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A phase based analysis of reaction dynamics

by

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ABSTRACT

The reaction dynamics of realistic molecular Hamiltonians including both mode coupling and anharmonicity may be profitably explored by classical trajectories. However, even if such trajectories begin in phase the energy dependence of individual orbital periods of anharmonic oscillators quickly results in an incoherent ensemble, thereby obscuring organization present in the reaction dynamics of a given Hamiltonian. One solution to these difficulties is to compare trajectories in phase on a cycle by cycle basis (i.e., coherently). In this work a model independent means for phase based, or coherent, comparison was developed utilizing the Hilbert transform.

Phase based analysis reveals that in particular unimolecular reactions correlated motion occurs when energy transfer between an orthogonal mode and the reaction coordinate forces synchronization in their motions, resulting in convergence of their phases. Thus a restricted and systematic set of states (i.e., points in phase space) precedes reaction, apparently contradicting the RRKM assumption that all states are equally likely to react. Detailed examination of the fundamental RRKM equation shows that this assumption differs from requiring that all states are equally likely to react per unit of time. States involved in correlated motion react sooner than others, but all states ultimately react, so their reaction probabilities are equal, therefore
correlated motion can be consistent with RRKM kinetics.

To explore the properties of different distributions of internal energy within a microcanonical ensemble a variant of phase space is proposed wherein every point is indexed by time remaining until reaction. (In the absence of trapping all unimolecular trajectories reside in the bound region of phase space for only a finite duration.) Under this variant points belonging to a particular allocation of internal energy are not scattered randomly across the lifetime distribution mapping (e.g. states in close time proximity to the transition state obviously all share the property of having sufficient energy in the reaction coordinate to clear the barrier). The microcanonical rate constant is an average of those for all component distributions of available internal energy, so the existence of rate constants with mode specificity can also be consistent with RRKM kinetics.
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Chapter 1

Introduction

The Chinese term for chemistry is huà xuè, which translates literally as "the study of changes". This neatly captures a central concern of chemistry, namely - what are the changes that occur in a molecule during the course of reaction, as atoms rearrange themselves and bonds break and form? Better understanding of the dynamics of reaction may bring us closer to the point of being able to influence the course of reaction on a microscopic scale, rather than resorting to the macroscopic interventions such as varying temperature or pressure.

There are three major interrelated themes in this thesis. First, reaction dynamics can be orderly rather than random. Certain atomic motions during reaction are systematic, akin to the sequence of moves in a formal dance. Second, analyzing reaction dynamics in terms of phase reveals underlying order. Third, the existence of order within reaction dynamics is consistent with RRKM kinetics. While demonstration of this last assertion is the focus of my thesis, strongly establishing the first two assertions makes the the third more interesting and important, so portions of this thesis are devoted to each.

This study explores the dynamics of reaction by treating molecules as a collection of coupled classical oscillators, so I will commence by establishing the foundation upon which my calculations are based. The first section of this chapter introduces concepts of general importance to classical trajectory calculations. The second section addresses subjects more specifically related to this thesis, and in the third section I detail the organization of this work.
1.1 Theoretical groundwork

Atoms have been postulated for millenia, but only since 1982 with the advent of STM microscopy [1] has it been possible to observe atoms directly. Most of the experimental physics which has illuminated the structure of the atom has occurred within the last century. Experiments from 1909 to 1911 by Rutherford and coworkers established that an atom consists a small dense positively charged nucleus surrounded by clouds of light negatively charged particles (electrons)[2] [3]. Molecules are in turn composed of interacting atoms, where the distribution of electrons forms a potential which determines the motion of the embedded nuclei. The positions of the nuclei then influence the distribution of electrons. The system would be hopelessly entangled without a means of decoupling these interactions, namely the Born-Oppenheimer approximation [4].

Born and Oppenheimer noted the mass difference between electrons and nuclei, which are some three orders of magnitude heavier. They concluded that the motions of electrons must be very fast in relation to those of nuclei. The differences in time scales for the motions of electrons versus nuclei allows a separation such that electrons in molecules may be treated, not as individual particles, but rather as the source of a potential field. It is the form of this potential field which governs the motion of the nuclei. In practice the Born-Oppenheimer approximation proves surprisingly robust, demonstrating that for most molecules electronic and nuclear motions are in fact separable. Once the Born-Oppenheimer approximation is made then a molecule may be treated as a collection of oscillators, where the force constants and couplings of the oscillators reflect the potential defined by the distribution of electrons.

By virtue of their size, molecules are governed by quantum mechanics, and the restrictions thereof, including quantization of energy and the uncertainty principle.
Spectroscopic data confirm that the vibrational energies of nuclei are quantized, and that in compliance with the uncertainty principle each oscillator has a "zero point energy" which prevents it from being stationary. (In a motionless oscillator both position and momentum would be specified to arbitrary precision, in contradiction to the uncertainty principle.) Calculation of the motions of nuclei under the influence of the molecular potential by classical mechanics requires a further approximation, namely neglect of vibrational quantization. Fortunately, nuclei are sufficiently massive that (particularly at higher energies) the effects of energy quantization are relatively small. By focusing on the motions of the nuclei only, one may reasonably approximate a molecule as a collection of classical oscillators, governed by classical equations of motion.

Given the number of approximations necessary for classical trajectory calculations one might well ask why the technique is used. The answers are twofold. First, the approximations involved are usually good ones, yielding results in reasonable agreement with direct observations. Second, the more exact approach of quantum dynamical calculations is not feasible for any but the smallest of molecules. In this work I have studied dynamics with both fully classical and semiclassical calculations, where in the latter case each oscillator has at least zero point energy, in conformance with the uncertainty principle.

1.1.1 The Hamiltonian

The foundations of classical mechanics lie in Newton's equations, which arise from observations of the motions of macroscopic objects, such as celestial bodies. For a single particle the essential physics is contained in Newton's second law of motion [5]:
\[ \vec{F} = \frac{d\vec{p}}{dt} \]  

(1.1)

where \( \vec{F} \) is the total force acting upon the particle, and \( \vec{p} \) is the linear momentum. Hamilton's equations are an alternate formulation of classical mechanics that are generally used in trajectory calculations because the equations of motion are first order differential equations. The Hamiltonian of a system is defined to be:

\[ H = T + V \]  

(1.2)

where \( H \) represents the total energy, which is constant for a conservative system, and \( T \) and \( V \) are the kinetic and potential energies respectively.

Having defined the Hamiltonian for a given molecule one can now explore its properties by running trajectories. The first stage in this process is selection of initial conditions. The manner in which initial conditions are selected determines the nature of the subsequent experiment. It is a matter of sufficient importance to warrant its own appendix, to which I refer the interested reader. Initial conditions become a trajectory by propagation of Hamilton's equations of motion [5]:

\[ \dot{s} = \frac{\partial H}{\partial p} \]  

(1.3)

\[ \dot{p} = -\frac{\partial H}{\partial s} \]  

(1.4)

where \( s \) is the coordinate, and \( p \) is its conjugate momentum. Each mode within the molecule has such paired equations of motion. Using the selected initial conditions, these first order differential equations may be numerically integrated (see the appendix on numerical integration) to yield a trajectory, i.e. the time evolution of the system, described by specifying coordinates and momenta at discrete times.
The molecule is the physical reality that we attempt to model with the Hamiltonian. A "complete" Hamiltonian would include terms for every conceivable interaction of that molecule, whether internal or with the rest of the universe. The form of a "complete" Hamiltonian will vary depending on the coordinate system in which it is expressed, but the underlying physics remain the same. In practice however only approximate Hamiltonians are used.

Potential energy

When constructing a Hamiltonian for a molecule much of the effort is focussed on creating an appropriate potential energy function. Ideally the Hamiltonian is fully specified once a coordinate system has been selected, but there is no standard procedure to guide in the construction of a practical potential energy function. Decisions must be made regarding which interactions to include, and which to neglect, based upon the nature of the problem to be studied. The challenge in creating a useful Hamiltonian lies in including only those terms of greatest relevance to the problem at hand, so that calculations are at once meaningful and as simple as is possible.

The potential energy function is a mathematical construct which permits calculation of potential energy for arbitrary molecular configurations. The form of the potential energy function depends upon the coordinate system used to specify atomic locations, but in general the function is of \(3N - 6\) dimensionality for \(N > 2\), where \(N\) is the number of atoms in the molecule. The potential energy function defines a hypersurface with \(3N - 6\) dimensions, commonly referred to as a potential energy surface (i.e. PES). For any molecule with more than two atoms the PES has too many dimensions to be simply plotted. Much of the art and the science of dynamics lies in discerning the specific properties of the hypersurface in the absence of direct visualization.
One standard system for specifying atomic locations is local mode coordinates, which have been used extensively in this work. Local modes (also referred to as bond modes) are an internal coordinate system which defines locations of atoms relative to each other. Adjacent atoms which are bonded are characterized by their internuclear separation, $s$, and positions in space are fixed by bending ($\theta$) and torsional ($\tau$) angles, or out of plane angles ($\phi$), depending upon the molecular geometry.

Typical Hamiltonians used in this study model bending local modes as variations of the harmonic oscillator potential

$$V = \frac{1}{2}k(\theta - \theta_0)^2$$

(1.5)

where $k$ is the force constant, and $\theta_0$ is the equilibrium angle. Stretching local modes are frequently defined in terms of the Morse potential, a relatively simple function that incorporates both harmonic and anharmonic behaviour.

$$V = D(1 - e^{-\alpha(s-s_0)})^2$$

(1.6)

$D$ is the dissociation energy, $s_0$ is the equilibrium separation, and $\alpha$ controls the curvature near equilibrium, and so functions in a manner similar to the harmonic force constant.

Local modes are a convenient choice for formulating a potential energy function because they correspond to the model of a molecule as a collection of coupled oscillators, and are readily visualized. However we will shortly see that this convenience comes at a cost.

**Kinetic energy**

The second part of the Hamiltonian is the kinetic energy function. It is simpler than the potential energy function, in that once a coordinate system is selected for
the Hamiltonian the form of the kinetic expression may in principle be generated
unambiguously in a systematic (but nontrivial) fashion, but it is no less important to
the dynamics, which respond to the entire Hamiltonian.

If the Hamiltonian is expressed in terms of cartesian coordinates (an orthogonal
coordinate system) then the kinetic energy is simply

\[ T = \frac{1}{2} \sum_{i=1}^{N} m_i (\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2) \]  \hspace{1cm} (1.7)

where \( N \) is the number of atoms in the molecule, \( m_i \) is the mass of an atom and
the \( \dot{q}_i \) are the corresponding cartesian components of its velocity. Usually the task
of formulating a PES directly in cartesian coordinates is formidable (but coordinate
transformations allow a PES expressed in local modes to be related to the correspond-
ing cartesians). When the PES is expressed in terms of local mode coordinates then
the kinetic energy of internal motions only is [6]

\[ T = \frac{1}{2} P^\dagger G P \]  \hspace{1cm} (1.8)

where \( P \) is the vector of local mode momenta, and \( G \) is the Wilson \( G \) matrix. Be-
because local modes are not an orthogonal basis their kinetic energy contributions are
not separable. Adjacent motions interact with each other in a manner first detailed
by Wilson [7]. (Please see the appendix on the Wilson \( G \) matrix for a discussion
more complete than the current one.) \( G \) is a \( M \times M \) matrix, where \( M \) is the number
of local modes in the molecule. Each element of \( G \) may be a complicated function
of atomic masses and any of the local mode coordinates. The total kinetic energy
involves summing the products of these terms with local mode momenta. The result-
ing contribution to the Hamiltonian is mechanical, in the sense that its exact form
can be specified explicitly, but future chapters will show that couplings in the kinetic
energy term can determine the form of reaction dynamics.
Given the added complications inherent in local mode coordinates one might question their utility, but in many systems high energy vibrational modes (including the reaction coordinate) are closely related to local modes, which makes local modes an appropriate coordinate system in which to study these motions.

Coupling

Reactions occur when there is sufficient energy in the reaction coordinate, but how does energy move between modes? It is apparent that energy can transfer from one local mode to another only when there are terms in the Hamiltonian that contain some product of the coordinates and/or the momenta of both modes. In the harmonic approximation the Hamiltonian may be expressed as [6]

$$2H = P^\dagger GP + S^\dagger FS$$

(1.9)

where $S$ is a vector of generalized vibrational coordinates and $F$ is the force constant matrix

$$F_{ij} = \frac{\partial^2 V}{\partial S_i \partial S_j}$$

(1.10)

In normal mode applications $S$ is chosen so that both $F$ and $G$ are diagonal. For a molecule with $N$ degrees of freedom the Hamiltonian is the sum of two $N \times N$ matrices. In the current case this corresponds to a system of $N$ independent harmonic oscillators. It is not a chemically interesting system, as (since no energy can be exchanged) all normal modes oscillate independently ad infinitum. One of the conditions for reaction is that the system be capable of transferring energy into a reactive mode. Such transfer occurs via the coupling terms of the full Hamiltonian. Both the kinetic and the potential portions of the full Hamiltonian contribute to coupling.
Coupling and coordinate transformations

Coupling terms pose a dilemma when constructing a Hamiltonian. Despite their importance they are often sacrificed to expediency, not because their effects are inconsequential, but rather because inclusion of coupling terms renders the Hamiltonian much more difficult to manipulate. When coupling terms are present the Hamiltonian is no longer separable into smaller, more easily handled subunits. The dilemma therefore is that excluding couplings can affect the validity of the model, while including couplings can make the problem intractable. Scientists attempt to deal with the problem of coupling by judicious selection of coordinates for the Hamiltonian, as an appropriate selection of coordinates can minimize or eliminate couplings.

The form of a Hamiltonian can vary greatly depending upon the coordinate basis. Ideal coordinates are those in which there is no coupling, so the Hamiltonian is separable without the necessity of neglecting terms. However, it is often the case that a single coordinate system will eliminate couplings in either the kinetic or the potential portion of the Hamiltonian, but in general one cannot find a coordinate system which eliminates couplings in both. In fact, as a rule, a transformation which diagonalizes one term of the Hamiltonian increases couplings in the other term, in essence forcing the full complexity of the problem into the undiagonalized term. Given that coordinate transforms seem to be a zero sum game why then would one wish to change bases? In an exact calculation the outcome is independent of the coordinate system selected, but most calculations are not exact, involving neglect of coupling terms, truncation errors, etc. The choice of coordinate system can minimize deleterious effects for approximate calculations. However, beyond these concerns, in the balance of this section I will show that some choices of coordinates yield greater physical insight than others.
We study reaction dynamics to understand the underlying causes of the observed motion. A small first step in this direction is to model a trajectory as the result of rolling a marble on a PES. This simple intuitive model incorporates the fundamental exchange of energy between kinetic and potential forms. Fig. 1.1 shows reactive trajectories superimposed upon the corresponding PES. The dashed lines are isoenergy contours of the PES for the following Hamiltonian comprised of two anharmonic stretching modes, expressed in local mode coordinates:

\[ H(s_1, s_2, p_1, p_2) = V_1(s_1) + V_2(s_2) + \frac{1}{2} p^\dagger G p \]  

(1.11)

where \( V_1 \) and \( V_2 \) are Morse oscillators. For this model all elements of the \( G \) matrix are constants, but the \( G \) matrix includes off diagonal terms. Superimposed upon this PES is the path of the final cycle of oscillation for fifty random reactive trajectories with the same total energy. (To increase clarity, in each trajectory the first half cycle is drawn with a solid line and the last half with a dotted one.) Fig. 1.1 shows the reaction dynamics for this simple system, but is not particularly illuminating in terms of how these arise. At the beginning of the final oscillation there is considerable spread in the distribution of the reactive trajectories. It is not immediately apparent that these trajectories are poised to react, nor is the path taken in harmony with our intuitive model of rolling a marble on the PES. (Particularly at the turning points the incident and the reflected angles of a given trajectory show that the path is not solely determined by the gradient of the PES.) The "rolling marble" model for trajectory generation is defective because in local mode coordinates the kinetic energy depends not only on the gradient of the PES, but also on kinetic coupling terms. These coupling terms undermine the validity of the simple and intuitive rolling marble model of dynamics.

To make the rolling marble model viable requires a change of basis to one in
Figure 1.1 The final oscillation for fifty reactive trajectories is superimposed upon the PES, which is that of two Morse oscillators. Both the trajectory paths and the energy contours are expressed in local mode coordinates.
which the kinetic coupling terms have been eliminated, and one must also account for mass differences between the modes. (In the current Hamiltonian both stretching modes have the same reduced mass, so mass effects are not a concern.) Fig. 1.2 shows the same trajectories as Fig. 1.1 in a basis where the $G$ matrix has been transformed into the identity matrix. This transformation has several advantages for analysis of reaction dynamics. First, the intuitive rolling marble model works in this basis. Trajectories respond to the gradient of the transformed PES rather than to unvisualizable kinetic coupling terms. Second, the spread in the reactive trajectories is small for the entire final oscillation, showing the fundamental similarities of all of these reactive trajectories. Third, in this transformed basis it is obvious that all trajectories are poised to react. They are clearly aligned with the reactive coordinate, and are positioned so that the sharp curve of the inner turning point flings them directly at the transition state (a surface orthogonal to the reaction path, which divides reactants from products [8]). For all of these reasons reaction dynamics are more easily interpreted in the transformed basis where the effects of kinetic couplings have been removed, showing up instead as features in the transformed PES.

In the preceding simple two dimensional model all terms of the $G$ matrix are constants, so a single transformation applies at every location. It is easy to specify another simple two dimensional model where this is no longer the case. Consider the Hamiltonian for a stretch $s_1$ coupled to a bend $s_2$,

$$H(s_1, s_2, p_1, p_2) = V_1(s_1) + V_2(s_2) + \frac{1}{2} P^\dagger G(s_1, s_2) P$$  \hspace{1cm} (1.12)

where now $V_1$ models the stretch as a Morse oscillator, and $V_2$ models the bend as a harmonic oscillator. The PES for this system is shown in the upper portion of Fig. 1.3. Importantly for the present discussion, the kinetic energy term for this Hamiltonian (expressed in local mode coordinates) now has functional dependence upon the values
Figure 1.2 The final oscillation for fifty reactive trajectories is superimposed upon the PES, which is that of two Morse oscillators. Both the trajectory paths and the energy contours are expressed in coordinates in which the kinetic energy term is diagonal.
of local mode coordinates, for elements both on and off of the diagonal. Now a separate transformation is required at every location to instantaneously diagonalize the kinetic energy term. The transformation from a local mode basis to one in which $T$ is diagonal is no longer a simple rotation. The lower plot in Fig. 1.3 shows how the PES has been changed under transformation to a diagonal $T$ basis. The most obvious effect of the transformation is to destroy the mirror symmetry of the local mode PES. In transferring complexity from the kinetic to the potential portion of the PES I have created a new PES with greater variation (and consequently less symmetry) than the old.

Of what benefit is the new PES? All that I have done is to move complexity in the Hamiltonian from the the kinetic to the potential term, but this more complex PES is a much better predictor of the dynamics than is the original PES. After mass scaling the axes, this is a PES for which the rolling marble model of trajectory generation is valid. In Fig. 1.3 the symmetry of the original PES suggests that the resulting dynamics should be fairly regular. This erroneous assumption is dispelled when one considers motion on the more complex PES. I shall refer to the PES which results from diagonalization of the kinetic energy term as the maximum complexity PES, because for a given Hamiltonian with a particular coordinate system it is the transformation wherein the kinetic term is as simple as is possible and so the potential term is correspondingly complex.

My research suggests that some couplings induce greater distortions into the maximum complexity PES than do others. Consider a normal mode which is a linear combination of two local modes. These modes tend to couple strongly, and this coupling seems to express itself as a distortion on the PES that spans a wide range of coordinate values. Conversely, small couplings, such as those between modes of different symmetries, seem to induce only small local distortions on the maximum complexity
Figure 1.3 The PES for an anharmonic stretch and a harmonic bend. The upper figure is the PES in a local mode basis, while the lower is the same PES in a basis where $T$ is diagonal.
PES. In the maximum complexity PES all couplings are expressed as topographic features on the PES, and the kinetic energy term is as simple as possible. The fundamental structure of this surface reflects the original potential energy function, but superimposed on this surface are distortions which arise when the effects of kinetic couplings are also included. In general the effects of couplings are perturbations to the base topography, but the magnitude of the perturbation can vary with the magnitude of the corresponding coupling. By incorporating the effects of all couplings, the maximum complexity PES is the one that is most directly relates to the observed dynamics.

The maximum complexity PES is a conceptual construct to help in qualitative interpretation of observed dynamics. It is not an analytic tool, since in describing this construct I have conveniently overlooked a number of complicating factors, including that when the $G$ matrix is a function of local mode coordinates diagonalization results in coordinates that are not simply a linear combinations of local modes, but rather have coefficients which vary with location. Despite these approximations, the maximum complexity PES has been very useful to me in rationalizing some of the observed subtleties of reaction dynamics.

1.2 Posing the problem

The preceding section described tools that (for the most part) are standard features in the study of reaction dynamics. In this section I focus on topics that are more specific to this study, and explicitly declare my thesis statement.

1.2.1 Oscillator phase

Within the Hutchinson group a standard technique for analysis of reaction dynamics of a given molecule is to create a large number of reactive trajectories and
then to compare the resulting reactions to identify consistent behavior. Prior to this work trajectories were compared using time as the independent variable [9] [10] [11] [12] [13] [14]. A major theme of this thesis is that for the study of reaction dynamics oscillator phase is superior to time as an independent variable. Coherent comparison of trajectories is not a new idea [15], but has been difficult to implement. Subsequent chapters will discuss the importance of phase and its implementation via the Hilbert transform. Coherent comparison of trajectories is superior because it relates behavior of local modes when the reaction coordinates are in similar regions of phase space, regardless of their arbitrary time indices. The results of phase analysis of reaction dynamics have proven to be sufficiently diverse and interesting to merit extensive study.

1.2.2 Correlated motion

Consistent behavior, which we have termed correlated motion, has been identified in simulations of the reactions of a number of molecules, including hydrazoic acid, hydrogen peroxide, diimide, methyl nitrite [12] [13] and formyl fluoride. During reaction one or more local modes show a pattern of behavior such that for a certain duration preceding reaction all trajectories will undergo similar motions in the correlated modes. Others have also noted evidence for orderly structures in phase space, including Davis [16] [17], Skodjie [18], Gray [19] and Ezra [20] who identified "bottlenecks" in vibrational phase space which constrain energy transfer. DeLeon [21] [22] [23] and coworkers report the existence of cylindrical manifolds which extend out from the transition state and regulate the rate of unimolecular reaction. In subsequent chapters I propose a model to account for structure in phase space, and show evidence that the interaction of oscillator phase and intramolecular vibrational relaxation (IVR) is critical to formation of phase space structures.
1.2.3 RRKM theory

Physical chemists are justifiably wary of evidence of nonstatistical behavior during reaction, because it appears to violate one of the key assumptions of RRKM theory, namely that all states are equally likely to react. RRKM theory is one of the most elegant in chemistry, producing remarkably accurate rate constants from a relatively small set of physical measurements and underlying assumptions. (To some extent RRKM theory is a victim of its own success. Molecules that are exceptions to RRKM theory are sufficiently rare as to merit individual study.) That most molecules obey RRKM kinetics is a tribute to the robustness of these assumptions, so it is entirely reasonable for chemists to question phenomena which appear to violate those assumptions.

1.2.4 Thesis statement

Abundant rate constant measurements support the validity of RRKM theory, which holds that all states are equally likely to react. A growing body of work also indicates that for many molecules a restricted set of states (i.e. those involved in correlated motion) precedes reaction. In this thesis I will demonstrate that despite this apparent contradiction, the existence of correlated motion is entirely consistent with RRKM kinetics.

1.2.5 Phase Space

A central problem in dynamics is how to handle the large number of dimensions that arise for any polyatomic molecule. Phase space (i.e. a space with separate dimensions for every coordinate and every momentum in a given Hamiltonian) can prove helpful. Because each coordinate and momentum has its own dimension every
possible molecular state is represented by a point in this space. As one state evolves into the next the resulting trajectory forms a nonintersecting space curve. Each trajectory is confined to the appropriate isoenergy hypersurface for the Hamiltonian. The isoenergy surfaces for any given Hamiltonian nest inside each other like layers of an onion, with outer layers corresponding to higher energy levels.

Phase space is a natural domain in which to study a statistical rate theory such as RRKM. (In the simplest terms the RRKM rate constant is a ratio of the flux across the transition state to the number of all bound states.) By contrast, correlated motion is a property of the system dynamics. To reconcile correlated motion and RRKM theory requires a bridge between kinetics and dynamics. While phase space has no explicit time dependence I will show that phase space can be parametric in time. A subsequent reordering of phase space based on time indices proves to be the desired bridge between kinetics and dynamics.

1.3 Thesis organization

This thesis is comprised of chapters addressing each of the three major themes of this work; reaction dynamics can be orderly, studying reaction dynamics in terms of phase can reveal this order, and such order is compatible with RRKM kinetics.

In Chap. 2 I discuss the process of generating trajectories and make the case that time is not the best framework in which to study dynamics. As a superior alternative I propose the use of phase, which allows coherent comparison of trajectories. Parameterizing trajectories by phase permits comparison when trajectories reside in similar regions of the Hamiltonian. I then show how the Hilbert transform can be used to assign phase in a manner appropriate for coherent trajectory comparison.

In Chap. 3 I introduce the concept of correlated motion and propose a model to account for it. Contrasting examples show how the extent and distribution of
couplings can have major impact upon the observed reaction dynamics.

I show in Chap. 4 how a variant of phase space can be used as an intermediary to connect kinetics and dynamics. In this way I show that correlated motion and RRKM kinetics are compatible.

In the course of this research I obtained interesting results regarding structure in phase space. While Chap. 4 validates the compatibility of orderly dynamics (arising from phase space structures) and RRKM theory, in subsequent chapters I show further supporting evidence for the existence of orderly dynamics, as follows.

Beginning in a contrary fashion, Chap. 5 is a case study of a molecule with disorderly reaction dynamics. I show how small differences in coupling can have major impact by taking a detailed look at the kinetics of nitrous acid. HONO is an interesting molecule, as (although the potential minima are very similar) the isomerization rate from cis to trans can be an order of magnitude greater than from trans to cis. I make the case that this difference in rates is a consequence of relatively small differences in the kinetic couplings of the two isomers.

In Chap. 6 I detail the Hamiltonian for HN₃, a molecule with large and extensive couplings whose reaction dynamics are very orderly. I further explore the nature of correlated motion and the structure of the phase space hose to show that when parameterized by phase, the reaction dynamics are quite regular.

As a contrast to the disorderly dynamics of HONO, in Chap. 7 I examine the kinetics and dynamics of hydrazoic acid, demonstrating by means of state specific reaction rates a relationship between phase and time until reaction.

In Chap. 8 I summarize the conclusions of the previous chapters:

- Phase is superior to time for analysis of dynamics.
- Couplings are key to dynamics, determining whether or not correlated motion
occurs.

- Correlated motion is consistent with RRKM theory.
- Mode specificity is consistent with RRKM theory.
- Phase plays a key role in IVR.

and also speculate on the implications of these findings for direct control of chemical reactions.

In a host of appendices I show a number of derivations and discuss mechanical details of implementation and verification of several computational techniques. The final appendix, on formyl fluoride, includes a brief discussion of my findings concerning the reaction dynamics of HFCO, which are of particular interest because in this molecule the reaction coordinate is not simply an extension of a local mode.
Chapter 2
Reaction dynamics and oscillator phase

Qui peut calculer la trajectoire d’une molécule? - V. Hugo

In this chapter I show that because of anharmonicity, time is often an unsatisfactory independent parameter for trajectory comparison, and describe two alternatives for characterizing “progress towards reaction”, commenting on the strengths and weaknesses of each. Unlike time, coherent comparison of trajectories (wherein reaction dynamics are parameterized by oscillator phase) relates trajectory behaviour when the trajectories are in similar regions of phase space. The Hilbert transform is one quite general means of implementing coherent comparison. In later sections I describe the transform, and apply it to a number of systems then compare the phase assigned to that generated by the action-angle transform, culminating in a system where, because of coupling, the action-angle transform is no longer applicable, but the Hilbert transform assigns physically meaningful phases. Finally, I discuss some details regarding implementation of the Hilbert transform and define the phase conventions used in this work.

2.1 Introduction

Depending upon molecular energy the duration of orderly reaction dynamics can be brief in comparison with the lifetime of the activated species which precedes it. The evanescent nature of the reactive process makes it difficult to study experimentally. Mathematical simulations of chemical reactions are useful because they have the potential for yielding insight into a process that is not currently amenable to direct experimental measurements. In this study I have explored reaction dynamics by computational simulation of unimolecular reactions.
To study reaction dynamics I follow trajectories until the specific reaction criterion is met for each particular molecule. Technical factors influence the choice of coordinates used to propagate the equations of motion, but irrespective of the integration coordinates, in this study the resulting dynamics were analyzed in terms of motion of local modes, shown in Fig. 2.1. Describing molecular motions in terms of local mode coordinates offers a number of advantages. As internal coordinates, local mode coordinates allow one to disregard over all translations and rotations. In addition, local modes (also called bond modes) are attractive because their motions are relatively easily visualized and because potential energy functions are often written in terms of local modes, but most importantly, the reaction coordinate is frequently closely re-
lated to a local mode. In dissociations, the reaction coordinate may be approximated as the limit of a local mode stretching motion, while a cis-trans isomerization may similarly be treated as the limit of a torsional local mode.

I analyzed reaction dynamics in large part by comparing the motions of each local mode over many trajectories. Since this study focusses on reaction dynamics, the span of each trajectory studied intensively is usually a window encompassing several oscillations of the reaction coordinate immediately prior to and including reaction. To compare motions between trajectories it is necessary to establish a criterion for how the reaction is progressing.

### 2.2 Reaction dynamics parameterizations

As has been previously noted, this work uses classical trajectories to study reaction dynamics. Classical equations of motion generate trajectories as time series. Does it therefore necessarily follow that time is the best parameterization in which to study dynamics? I will make the case in the next section that due to anharmonicity in the reaction coordinate time is actually a rather poor choice of independent parameter with which to study reaction dynamics. In subsequent sections I will propose two new independent parameters of reaction progress and discuss the strengths and weaknesses of each.

#### 2.2.1 Time and anharmonicity

If, as we often pretend, the whole universe were harmonic, time would be a satisfactory parameter for trajectory comparisons. However there would also be no chemical reactions whose dynamics we could study. Reaction can only occur when the reaction coordinate potential allows unbound, anharmonic motion. Given that reactions are intrinsically anharmonic, why does this render time a poor independent
parameter? To identify common features of reaction dynamics one must compare the characteristics of many trajectories during the course of reaction. To compare reactive trajectories requires selection of an independent parameter which is the measure of progress towards reaction for each trajectory. The first problem with time is to define its starting point. For unimolecular reactions a reasonable choice for the zero of time is at the beginning of a trajectory, where the initial conditions may be equated with the state of the molecule at the time of excitation. (By contrast, bimolecular reactions lack even this rudimentary a time origin.) Creating a trajectory by forward time propagation of the selected initial conditions results in reactions at arbitrary times. While this procedure is perfectly correct, the reactive portions of trajectories cannot be compared with this time origin. One alternative which guarantees that that reactions occur in the same range of time indices is to set the time origin at the transition state, and to propagate reactive initial conditions backwards in time towards bound states. However, even trajectories so aligned in time are only directly comparable for a brief span. Because of anharmonicity, the final stages of reaction occur over different time scales depending upon the energy in the reaction coordinate. In an ideal harmonic universe all oscillations in a given mode have the same period, irrespective of energy. In the real anharmonic universe the duration of the final half oscillation preceding reaction is energy dependent, as shown in Fig. 2.2. This figure shows the transit time from the inner turning point to either the outer turning point in the case of bound motion, or to the transition state in the case of unbound motion. (The curves shown are qualitative, representing the trends indicated by calculated time values for discrete energies, not a curve fit to any particular set of data.)

In the low energy limit the half oscillation time is related to the period of the harmonic oscillator that approximates the curvature of the anharmonic PES near equilibrium. As energy in the oscillator increases anharmonicity becomes significant,
Figure 2.2  Transit time for a half oscillation, from the last inner turning point to either the transition state or the outer turning point, depending upon the energy in the reaction coordinate, versus energy in the reaction coordinate. The pole corresponds to a reaction coordinate energy equal to that of the barrier. The inset figure shows an example anharmonic potential, with the arrows indicating reactive, asymptotic and bound energies from top to bottom respectively.
and increases the time per oscillation, culminating in a pole in the function when the energy in the reaction coordinate equals the barrier energy $E_b$. Thereafter time for a half oscillation diminishes as energy in the reaction coordinate increases. Trajectories clear the reaction barrier with increasing velocity, thus the time that a trajectory spends in the final half cycle preceding reaction (and to some extent in the crucial cycles preceding that one) is critically dependent upon the energy in the reaction coordinate. Especially in the vicinity of the pole at $E = E_b$, trajectories differing only slightly in energy can have markedly different time responses, rendering a time based comparison of the two trajectories ineffective. Consider two trajectories, both with the same total energy, but differing in the amount of energy in the reaction coordinate. Fig. 2.3A shows the time response of two such trajectories, beginning at the transition state and running backwards in time towards bound states. If we were to look for correlated motion by averaging these two time responses, within a single oscillation of the reaction coordinate (by 2300 time units) the trajectories are completely out of phase, so the contributions of each result in an average near to the equilibrium value. What then are the alternatives to time parameterization?

2.2.2 Reactive mode arc length

The objective in comparing trajectories is to identify similarities in behavior during reaction. The "progress towards reaction" parameter should permit comparison of trajectories when their reaction coordinates are in similar regions of phase space, irrespective of the time indices of these occurrences. Because molecules are readily viewed as a collection of coupled oscillators, parameterizations related to oscillation of the reaction coordinate seem like a natural place to begin.

A parameterization that has the advantage of simplicity involves generating a "progress of reaction" parameter by taking a line integral along the reaction coordi-
Figure 2.3 Position of the reaction coordinate versus a "progress of reaction" independent parameter. In part A the independent parameter is time, while in part B it is reaction coordinate arc length.
nate oscillator:

\[ A = \int ds \]  \hspace{1cm} (2.1)

\[ ds = \sqrt{dp'^2 + dq'^2} \]  \hspace{1cm} (2.2)

where \( A \) is the reaction coordinate arc length and \( dp' \) and \( dq' \) are respectively the incremental momenta and coordinates for this oscillator, scaled in a manner that eliminates the effects of the fundamental differences in their units [13]. Fig. 2.3B shows the same two trajectories plotted against the arc length parameter \( A \). This "progress of reaction" parameter is somewhat better than time in preserving coherence when comparing trajectories. The inner turning points are more closely aligned, and coherence between the trajectories is preserved for an additional half cycle when compared to time, with cancellation occurring at about one and a half cycles of the trajectory with the greater period.

The reaction arc length parameter is an improvement over time as an independent parameter for coherent addition of trajectories. It is easily calculated and can be used for the entire span of a trajectory. When used as the independent parameter one can produce plots (discussed further in Chap. 3) which display a striking visual representation of correlated motion. Given the high dimensionality of the systems studied, this is otherwise not easily achieved. However, since a trajectory with more energy in the reaction coordinate will have a longer arc length per oscillation, there is a gradual slippage between two trajectories compared in arc length, which is cumulative. While arc length is a useful display parameter, it is not one which will keep trajectories in proper registration to allow quantitative comparison. In properly aligned trajectories I can compare behavior of orthogonal modes at any location of the reaction coordinate, whether at an inner turning point, an outer turning point, at equilibrium, or in
between. In this way I can look for consistent behavior of the orthogonal modes over many trajectories whilst the reaction coordinate is at a specific stage of the reaction process, and is in a well defined region of phase space.

2.2.3 Phase

What parameter will permit coherent comparisons of trajectories? The clues come from defining the locales where comparison is desired. Turning points and equilibria are easily defined in terms of the phase of an oscillator. What is needed is a way to assign a meaningful phase parameter to the arbitrary time series which is the motion of a local mode oscillator. In separable systems a phase angle may in principle be uniquely assigned to the motion of each oscillator by means of the action-angle transform [5]. However, this technique is analytical, and becomes intractable as soon as the modes are coupled. I have developed a numerical technique which permits the assignment of phase angles to any oscillator, by means of the Hilbert transform (to be discussed shortly). When trajectories are transformed into unwrapped phase they can be added coherently.

Fig. 2.4 shows a comparison of the same two trajectories as shown in Fig. 2.3, but with continuous phase (also referred to as unwrapped phase) of the reaction coordinate as the independent parameter. For technical reasons the oscillators are characterized by momentum, rather than coordinate, but both trajectories are clearly in registration for their entire duration. As is evident at $\phi = 15$, phase assignment is subject to certain idiosyncrasies. High frequency "wiggles" in the oscillator motion can induce temporary phase reversals as a small high frequency oscillation cycle rides on top of the carrier wave. The resulting nonmonotonic phase relationship is physically valid, but can appear anomalous. More seriously, there is a "blackout" zone as trajectories approach the transition state wherein phase values can not be
Figure 2.4 Comparison of the reaction coordinate momenta for two trajectories with reaction coordinate phase as the independent parameter.

meaningfully assigned. Phase is only relevant to cyclic motion, and as trajectories approach the transition state the motion of the reaction coordinate local mode becomes intrinsically aperiodic in both amplitude and frequency. However, the range of aperiodic behavior wherein phase can not be meaningfully assigned encompasses at most a quarter of an oscillation. This will be discussed at greater length in the subsequent section on the Hilbert transform.

Despite these imperfections, unwrapped phase is an independent parameter which will permit direct comparisons of trajectories at well defined stages of the process of reaction. Coherent comparison of trajectories, parameterized by continuous phase of the reaction coordinate, makes it possible to compare the motions of orthogonal oscillators for many cycles of oscillation preceding reaction without differences in reaction coordinate periodicity (caused by energy differences and anharmonicities) blurring the response. As will be discussed in Chap. 3, unwrapped phase is also key
to developing a quantitative assessment of correlated motion.

2.3 Phase assignment by the Hilbert transform

The Hilbert transform is one means by which phase may be assigned to oscillator motions. Its advantages over the action-angle transformation are in being more generally applicable and in assigning a more appropriate phase to anharmonic oscillations. Following a short introduction, Sec. 2.3.2 contains a brief derivation showing how to obtain oscillator phase from the Hilbert transform. In Sec. 2.3.3 action-angle phases are compared to those of the Hilbert transform for systems of increasing complexity, culminating in a coupled oscillator system for which the action-angle transform is no longer feasible. I briefly discuss the implementation of the numerical Hilbert transform in Sec. 2.3.4, and present conclusions in Sec. 2.3.5.

2.3.1 Introduction

Phase of an oscillator is a quantity of interest in a number of chemical problems. Typical applications involve examining the interactions of coupled oscillators, such as surfaces of section in action angle coordinates [24], or in configuration space where phase is instrumental for coherent comparison of trajectories. The latter application is the emphasis of this chapter. Coherent comparison of trajectories is not a new idea [15], but is difficult to implement. Previous techniques for assigning phase have been limited to simple separable systems. The standard means of assigning phase is by the action-angle transform [5]. This technique is a canonical transformation of $H(q,p)$ to $H(J,\phi)$ where the action $J$ is related to the energy of the oscillator and $\phi$ is its phase. The transform is an analytical technique which can only be readily applied to uncoupled harmonic and Morse oscillators. For many systems of chemical interest because of coupling and/or chaos the exact action-angle transform does not exist,
so use of the technique requires neglect of all couplings. By contrast, the numerical Hilbert transform is independent of the complexity of the Hamiltonian, so strongly coupled modes may be treated without approximation.

Molecules may reasonably be modeled as collections of coupled oscillators. Typical potential energy functions describe bound molecular motions in terms of harmonic oscillators and dissociative motion in terms of anharmonic oscillators. Despite the clearly cyclic nature of local mode motion, the behaviour of trajectories is usually characterized by comparing positions as a function of time. A coordinate system that is better suited to the oscillatory nature of local mode motion is one wherein the motion is defined in terms of an oscillator amplitude component \( r \) and a phase \( \phi \). If a phase can be meaningfully assigned to local mode motion it becomes possible to compare trajectories coherently, obviating many of the more unpleasant aspects of anharmonicity and coupling.

### 2.3.2 The Hilbert transform

The Hilbert transform is used in fields as diverse as engineering, [25] optics, [26] and geophysics. [27] Within chemistry, it has already been applied to a number of problems, primarily in the area of spectroscopy. [28] [29]. Absorption and dispersion spectra are Hilbert transforms of each other [30], and may be combined to diagnose line broadening mechanisms in NMR [31] and ESR spectra [32]. In a similar fashion coordinates and momenta, once scaled to account for differences in units, are also a Hilbert transform pair. Consequently oscillator phase may be assigned by taking the Hilbert transform of either coordinates or momenta.

The Hilbert transform, as shown in Bracewell [33], is a relatively simple technique,
defined as the principal part of the following integral.

\[ F(t) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{f(t')dt'}{t' - t} \]  \hspace{1cm} (2.3)

Fig. 2.5 shows an arbitrary time series in Part A and Parts B through E are successive Hilbert transforms. Comparing any pair of functions one finds that after transformation the zeros and extrema of each function have been interchanged, corresponding to a ninety degree phase shift in the function. (The prototypical Hilbert transform pair are the sine and cosine.) A second cycle of transformation results in a function whose polarity is inverted with respect to the original time series, and four transformations return the function to its original form (compare Parts A and E of Fig. 2.5).

Note that this integral is equivalent to convolving \( f(t) \) with \( \frac{i}{\pi t} \). Bracewell [33] shows an alternative implementation of the Hilbert transform wherein the time series \( f(t) \) is Fourier transformed to \( F(s) \), which is then multiplied by the function \( i \text{sgn}(s) \), followed by inverse Fourier transformation. (Multiplication by \( i \text{sgn}(s) \) in the transform domain is equivalent to time domain convolution by \( \frac{i}{\pi t} \).) Note that \( i \text{sgn}(s) \) is a function that has no effect on the frequency content of a function, but multiplies negative frequency values by \(-i\) and positive ones by \(i\). This alternative implementation more clearly shows how the Hilbert transform induces the ninety degree phase shift in each application. As the Hilbert transform affects the phase but not the frequency of a given time series, the power spectrum should remain unchanged under Hilbert transformation. Fig. 2.6 verifies this by superimposing the power spectrum of the original time series and that of its Hilbert transform. Except for small truncation effects visible at the lowest frequencies, the two spectra are the same.

The phase shifted data \( F(t) \) may be combined with the original time series data \( f(t) \) to form what Bracewell terms the quadrature function,

\[ Q(t) = f(t) + iF(t) \]  \hspace{1cm} (2.4)
Figure 2.5  Successive Hilbert transformations of an arbitrary time series. Part A is the original time function, and Parts B through E are each Hilbert transformations of the preceding function. Note that any transform pair corresponds to an interchange of extrema and zero crossings, while two transformations correspond to a polarity inversion, and four transformations return the function to its original form.
Figure 2.6  Power spectrum of a function $f(t)$ and its Hilbert transform, showing that aside from minor truncation effects at zero frequency the Hilbert transform has no effect on the frequency content of a function.
a function in complex cartesian coordinates. When $Q(t)$ is transformed into complex polar coordinates $re^{i\phi}$ the following quantities emerge [34]:

$$r(t) = \left( f(t)^2 + F(t)^2 \right)^{\frac{1}{2}}$$

(2.5)

$$\phi(t) = \tan^{-1} \left( \frac{f(t)}{F(t)} \right)$$

(2.6)

The angle coordinate $\phi$ arising from the Hilbert transform varies by $2\pi$ over one period of oscillation, and so is the oscillator phase angle which we seek. The amplitude $r$ relates to oscillator amplitude, so $r^2$ is proportional to oscillator energy, and thus is analogous to the action $J$ of action-angle coordinates.

### 2.3.3 Comparison of the action-angle and Hilbert transforms

The two cases for which the action-angle transform may most easily be applied without approximation are the uncoupled harmonic and the Morse oscillators, each of which is considered. The final system is one in which a Morse and an harmonic oscillator are coupled. This case can no longer be treated exactly using the action-angle transform, but I show that phases can readily be applied to the motion by using the Hilbert transform.

The Hamiltonians used are models only, and all calculations were done in atomic units. For technical reasons (touched on in Sec. 2.3.4) the Hilbert transform is more easily implemented using momentum, so in all subsequent figures oscillator motion will be characterized by momentum values, scaled for convenience to range over roughly $-\pi$ to $\pi$. The solid line in each plot represents the scaled momentum, and the dashed line the assigned phase.
Harmonic oscillator

The Hamiltonian is

$$H = \frac{p^2}{2m} + \frac{ks^2}{2}$$

(2.7)

where $m$ is 2000 au and the force constant is 0.1 au. Fig. 2.7 shows the phases assigned to harmonic oscillator local mode motion. Part A shows three cycles of harmonic oscillation characterized by momentum, with the corresponding phase assigned by the action-angle transform superimposed as a dashed line. Part B shows the same, save only that the phase has been generated by a numerical Hilbert transform. The plots are unremarkable, but demonstrate clearly that for the harmonic oscillator similar phases are assigned by the two techniques.

Morse oscillator

The Hamiltonian for this anharmonic oscillator is

$$H = \frac{p^2}{2m} + D(1 - e^{-\alpha s})^2$$

(2.8)

where the mass is 2000 au, $D$ is 0.1 au and $\alpha$ equals 1.0 au. The action-angle transform phase relationship for the Morse oscillator is

$$\phi = -\frac{\pi}{2} - \sin^{-1}([\frac{1 - \epsilon^2}{\epsilon}][1 - e^{-\alpha s}])$$

(2.9)

where $\epsilon$ is $\frac{E}{D}$, the ratio of total energy to the dissociation energy.

For the Morse oscillator I consider two limiting cases. The low energy limit is shown in Fig. 2.8. In this instance the total energy is one percent of the dissociation energy, and not surprisingly the results are virtually indistinguishable from the harmonic oscillator. Fig. 2.9 shows the high energy case in which the total energy
Figure 2.7  Harmonic oscillator scaled momentum (solid line) and phase (dashed line) values. In part A phase was assigned by the action-angle transform, while in part B it was assigned by the Hilbert transform.
Figure 2.8 Low energy limit of Morse oscillator ($\frac{E}{D} = .01$). The phase in part A is assigned by the action-angle transform, and in part B by the Hilbert transform.
is 0.9D. The effects of anharmonicity upon the momentum are clearly visible. The portion of time spent in the vicinity of the inner turning point for each oscillation is small. The lion's share of each oscillation is spent in the neighborhood of the outer turning point. In this anharmonic case there is a clear difference between the phases assigned by the action-angle and the Hilbert transforms. Each spans $2\pi$ in the course of an oscillation, but the action-angle transform distributes phase uniformly in time, while the Hilbert transform does not.

The Hilbert transform phase differs from that of the action-angle when the oscillator has significant anharmonicity, and the phase assigned by the Hilbert transform is clearly superior for coherent trajectory comparison. Fig. 2.10 shows a single cycle of anharmonic oscillation (the solid line) with both phase assignments superimposed. The action-angle phase (shown by a dot dashed line) is directly proportional to time, so most of the $2\pi$ phase values occur in the vicinity of the outer turning point (i.e. the transition from positive to negative momentum). Action-angle phase therefore suffers from the same limitations as time when the system is anharmonic, i.e. an inability to relate a phase angle to a unique stage of the oscillation. Depending upon the energy in the anharmonic oscillator (and so upon the degree of anharmonicity experienced), the phase angle assigned by the action-angle transform to (for example) the equilibrium location will vary from oscillation to oscillation as the energy in the mode changes. By contrast, the Hilbert transform (dashed line) distributes $\pi$ phase values near the inner turning point as well as near the outer. This can be verified by noting that the phase value assigned by the Hilbert transform to an equilibrium location (i.e. a momentum extremum) is $\pm \frac{\pi}{2}$. The action-angle phase at these locations is nearly $\pm \pi$. For the action-angle transform the exact phase value of the equilibrium location depends upon the degree of anharmonicity in the system, while for the Hilbert transform it does not. Thus, unlike the action-angle transform,
Figure 2.9 High energy limit of Morse oscillator \( \left( \frac{E}{D} = 0.90 \right) \). The phase in part A is assigned by the action-angle transform, and in part B by the Hilbert transform.
Figure 2.10  A single cycle of oscillation for a Morse oscillator with $\frac{E}{D} = .90$. The solid line is scaled momentum, the dot dashed line is action-angle transform phase, while the dashed one is Hilbert phase. The dotted lines demonstrate that at equilibrium (i.e. the extrema of momentum) the Hilbert phase is $\pm \frac{\pi}{2}$, while the corresponding action-angle phase is nearly $\pm \pi$. 
the Hilbert transform phase allows coherent comparison of trajectories, as a specific phase value can be uniquely associated with a particular stage of oscillation, and so with a fixed location on the PES. In this manner the behavior of orthogonal modes can be compared when the reaction coordinate is in a particular region of phase space irrespective of the arbitrary time indices of these occurrences.

Coupled oscillators

The final system considered is a harmonic oscillator coupled to a Morse oscillator, as follows:

\[ H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + V_1 + V_2 + V_c \tag{2.10} \]

where \( V_1 \) is the harmonic potential from part A, \( V_2 \) is the Morse potential from part B and the coupling potential is

\[ V_c = k_c s_1 (1 - e^{-\alpha s_2}) \tag{2.11} \]

where \( k_c \) is 0.025 au and \( \alpha \) is 1.0 au. Fig. 2.11 shows the scaled momenta for each oscillator along with the phases assigned by the Hilbert transform. Note that coupling in the system renders cycles of oscillation nonperiodic, and that some of the oscillations are perceptibly anharmonic, reflecting the structure of the generating Hamiltonian. Despite these complications the Hilbert transform assigns a physically meaningful phase to these local mode motions, in a system where the action-angle transform is no longer applicable.
Figure 2.11  Coupled Morse and harmonic oscillators. Part A shows the scaled momentum and Hilbert phase for the harmonic oscillator, and part B shows the scaled momentum and Hilbert phase for the Morse oscillator. The Hilbert phases are appropriate to the nonperiodic and slightly anharmonic oscillations of this Hamiltonian. The action-angle transform can not be applied to this case.
2.3.4 Implementation

As shown in Eq. 2.3, the analytical form of the Hilbert transform of a function $f(t)$ involves convolution of that function with $\frac{1}{\pi t}$ over an infinite range. This poses two potential complications in implementing the transform. First, a numerical implementation, which is restricted to a finite range, is necessarily only an approximation to the analytical form. Second, convolution operations, particularly of long series, are very demanding of computer resources. An alternative implementation that is more efficient replaces convolution of the time series $f(t)$ by $\frac{1}{\pi t}$ with the equivalent operations in the Fourier transform domain. Thus, one Fourier transforms $f(t)$ to $F(s)$ and $\frac{1}{\pi t}$ to $i\text{sgn}(s)$. One then inverse Fourier transforms the product $i\text{sgn}(s)F(s)$, yielding the equivalent of a time domain convolution [33].

By its finite nature, numerical implementation of the Hilbert transformation necessarily involves approximations, and as always with numerical techniques, care must be taken to prevent introducing artifacts. Most of these are consequences of the periodic nature of the Fourier transform, and proper treatment of edge effects will remedy them. Idiosyncracies of the Hilbert transform which can cause problems independent of FFT concerns are discussed next.

When generating phase values with the Hilbert transform one can use either coordinates or momenta to represent the waveform. Momenta, which vary about zero, are more easily utilized than coordinate data, which most often vary about a nonzero equilibrium value. (The Hilbert transform defines cyclic motion in terms of maxima, minima and zero crossings.) Should it be preferable to use coordinate data, one must subtract off the value of the equilibrium position. In either case, a sensible precaution to ensure a well behaved waveform consists of removing any residual DC level in the time series by setting the value of the zero frequency component of the Fourier
transform to zero.

Any attempt to assign a phase value to an intrinsically noncyclic motion will necessarily result in an unsatisfactory outcome since assignment of a phase presupposes oscillatory behavior. The action-angle transform fails when the energy in a given mode exceeds the dissociation energy, and the mode becomes capable of noncyclic motion. The Hilbert transform however will attempt to use all data given, but when the data include inherently noncyclic phenomena (such as motion across a transition state) the resulting values of $\phi$ are shifted with respect to the maximum or minimum of the motion. The solution to this problem is to back off of the approach to the transition state until the motion included in the data set to be transformed lies only within the range of typical oscillations. How large a portion of the final cycle must be omitted depends on the nature of the transition state and on the energy in the mode. For example, if the reaction coordinate involves cis to trans isomerization in a typical torsional double well potential the approach to the transition state is basically cyclical, and nearly all portions of the motion can be used. On the other hand, in systems where the reaction coordinate is a Morse oscillator and the energy is only slightly more than that of the dissociation energy, the approach to the transition state can be highly nonperiodic, and it may be necessary to omit all motion after passing the equilibrium position for the final time. In such a system reaction involves larger amplitude motion than that of ordinary oscillations, but more importantly the final approach to the transition state can occur over a span of time that approaches infinity as the energy in the reaction coordinate approaches that of the barrier. Therefore motion beyond the equilibrium point is inherently noncyclic and must be omitted from any analysis which seeks to assign phase values.
2.3.5 Conclusions

When the data are properly conditioned, the Hilbert transform is quite robust. I have used the technique to analyze local mode motions from systems ranging from a single Morse oscillator to polyatomic molecules with complex Hamiltonians. The Hilbert transform has the useful attribute of distributing phase angles equally throughout the oscillation (such that $\frac{\pi}{2}$ phase values span any quarter cycle), unperturbed by the degree of anharmonicity in the system. Therefore a phase assigned by the Hilbert transform may be interpreted with confidence in relation to the stage of oscillation. Coherent comparison of trajectories allows dynamical information to illuminate features of the PES by observing average trajectory behavior at turning points, equilibria, and elsewhere.

2.4 Phase conventions

In subsequent chapters continuous phase will be used extensively as a "progress of reaction" independent parameter. Oscillatory motions are intrinsically cyclic, so the phase origin for these motions is necessarily arbitrary. The following figures show the phase conventions used throughout this study. Fig. 2.12 shows typical vibrational motions within a Morse oscillator, and Fig. 2.13 is the corresponding phase space ellipse, each annotated with phase values. Tab. 2.1 summarizes the phase conventions.
Figure 2.12  Morse potential curve annotated with the corresponding momentum and phase values for a cycle of oscillation

<table>
<thead>
<tr>
<th>location</th>
<th>momentum</th>
<th>phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>outer turning point</td>
<td>p &lt; 0</td>
<td>0</td>
</tr>
<tr>
<td>near equilibrium</td>
<td>p &lt; 0</td>
<td>π/2</td>
</tr>
<tr>
<td>inner turning point</td>
<td>p = 0</td>
<td>π</td>
</tr>
<tr>
<td>near equilibrium</td>
<td>p &gt; 0</td>
<td>3π/2</td>
</tr>
<tr>
<td>outer turning point</td>
<td>p &gt; 0</td>
<td>2π</td>
</tr>
</tbody>
</table>

Table 2.1  Phase conventions used in this study.
Figure 2.13  The phase space ellipse of a Morse oscillator annotated by instantaneous phase values.
Chapter 3
A model for correlated motion

In this chapter I define the term “correlated motion” and propose a model for this phenomenon. The model makes a number of predictions regarding the expected behavior of correlated motions. I test these predictions with two molecules, HN$_3$, a molecule with strong couplings, and HONO, a molecule with weak couplings to the reaction coordinate.

3.1 Introduction

Previous work in this group and others [11] [12] [13] [14] [35] [36] [37] has shown that for many molecules some of the local modes execute a distinct pattern of motions immediately preceding reaction, akin to the steps of a formal dance. The pattern of interaction involves one or more local modes moving in synchronization with the reaction coordinate. In this “correlated motion” there exists a relationship between the phase of the local mode and that of the reaction coordinate, so for local modes with correlated motion a distinct and restricted set of points in phase space precedes reaction. (In subsequent discussions I use the term “state” to refer to a point in phase space, i.e. a space with separate dimensions for each local mode coordinate and momentum.) Correlated motion is restricted in that while it is ongoing, bundles of trajectories are nondivergent, exploring only a small and distinct portion of the accessible phase space. After several oscillations of the reactive coordinate when correlated motion has ceased the bundles of trajectories lose coherence and diverge, thereby exploring phase space more extensively.

Prior to this work typical means of identifying correlated motion has been to demonstrate non-statistical distributions in reactant or product states, or to com-
pare the time behavior of local modes from many trajectories, looking for consistent
patterns of motions [13]. When correlated motion exists, it manifests itself in the
motions of oscillators such that at various stages of the reaction process motion of a
particular oscillator will be restricted to a specific region of phase space [38], rather
than ranging over the full set of accessible values. DeLeón and coworkers describe
correlated motion in terms of “reactive cylinders” [21] [22] [23] [39], which our group
refers to colloquially as a “hose”, because for the duration of the correlated motion
trajectories cluster in phase space as a cylindrical hose. When the correlation ends
trajectories diverge exponentially and the hose ceases to be an identifiable entity [13].
I will return to this topic in greater detail in Chap. 6.

3.2 Definition of correlated motion

The existence of a restricted set of states preceding reaction is at first glance only
an obvious consequence of having a system governed by deterministic equations of
motion. For each state at the transition state there exists an immediate precursor
at one integration time step preceding reaction. This set of immediate precursors
is also limited when compared with the full range of bound states. Each immediate
precursor state has a unique precursor of its own. Working deterministically back from
the transition state along the paths of all possible reactive trajectories we traverse a
restricted subset of all energetically allowed bound phase space values. What makes
correlated motion interesting and nontrivial is that in some molecules, for a few cycles
of motion of some local modes, the set of all precursors is confined to a region of phase
space that is small and compact when compared to the full range of phase space that
is energetically accessible. Something about the process of reaction limits the range
of oscillator values at certain stages, resulting in trajectories that bundle together as
a hose. Some intriguing questions about correlated motion are:
• Why are the motions of some oscillators restricted, while others are not?

• Why do the oscillators exhibiting correlated motion follow the paths observed?

In the next section I will propose a model for correlated motion which addresses these questions.

3.3 A model for correlated motion

Consider a system with barely sufficient energy to react. There is only a single trajectory that can transit the lowest potential energy position of the transition state with essentially zero momentum. What are the necessary characteristics of this lowest energy reactive trajectory? In all oscillations preceding the final one, the reaction coordinate has less energy than that required for reaction. Since the system contains barely sufficient energy to permit reaction, this lowest energy reactive trajectory must be the most efficient one in gathering all possible energy from other modes. The oscillations preceding reaction must allow the lowest energy trajectory to visit regions of phase space with large couplings, so that energy may be transferred from orthogonal modes into the reaction coordinate, thereby enabling reaction. The lowest energy reactive trajectory must therefore follow a very specific path, i.e. the one that permits maximum energy transfer so that sufficient energy accrues in the reaction coordinate to permit crossing the transition state.

Let us now slightly increase the energy available to the system, so that the energy required for reaction is a somewhat smaller proportion of the total energy. This corresponds to sampling a small region at the transition state, rather than a single point. These nearly lowest energy trajectories are also constrained to visit regions of phase space with high couplings to gather sufficient energy to react. Whether or not a system demonstrates correlated motion (i.e. an organized pattern of restricted states)
depends upon the nature of the Hamiltonian. If the Hamiltonian is such that one or more orthogonal modes couple strongly to the reaction coordinate, and the regions of strong coupling are restricted, then the system will demonstrate correlated motion, because all the nearly lowest energy trajectories will traverse substantially the same region of phase space as the lowest energy trajectory. However, if the Hamiltonian is such that no mode couples strongly to the reaction coordinate, and such coupling regions as do exist are small and scattered, then the next to lowest energy trajectories may easily diverge from the vicinity of the lowest energy trajectory, and no correlated motion will be observed.

In subsequent sections I will use studies of HN_3, which shows strongly correlated motion, and HONO, which shows no correlated motion, to illustrate the preceding two cases. (It should be noted that both of these molecules react in a non RRKM manner, implying that obeying RRKM kinetics is a separate issue from the presence of correlated motion.)

In light of the preceding arguments regarding the behavior of low energy reactive trajectories, my proposed model for correlated motion is as follows:

*Correlated motion is a consequence of energy transfer from orthogonal modes into the reaction coordinate via high coupling regions. When these high coupling regions of the Hamiltonian are compact in comparison with the full range of phase space values accessible, the molecule will exhibit correlated motion.*

This model for correlated motion makes a number of testable predictions, including:

1. Coupling during the final stages of reaction should be greater than in preceding oscillations.

2. Modes that do not exhibit correlated motion are ones that do not couple to the
reaction coordinate. Conversely, modes with correlated motion should couple to the reaction coordinate.

3. The extent of correlated motion should correspond to the degree of coupling between the reaction coordinate and the orthogonal mode.

4. In systems with correlated motion, the strength of that correlation should decrease with increasing energy in the system.

To demonstrate the validity of several of these predictions I utilize coherent comparison of trajectories, as described in Chap. 2. Oscillator phase is assigned following the conventions set forth in Sec. 2.4. Although the Hilbert transform finds use in many branches of science, this is the first time it has been used to implement coherent comparison of trajectories. In this and subsequent chapters I apply the Hilbert transform (as outlined in Sec. 2.3.4) to compare trajectories in phase, thereby revealing underlying order to reaction dynamics which is not evident in a time analysis. Evidence for this underlying order is of critical importance to both development and verification of the proposed model for correlated motion.

3.4 HN₃: A system with strongly correlated motion

To develop and test this model I have created a number of diagnostics, both qualitative and semiquantitative, for correlated motion. In the following sections I will explain the significance of these diagnostics and use them to test the predictions for this model. Since the focus of this chapter is the model for correlated motion, I have deferred discussion of the HN₃ Hamiltonian to Chap. 6, to which the reader is referred for details regarding the form of the Hamiltonian used.
3.4.1 Verifying prediction 1.

To test the first prediction I need a measure of coupling. One such simple measure is to define coupling energy \( E_c \) as the absolute energy difference between the full Hamiltonian \( H \) and the Hamiltonian \( H_0 \) in which all coupling terms have been set to zero:

\[
E_c = |H - H_0|
\]  

A fundamental test of this model for correlated motion is to compare values of the coupling energy during the final oscillation to those in preceding oscillations. Fig. 3.1 shows \( E_c \) versus oscillator phase for one hundred HN₃ trajectories when the available energy is 1.05\( E_b \), where \( E_b \) is the barrier energy to the N-N dissociation. As will be shown shortly, these trajectories exhibit strongly correlated motion. There is clearly on average a much higher level of coupling energy in the final oscillation (\( \phi = 0, 2\pi \)) than in the preceding one, in accordance with the prediction.

However, Fig. 3.1 reveals other interesting trends. In the next to last cycle (\( \phi = 2\pi, 4\pi \)) the coupling energy for almost all trajectories is much less than that of the final cycle, and occurs at random stages within the oscillation. In stark contrast, during the last oscillation prior to reaction (\( \phi \approx 0, 2\pi \)) the coupling is both large and systematic. For phases in the range of \( \frac{\pi}{2} \) to \( 2\pi \) there is a clear pattern. \( E_c \) is nearly zero at \( \phi = \pi \) and \( 2\pi \), and reaches peak values at \( \frac{\pi}{2} \) and \( \frac{3\pi}{2} \). Relating these phase values to motion of the oscillator reveals that during the last cycle coupling energy is least at the inner and outer turning points of the oscillation, and is greatest near equilibrium. The greatest coupling occurs when the momentum is maximum, suggesting that kinetic coupling plays a significant role in this system, even though the potential energy function for this Hamiltonian includes sizable potential coupling
Figure 3.1  Coupling energies for 100 HN₃ trajectories with 1.05E₅ as a function of continuous reaction coordinate phase.
terms (See Chap. 6 for a discussion of the HN$_3$ Hamiltonian). Little emphasis should be placed upon the observations for the phase range of $\phi = 0$ to $\pi$, since (as was discussed in Chap. 2) these phase values are susceptible to edge effects from the transform. It is therefore difficult to ascertain if the loss of organization in $E_e$ in this range is real or is an artifact of the transformation to phase.

3.4.2 Verifying prediction 2.

Testing the second prediction requires a qualitative diagnostic for correlated motion. I use an intuitive diagnostic that permits direct visualization of the correlation between the modes. For reasons that will become evident I call this diagnostic a "tornado" plot. The "progress of reaction" independent variable for tornado plots is the reaction coordinate arc length, as was described in Chap. 2. By plotting local mode coordinate and momentum values against reaction arc length I obtain an approximately spiral space curve which is the motion of that oscillator for a single trajectory. The spiral path of each trajectory corresponds to a progressive unfolding of the motion of an oscillator around its phase space ellipse. Although the data are plotted in terms of coordinate and momentum, the plots can readily be interpreted in terms of an $r, \phi$ coordinate system, where $r$ and $\phi$ are the coordinates described in Chap. 2 associated with the Hilbert transform of the trajectory data. When a local mode oscillator has small energy, the radius $r$ of the spiral will be small. As energy in the oscillator increases so does the value of $r$. When a large number of trajectories with similar constraints upon their initial conditions are plotted together, two patterns emerge. For each local mode oscillator the trajectory phases either vary randomly, so that a featureless cylinder results, or there is a convergence of phases such that for a certain span of the reaction process trajectories tend to cluster together in restricted regions of phase space. It is the latter case that we identify as correlated motion.
When trajectories are unconstrained their relative phases are random, and a set of trajectories will tend to generate a featureless cylinder as the trajectories fill space. However, if the oscillator is involved in transferring energy then the oscillator phases are constrained. Reactive trajectories must all visit similar regions of phase space to effect the energy transfer. For this reason certain oscillator phase relationships are preferred and trajectories tend to bunch together. For systems with correlated motion the reactive cylinder has clear features which in some instances resemble a twister, hence the name "tornado" plots.

Fig. 3.2 shows tornado plots of all local mode oscillators for the final two oscillations leading to reaction for HN₃ when the energy in the system is 1.05E₄. (A reaction progress value of zero corresponds to the transition state.) The two forms of cylinders are clearly shown. The featureless cylinders are for the H-N and torsional modes, neither of which is expected a priori to interact with the reaction coordinate, since the H-N stretch is isolated from the other modes by its high frequency and torsion by its symmetry. Neither mode interacts with the reaction coordinate, and neither shows correlated motion, in accordance with prediction two. But what of the modes which do interact? When oscillators interact energy is transferred, thereby changing the radius of phase space gyration. Those modes which interact therefore display some systematic variation in the diameter of the cylinder as reaction progresses.

The mode with the greatest degree of organization is the reaction coordinate, the N-N stretch. At the transition state (arc length of zero) all trajectories are tightly clustered in coordinate and momenta and almost all energy is potential so the ranges of coordinate and momenta values are greatly restricted. As the trajectories leave the transition state in backwards time, heading back towards bound states, initially they all follow a similar path, with divergence between the paths only becoming significant after a full cycle of oscillation. However, as the reaction coordinate, the
Figure 3.2 Tornado plots of HN₃ local modes when the total energy is 1.05E₉
N-N stretch is the reference for correlation, so organization in this mode does not constitute correlated motion.

It is the final three modes that are of greatest interest. The N=N stretch in particular shows a very strong pattern of organization amongst the trajectories. At the transition state the radius of gyration for this mode is very small when compared to its radius at an arc length of 20, which corresponds to the final half cycle of oscillation of the reaction coordinate. We know from previous work [13] that the N=N mode transfers energy impulsively into the reaction coordinate. The N=N tornado plot strikingly illustrates this energy transfer by the change in radius, but also shows by the phase convergence of the trajectories that the conditions which permit the energy transfer are limited. Based on this diagnostic one would argue that in this system the N=N stretch shows strong correlation, while the H-N-N and N-N=N bends show weaker correlation to the reaction coordinate.

In qualitative terms the tornado plots verify both aspects of prediction two. The modes that do not interact with the reaction coordinate (the H-N stretch and torsion) show no correlation, while those that do interact with the reaction coordinate (the N=N stretch as well as the H-N-N and N-N=N bends) show at least some degree of correlation. However, a more quantitative diagnostic of correlated motion is needed to test the third prediction.

3.4.3 Verifying prediction 3.

In Chap. 2 I showed that unwrapped phase of the reaction coordinate is an independent parameter which allows coherent comparison of trajectories. When trajectories are so compared one can look for similarities in behaviour of the orthogonal modes when the reaction coordinate is in roughly the same region of phase space, regardless of the time of that occurrence. (Coherent comparison aligns trajectories
by phase of the reaction coordinate, but those oscillations can still differ in amplitude, thereby allowing some variation in the phase space location of the reaction coordinate.) Coherent comparison of trajectories is key to demonstrating the validity of prediction 3.

Unwrapped phase is the independent parameter which will ultimately lead to the quantitative diagnostic for correlated motion which is needed to test the third prediction of the model. A simple diagnostic of local mode behavior is to assign a continuous (i.e. unwrapped) value of phase to the motion of all oscillators beginning at the transition state and running backwards towards bound states. When the phase values of an orthogonal mode are plotted as a function of the phase of the reaction coordinate the result is as is shown in Fig. 3.3, and will hereafter be referred to as a "horsetail" plot. Roughly one hundred trajectories with an energy of 1.1E₆ were plotted for many oscillations of the reaction coordinate. Recall that the tornado plots suggest that in HN₃ the N=N mode is strongly correlated to the reaction coordinate, while N-N=N and H-N-N are weakly correlated to the reaction coordinate, and H-N is uncorrelated. Recall also that correlated motion manifests itself as a restriction in observed phase values [38]. The local modes are independent, so for any given value of the reaction coordinate the phase values of the orthogonal mode should range over at least 2π in the absence of correlation. Convergence of observed phase values to a range of less than 2π is evidence of correlated motion. In Fig. 3.3 the N=N oscillator shows strong phase convergence (hence strong correlation) up to φ = 2π for the reaction coordinate. The horsetail plot for N-N=N suggests some correlation in the phase range between π and 3π in the reaction coordinate as indicated by a greater concentration of trajectories in the lower part of the distribution, while the H-N-N plot shows little and the H-N plot shows no evidence of correlation.

Horsetail plots are consistent with tornado plots in assessing the presence or ab-
Figure 3.3  Phase of a local mode oscillator versus phase of the reaction coordinate for the final four cycles of oscillation. There are 100 HN₃ trajectories with 1.1E₆ total energy.
sence of correlated motion, but both are qualitative. A semi-quantitative measure of correlated motion can be extracted from the data of a horsetail plot as follows. I create a grid of bins whose $x$ values correspond to short ranges of values of the unwrapped phase of the reaction coordinate, and whose $y$ values are short ranges of the wrapped phase of an orthogonal coordinate. Each phase pair for every integration cycle and every trajectory is assigned to the appropriate bin. The result is a two-dimensional histogram of phase relationships between the reaction coordinate and the orthogonal mode. If there were no systematic relationship between the phases of these two modes every bin would contain roughly an average number of points determined by the number of trajectories in the dataset. However, if the orthogonal mode in this system is correlated with the reaction coordinate (which is manifest as a convergence of phases) then certain bins corresponding to favored phase relationships gain population at the expense of those bins corresponding to unfavorable phase pairings. To determine which phase relationships are favored, and to what extent, I contour the binned data grid, identifying those phase relationships whose bins contain twice, three times and four or more times the expected number of data points. In the absence of correlation this contour plot would have only small random features because (given a sufficient number of trajectories) the population of each bin will have only small random fluctuations about the average value. The contoured phase map for the H-N stretch mode in Fig. 3.4 illustrates the random nature of a phase map in the absence of correlated motion.

When correlated motion is present the contoured phase map identifies which phase pairings are favored and quantifies the extent of the correlation. This is the tool by which I will test prediction three of the correlated motion model. Fig. 3.4 has contoured phase maps for orthogonal modes of HN$_3$ which show variation in correlation from none for the H-N stretch to strong for the N=N stretch. This measure of corre-
Figure 3.4 Contoured phase maps of the local modes for 100 HN$_3$ trajectories with 1.1E$_6$ total energy. Note that the local mode phase is modulus $2\pi$ while that of the reaction coordinate is continuous. The contours respectively enclose areas with 2,3 and 4 times the average population, thus identifying favored phase relationships.
lated motion agrees with, and quantifies the results of the tornado plots. The N=N stretch local mode oscillator has the greatest degree of correlation, demonstrated by the behavior of the highest population contour. For this local mode there are relatively many bins that contain four or more times the average population, and these bins show a very well defined trend. The phase relationship between these two modes is clearly defined and closely obeyed, illustrating strong correlation. Turning now to the phase map for the N-N=N bending local mode we find that the area encompassed by the highest population contour line has a smaller extent than that of the N=N mode, and that the pattern of favored phase pairings, while not as sharply defined as that of N=N, is still distinct. I therefore conclude that the N-N=N bending mode shows moderate correlation. In contrast, the phase map for the H-N-N bending mode has few phase pairings with populations exceeding three times the average value. The pattern of phase pairings enclosed by the contour for twice the average population is indistinct. H-N-N is a mode with only weak correlation, and as discussed previously, the H-N stretching mode has no correlation with the reaction coordinate.

In summary, the results of prediction three are partially verified. The interactions of most local modes with the reaction coordinate are consistent with the local mode composition of the N-N normal mode (see Tab. 6.2). Full verification requires an independent means of measuring the coupling between a given orthogonal mode and the actual reaction coordinate (not just the nearest local mode), which remains to be developed.

Analysis of phase maps

Beyond simply delineating the existence of favored phase pairings, the contoured phase maps of Fig. 3.4 reveal interesting insights into the nature of preferred phase relationships during the process of reaction. Examining first the map for the N=N
local mode we find that the N=N oscillator is in a roughly 1:1 resonance with the N-N oscillator over the phase range of $\phi = \pi$ to $3\pi$ of the reaction coordinate. There is clearly a change of behavior at $\phi = \pi$, and the relationship changes to a 1:2 resonance. By cross referencing to the corresponding tornado plot in Fig. 3.2 it becomes apparent that the change in behavior at $\phi = \pi$ occurs when the energy is impulsively transferred from this mode into the reaction coordinate. The N=N mode shows some correlation during the next to last oscillation of the reaction coordinate, and strong correlation during the final cycle, which encompasses nearly three cycles of N=N oscillation. Turning to the N-N=N oscillator we find measurable correlation during the last two cycles of oscillation of the reaction coordinate, which is strong during the final cycle. This corresponds to roughly one and a half cycles of the N-N=N bend (which is a lower frequency motion). During the final cycle prior to reaction the correlation is strongest and N-N=N and N-N are in a nearly 1:1 resonance but are roughly $\frac{\pi}{2}$ out of phase.

### 3.4.4 Verifying prediction 4.

With contoured phase maps as a quantitative measure of correlated motion I am able to assess the validity of prediction four, namely that correlated motion should decrease with increasing energy. Fig. 3.5 through Fig. 3.9 show tornado plots for each local mode for trajectories ranging in energy from $1.1E_b$ up to the H-N dissociation limit, which is $3.2E_b$. This qualitative assessment of correlated motion shows clearly the decrease in the organization of orthogonal mode trajectories as the energy in the system increases.

Let us focus on the mode with greatest correlated motion. Fig. 3.10 contains contoured phase maps for the N=N local mode which span this energy range. At an energy of $1.1E_b$ the phase convergence is strict and is long lived, lasting up to one
Figure 3.5  Tornado plots of HN₃ local modes when the total energy is 1.1E₆.
Figure 3.6  Tornado plots of HN$_3$ local modes when the total energy is 1.5E$_6$
Figure 3.7  Tornado plots of HN₃ local modes when the total energy is 1.8E₆
Figure 3.8 Tornado plots of HN₃ local modes when the total energy is 2.2E₆
Figure 3.9  Tornado plots of HN₃ local modes when the total energy is 3.2E₅
Figure 3.10  Contoured phase maps of the N=N stretch local modes for 100 HN$_3$ trajectories with energies varying between 1.1E$_b$ and 3.2E$_b$. 
and a half cycles of the N=N oscillation. An increase in energy to 1.8E₆ is sufficient to relax the phase convergence requirement to the point where the bins containing greater than four times the average number of data points no longer form a continuous domain. When the energy is further increased to 2.2E₆ correlation has relaxed to the point where the most favored phase pairings are few and scattered. With a total energy of 3.2E₆ correlation has all but vanished. The remnants of correlated motion persist as an echo of the strong constraint at lower energies, but the most strongly favored phase pairings are all but gone. In this energy range the reaction coordinate is no longer strictly dependent upon impulsive energy transfer from the N=N stretch to react. Certainly energy transfer from the N=N local mode is one important means by which reaction occurs, given the evidence of the residual correlation shown, but by the same token, it is no longer the condition sine qua non for reaction. Apparently at this high energy the reaction coordinate can also gain sufficient energy to react by coupling to other modes.

3.4.5 The nature of HN₃ couplings

Having postulated that couplings between the reaction coordinate and orthogonal local modes are responsible for the correlated motion exhibited by HN₃, I must identify the portion of the Hamiltonian that gives rise to correlated motion. Since it is by far the strongest component, I will focus on the correlated motion of the N=N local mode. This mode couples to the dissociative N-N mode in both the potential and the kinetic portions of the Hamiltonian. When trajectories are run without the potential couplings the reaction dynamics are virtually unchanged. However, when trajectories are run with the full Hamiltonian, save only that the G matrix element that couples the N-N momentum to the N=N momentum is zero, the resulting reaction dynamics are greatly changed. As Fig. 3.11 shows, zeroing of the appropriate kinetic coupling
Figure 3.11  Tornado plots of HN₃ local modes when the G matrix term coupling $p_{N-N}$ to $p_{N=N}$ is set to zero. (Total energy is $1.1E_4$.)

term destroys the correlation between N=N and the reaction coordinate, with N=N showing the featureless plume of an uncoupled mode. Removing this coupling has altered the topography of the maximum complexity PES, and changed the path taken by reactive trajectories.

3.5 HONO: A system with no correlated motion

HONO is a molecule of particular interest, and will be treated at length in a subsequent chapter (so for details of the HONO Hamiltonian see Chap. 5), but a short introduction is required at this point to show why HONO is relevant to my model for correlated motion. Both experimental [40] and theoretical [41] investigations of this molecule have found substantial (order of magnitude) differences in the rates for cis to trans isomerization versus that for trans to cis, despite the fact that the local minima in the PES for these two isomers are nearly identical. (The difference in barrier height is only about 0.6 kcal/mole [41].) The isomerization reaction for HONO differs from the HN₃ dissociation in several important respects. For this molecule the reaction coordinate is the torsional mode, which is isolated by symmetry from all other local modes. Normal mode analysis shows that the torsional normal mode is identically the local mode so that to first order there are no couplings between the reaction coordinate and the orthogonal modes. Clearly couplings must exist, or there could be no energy transfer into the reaction coordinate, and so no reactions, but we must look for the couplings in higher order derivatives. Such terms are apt to be small, so my model for correlated motion predicts that HONO will show no correlated motion, because there are no local modes that couple strongly to the reaction coordinate.

The argument concerning the path of the minimum energy trajectory is as valid for this system as for any other. There can be only a single trajectory with barely sufficient energy to react, and to do so it must extract all possible energy from all
orthogonal modes. Correlated motion fails in this system when we consider the nearly minimum energy reactions. Couplings in this Hamiltonian must be of small extent and scattered throughout the PES, because at energies only slightly greater than the minimum, reactive trajectories have many choices of paths leading to reaction and so diverge from the path of the minimum energy trajectory. Figures 3.12 through 3.15 support the preceding argument. Fig. 3.12 shows tornado plots for the final oscillation in the cis to trans isomerization when the energy in the system is only 1.02E₄. At this low energy level these trajectories are good approximations of the minimum energy trajectory (which as a practical matter is itself unobtainable since the period of reaction is infinite). In this low energy limit we see slight phase convergence in some of the modes, and we see changes in diameter of the reactive cylinder as energy is transferred. However, proceeding on to Fig. 3.13 we find that by increasing the energy in the system to only 1.1E₄ the hints of correlation contained in the slight phase convergences of the low energy limit have already essentially disappeared. (Recall that for HN₃ evidence of correlated motion persisted up to energies of 3.2E₄.) Figures 3.14 and 3.15 show substantially the same results for the trans to cis isomerization, except that the lowest energy trajectories show even less residual correlation than the corresponding cis ones. Apparently we must look elsewhere to explain the order of magnitude differences in the two rate constants. I will revisit this issue in Chap. 5.

In conclusion, HONO shows only ephemeral correlations, which vanishes at energies as low as 1.1E₄. Symmetry considerations prohibit any orthogonal mode from coupling strongly to the reaction coordinate, so these results are entirely consistent with prediction two of the model for correlated motion.
Figure 3.12  Tornado plots of cis HONO local modes when the total energy is 1.02E₄
Figure 3.13  Tornado plots of cis HONO local modes when the total energy is $1.1E_0$
Figure 3.14  Tornado plots of trans HONO local modes when the total energy is 1.02Eₘ
Figure 3.15  Tornado plots of trans HONO local modes when the total energy is 1.1E6
3.6 Conclusion

I have proposed a model for correlated motion as a consequence of energy transfer between modes. To gain sufficient energy to clear the transition state the reaction coordinate must acquire energy from orthogonal modes, and energy can be transferred between modes only when the modes couple. (For this reason modes that do not couple to the reaction coordinate show no correlated motion.) If the form of the Hamiltonian is such that regions which permit strong coupling to the reaction coordinate are well defined and of limited extent in phase space, then the result is correlated motion. Reactive trajectories cluster around the path of the minimum energy trajectory, thereby visiting regions of phase space with large couplings and large energy transfers. Reactive trajectories are therefore constrained in their motions, and it is this restriction that we term correlated motion. The form of the specific path for any particular system will depend upon the Hamiltonian and the details of its couplings.

All available tests to date are consistent with the predictions of this model for correlated motion. Future work may include developing an independent means to assess coupling between the reaction coordinate and local modes, and to explore the possibility of a priori assessments of correlated motion based on analysis of couplings in the Hamiltonian.

Correlated motion may be considered to be a consequence of resolving the reaction coordinate into its local mode components. When the reaction coordinate is a pure local mode, such as in the case of isolation by symmetry or frequency considerations, there is no correlated motion (e.g. HONO), since no orthogonal mode contributes substantially to the reaction coordinate. However, when the reaction coordinate is a linear combination of local modes then the component local modes will show
correlation proportional to their contributions to the reaction coordinate. When
the reaction coordinate is a nearly equal mix of two local modes, such as is the
case for HN\textsubscript{3}, then there is strongly correlated motion. Local modes showing lesser
degrees of correlation make a smaller contribution to the reaction coordinate. If this
interpretation of correlated motion is correct (and more work is needed to test this
conjecture), then correlated motion may occur to varying extents in many systems,
depending upon how frequently the reaction coordinate is a combination of local
modes.
Chapter 4
RRKM theory and correlated motion

In this chapter I explore the nature of RRKM theory, focussing on the key RRKM assumption that all states are equally likely to react. I reconcile the apparent conflict between this assumption and correlated motion by proposing a novel variant of phase space which serves as a bridge between kinetics and dynamics.

4.1 Introduction

RRKM (Rice Ramsperger Kassel and Marcus) theory is one of the most elegant in chemistry, permitting calculation of rate constants of very good accuracy from remarkably few parameters [42]. It is a sign of the success of this theory that molecules which are exceptions are sufficiently rare as to merit individual study (hence the proliferation of titles in the literature featuring the term “non RRKM”.) While RRKM theory is broadly applicable, one active area of research consists of creating refinements to increase its accuracy and extending it to cover the exceptional cases [23] [43] [44]. Given both the success and the adaptability of the theory it is only natural that chemists should greet with healthy skepticism any claims of phenomena that appear to contradict its underlying assumptions. RRKM theory is a unimolecular microcanonical transition state theory [8] and as such is based on a number of assumptions regarding the process of chemical reaction. In its most pristine form the essential RRKM equation is [8]

$$k(E) = \frac{1}{\hbar} \frac{G(E^\dagger)}{N(E)}$$

(4.1)

where $G(E^\dagger)$ is the sum of states at the transition state, and $N(E)$ is the density of states for the reactant portion of phase space. The equation asserts that the mi-
crocanonical rate constant $k(E)$ is proportional to the ratio of the flux across the transition state $G(E_\dagger)$ to the total number of bound states $N(E)$. (The flux term $G(E_\dagger)$ may in turn be regarded as the number of states capable of reacting within a time $\delta t$.) What are the underlying assumptions in this equation? Consider the right hand term $k(E)$, which is constant for a fixed energy. This limits consideration to microcanonical systems which obey first order kinetics, since only for these systems will $k$ be constant at all times for a particular energy. In this simplest formulation *RRKM theory is only applicable to unimolecular reactions which obey first order kinetics*. Therefore the constraints posed by the $k(E)$ term are:

1. A microcanonical system.

2. First order kinetics.

On the left hand side the requirements imposed by the $G(E_\dagger)$ term are:

3. The existence of a transition state.

4. Reactive trajectories cross the transition state only once.

The necessity for a transition state is self evident. The fourth constraint arises because the fundamental RRKM ratio depends upon the flux across the transition state being equal to the number of reactions, and recrossings upset that relationship. Finally, aside from reiterating the microcanonical constraint, the $N(E)$ term requires:

5. All bound states are reactive.

The final constraint prohibits trapped trajectories, as those will contribute to the total number of bound states $N(E)$, but not to the reactive flux $G(E_\dagger)$, thereby upsetting the ratio.
As expressed above, all of the fundamental RRKM constraints are consistent with the existence of correlated motion (i.e. a restricted set of states immediately preceding reaction). Confusion arises because requirements 2 and 5 are often combined in a statement similar to the following; RRKM theory requires that all states are equally likely to react. (Hereafter I will use the term "the RRKM assumption" to refer to this statement.) This assumption is in apparent contradiction with the observed phenomenon of correlated motion, and in the balance of this chapter I show that the preceding statement is an inaccurate representation of RRKM requirements (and propose an alternative, more accurate formulation), and show that RRKM theory is consistent with correlated motion.

To resolve this apparent conflict it is necessary to explore in some detail the physical significance of both the RRKM assumption and correlated motion. In Chap. 3 I explored the phenomenon of correlated motion in some detail, showing that for some molecules a degree of correlated motion is inevitable. In the following section I develop arguments regarding the relationship between RRKM theory and the structure of phase space which illuminate the nature of the RRKM restriction. Once the true purpose of the RRKM assumption is shown, it is easily demonstrated that RRKM theory is in fact compatible with correlated motion.

4.2 RRKM theory and phase space structure

Although RRKM theory is often referred to as a unimolecular rate theory, it is more appropriately described as a first order rate theory. This distinction will become important in subsequent discussions as we examine the RRKM assumption in greater detail. In an appendix devoted to calculation of RRKM rate constants I show that for the classical microcanonical case \( N(E) \) is equivalent to the area of the constant energy hypersurface which is the set of all possible reactant states. Subsequent arguments
rely upon the observation that the RRKM rate constant depends on the number of states that are capable of reacting, i.e. the area of the hypersurface. (For a more complete treatment of the derivation of classical RRKM theory, as well as several techniques for calculating RRKM rate constants please see the RRKM appendix.)

To reconcile correlated motion with RRKM theory we need to take a closer look at what this assumption really means, and what constraints it actually places on the system. For the sake of simplicity the following arguments pertain to the microcanonical case, but are extensible to the canonical case in the usual manner.

4.2.1 Reordering phase space

An important part of resolving the central contradiction between RRKM theory and correlated motion consists of constructing a bridge between kinetics, the province of RRKM theory, and dynamics, the domain of correlated motion. Phase space proves to be a useful intermediary. In the following discussion I develop arguments regarding a new reordering of phase space that has useful properties in terms of relating kinetics and dynamics. The reordering is fundamentally a rearrangement of phase space points indexed by time to the transition state and by the trajectory to which a given point belongs.

Since RRKM theory pertains specifically to unimolecular reactions, those will form the basis for subsequent discussions. Consider the following thought experiment; Select an arbitrary point $A$ in phase space. Since the system in question is both unimolecular and has sufficient energy to react, $A$ is a member of a continuum of phase space points (related by the equations of motion) which run from the transition state into the bound region of phase space and then ultimately back out into the unbound region. In this chapter I will refer to such a set of points as a trajectory. To satisfy RRKM requirements, each trajectory must cross the transition state exactly twice,
Figure 4.1 Example of a trajectory beginning and ending at the transition state
once in the direction of bound states, and once towards unbound states. (To cross more than once heading towards unbound states invalidates the flux relationship, while failure to cross the transition state at all will result in a trapped trajectory, which violates the requirement that all bound states in $N(E)$ are reactive.) Fig. 4.1 shows an example trajectory.

Our arbitrary point thus becomes a member of a set of phase space points running from the transition state back to the transition state. Every point in phase space is a member of a unique nonintersecting trajectory with a specific duration. In principle one can order trajectories by duration, and can map all points in a multidimensional phase space into a two dimensional representation. If all trajectories were of equal duration phase space would map into two dimensions as shown in Fig. 4.2 where each horizontal line represents a single trajectory.

Fig. 4.2 represents a rearrangement of phase space so that every point is shown by its time proximity to the transition state. To obtain the number of reactions as a function of time one can integrate the distribution with respect to time. To do so however requires assigning an appropriate $\delta y$ increment between trajectories. If $\delta y$ is selected such that the area of the distribution is equal to the total number of bound states $N_0$, then the distribution is properly normalized, and integration from zero to $t$ yields the cumulative number of reactions $N$. Integration of Fig. 4.2, the trajectory map, results in the relationship shown in part A of Fig. 4.3 for the number of reactions as a function of time. The fraction of accessible phase space points that react at any time comes from dividing by $N_0$, which is the area of the map and corresponds to all points in phase space. The fraction unreacted at any time is $\frac{A}{A_0} = 1 - \frac{N}{N_0}$, and is shown in part B of Fig. 4.3.

Fig. 4.3B shows a linear decay curve, and so is clearly not representative of first order reactions, which are characterized by decay curves corresponding to a single
Figure 4.2  Equal time duration trajectories
Figure 4.3 Part A is the number of phase space points which have undergone reaction, as a function of time, and part B is the proportion of phase space points which have yet to react.
exponential. The starting assumption that all trajectories have equal duration has no physical validity. However, the thought process may be reversed, so that we can proceed from the observation of exponential decay for first order reactions to infer the distribution of trajectories for a given system. Consider a first order reaction characterized by a reaction rate constant $k$. The corresponding decay curve is $y = e^{-kt}$, shown in Fig. 4.4A. The curve in Fig. 4.4A can be inverted to yield instead the fraction of reactions as a function of time $\frac{N}{N_0} = 1 - \frac{A}{A_0}$, whose equation is $y = 1 - e^{-kt}$, as shown in Fig. 4.4B.

Recall that the cumulative number of reactions as a function of time was the integral of the phase space time distribution map Fig. 4.2, so we can obtain the time distribution map for this system by differentiating $y = 1 - e^{-kt}$, the cumulative number of reactions, with respect to time, obtaining $\dot{y} = ke^{-kt}$. This curve marks the boundary for trajectory durations for a first order reaction with rate constant $k$. As Fig. 4.5 illustrates, when trajectories for this system are ordered by duration, they fill the space under the $y = ke^{-kt}$ curve.

Fig. 4.5 is the time distribution of phase space points that will result in a reaction rate of $k$. What is the importance of this distribution? This mapping is essentially a way to emphasize that phase space points have different time proximities to the transition state. While the probability of reacting per unit of time decreases exponentially, the (time independent) probability of reacting is the same for every point. Given sufficient time (and the RRKM prohibition of bound trajectories), each point in phase space will evolve until it encounters the transition state, so the probability of reacting is in fact a certainty, therefore all points have an equal probability of reacting, namely one. What then is the purpose of the RRKM assumption requiring all phase space points to have an equal probability of reacting? It appears that this requirement is satisfied trivially. However, the requirement is a valid one, but is one
Figure 4.4  Part A is the decay curve for first order reaction, and part B is the proportion of phase space points which have reacted versus time for a first order reaction.
Figure 4.5 The time duration distribution of trajectories for a first order reaction
that needs to be stated in a more careful manner. The assumption that all phase space points have an equal probability of reacting is simply a safeguard restricting the systems in question to first order behavior by disallowing systems with internal bottlenecks or with trapped trajectories, both of which we now consider.

4.2.2 Hamiltonians with bottlenecks

The energy hypersurface of the Hamiltonian in the previous case can be visualized as a roughly spherical balloon, where the mouth of the balloon represents the transition state. Any particular initial conditions on this surface can be propagated in time and will eventually encounter the transition state and so react. The important aspect here is that no phase space point encounters greater hindrance to reaching the transition state than does any other. However, if instead of being roughly spherical our energy hypersurface balloon suffers an embolism the picture changes dramatically. Consider now a hypersurface with a restricted set of points which in order to react must traverse not only the transition state but also an internal bottleneck, as shown in Fig. 4.6.

The trajectories for these points consist of two stages, the first being to traverse the internal bottleneck and so escape the restricted zone, and the second, once having entered the main surface, being to locate the transition state and react. In terms of the previously developed map of phase space trajectories, two types of trajectories now exist. Trajectories residing solely in the main region of phase space have a distribution corresponding to one rate constant. Trajectories residing in part in the restricted region have a different rate constant, reflecting their need to traverse not one, but two constrictions in phase space. In general there will be overlap in the duration of trajectories of each type, so the observed decay curve is a complex one.

The rate constant for trajectories within the restricted region depends upon not
Figure 4.6 Isoenergy contour for a Hamiltonian with an internal bottleneck.
one, but two processes. These trajectories must first escape the restricted region, and then react. The rate constant for the first step depends upon the narrowness of the internal constriction, which in the limit can reach zero, resulting in strictly trapped motion for the set of phase space points which now have no access to the transition state. (Davis et.al. [16] [17] have developed theories for identifying internal bottlenecks and for calculating flux across them.) A system with an internal bottleneck is therefore characterized by a nonlinear logarithmic decay curve. Different regions on this decay curve correspond to the interactions of the rate constants for the processes involved. Fig. 4.7 shows the curved nature of a logarithmic decay curve when there are two competing first order processes.

Although only one molecule is involved, such systems violate the requirements of first order kinetics, namely that the decay curve be fit by a single exponential. When a single exponential is insufficient this is an indication that some trajectories require two or more distinct processes in order to react. The RRKM assumption that all states have equal probability of reacting may instead be better phrased as no reactive state may encounter greater hindrance to reaction than any other. The purpose of this RRKM assumption is to exclude systems such as the preceding from consideration because they have no single well defined rate constant. Examples of molecules which fit this pattern include those with hydrogen bonded to a much heavier atom. The frequency of this vibration is often much higher than that of any other vibration in the molecule. This precludes resonant energy transfer so the coupling of that mode to the rest of the system is poor. This effect can be verified for HN$_3$. Table 4.1 summarizes the normal vibrational mode frequencies for MN$_3$, when M has a mass of one amu and of eight amu. No other change was made to the Hamiltonian.

Fig. 4.8 shows decay curves for HN$_3$. Both data sets have microcanonically sampled initial conditions and use the same Hamiltonian. As with the preceding cal-
Figure 4.7 Logarithmic decay curve for a system with two exponential processes.
Figure 4.8 Logarithmic decay curves for MN$_3$. In plot A the mass of M is one amu, while in plot B it is eight amu.
culation of vibrational frequencies, the only difference between them is in the mass specified for hydrogen. Setting the mass of hydrogen to one amu results in a system with a kinetic bottleneck that demonstrates biexponential decay. With the same Hamiltonian, but with the mass of hydrogen set to eight amu the resulting vibrational frequencies are now sufficiently low to permit the H-N stretch to couple to other vibrational modes. The result is the elimination of the kinetic bottleneck, yielding a more nearly first order decay curve. Molecules with kinetic bottlenecks are non RRKM because their kinetics are not first order. Bunker and Hase have presented similar arguments for intrinsically non RRKM behavior [45]. (To qualify as first order, all reactions must undergo similar processes, but first order kinetics does not by itself imply a single bottleneck. In Chap. 7 I show that trajectories whose initial conditions all fall within the embolism exhibit log linear decay curves although each must traverse two bottlenecks. By contrast, selection of initial conditions which span both the embolism and the main region of bound phase space results in decay curves of more complex character.)

4.3 Conclusion

In Chap. 3 I showed that the phenomenon of correlated motion follows from the equations of motion and the form of the Hamiltonian, such that at low energies for systems with modes strongly coupled to the reaction coordinate, classical trajectories will necessarily exhibit correlated motion during reaction. In this chapter I showed that the RRKM requirement that all phase space points be equally likely to react is better phrased as no phase space point shall have greater hindrance to reaction than any other. This requirement therefore does not imply that that all phase space point must have the same probability of reacting per unit of time. Thus the existence of an organized and restricted set of phase space points (i.e. correlated motion) in the time
immediately preceding reaction poses no conflict with the critical RRKM assumption. The other underlying assumptions of RRKM theory (i.e. the existence of a transition state, and the absence of trapped or back reacting trajectories) have no relevance to the phenomenon of correlated motion. I therefore conclude that correlated motion is entirely consistent with RRKM theory.
frequency (cm\(^{-1}\))
M = 1 amu  M = 8 amu

normal mode

<table>
<thead>
<tr>
<th>Mode</th>
<th>M = 1 amu</th>
<th>M = 8 amu</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-N stretch</td>
<td>3496</td>
<td>1926</td>
</tr>
<tr>
<td>N=N stretch</td>
<td>2138</td>
<td>2153</td>
</tr>
<tr>
<td>N-N stretch</td>
<td>1225</td>
<td>1165</td>
</tr>
<tr>
<td>M-N-N bend</td>
<td>1146</td>
<td>293</td>
</tr>
<tr>
<td>N-N=N bend</td>
<td>523</td>
<td>629</td>
</tr>
<tr>
<td>torsion</td>
<td>607</td>
<td>584</td>
</tr>
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</table>

Table 4.1  Comparison of normal mode vibrational frequencies for MN\(_3\) for different masses of M.
Chapter 5

HONO: A system with an isolated reaction coordinate

Despite very similar potentials, HONO isomerization rates vary greatly. In this chapter I propose a model accounting for the differences in terms of kinetic couplings, and then verify and interpret the model.

5.1 Introduction

Nitrous acid, hereafter referred to as HONO, is an interesting molecule. Despite a difference in barrier heights of only 0.6 kcal/mole the rates for cis to trans isomerization can be as much as an order of magnitude faster than the rates for trans to cis isomerization [41]. This molecule is strongly non RRKM in behavior and shows evidence of mode specificity both experimentally [40] and theoretically [41]. In Chap. 3 I used HONO as an example of a molecule without correlated motion. In this chapter I show that correlated motion is independent of mode specificity, and propose a mechanism that accounts for both the observed differences in reaction rates and the mode specificity.

The chapter is organized as follows. I review the form of the Hamiltonian used in these calculations in Sec. 5.2 and discuss briefly its implications. In Sec. 5.3 I show computational evidence for mode specific behavior, and elaborate on why HONO isomerization must inevitably be non RRKM. Sec. 5.4 discusses the impact of couplings on both correlated motion and HONO's mode specificity. In Sec. 5.5 I propose and test a mechanism to account for the observed rate differences. Finally, in Sec. 5.6 I interpret the proposed model in terms of the maximum complexity PES.
5.2 The HONO Hamiltonian

The Hamiltonian used for this study is that of Thompson and coworkers [41], and is defined in terms of local mode coordinates $R_1$, $R_2$, $R_3$, $\theta_1$, $\theta_2$ and $\tau$, as shown in Fig. 5.1.

\[ V_t(\tau) = a_0 + a_1 \cos(\tau) + a_2[2 \cos^2(\tau) - 1] \]
\[ + a_3[4 \cos^3(\tau) - 3 \cos(\tau)] \]
\[ + a_4[8 \cos^4(\tau) - 8 \cos^2(\tau) + 1] \]
\[ + a_5[16 \cos^5(\tau) - 20 \cos^3(\tau) + 5 \cos(\tau)] \]  
(5.1)

In the resulting double well potential the minima for the cis and trans isomers are nearly identical and, at $85^\circ$, the transition state is nearly symmetrically located with respect to the cis and trans isomers.
Each stretching mode is modeled by a Morse oscillator

\[ V_{R_i} = D e_{R_i} (1 - e^{-\alpha_{R_i}(R_i - R_{i_{eq}})})^2 \]  \hspace{1cm} (5.2)

and each bending mode by an harmonic oscillator

\[ V_{\theta_i} = \frac{1}{2} F_{\theta_i} (\theta_i - \theta_{i_{eq}})^2 \]  \hspace{1cm} (5.3)

The total potential is

\[ V(s) = \sum_{i=1}^{3} V_{R_i} + \sum_{i=1}^{2} V_{\theta_i} + V_{\tau} \]  \hspace{1cm} (5.4)

and the full Hamiltonian is

\[ H = V(s) + \frac{1}{2} P_{\tau}^\dagger G(s) P \]  \hspace{1cm} (5.5)

Each isomer is treated separately rather than attempting to switch smoothly at the transition state. Since this study deals only with the dynamics leading to the transition state this is not a liability. Tab. 5.1 summarizes parameters for the PES, and Tab. 5.2 compares the normal mode frequencies of this PES to experimentally measured values. Normal mode analysis (Tab. 5.3) shows, as expected, that the torsional local mode \( \tau \) is also a normal mode.

Please note that this potential for HONO involves no terms which couple local modes. All coupling between local modes in this Hamiltonian occurs within the kinetic energy term. Furthermore, since the reaction coordinate \( \tau \) is itself a normal mode, to second order there are no couplings between \( \tau \) and the other modes. Clearly torsion must couple to other modes for sufficient energy to reach the mode and allow reaction, but normal mode analysis shows that in such coupling terms only the third and higher order contributions are nonzero. The mechanism that couples torsion to
**Morse Oscillators**

<table>
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<th>N=O</th>
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<tr>
<td></td>
<td>cis</td>
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<td>cis</td>
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<td>$D\epsilon(eV)$</td>
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<td>$r_e(\text{Å})$</td>
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**Harmonic Oscillators**

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<td></td>
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<td>trans</td>
</tr>
<tr>
<td>$k(\text{mdynÅ})$</td>
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<tr>
<td>$\theta_e(\text{o})$</td>
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**Torsion (mdynÅ)**

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</tr>
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<td>$a_5$</td>
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**Table 5.1** HONO PES parameters.
Table 5.2  HONO normal mode vibrational frequencies.

<table>
<thead>
<tr>
<th></th>
<th>O-H ($\nu_1$)</th>
<th>N=O ($\nu_2$)</th>
<th>H-O-N ($\nu_3$)</th>
<th>O-N ($\nu_4$)</th>
<th>O-N=O ($\nu_5$)</th>
<th>$\tau$ ($\nu_6$)</th>
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<tr>
<td>cis</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>theor.</td>
<td>3443.7</td>
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<td>1273.2</td>
<td>980.4</td>
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<td>679.5</td>
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<td>exper.</td>
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<tr>
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### Cis isomer

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<tr>
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<tr>
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<td>0.0000</td>
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### Trans isomer

<table>
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<th>$S_{N=O}$</th>
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<th>$S_{ONO}$</th>
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<tbody>
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<td>0.6523</td>
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<td>0.0000</td>
<td>-0.0002</td>
<td>1.0000</td>
</tr>
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</table>

Table 5.3 Relationship between local and normal modes for HONO.
the other modes is discussed in Sec. 5.5, and involves a detailed look at both the PES
and the terms of the kinetic energy function.

Reviewing the parameters for the HONO PES it is not obvious why there can be
an order of magnitude difference in the rate constants for isomerization. None of the
parameters is greatly different. The minimum of each well is nearly the same, and the
transition state value for the torsional coordinate (85° [41]) is nearly symmetrically
placed between the cis and trans configurations. In the next section I show that
despite these apparent similarities, rate constants calculated from trajectories do
indeed exhibit major differences.

5.3 Evidence for mode specific behavior

Significant differences (up to an order of magnitude) have been reported both
experimentally [40] and theoretically [41] for the rates of interconversion from cis to
trans versus from trans to cis. This indicates that HONO isomerization is a non
RRKM process. To verify these results I began by generating two sets (cis and trans)
of two thousand trajectories, with microcanonically sampled initial conditions, shown
in Fig. 5.2.

Two features stand out clearly in Fig. 5.2. Firstly, this isomerization is not a
first order reaction which can be neatly characterized by fitting a single exponential.
In fact, a linear least squares fit to data such as these is uninformative because
it is excessively influenced by the long lived outlying trajectories, which tend to
be nonreproducible. For that reason, rather than trying to equate reaction rates
between data sets by an inappropriate rate constant I will instead present the actual
data, plotted at the same scale for direct comparison. The nonlinearity of these
microcanonically sampled logarithmic decay curves confirms that this reaction is non
RRKM, and we may reasonably infer that there are modes within HONO that are
Figure 5.2 Logarithmic decay curves for both cis and trans isomerization. Each data set consisted of two thousand trajectories with microcanonically sampled initial conditions at a total energy of 4.06E₆.
kinetically isolated, resulting in internal constraints to IVR. Secondly, although the rates of reaction can’t be neatly fit by a single exponential, the rate of reaction for cis is clearly much greater than for trans, thus verifying previous observations.

Given the great similarities between the cis and the trans Hamiltonian, what causes the observed differences in reaction rates? I began my exploration by testing reaction rates for high overtone states. The initial conditions were semiclassical in that zero point energy was allocated to each normal mode oscillator, then the balance of available energy was placed in a single normal mode. The results for cis to trans isomerization are displayed in Fig. 5.3 and for trans to cis in Fig. 5.4. The initial vibrational state for each trajectory is indicated on every plot. Please note that for the cis isomer the O-N=O bending frequency is lower than that of the torsional mode, so for this isomer $\tau$ is $\nu_5$, and the O-N=O bend is $\nu_6$, reversed in order with respect to the trans isomer.

Fig. 5.3 contains several interesting results, the most important being that excitation of $\nu_3$, the H-O-N bending mode, induces reaction nearly as efficiently as placing the excitation directly in the reaction coordinate, the $\nu_5$ torsional mode. (Thompson and coworkers have previously noted mode specificity for the H-O-N mode [41]). The reaction rates for all other excitations are much slower than for either of these two modes, with excitation of $\nu_2$, the N=O stretch, being significantly slower than all other rates. When we compare the reaction rates for overtone excitations of the cis isomer in Fig. 5.3 to the corresponding trans ones in Fig. 5.4 clear differences in behavior emerge. Unlike the cis isomer, the trans reaction rate for $\nu_3$ excitation is no faster than for any other overtone excitation. Behavior of the torsional mode also shows interesting contrasts. In the cis isomer $\tau$ excitation results in many early reactions, but even the later ones react with an instantaneous rate value that is fast compared to all other excitations save that of $\nu_3$. In the trans isomer, $\tau$ excitation
Figure 5.3  Decay curves for normal mode overtone excitations of cis HONO. The total energy is 0.065 \( \text{ht} \), which is 4.06E\(_{\text{a}}\). Each data set consisted of three hundred trajectories.
Figure 5.4  Decay curves for normal mode overtone excitations of trans HONO. The total energy is 0.065 \text{ ht}, which is 4.06E_6. Each data set consisted of three hundred trajectories.
results in a great majority of trajectories that react almost immediately, but a handful of trajectories react later, and at a rate that is scarcely any faster than that for the other overtone excitations.

5.4 Couplings, correlated motion and mode specificity

In Chap. 3 I used HONO as an example of a molecule that has no correlated motion, and explained the observed behavior in terms of the small couplings present in the HONO Hamiltonian. In this chapter we find that although HONO has no correlated motion, it has strong mode specific effects. I must account for the observed mode specificity and differences in reaction rates within the framework of a Hamiltonian with very small couplings between the reaction coordinate and the orthogonal modes.

Because couplings between the torsional modes and the others are so small, very slight differences in the extent of these couplings can have a large effect. This is essentially a situation where we are comparing numbers close to zero, whose ratios vary greatly with only slight changes in the values themselves. The restricted nature of the couplings to the reaction coordinate makes HONO particularly susceptible to mode specific effects, so one would expect that by altering the couplings one would significantly change the system.

5.5 A model for HONO isomerization

Reaction rates for high overtone excitations (Fig. 5.3 and Fig. 5.4) show clear differences between the two isomers. It is not unreasonable to expect that the striking difference in behavior for the H-O-N bend is related to the observed differences in reaction rates for the isomers. In the next section I propose a model to account for these observations, and then test the model.
5.5.1 Description of the model

Based on the observations arising from Fig. 5.3 and Fig. 5.4 I propose that differences in the reaction rates for cis and trans isomers are a consequence of differences between the isomers in the coupling of the H-O-N bending mode to the torsional mode. In the cis conformer these two modes find a way of coupling, while in the trans one they do not. Such coupling is very important because in the cis isomer the H-O-N bend serves as a conduit to the reaction coordinate, coupling with other orthogonal modes as well as to the reaction coordinate, thereby facilitating IVR. Closer inspection of the decay curves in Fig. 5.3 shows several interesting trends. Apparently H-O-N and $\tau$ couple efficiently, because exciting H-O-N leads to reaction almost as efficiently as direct excitation of $\tau$. Three other orthogonal modes react at roughly the same intermediate rate, suggesting that they couple to nearly the same degree with H-O-N, and so convey their energy to the reaction coordinate with roughly equal efficiency. Only $\nu_2$ is the odd one out, reacting much more slowly than the other cis excitations, at a rate comparable to any of the trans excitations. From this I infer that the N=O excitation couples only weakly with the other vibrational modes.

The data in Fig. 5.4 are also open to interesting interpretations in terms of this model. The primary inference is that in the trans isomer the H-O-N bend does not couple to $\tau$ any more efficiently than any other mode. The reaction rates for each normal mode are roughly equal, suggesting each mode has an equally difficult time conveying energy to the reaction coordinate. The orthogonal modes may couple amongst themselves, but none can act as a conduit to the torsional mode. Interestingly, the torsional mode is strongly biexponential, with one set of trajectories reacting rapidly while a second set reacts no faster than any other excitation. The rapidly reacting trajectories clearly represent those wherein the initial conditions re-
sult in immediate reaction. By constraint, I infer that the longer lived trajectories somehow manage to divest themselves of sufficient energy in the torsional mode to avoid immediate reaction. Having relinquished the energy required for reaction, the trajectories evolve, waiting to reacquire sufficient energy for reaction. Once having shed the energy needed for reaction, these trajectories can not regain said energy any faster than any other initial excitation. Therefore the reaction rate for these slower torsionally excited trajectories is roughly the same as for any of the other excitations.

5.5.2 Testing the model

Having claimed in the preceding model for HONO isomerization that the H-O-N bend couples more strongly to the reaction coordinate in the cis isomer than in the trans, to verify the model I must now prove this assertion. To do so I must isolate those terms in the Hamiltonian responsible for the coupling. Recall from Sec. 5.2 that the HONO Hamiltonian used in this study has no potential energy coupling terms. I must therefore look to the kinetic energy portion of the Hamiltonian for off diagonal terms which can connect modes, and so allow energy transfer. Here the observation that H-O-N apparently couples more strongly to the reaction coordinate gives guidance in searching for which off diagonal elements are important. Recall that the Wilson $G$ matrix for HONO is a 6x6 symmetric matrix whose diagonal terms are effective masses for the interaction of each local mode motion with itself. There are therefore fifteen unique off diagonal elements which can potentially influence couplings. Of these fifteen terms, ten are expressions which involve terms for both the H-O-N bend and torsion (either the coordinates or the momenta of each local mode, or both).

I tested the model by seeking to disable the H-O-N/τ coupling in the cis mode, thereby reducing the cis reaction rate to that of the trans. Rather than subject the reader to the details of the ensuing trial and error search, I will simply present the
final outcome. I was able to reduce the microcanonical reaction rate of cis HONO to nearly that of trans HONO by setting to zero three of the ten off diagonal $G$ matrix elements which couple H-O-N and $\tau$, and by addressing a subtle asymmetry in the potential. Zeroing the kinetic coupling terms alone was insufficient to slow the cis reaction rates to those of trans, so I looked more closely at the form of the torsional potential, and realized that with the maximum at 85° the transition state was slightly skewed towards the cis isomer. By a change of variables I was able to alter the form of the potential to skew it instead to the trans side. (The original and the modified torsional potentials are shown in Fig. 5.5.) This small modification to the form of the potential proved to be the final component that in conjunction with the three zeroed kinetic coupling terms leads to a Hamiltonian whose reaction rate for the cis isomer is comparable to the trans.

Fig. 5.6 summarizes the results. Part A shows the reaction rate for cis trajectories with a complete Hamiltonian. Part B shows the reaction rate for cis trajectories when three off diagonal $G$ matrix elements unrelated to H-O-N/$\tau$ coupling are set to zero. Part C shows the reaction rate for cis trajectories when three $G$ matrix terms vital to H-O-N/$\tau$ coupling are set to zero, and the transition state is slightly shifted. Part D shows for comparison the reaction rate for the trans isomer with the full Hamiltonian. When we compare parts A and B it becomes apparent that loss of arbitrary coupling terms does not greatly influence the kinetics. Comparison of parts C and D shows that loss of very specific coupling terms related to H-O-N/$\tau$ coupling can reduce the cis reaction rate to one comparable to that of trans, where apparently these same coupling terms are not as effective, else the reaction rate for trans would be comparable to that of cis. (The reduction in reaction rate in part C is a consequence of both zeroing kinetic coupling terms and of modifying the torsional potential. Both changes to the Hamiltonian are required, because neither singly has
Figure 5.5 Comparison of the original torsional potential (solid line) with the transition state at 85°, and the modified potential (dashed line) with the transition state at 95°.
Figure 5.6 Decay curves showing reaction rates for 300 trajectories with micro-canonical sampled initial conditions and total energy of 4.06E4. See the text for further explanation of each data set.
sufficient impact upon the rates of reaction.)

For completeness' sake in Tab. 5.4 I note the $G$ matrix terms set to zero in the following tests, but it is not obvious to me why the three terms in Part C should have a greater effect on the kinetics than other possible combinations.

**Modifications to the Hamiltonian**

<table>
<thead>
<tr>
<th>Part B</th>
<th>Part C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(no effect)</td>
<td>(affects kinetics)</td>
</tr>
<tr>
<td>$P_{HO}P_{ON}G_{HO,ON}$</td>
<td>$P_{ONO}P_{O,GONO,\tau}$</td>
</tr>
<tr>
<td>$P_{ONO}P_{ON}G_{ONO,ON}$</td>
<td>$P_{HON}P_{O,GHON,\tau}$</td>
</tr>
<tr>
<td>$P_{N=0}P_{ONO}G_{N=0,ONO}$</td>
<td>$P_{HON}P_{N=0,GHON,N=0}$</td>
</tr>
<tr>
<td>original torsional potential</td>
<td>modified torsional potential</td>
</tr>
</tbody>
</table>

*Table 5.4* HONO kinetic energy terms zeroed out to test the effect of H-O-N/\tau coupling upon reaction kinetics.

### 5.6 Conclusions

In the prior discussion on correlated motion we saw that because of poor coupling between the reactive and the orthogonal modes HONO lacks correlated motion (as demonstrated by the tornado plots, Fig. 3.12 to Fig. 3.15). Any model for the demonstrated mode specificity of HONO must also be consistent with the previous correlated motion model.

I interpret the observations of HONO's behavior as follows. HONO lacks strong couplings between the reaction coordinate \( \tau \) and the orthogonal modes. Strong couplings, such as those found in HN$_3$ result in a reaction coordinate that is a linear combination of local modes, as demonstrated in Fig. 1.2. In systems with strong
couplings over a substantial portion of the PES the resulting gradient is one which strongly focusses trajectories upon the transition state. By contrast, HONO's weak couplings have only local effects. Trajectories must locate the transition state without the benefit of prior focussing (such as in the HN$_3$ reaction coordinate). Once in the neighborhood of the transition state, reactivity is critically dependent upon the local characteristics of the PES. This makes HONO extraordinarily susceptible to small variations in weak couplings. I believe that the difference between the cis and trans isomerization rates depends upon the details of the PES gradient near the transition state. Each of the factors which affected the reactivity of the cis isomer has the ability to locally modify the character of the PES near the transition state. The first (and smaller) factor in reducing the cis reaction rate involved inverting the transition state so that it was slightly to the trans rather than the cis side (at 95° rather than 85°). (This makes a great difference to the local gradient of the PES at angles close to the transition state.)

The second, more significant factor in reducing the cis reaction rate was setting to zero some of the kinetic coupling terms. Recall from Chap. I my arguments concerning the influence of couplings on the maximum complexity PES. In the proper frame, kinetic couplings may be regarded as perturbations to the base PES which can locally modify the gradient of the PES. I propose that the $G$ matrix elements I removed from the cis Hamiltonian (by setting them to zero) have the effect (over short ranges near the transition state) of directing trajectories towards the transition state. By the nature of the HONO PES, in the cis isomer these perturbations tended to lead trajectories towards the transition state. When I zeroed out the selected kinetic coupling terms I removed the effects of the perturbations, so trajectories are no longer guided towards the transition state. Trajectories must now find the transition state unaided, much as they do in the trans isomer, which shows no mode specific effect for
the H-O-N bend. It bears repeating that only because the reaction rate is so slow do these minor effects have so major an impact. (Small differences in the local geometry of the transition state can mean that for the cis isomer perhaps one oscillation in one hundred of the reaction coordinate will lead to reaction, while for the trans isomer it may be only one in one thousand.)

Because of the high dimensionality of the HONO system it is not possible to test these ideas directly by plotting the PES with couplings, but this model for HONO reactivity accounts for all results obtained to date.

While differences in the reaction dynamics of the two isomers can account for differences in reaction rates, consideration of statistical mechanics and microscopic reversibility suggests that the trans isomer must have a much larger density of states than the cis one. My conjecture is that couplings in the cis isomer render the harmonic approximation poor for this isomer, so a density of states (or subsequent RRKM rate constant) calculated with this approximation will be inaccurate. More work remains to test this conjecture.
Chapter 6
HN₃: Structure of the hose

In this chapter I document the Hamiltonian for HN₃, and explore the nature of the phase space hose in a system with strong couplings.

6.1 Introduction

In Chap. 3 I used HN₃ as an example of a system with strong couplings, and showed that those couplings result in correlated motion between reactive and orthogonal modes. Correlated motion implies a nonuniform phase space distribution of trajectories. The portion of each reaction where trajectories cluster together in phase space I referred to as the hose. Because of its strong couplings the hose for HN₃ is well defined. In this chapter I explore the nature of the hose, focussing especially on the phase dependence of hose dissolution. To set the stage for these investigations I begin with a discussion of the HN₃ Hamiltonian.

6.2 The HN₃ Hamiltonian

Hydrozoic acid (hereafter referred to as HN₃) decomposes into HN and N₂ via a singlet to triplet transition as the central N-N bond extends [48] [49]. I have neglected the singlet to triplet transition in the Hamiltonian used, on the assumption that the details of the reaction dynamics are the same whether or not this transition occurs. The advantage of doing so is that a far larger fraction of trajectories are reactive, but the disadvantage is that as a consequence, computed reaction rates can not be compared to experimentally measured values. Since the objective is to unravel the details of the dynamics the benefits of larger numbers of reactions makes this compromise worthwhile. I therefore deem that a reaction has occurred when the
central N-N bond reaches 3.5 $\alpha$, the location where crossing would occur, were that possibility built into the Hamiltonian. In this fashion 3.5 $\alpha$ is designated as the transition state for this reaction although in reality it is simply a rather distant point on the reaction coordinate Morse oscillator. The HN$_3$ Hamiltonian for these studies is that used by Julien [13], and is defined in terms of internal coordinates $R_1$, $R_2$, $R_3$, $\theta_1$, $\theta_2$, and $\tau$, as shown in Fig. 6.1.

![Diagram of HN3 molecule showing internal coordinates](image)

**Figure 6.1** HN$_3$ local modes.

Each stretching mode is modeled by a Morse oscillator

$$ V_{R_i} = D_{R_i}(1 - e^{-\alpha_{R_i}(R_i - R_{i_{eq}})})^2 $$

and each bending mode by an harmonic oscillator

$$ V_{\theta_i} = \frac{1}{2} F_{\theta_i}'(\theta_i - \theta_{i_{eq}})^2 $$

where the values of the bending force constants $F_{\theta_i}$ are tapered by a switching function

$$ F_{\theta_i}' = F_{\theta_i}[1 - tanh(\gamma(R_2 - \beta)^9)] $$

(6.1)

(6.2)

(6.3)
to diminish their values as dissociation occurs. In Eq. 6.3 $\gamma = 1 \times 10^{-4} \AA^{-9}$ and $\beta = 1.3 \AA$. The torsional mode is a sine function

$$V_\tau = F_\tau \sin(\tau - \tau_{eq} - \frac{\pi}{2})$$  \hspace{1cm} (6.4)

and a number of coupling terms are included which link the bends together,

$$V_{\theta_1 \theta_2} = F_{\theta_1 \theta_2} (\theta_1 - \theta_{1eq})(\theta_2 - \theta_{2eq})$$  \hspace{1cm} (6.5)

and both NN stretches,

$$V_{R_2R_3} = \frac{F_{R_2R_3}}{\alpha_{R_2} \alpha_{R_3}} (1 - e^{-\alpha_{R_2}(R_2-R_{2eq})})(1 - e^{-\alpha_{R_3}(R_3-R_{3eq})})$$  \hspace{1cm} (6.6)

and the HNN bend to the dissociative N-N stretch:

$$V_{\theta_1R_2} = \frac{F_{\theta_1R_2}}{\alpha_{R_2}} (\theta_1 - \theta_{1eq})(1 - e^{-\alpha_{R_2}(R_2-R_{2eq})})$$  \hspace{1cm} (6.7)

Thus the total potential energy function is:

$$V(s)_{tot} = \sum_{i=1}^{3} V_{R_i} + \sum_{i=1}^{2} V_{\theta_i} + V_\tau + V_{\theta_1 \theta_2} + V_{R_2R_3} + V_{\theta_1R_2}$$  \hspace{1cm} (6.8)

and as is customary the Hamiltonian is

$$H(s, p) = V(s)_{tot} + \frac{1}{2} P^\dagger G(s) P$$  \hspace{1cm} (6.9)

Values for parameters are listed in Tab. 6.1. Normal mode vibrational frequencies for HN$_3$ are listed in Tab. 4.1 and local mode components of normal modes are given by Tab. 6.2.
### Stretching Modes

<table>
<thead>
<tr>
<th></th>
<th>H-O (R₁)</th>
<th>N-N (R₂)</th>
<th>N=N (R₃)</th>
</tr>
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<tr>
<td>( D_R (\text{au}) )</td>
<td>0.1766</td>
<td>0.0662</td>
<td>0.290</td>
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<tr>
<td>( \alpha_R (\text{a.u.}^{-1}) )</td>
<td>1.1083</td>
<td>2.1865</td>
<td>1.3311</td>
</tr>
<tr>
<td>( R_{eq} (\text{Å}) )</td>
<td>1.015</td>
<td>1.243</td>
<td>1.134</td>
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</tbody>
</table>

### Bending Modes

<table>
<thead>
<tr>
<th></th>
<th>HNN ((\theta_1))</th>
<th>NNN ((\theta_2))</th>
<th>torsion ((\tau))</th>
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<tr>
<td>( k(10^{-11} \text{erg rad}^{-2}) )</td>
<td>0.729</td>
<td>0.611</td>
<td>0.0168</td>
</tr>
<tr>
<td>( \theta_{eq} (°) )</td>
<td>108.8</td>
<td>171.3</td>
<td>180</td>
</tr>
</tbody>
</table>

### Coupling Terms

\[
\begin{align*}
V_{R_2R_3} & \quad (10^5 \text{erg cm}^{-2}) \\
V_{\theta_1,\theta_2} & \quad (10^{-11} \text{erg rad}^{-2}) \\
V_{\theta, R_3} & \quad (10^{-3} \text{erg cm rad})
\end{align*}
\]

<table>
<thead>
<tr>
<th></th>
<th>force constants</th>
<th>( V_{R_2R_3} )</th>
<th>( V_{\theta_1,\theta_2} )</th>
<th>( V_{\theta, R_3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.730</td>
<td>0.048</td>
<td>0.838</td>
<td></td>
</tr>
</tbody>
</table>

**Table 6.1**  HN₃ PES parameters.
6.3 \( \text{HN}_3 \) and the structure of the hose

Hydrazoic acid has already been discussed extensively in Chap. 3, having been cited as an example of a molecule with strong couplings. In Chap. 3 I showed that several local modes of \( \text{HN}_3 \) exhibit correlated motion. The behavior of the \( \text{N=N} \) stretching mode was particularly dramatic. Fig. 3.3 illustrates that phases converge for this mode far more rigorously than for other local modes. This convergence of phases brings trajectories together into a configuration that we have termed a phase space hose.

In my model for correlated motion I equated the specific path of the hose with phase space regions of high coupling. The hose is particularly well defined (i.e. the phases are most constrained) during the critical final one or two oscillations of the reaction coordinate. This is the stage in which energy is transferred into the reactive mode, and dissociation results. How closely the \( \text{N=N} \) stretch must be correlated with the \( \text{N-N} \) reactive mode during this critical period is apparent in Fig. 3.3, where all trajectories reside within a \( \frac{\pi}{2} \) range for a full oscillation of the reaction coordinate. (If there were no constraints phases would range over \( 2\pi \).) For a certain critical period preceding reaction, the requirements of energy transfer constrain modes that couple with the reaction coordinate to a specific path.

6.3.1 Evolution of the hose

Whilst trajectories are so constrained they reside within a phase space hose. What process converts a trajectory freely roaming phase space into one wherein two modes are strictly correlated? In search of an answer to this question I decided to examine the phase relationships between the \( \text{N-N} \) dissociative mode and the closely correlated \( \text{N=N} \) mode for many cycles preceding reaction, to capture behavior both inside and
Figure 6.2  This shows the relationship between the continuous phases (in radians) of the reaction coordinate and the correlated N=N mode. This data set consists of one hundred trajectories with a total energy of 1.1E₆
outside the hose. The results are shown in Fig. 6.2, wherein trajectories have been plotted as a series of dots. Where the phases of trajectories converge their density is greater, and the hose is evident as a darker region.

6.3.2 Hose bifurcations

Fig. 6.3 is an enlargement of Fig. 6.2, and allows close examination of the region between zero and $4\pi$, which has several interesting features. In the range of zero to $2\pi$ the hose is clearly evident by the narrow range of phase values. At reaction coordinate phase values slightly larger than $2\pi$ the range of N=N phase values broadens greatly. Choosing momentarily to adopt a "forward time" framework, the sudden constriction in phases circa $2\pi$ corresponds to trajectories entering the outer turning point region of the PES, ready to embark upon the final oscillation. While approaching the penultimate outer turning point the trajectories converge rapidly and strongly. Does this convergence at $2\pi$ mark the limit of the hose? I would argue that it does not. In the range between $2\pi$ and $4\pi$ Fig. 6.3 shows a bifurcation in the hose, with regions of preferred phase relationships (identifiable as darker regions in the plot) persisting to values of $8\pi$ or more. The bifurcation at $\phi = 10$ is an interesting feature. The (lower) main branch of the hose progresses smoothly towards the outer turning point, beyond which the N-N and N=N stretches are in phase for the final oscillation. The path of the upper branch of the hose is not as direct. Note the phase reversals in the upper branch circa $\phi = 10$. At this location the phase values in the upper branch are roughly $\pi$ greater than those of the lower, more direct one. To join the main hose (with its carefully constrained phase relationships) these trajectories must accomplish a $\pi$ change in their N=N oscillator phase. They do so by executing a "pirouette" (in evidence as the backtracking phases at $\phi = 10$) which is an abbreviated cycle that brings their phases into accord with those of the main branch of the hose. Further
Figure 6.3  A closer view of the phase relationships between the reaction coordinate and the correlated N=N mode during the process of reaction. Phase convergence occurs whenever the distribution of N=N phases is less than $2\pi$, indicating that the N-N and N=N motions are correlated. Vertical lines occur at intervals of $2\pi$. 
examination reveals that this upper branch of the hose itself diverges in the vicinity of $4\pi$.

6.3.3 Hose duration

Evidence of periodic divergences led me to attempt to track the main branch of the hose out to the vicinity of $8\pi$, beyond which no further hose structure is evident. The results are in Fig. 6.4, where solid lines show trajectories in the main branch of the hose. Dashed lines show trajectories that converge with the main branch prior to $4\pi$, and dotted trajectories are those that join in the interval of $2\pi$ to $4\pi$, the penultimate oscillation. Fig. 6.4 suggests that the hose retains some structure until a final divergence circa $8\pi$ (four oscillations of the reaction coordinate).

6.3.4 Hose convergence and PES curvature

One intriguing aspect is the cyclic convergence of phases shortly after the momentum reversal at the outer turning point. These periodic convergences suggest that outer turning points play an important role in shaping dynamics. My speculations in this regard are as follows. The PES at the outer turning point for stretching modes whose potentials are modeled as Morse oscillators (such as N-N and N=\text{N}) is characterized (unlike other regions) by negative curvature. When one calculates Lyapunov exponents in such regions one discovers that here trajectories are capable of either exponential divergence or exponential convergence. To arrive at the transition state, the process of interest for hose formation is exponential convergence. The phase space structure that we have termed a "hose" is perhaps more accurately characterized as a tree, where at every outer turning point another branch of trajectories exponentially converges with the trunk. It is by repeated cycles of convergences from twig
Figure 6.4 The phase space hose unravels in stages. Trajectories plotted in solid lines are those that comprise the hose until its final dissolution after the fourth cycle. Dashed trajectories are those which converge upon the main hose prior to the second cycle, while dotted ones are those converging during the second cycle. There are one hundred HN$_3$ trajectories with a total energy of 1.1E$_4$. 
to branch to trunk that trajectories pass from random phase relationships into the lockstep of the final cycle. This structure thus has no single origin, but rather assembles gradually by successive cycles of convergences, arriving ultimately at the phase configuration required to clear the transition state and so react.
<table>
<thead>
<tr>
<th>local mode</th>
<th>H-N</th>
<th>N=N</th>
<th>N-N</th>
<th>N-N=N</th>
<th>H-N-N</th>
<th>torsion</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-N stretch</td>
<td>0.9986</td>
<td>-0.0179</td>
<td>-0.0292</td>
<td>-0.0229</td>
<td>-0.0081</td>
<td>-0.0000</td>
</tr>
<tr>
<td>N-N stretch</td>
<td>-0.0474</td>
<td>-0.3992</td>
<td>-0.7425</td>
<td>-0.0421</td>
<td>0.6564</td>
<td>0.0000</td>
</tr>
<tr>
<td>N=N stretch</td>
<td>0.0069</td>
<td>0.9125</td>
<td>-0.5898</td>
<td>-0.0487</td>
<td>0.4097</td>
<td>0.0000</td>
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<tr>
<td>H-N-N bend</td>
<td>-0.0194</td>
<td>-0.0874</td>
<td>-0.3138</td>
<td>0.1855</td>
<td>-0.6055</td>
<td>0.0000</td>
</tr>
<tr>
<td>N-N=N bend</td>
<td>-0.0100</td>
<td>-0.0061</td>
<td>-0.0394</td>
<td>-0.9803</td>
<td>-0.1863</td>
<td>0.0001</td>
</tr>
<tr>
<td>torsion</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
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</tr>
</tbody>
</table>

Table 6.2  The relationship between normal modes and local modes for HN$_3$. 
Chapter 7
HN$_3$: Phase and IVR

In this chapter I show that there is a consistent relationship between the phase of an initial excitation and the lifetime of the resulting excited molecule. This phase relationship suggests a possible mechanism for IVR.

7.1 Introduction

Much of this thesis has been an exercise in comparing and contrasting the reaction dynamics of HN$_3$, a system with strong couplings between local modes and the reaction coordinate, to those of HONO, a system wherein the reaction coordinate couples only weakly to the orthogonal modes. In Chap. 5 we saw that cis HONO has very distinct state specific reaction rates. In this chapter I examine reaction rates for a series of overtone excitations of HN$_3$, looking for evidence of mode specific reaction rates in this system. For every state studied the initial conditions of each trajectory specify one particular distribution of internal energy, yet some trajectories react immediately, while others survive for picoseconds. I explore the differences between trajectories which react rapidly and those that do not, and find that for many states there is a strong correlation between oscillator phase and lifetime of the trajectory.

This chapter involves a synthesis of many of the themes of previous chapters, so there are a number of points to be made:

- Mode specificity can be consistent with RRKM kinetics.

- A relationship exists between the phases of the initial excitation and the lifetime of a trajectory.
• The relationship between initial phase and trajectory lifetime is consistent with previous findings concerning the nature of the hose.

• The phase relationships demonstrated have implications for a mechanism for IVR.

7.2 State specific reaction rates

This section outlines the rationale for the overtone excitations used and shows the resulting decay curves. Each selected state represents a contribution to the microcanonical ensemble. I show that the existence of state specific rate constants does not preclude the existence of a microcanonical first order (i.e. RRKM) rate constant.

7.2.1 Design of the calculations

High overtone excitations permit some insight into IVR, in that the resulting rate of reaction must depend upon the rate at which energy can move from the initially excited mode into the reaction coordinate. In addition, in HN₃ (because of the kinetic bottleneck which isolates the H-N stretching mode) energy can be sequestered in the H-N stretch, so that the initial rates of reaction will reflect only the energy available in other modes. For these reasons I embarked upon an investigation of the reaction kinetics of HN₃ by using a series of overtone excitations. The calculations are semiclassical, as in every case each normal mode had at least zero point energy, and the total energy in the system was 3.2E₄. For each data set (varying by initial conditions) I calculated five hundred trajectories and recorded the time until reaction. The resulting decay curves give insight into mode specificity in the kinetics of HN₃.

The first set of experiments involved trajectories whose initial conditions placed all but the zero point energy separately into each successive normal mode, for a total
accessible excitation of $3.0E_4$. The next set of calculations, while conducted at the same total energy ($3.2E_4$), placed three quanta of vibrational excitation into the H-N stretch, thereby reducing the immediately available energy to roughly $2.0E_4$. This energy was successively allocated to each of the other local modes. In the final set of experiments six vibrational quanta were reserved in the H-N stretch, leaving about $1.1E_5$ of energy to be sequentially distributed to each local mode. In this fashion I was able to examine excitations of varying energies while preserving a single total energy for the whole study. In semiclassical trajectory calculations one can specify (by assignment of vibrational quanta) the distribution of internal energy, but since the oscillators are not quantized, energy can be scaled to a single value. In this study vibrational quanta were allocated to be as close as possible to the target energy, but then the total energy was scaled, resulting in a uniform total energy for all cases.

7.2.2 Decay curve for microcanonical sampling

Each of the preceding normal mode excitations is a part of the microcanonical distribution. The purpose of this study is to gain insight into how each component of a microcanonical ensemble shapes the resultant whole. Recall Fig. 4.5 wherein every possible trajectory in phase space is ordered by time duration. Zero time corresponds to reaction, so times near zero must involve states with high excitations of the reaction coordinate. Highly excited reactive states are not scattered randomly throughout this distribution, but rather cluster near time zero. This raises the question: must other initial excitations also be distributed randomly (resulting in a rate constant the same as in the microcanonical case), or can they preferentially occupy regions of this distribution, thereby incurring reaction rates different from the microcanonical one? The latter case is termed a mode specific rate constant.

Just as in the case of HONO, because many of the decay curves do not correspond
Figure 7.1  Logarithmic decay curves for HN$_3$ under various initial conditions. Part A represents two thousand trajectories sampled microcanonically. Part B is five hundred trajectories with high initial excitation of the H-N stretch. Part C is five hundred trajectories with energy distributed evenly between normal modes.
to first order processes, the actual data will be presented at uniform scales to allow comparison of reaction rates, rather than by comparing values of inappropriate linear curve fits. Fig. 7.1 shows three decay curves with part A resulting from microcanonically sampled initial conditions. The curve can be divided into three approximately linear regions. The first region, up to roughly 0.1 ps has the fastest reaction rate. The second (from 0.1 ps to 0.5 ps) has an intermediate rate, while that of the third (encompassing times greater than 0.5 ps) has the slowest rate. This is the reference case, whose shape we seek to understand. As was discussed in Chap. 4, HN$_3$ dissociation is not a first order process. Detailed study may reveal the underlying processes whose different rates cause HN$_3$'s decay curve to be multiexponential.

Part B is the decay curve for high overtone excitation of the H-N stretch. This curve shows a number of interesting features. Clearly the reaction rate for this excitation is much slower than that of the microncanonical case, implying that H-N excitations occupy a larger than average portion of distant times in the time distribution map of trajectories. Also, the slope of the excited H-N decay curve is similar to the final slope for the microcanonical case, indicating that the slow reactions in the microcanonical distribution may represent trajectories whose initial conditions have much of their available energy in this kinetically isolated region of phase space. Finally, this excitation has a first order decay curve. I interpret this to show that all the trajectories for the high overtone H-N excitation have initial conditions which lie within the kinetically isolated region of the Hamiltonian (as illustrated in Fig. 4.6), so all trajectories are equally hindered in the process of reaction (all having to clear the internal bottleneck on the way to the transition state), thus satisfying the requirements for a first order process.

Part C of Fig. 7.1 shows the reaction rate for initial conditions which allocate equal energy to each normal mode. The rate for these average excitations is closest
to the middle portion of the microcanonical decay curve, leading me to believe that in this range of the microcanonical curve reaction rates are dominated by trajectories whose initial conditions have states wherein the energy is distributed roughly equally.

We have yet to determine what initial conditions result in the rapid reactions of the first region of the microcanonical decay curve, but with only minimal shrewdness, I will next examine mode specific rates for high overtone excitations of modes which are not kinetically isolated.

7.2.3 Overtone excitation decay curves

Fig. 7.2 and Fig. 7.3 show decay curves for overtone excitations for each normal mode (as annotated), with increasing amounts of energy reserved in the H-N stretch. Because each normal mode will be discussed at length, each will be treated in a separate subsection, from highest to lowest frequency value. From the observed kinetics I will make inferences regarding the dynamics.

N=N excitations

The (0 15 0 0 0 0) state has the single fastest reaction rate, greater than that of placing the excitation (which is 3.0E₅) directly into the reaction coordinate. When energy in this mode is reduced to roughly 2.0E₅ (in the (3 10 0 0 0 0) state) the reaction rate slows somewhat, but is still faster than nearly all other states. Only when the excitation is reduced to 1.1E₅ in the (6 6 0 0 0 0) state does the rate decrease to one that is comparable to many other states.

In light of the previous discussion of correlated modes in HN₃ I interpret these results as follows. The N=N mode is known (by normal mode analysis) to be strongly coupled to the N-N dissociative mode, and to transfer energy impulsively into this
Figure 7.2 Logarithmic decay curves for N=N, N-N and HNN normal mode excitations of HN$_3$. Each data set represents five hundred trajectories whose total energy is 3.2E$_b$. 
mode during reaction [13]. The (0 15 0 0 0 0) decay curve shows, by its lack of slow reactions, that energy placed in this overtone does not dissipate randomly, but rather couples preferentially with the reaction coordinate. Thus reaction occurs before the excitation is able to divert sufficient energy into other modes to avoid reaction. This is contrary to the standard model of IVR, which holds that this excitation should randomize and disperse long before reaction. High overtone states which may exhibit this kind of behavior are very difficult to prepare experimentally.

In very rare cases the (3 10 0 0 0 0) excitation is able to disperse sufficient energy to survive up to a picosecond. However, most trajectories in this state proceed to react promptly. I account for the relative slowness of the reactions of the (6 6 0 0 0 0) state (an excitation of 1.1E₆) by noting that even a small energy leakage out of the excitation is sufficient to reduce the energy below that required for reaction. This initial excitation is basically inadequate for rapid reaction (with only a few trajectories reacting promptly), and the observed reaction rate reflects the rate of random energy transfers.

N-N excitation

What happens when the excitation is placed directly in the reaction coordinate? The (0 0 27 0 0 0) state corresponds to an initial excitation three times greater than that required to clear the barrier. The surprise in this experiment is that some trajectories last for more than a single oscillation period. (This suggests that the normal mode is not identically the reaction coordinate.) A small minority of trajectories, represented by the slower reacting portion of the curve, manage to divest themselves of sufficient energy to survive for a few oscillations.

As the excess of energy in the reactive mode is decreased to 2.0E₆ in the (3 0 18 0 0 0) state two linear regions clearly emerge. The fast portion represents
prompt reactions (i.e. within one or two cycles), while the slower portion represent trajectories that have shed sufficient energy to survive for several oscillations. The latter are clearly more numerous in the $(3\ 0\ 18\ 0\ 0\ 0)$ case than in the $(0\ 0\ 27\ 0\ 0\ 0)$ case.

When the initial excitation is reduced to $1.1E_b$ in the $(6\ 0\ 10\ 0\ 0\ 0)$ state surprisingly few trajectories react promptly, as shown by the tiny fast segment near time zero. Most trajectories undergo random IVR, reacting at a rate comparable to all other states with insufficient energy for prompt reaction. These results indicate that once a trajectory has shed sufficient energy from the initially excited reactive mode to avoid prompt reaction then the process of reacquiring enough energy to react is the same as for any other excitation.

**HNN excitation**

Reaction rates for HNN excitation are remarkably consistent (and rather slow), irrespective of the size of the initial excitation. Recall from the discussion of correlated modes that the HNN bend showed only slight correlation at very low energies $(1.1E_b)$. Apparently at the high total energy of these experiments $(3.2E_b)$ HNN couples only poorly to the reaction coordinate. Lacking any direct connection to the reaction coordinate, in order to react energy in this mode must first randomly disperse into other modes, yielding a slow and consistent rate of reaction.

**NNN and torsional excitations**

Fig. 7.3 shows the decay curves for these two modes, which will be discussed jointly because their behaviors are so similar. The surprise in this data set is that a high excitation of the torsional mode $(0\ 0\ 0\ 0\ 0\ 64)$ can result in rapid reaction.
High excitations of both NNN and $\tau$ apparently do not disperse rapidly and so are able to convey their energy to the reactive coordinate before dispersing to the point where the available energy is insufficient for reaction. The surprising ability of these modes to couple to the reactive N-N stretching mode at high energies may be one of the factors behind the diminishment of N=N correlated motion at high energy.

As the initial excitation in these modes is diminished the reaction rates for the (3 0 0 0 38 0) and the (3 0 0 0 0 44) states slow, but are still substantially faster than those states reduced to random IVR, such as the (6 0 0 0 20 0) and the (6 0 0 0 0 24) excitations which have rates comparable to other states where the initial excitation has insufficient energy to permit immediate reaction.

7.2.4 Summary

The purpose of the preceding experiments is to examine the structure of phase space in terms of local rates of reaction. Normal mode excitations prove to be a useful tool in this undertaking, as their resultant decay curves tend to have fairly simple shapes which can be readily explained in terms of couplings and energy transfer.

Many of the excitations have decay curves with a segment of extremely fast reactions near time zero. These are reactions where sufficient energy either resides in, or else reaches the reaction coordinate quickly enough to allow reaction to occur within one or two oscillations. This behavior is characteristic of states whose initial conditions include an excitation of sufficient size to permit reaction, should the excitation reach the reaction coordinate prior to dispersion. Because of the greater total energy in this series of calculations these fast reactions may or may not involve the same hose as discussed in Chap. 3. It is reasonable to infer that the N=N excitation will transfer energy in a manner similar to that at lower energies, comprising a hose with one set of characteristic correlated motions. However, at high energies NNN and $\tau$ become
Figure 7.3 Logarithmic decay curves for N-N=N, and torsional normal mode excitations of HN₃. Each data set represents five hundred trajectories whose total energy is 3.2Eₒ.
capable of strong coupling to the reaction coordinate. I infer that either separately, or together, these two modes have a separate small hose or hoses which involve their energy transfer to the reaction coordinate. The characteristic correlated motions of these small hoses are lost in the tornado plots because in those plots trajectories are microcanonically sampled, and these high overtone states are but a small component of the ensemble. (Tornado plots will only reveal the existence of a hose that all, or most trajectories traverse.) We can see remnants of small hoses in the horsetail plots, where they appear as small bundles of trajectories moving together within an otherwise random distribution. The difference between the small hose for high energy NNN and \( \tau \) and the large hose for low energy \( N=N \) is that in the former case only a small portion of a microcanonical ensemble traverse a small hose, whereas in the latter case essentially all members of the microcanonical ensemble traverse the large \( N=N \) hose.

The decay curves for most excitations have a portion corresponding to slow reactions. The reaction rates for these long lived trajectories are fairly consistent irrespective of excitation. These slower reactions represent trajectories wherein the initial excitation did not arrive in the reaction coordinate as a neat bundle, but rather had to find its way to the reaction coordinate via random IVR. Thus it is not surprising that the slow reaction rates are independent of excitation. What is a surprise is that the HNN mode is apparently nearly as poorly coupled to other oscillators as the H-N stretching mode.

Lastly I wish to make a very important point. In Chap. 4 I proposed an entity I called the phase space trajectory distribution map (or distribution map for short) which is a reordering of phase space points by time proximity to reaction. I also showed that the shape of this distribution map can be inferred from the observed kinetics, and that there is a map shape which corresponds to garden variety first
order RRKM kinetics. One purpose of the preceding experiments is to show that when we sample the Hamiltonian locally (as in normal mode excitations) we may observe different kinetics (i.e. mode specific reaction rates) than when we sample the whole Hamiltonian globally and randomly (i.e. microcanonically). However, each local sampling is a subset of the whole. If we were to examine any particular time slice of the distribution map, some normal modes would have greater representation and some lesser, depending upon their separate mode specific kinetics, but the ensemble response of all possible state specific responses can result in first order decay. So, the existence of mode specific rate constants is entirely consistent with RRKM kinetics.

7.3 Initial conditions and trajectory lifetimes

In this section I explore the relationship between phase and trajectory lifetimes, emphasizing conditions which result in long lived trajectories. I will show that long lived trajectories are those whose phase relationships allow the initial excitation to disperse into other modes prior to encountering the reaction coordinate. These trajectories then survive until sufficient energy reaches the reaction coordinate to cause dissociation. Fig. 7.2 and Fig. 7.3 show that the rate for this slow process is independent of the initial excitation.

7.3.1 Normal mode behaviors

In the experiments of the preceding section, each trajectory within a given data set had the same total energy and the same distribution of normal mode energies as any other, yet some trajectories react immediately while others survive for picoseconds. What accounts for these differences in behavior?

As usual, phase is a chief suspect. To check the effect of phase on trajectory duration I used the same initial mode excitations and the same total energy as before,
but this time I calculated three hundred trajectories in each data set. For the new sets of trajectories I saved the phase angles for the initial normal mode excitations along with the corresponding lifetime of the trajectory. Thus armed with information regarding both initial phases and lifetimes I was now able to see if any relationship exists.

If we disregard the energy in the kinetically isolated H-N mode, each data set has only a single normal mode which is excited. I therefore am looking for a relationship between phase of the orthogonal coordinate, which must transfer energy, to phase of the reaction coordinate, which must receive it, as a function of time to reaction, which indicates how long after the inception the exchange took place. To check for a relationship amongst these three factors in the most direct fashion possible, I created a three dimensional plot of the data set, with time along the z axis, and draped a mesh grid across the resulting points to give a better 3D perspective. In the resulting plots the plains correspond to phase relationships resulting in rapid reaction, while the mountainous regions correspond to phase relationships which result in long lived trajectories. As before, each normal mode will be discussed separately.

N=N excitation

The (0 15 0 0 0 0) excitation in Fig. 7.4 shows a stark relationship between the phase of excitation and the lifetime of a trajectory. Recall that the N=N mode correlates strongly with the reaction coordinate. If the initial excitation is deposited in this mode with a phase between $\pi$ and $2\pi$ (corresponding to positive momentum) then reaction occurs promptly. Only if the initial excitation has negative momentum do the trajectories manage to survive for a few oscillations.

When the size of the initial excitation is reduced to 2.0E6 Fig. 7.5 shows that the phase relationship becomes more complex, but there is still a region where reactions
Figure 7.4  Relationship for the \((0\ 1\ 5\ 0\ 0\ 0\ 0)\) state between time to reaction and the initial phases (in radians) of the reactive N-N normal mode and the N=N normal mode.
Figure 7.5  Relationship for the \((3\ 1\ 0\ 0\ 0\ 0)\) state between time to reaction and the initial phases (in radians) of the reactive \(N-N\) normal mode and the \(N=N\) normal mode.
Figure 7.6  Relationship for the (6 6 0 0 0 0) state between time to reaction and the initial phases (in radians) of the reactive N-N normal mode and the N=N normal mode.
occur rapidly, when the initial phase of N=N is between π and 2π and that of N-N is circa π. This region defines the phase relationship required for energy transfer. All trajectories in this state with other phase relationships must evolve until their phases so coordinate as to be able to transfer energy. As shown by the random distribution of long lived trajectories, evolution from an arbitrary initial phase to one that allows energy transfer is random.

Once the excitation is reduced to 1.1E₆ (Fig. 7.6) any preferred phase relationship which allows rapid reaction is lost in the jumble of random long lived trajectories.

N-N excitation

Recall that when a large initial excitation (3.0E₆) was placed in the reaction coordinate a few trajectories still managed to survive for up to a picosecond. Fig. 7.7 shows that these anomalously long lived trajectories share the characteristic that the initial excitation occurs in the vicinity of zero/2π. All other trajectories proceed to react promptly, but the few trajectories whose initial excitation occurs very close to the outer turning point manage to leak sufficient energy into other modes to prevent immediate reaction. This is yet another piece of evidence that outer turning points are critically important to the process of IVR.

When the excitation is reduced Fig. 7.8 shows that now a greater range of phase relationships are capable of siphoning energy out of the reactive mode. The pattern is more complex, but trajectories with the initial excitation at the outer turning point still tend to be longer lived.

By the time the excitation is reduced to 1.1E₆ Fig. 7.9 shows that nearly all trajectories are long lived. Only a small region, with N=N phases between π and 2π and N-N phases circa π continue to react rapidly. This figure also shows that the algorithm for draping the mesh across the data points has occasional problems with
Figure 7.7 Relationship for the \((0 \ 0 \ 27 \ 0 \ 0)\) state between time to reaction and the initial phases (in radians) of the reactive N-N normal mode and the N=N normal mode.
Figure 7.8  Relationship for the (3 0 1 8 0 0 0) state between time to reaction and the initial phases (in radians) of the reactive N-N normal mode and the N=N normal mode.
Figure 7.9  Relationship for the (6 0 1 0 0 0 0) state between time to reaction and the initial phases (in radians) of the reactive N-N normal mode and the N=N normal mode.
rapid changes in the data set, and will then introduce artifacts to the resulting surface. (The spike in the figure near the N-N phase value of 2 is an example.) However the artifacts, while difficult to remove, are easily identified and can readily be ignored.

HNN excitation

This mode is of interest because its reaction rate is slow regardless of the initial excitation. Fig. 7.10 shows that even the greatest excitation results in basically long lived trajectories. There is a small region in the middle where trajectories react rapidly, but in general this initial excitation does not lead directly to reaction. Fig. 7.11 and Fig. 7.12 show that as energy in the initial excitation diminishes even the traces of a cohesive region of preferred phase relationships for rapid reaction disappear. Time to reaction and initial phase values are uncorrelated, resulting in randomly distributed peaks and valleys, with the pronounced peak in the middle of Fig. 7.12 simply representing the extreme value of the random distribution.

Torsional excitation

Recall from Fig. 7.3 that high overtone excitation of the \( \tau \) mode leads to rapid reaction. Fig. 7.13 shows that with an initial excitation of 3.0E6 rapid reaction occurs if the initial phases are near zero, \( \pi \) or \( 2\pi \), with all other phase relationships reacting more slowly. (The rapidly reacting trajectories correspond to an initial excitation atop a torsional barrier, but torsion is isolated by symmetry from the reaction coordinate and the torsional barrier has far less energy than that required for this dissociative reaction.) Recall that for a torsional mode a phase of zero or \( 2\pi \) corresponds to the right hand side potential maximum, and a phase of \( \pi \) corresponds to the left hand side potential maximum. In either case these locations \((0,\pi,2\pi)\) are regions of the
Figure 7.10  Relationship for the (0 0 0 29 0 0) state between time to reaction and the initial phases (in radians) of the reactive N-N normal mode and the HNN normal mode.
Figure 7.11 Relationship for the (3 0 0 2 0 0 0) state between time to reaction and the initial phases (in radians) of the reactive N-N normal mode and the HNN normal mode.
Figure 7.12  Relationship for the $(6 \, 0 \, 0 \, 1 \, 1 \, 0 \, 0)$ state between time to reaction and the initial phases (in radians) of the reactive N-N normal mode and the HNN normal mode.
Figure 7.13  Relationship for the (0 0 0 55 0) state between time to reaction and the initial phases (in radians) of the reactive N-N normal mode and the $\tau$ normal mode.
Figure 7.14  Relationship for the (3 0 0 0 38 0) state between time to reaction and the initial phases (in radians) of the reactive N-N normal mode and the $\tau$ normal mode.
Figure 7.15  Relationship for the (6 0 0 0 2 0 0) state between time to reaction and the initial phases (in radians) of the reactive N-N normal mode and the $\tau$ normal mode.
PES marked by negative curvature, so this figure shows that the relationship between PES position and rapid reaction is not simply between the outer turning point and rapid energy transfer, but rather between regions of negative curvature and rapid energy transfer. The inference I draw from these results is that negative curvature of the PES facilitates energy transfer from \( \tau \) into the reaction coordinate, permitting rapid reaction. This figure is yet more evidence that negative curvature regions are important to energy transfer. (In the next section we will see evidence that at high energies \( \tau \) and the N-N=N bend act as a single mode, suggesting that the N-N=N bend can act as a conduit between \( \tau \) and the reaction coordinate.)

Fig. 7.14 shows that the same pattern continues to hold even in the case of an initial excitation of 2.0E6. It is only when the excitation is reduced to 1.1E6 (Fig. 7.15) that no significant impulsive energy transfer is immediately possible. Under these conditions no pattern is discernible in the IVR, as the random distribution of long and short lived trajectories shows.

**NNN excitation**

The shape of the decay curves (Fig. 7.3) for the high overtone excitations of NNN and \( \tau \) are amazingly similar, leading me to speculate that at high energies these two modes act as one. Certainly Fig. 7.16 supports this notion. Just as in the case of the (0 0 0 0 55 0) excitation, the (0 0 0 0 0 64) state shows a strong pattern of phase correlations, such that rapid reactions occur when the NNN initial phase is either zero, \( \pi \) or 2\( \pi \). Trajectories whose initial phase is not associated with a turning point tend to be longer lived. This trend persists when the initial excitation is 2.0E6 (Fig. 7.17). Only when the initial excitation is reduced to 1.1E6 (Fig. 7.18) does the distribution of lifetimes become random with respect to initially assigned phases.
Figure 7.16 Relationship for the (0 0 0 0 64) state between time to reaction and the initial phases (in radians) of the reactive N-N normal mode and the NNN normal mode.
Figure 7.17  Relationship for the (3000044) state between time to reaction and the initial phases (in radians) of the reactive N-N normal mode and the NNN normal mode.
Figure 7.18  Relationship for the (6 0 0 0 0 24) state between time to reaction and the initial phases (in radians) of the reactive N-N normal mode and the NNN normal mode.
Summary

The duration of any given trajectory depends upon how long after excitation it takes for sufficient energy to arrive at the reaction coordinate. If the initial excitation is already in the reaction coordinate then reaction is simply a matter of retaining energy in that mode until the transition state is crossed. If the initial excitation is elsewhere then reaction depends upon transferring energy into the reaction coordinate. Results of several of the previous experiments indicate that negative curvature regions are critical to energy transfer. When the reaction coordinate is excited only those trajectories whose initial conditions place them at the outer turning point (i.e. in negative curvature) manage to transfer sufficient energy to last for several oscillations. When the torsional mode is excited only those trajectories whose initial conditions place them on local maxima (within negative curvature) are able to transfer energy into the reaction coordinate, and so react rapidly. In either case for HN₃ IVR seems to occur most readily in association with regions of negative curvature of the PES. These results are in accord with the previous observation for HN₃ in Chap. 6 that trajectories tend to converge in phase in the vicinity of outer turning points. The process of convergence of trajectories corresponds to IVR, and Fig. 6.3 shows that this occurs predominantly at intervals of 2π, when the reaction coordinate is at the outer turning point, in negative curvature regions of the PES.

7.4 Phase relationships for rapid reactions

This section focusses on the initial phase conditions which allow trajectories to react rapidly. I will show that these trajectories are characterized by phase conditions which permit facile energy transfer from the excited mode into the reaction coordinate. Some modes allow energy transfer under a wide set of phase relationships, while
others are far more selective. When there are few trajectories for a given state which are capable of rapid reaction, I find that those trajectories have sharply defined phase criteria. The initial phase relationships for rapidly reacting trajectories are an alternative expression of the phase space hose. Because this series of calculations occurs at high total energy (3.2E₄) the form of these hoses is different from the previously discussed low energy limit, and trajectories may traverse any of several possible hoses, but similarities can readily be identified.

7.4.1 Normal mode behaviors

The previous analysis of initial phase and reaction time has tended to emphasize the conditions which cause trajectories to be long lived, but even more important are the conditions which result in rapid reaction. To examine these conditions more closely I will begin by redisplaying the decay curves for the overtone excitations at a scale which emphasizes rapid reactions, in Fig. 7.19 and Fig. 7.20. The decay curves tend to have two linear regions, with the first (which has the faster rate) comprised of the earlier "prompt" reactions, while the second region with later reactions has a slower reaction rate. The purpose of this section is to discover what differentiates the faster region from the slower, so I will emphasize those states which have an appreciable number of prompt reactions.

To ascertain if phase correlations determine which trajectories react promptly I again sought a relationship between the phases of the initial excitations of the reaction and each orthogonal mode, but in this analysis the z axis is the reciprocal of time to reaction, thereby emphasizing trajectories which react quickly. Hereafter the mountainous regions are fast reactions and the plains are slow ones. As before, each normal mode will be discussed separately.
Figure 7.19  Logarithmic decay curves for N=N, N-N and HNN normal mode excitations of HN$_3$. Each data set represents five hundred trajectories whose total energy is 3.2E$_6$. This data set is the same as the previous, just redisplayed to emphasize rapid reactions.
Figure 7.20  Logarithmic decay curves for N-N=N and torsional normal mode excitations of HN$_3$. Each data set represents five hundred trajectories whose total energy is 3.2E$_b$. This data set is the same as the previous, just redisplayed to emphasize rapid reactions.
N=N excitation

The (0 15 0 0 0 0) excitation results in very fast reactions, but as Fig. 7.19 shows the rate is not uniform. Fig. 7.21 shows that the fastest reactions occur when the initial excitation has positive momentum. Recall that the correlated motion between N=N and N-N places both in phase during the final oscillation, so positive momentum for N=N is equivalent to also specifying positive momentum for the reaction coordinate. These trajectories head straight for the transition state (2π), with those closest reaching it first. However, the decay curve in Fig. 7.19 shows intriguing discontinuities at roughly 0.04 and 0.07 ps. To further investigate these I plotted separately all trajectories reacting in less than 0.045 ps (Fig. 7.22) and those that react between 0.045 and 0.070 ps (Fig. 7.23). Almost all trajectories reacting within 0.045 ps have initial N=N momentum directed towards the outer turning point, while those trajectories reacting between 0.045 and 0.070 ps have initial momenta directed away from the outer turning point. (The earlier time span thus corresponds to the final half cycle of oscillation, while the later time span corresponds to the half cycle preceding that.) For the (0 15 0 0 0 0) state (which is a high overtone of a mode that couples strongly to the reaction coordinate) the direction of the initial momentum is the primary determinant of trajectory duration.

When I decreased the excitation Fig. 7.24 shows that the prompt reactions (i.e. those within 0.045 ps), while less numerous, still largely correspond to those with initial positive momentum. When the initial excitation is reduced to 1.1E₆, the (6 6 0 0 0 0) case shows (in Fig. 7.25) that prompt reactions (within 0.045 ps) are few and very specific. The prompt trajectories have initial N=N excitations with positive momentum and have the N-N oscillator initially in the vicinity of π.
Figure 7.21 Relationship for the (0 15 0 0 0 0) state between the inverse time to reaction and the initial phases of the reactive N-N normal mode and the N=N normal mode. This plot includes all reactions.
Figure 7.22  Relationship for the (0 1 5 0 0 0 0) state between the inverse time to reaction and the initial phases of the reactive N-N normal mode and the N=N normal mode. This plot includes only those trajectories reacting within 0.045 ps.
Figure 7.23 Relationship for the (0 15 0 0 0 0) state between the inverse time to reaction and the initial phases of the reactive N-N normal mode and the N=N normal mode. This plot includes only those trajectories reacting between 0.045 and 0.072 ps.
Figure 7.24 Relationship for the (3 1 0 0 0 0 0) state between the inverse time to reaction and the initial phases of the reactive N-N normal mode and the N=N normal mode. This plot includes only those trajectories reacting within 0.045 ps.
Figure 7.25  Relationship for the (6 6 0 0 0 0) state between the inverse time to reaction and the initial phases of the reactive N-N normal mode and the N=N normal mode. This plot includes only those trajectories reacting within 0.045 ps.
N-N excitation

Nearly all trajectories in the \(0 0 27 0 0 0\) state react in less than 0.05 ps, and we have already determined that those few that do not react have initial excitations near the outer turning point. Fig. 7.26 is consistent with these observations, showing that trajectories reacting most rapidly are those with initial N-N phase near \(2\pi\). Close examination of the \(0 0 27 0 0 0\) decay curve in Fig. 7.19 shows that even the prompt reactions do not occur at a uniform rate. For that reason I have plotted separately prompt reactions occurring before and after the knee in the curve at roughly 0.02 ps. Fig. 7.27 and Fig. 7.28 show the results. As expected, the fastest reactions are those with initial phases between roughly \(\pi\) and \(2\pi\). The somewhat slower reactions, occurring between 0.019 and 0.045 ps all have initial phases between zero and nearly \(\pi\). The surprise in this data set is that the knee in the curve that divides the two regions of the decay curve does not coincide precisely with \(\pi\).

When I decrease the excitation to \(2.0E_6\) prompt reactions are not nearly as well organized as before (see Fig. 7.29). The fastest reactions tend to have initial phases between \(\pi\) and \(2\pi\), but there are dramatic local variations within that trend.

When the initial excitation is reduced to \(1.1E_6\) Fig. 7.30 shows that conditions for prompt reactions are now somewhat restricted. The most favorable conditions for prompt reaction occur when the initial N-N stretch is near \(\pi\). Recall from the discussion of correlated motion that impulsive energy transfer between N=N and N-N occurs when N-N is close to the inner turning point.

HNN excitation

Fig. 7.19 shows that in general HNN couples only poorly to the reaction coordinate, since very few trajectories result in prompt reaction. However, to varying
Figure 7.26  Relationship for the (0 0 27 0 0 0) state between the inverse time to reaction and the initial phases of the reactive N-N normal mode and the N=N normal mode. This plot includes all reactions.
Figure 7.27  Relationship for the (0 0 27 0 0 0) state between the inverse time to reaction and the initial phases of the reactive N-N normal mode and the N=N normal mode. This plot includes only those trajectories reacting within 0.019 ps.
Figure 7.28 Relationship for the (0 0 27 0 0 0) state between the inverse time to reaction and the initial phases of the reactive N-N normal mode and the N=N normal mode. This plot includes only those trajectories reacting between 0.019 and 0.045 ps.
Figure 7.29  Relationship for the (3 0 18 0 0 0) state between the inverse time to reaction and the initial phases of the reactive N-N normal mode and the N=N normal mode. This plot includes only those trajectories reacting within 0.045 ps.
Figure 7.30  Relationship for the (6 0 1 0 0 0 0) state between the inverse time to reaction and the initial phases of the reactive N-N normal mode and the N=N normal mode. This plot includes only those trajectories reacting within 0.045 ps.
Figure 7.31 Relationship for the \((0 \ 0 \ 29 \ 0 \ 0)\) state between the inverse time to reaction and the initial phases of the reactive N-N normal mode and the HNN normal mode. This plot includes only those trajectories reacting within 0.050 ps.
Figure 7.32  Relationship for the \((3 \ 0 \ 0 \ 20 \ 0 \ 0)\) state between the inverse time to reaction and the initial phases of the reactive N-N normal mode and the HNN normal mode. This plot includes only those trajectories reacting within 0.050 ps.
Figure 7.33  Relationship for the (6 0 0 11 0 0) state between the inverse time to reaction and the initial phases of the reactive N-N normal mode and the HNN normal mode. This plot includes only those trajectories reacting within 0.050 ps.
degrees each HNN decay curve shows an inflection point or a discontinuity at about 0.05 ps. For that reason the following plots will focus on reactions occurring prior to 0.05 ps.

Fig. 7.31 shows that for the (0 0 0 29 0 0) state all prompt reactions have initial phases between $\pi$ and $2\pi$. When the initial excitation is reduced to $2.0E_6$, Fig. 7.32 shows that the location for prompt reaction shifts, but that the conditions for prompt reaction are fairly restricted. When the initial excitation is reduced to $1.1E_6$ Fig. 7.33 shows that the initial conditions for the few trajectories that do react quickly are quite specialized, centering on a region where the initial phase of N-N is $\pi$ and that of HNN is roughly $\frac{3\pi}{2}$. This corresponds to placing the N-N normal mode at its inner turning point while the H-N-N bending normal mode is near equilibrium, heading towards the outer turning point. (As Tab. 6.2 shows, each of these normal modes is a linear combination of local modes, so the exact molecular configuration corresponding to this phase relationship is not easily specified.)

**Torsional excitation**

One of the surprises in the HN$_3$ overtone calculations was that high torsional excitation results in rapid reaction. Fig. 7.20 shows that while reaction rates are rapid for the (0 0 0 0 55 0) state, they are not uniform. I chose to examine phase relationships in two time ranges, from zero to 0.033 ps and from 0.033 to 0.070 ps. In both cases the upper time boundary corresponds with a local slowing in the rate of reaction. Fig. 7.34 shows the phase relationships for the fastest reactions. Trajectories whose $\tau$ mode couples readily to the reaction coordinate all have phases clustered about 0, $\pi$ or $2\pi$; the regions of the PES where the torsional potential has negative curvature. Fig. 7.35 shows the phase distribution for the next most rapid set of reactions. Except for local depletions right at 0, $\pi$ and $2\pi$ (all of which trajectories
Figure 7.34  Relationship for the (0 0 0 55 0) state between the inverse time to reaction and the initial phases of the reactive N-N normal mode and the torsional normal mode. This plot includes only those trajectories reacting within 0.033 ps.
Figure 7.35  Relationship for the (0 0 0 0 55 0) state between the inverse time to reaction and the initial phases of the reactive N-N normal mode and the torsional normal mode. This plot includes only those trajectories reacting between 0.033 and 0.070 ps.
Figure 7.36 Relationship for the (3 0 0 0 3 8 0) state between the inverse time to reaction and the initial phases of the reactive N-N normal mode and the torsional normal mode. This plot includes only those trajectories reacting within 0.044 ps.
Figure 7.37  Relationship for the (6 0 0 0 20 0) state between the inverse time to reaction and the initial phases of the reactive N-N normal mode and the torsional normal mode. This plot includes only those trajectories reacting within 0.044 ps.
belong to the set of most rapid reactions) the phase distribution is fairly random.

Fig. 7.36 shows the phase relationships for the most rapid reactions of the \((3 \, 0 \, 0 \, 0 \, 38 \, 0)\) state. As before, these center on the negative curvature region of the PES. Fig. 7.37 shows the phase relationship for the few trajectories in the \((6 \, 0 \, 0 \, 0 \, 20 \, 0)\) state which do react rapidly. As with the higher torsional excitations these rapidly reacting trajectories cluster about \(0, \pi\) and \(2\pi\) in initial phase.

**NNN excitation**

Another surprise in the outcome of measuring mode specific rate constants was that at high excitations \(\tau\) and the NNN bend behave so similarly. Fig. 7.20 shows that the decay curves for the \((0 \, 0 \, 0 \, 0 \, 55 \, 0)\) and the \((0 \, 0 \, 0 \, 0 \, 64)\) states are virtually identical up to 0.10 ps. One possible explanation is that at these very high excitations both modes have merged, forming a single mode. One can visualize the motion as a combination of the NNN bend and the torsion such that as the NNN bend heads towards its outer turning point the bending angle exceeds \(\pi\). The bending motion likely includes a small out of plane (torsional) component which prevents the terminal N atom from becoming collinear, and the net result of the excited bending motion is a torsion. The results shown in Fig. 7.38 and Fig. 7.39 are consistent with this hypothesis. These figures show that the phase relationships for the \((0 \, 0 \, 0 \, 0 \, 0 \, 64)\) state are virtually identical to those of the \((0 \, 0 \, 0 \, 0 \, 55 \, 0)\) state.

The apparent coupling of NNN and \(\tau\) persists even at lower energies. The decay curves for the \((3 \, 0 \, 0 \, 0 \, 38 \, 0)\) and the \((3 \, 0 \, 0 \, 0 \, 44)\) states are very similar, as are the phase relationships expressed in Fig. 7.36 and Fig. 7.40. Even at excitations as low as \((6 \, 0 \, 0 \, 0 \, 0 \, 24)\) the phase relationships for the NNN bend, shown in Fig. 7.41 are very similar to the corresponding torsional excitation. (The sharp peak near the N-N=N phase of 2 is an artifact of the mesh draping process within MATLAB, and
Figure 7.38  Relationship for the (0 0 0 0 0 64) state between the inverse time to reaction and the initial phases of the reactive N-N normal mode and the NNN normal mode. This plot includes only those trajectories reacting within 0.033 ps.
Figure 7.39  Relationship for the (0 0 0 0 0 64) state between the inverse time to reaction and the initial phases of the reactive N-N normal mode and the NNN normal mode. This plot includes only those trajectories reacting between 0.033 and 0.070 ps.
Figure 7.40  Relationship for the (3 0 0 0 0 44) state between the inverse time to reaction and the initial phases of the reactive N-N normal mode and the NNN normal mode. This plot includes only those trajectories reacting within 0.044 ps.
Figure 7.41 Relationship for the $6000024$ state between the inverse time to reaction and the initial phases of the reactive N-N normal mode and the NNN normal mode. This plot includes only those trajectories reacting within 0.044 ps.
should be ignored.)

Summary

Trajectories which react quickly have two characteristic traits:

- An excitation with greater than $E_b$ energy in a single mode.

- Phase relationships conducive to transferring energy into the reactive coordinate, or to maintaining it there.

7.5 Conclusions

In many respects the previous series of calculations for overtone excitations of HN$_3$ is the culmination of my research, in which I used concepts developed in previous investigations to explain in detail the observed results. In this section I revisit two principal conclusions arising from this body of work.

7.5.1 The significance of negative curvature regions

In HN$_3$ negative curvature regions of the PES (typically outer turning points) are critical to coupling, and therefore to subsequent energy transfer. Numerous observations support this contention. I will revisit in detail only two.

In the previous chapter, Fig. 6.4 shows that sets of trajectories converge with the hose at intervals of roughly $2\pi$. These regions of convergence correspond to successive visits by the reaction coordinate oscillator to the outer turning point.

In this chapter the series of overtone excitations reinforce the importance of the outer turning point to energy transfer. When the initial excitation was in an orthogonal mode with facile energy transfer, the most rapid reactions corresponded to initial excitations at the outer turning point. These trajectories were able to transfer energy
swiftly into the reaction coordinate. Conversely, when the initial excitation was in the reaction coordinate, all long lived trajectories had initial excitations at the outer turning point. Only those trajectories were able to transfer sufficient energy to the orthogonal modes to avoid immediate reaction.

I rationalize the relationship between energy transfer and negative curvature of the PES in terms of the maximum complexity PES. Recall that the maximum complexity PES is a conceptual construct wherein by coordinate transformation all effects of kinetic couplings have been forced into the potential portion of the Hamiltonian. The resulting PES, while related to the original untransformed one, is now less symmetric and more complex than previously, as it incorporates the effects of kinetic couplings. This rather irregular surface is one for which a trajectory may be modelled as the outcome of rolling a marble, and subsequent arguments regarding the interaction between negative curvature and IVR will be based on the rolling marble model.

When a trajectory visits an outer turning point there is often a reversal of momentum on a surface with negative curvature. Approaching the transition state along the reaction coordinate the PES changes from positive to negative curvature, and is momentarily flat at the saddle point. This has two effects, namely that the time which a trajectory spends in the vicinity of an outer turning point can be considerable as the momentum decreases to zero, and that the relative effect of perturbations (induced by incorporating the effects of kinetic couplings) on a nearly flat surface will be greater. When the marble (representing the trajectory) interacts with local variations in the gradient at low velocity it can emerge from the encounter with a significantly different direction. (However should that encounter occur near equilibrium on the PES where the momentum is maximum, the marble can fly right across the perturbation without being significantly deflected.) It is the deflection of a trajectory into a new direction that results in energy transfer from one mode to another. The properties of the outer
turning point that facilitate energy transfer are:

- Local curvature is negative and the slope is zero briefly at the transition state. The gradient of a negative curvature surface diverges, while that of a positive curvature surface converges.

- Momentum slows to zero and reverses. If the PES curvature is gradual, so too is the deceleration, allowing plenty of time for interaction with local features along other directions. Particularly at the instant when momentum is zero the trajectory is susceptible to local variations in the gradient, which can greatly influence the direction of departure from the outer turning point, especially if (as in the case of zero slope) the variations are large with respect to the local gradient.

These arguments have been developed based on observations of the behavior of HN$_3$. While each of the preceding properties of negative curvature of the PES is general (i.e. not simply a characteristic of the HN$_3$ PES) further work remains to determine whether this model for IVR is broadly applicable.

7.5.2 Mode specific rates and RRKM kinetics

*Mode specific rates are compatible with RRKM kinetics.*

A microcanonical rate constant is determined by sampling the Hamiltonian in a manner that is both random and global. State specific rate constants are a consequence of sampling the Hamiltonian locally, and so need not have the same value as the microcanonical rate constant. The global Hamiltonian is the sum of its local regions, so the microcanonical rate constant reflects contributions from all component state specific rate constants. States which are on average close to the transition state
(such as highly excited reaction coordinate modes) will have a reaction rate faster than the microcanonical case. States which are on average far removed from the transition state (such as states where the energy is evenly distributed, in which energy for reaction cannot be transferred impulsively) will have reaction rates slower than the microcanonical rate. The observed microcanonical rate constant is an average of all contributing mode specific rate constants, so the existence of a single measurable first order microcanonical rate constant can be consistent with the simultaneous existence of mode specific rate constants.
Chapter 8
Conclusions

8.1 Summary of findings

In real molecules energy moves between modes and bonds break. Any worthwhile mathematical simulation of a molecule must therefore include both coupling and anharmonicity. However, period varies with energy for anharmonic oscillators, and coupling permits energy transfer between modes, so the period of oscillation for an anharmonic local mode can be quite variable. When trajectories are compared in time, differences in the periodicity of oscillations soon cause local modes to be out of phase, even when they begin in phase. Coherent comparison of trajectories avoids this problem by comparing trajectories cycle by cycle, irrespective of the arbitrary time index of the motion. *Phase based comparison of trajectories is superior to time based comparison* because the local mode motions being averaged over all occur when the reaction coordinate is in a fixed region of phase space. Coherent comparison of trajectories reveals considerable structure to reaction dynamics that is not evident in time. However, to uncover this structure requires the ability to assign a physically meaningful phase to rather irregular motions. Fortunately, the Hilbert transform is able to accomplish this, assigning consistent phase angles irrespective of the aperiodicity and anharmonicity of the system.

Not all modes show structure in their reaction dynamics, even when viewed from a phase perspective. During reaction the motion of some modes correlates with the reaction coordinate, while that of other modes does not. *Modes with correlated motion couple strongly to the reaction coordinate. The synchronization of phases between these modes which permits energy transfer causes the correlated mode to have only a narrow range of phases compared to the energetically allowed set.* Modes which do
not transfer energy into the reaction coordinate are unconstrained, and their reaction dynamics show no phase convergence.

A growing body of evidence (both experimental and theoretical) indicates that a restricted set of states may lead to and depart from the transition state. The existence of states with correlated motion that lead directly to the transition state has been problematical for physical chemists because correlated motion appears to contradict a fundamental assumption of RRKM kinetics, namely that all states are equally likely to react. (Although there are classes of molecules which violate RRKM theory, it is still broadly applicable, so it is important to reconcile correlated motion with RRKM theory, if possible.) Only by detailed examination of the implications of this RRKM assumption does it become apparent that the requirement that all states be equally likely to react is not the same as the requirement that all states be equally likely to react per unit of time. States involved in correlated motion will react sooner than other states, but (in the absence of trapping) ultimately all states react, so the reaction probability for any state is the same.

To bridge the gap between kinetics, the realm of RRKM theory, and dynamics, the realm of correlated motion I proposed a variant of phase space. Conceptually, every point in phase space may be labelled with a time index identifying how long until that point evolves to the transition state and reacts. These time indices can be mapped into a histogram which shows the distribution of phase space points as a function of time. Random sampling of this mapping is equivalent to microcanonical sampling of the isoenergy hypersurface in phase space, and will result in a microcanonical decay curve. However, phase space points are not distributed randomly by time index. Points right at the transition state (with time index of zero) whatever their other properties, share the common feature of having at least $E_0$ in the reaction coordinate. Since the distribution of phase space points is nonrandom at zero time, there is no
intrinsic reason why phase space points must be randomly distributed at any arbitrary time index. The only constraint on the system is that the overall distribution of time indices conforms to the microcanonical rate constant. Conversely, when only a local region of phase space is sampled (such as for mode specific kinetics) the decay curve may differ from the microcanonical case. The only constraint is that the average rate constant resulting from the ensemble of states that comprise the microcanonical case is equal to the microcanonical rate constant. Therefore mode specific reaction rates are compatible with RRKM kinetics.

Study of mode specific reaction rates showed that trajectories which have the same distribution of energy may react promptly, or may survive for many oscillations, with the outcome depending upon the phase of the initial excitation. In HN$_3$ when rapid reaction depends upon conserving the initial excitation in the reaction coordinate only those trajectories whose initial excitation was at the outer turning point were able to transfer sufficient energy to avoid prompt reaction. Evidence from the torsional mode (where rapid reaction is associated with excitations at local maxima) suggests that the salient feature of the outer turning point is the negative curvature of the PES. Also the structure of the HN$_3$ hose showed periodic convergence of trajectories after they have visited regions of negative curvature. These results suggest that for HN$_3$ negative curvature is critical to the process of IVR. Further work remains to ascertain if the relationship between negative curvature and IVR is unique to HN$_3$, or is more broadly applicable, but the properties of negative curvature of the PES which can enhance IVR are not specific to HN$_3$.

These results, along with those of HONO, imply that considerable care should be taken in the construction of the PES in the vicinity of outer turning points in general, and the transition state in particular, as details of couplings can influence the observed reaction dynamics.
8.2 Implications for further work

Lasers were greeted by chemists with great enthusiasm as the tool which would make possible active control of chemical reactions. Chemists harbored hopes of being able to increase reaction rates or even to select reaction channels. To date the promise of lasers for active control has borne little fruit. Rapid excitation of a single mode is tricky business. If the laser pulse is sufficiently monochromatic to excite a single mode then its time duration relative to molecular motions must be long. Conversely, a laser pulse that is brief compared to molecular motions is not sufficiently monochromatic to excite only a single mode.

On a positive note, the HN$_3$ results (i.e. for most modes in HN$_3$ high overtone excitations resulted in rates of reaction faster than the microcanonical one) suggest that if high overtone excitations can be achieved, the particular mode being excited may not be critical to achieving rates of reaction that are faster than the statistical case. It is unlikely that such a brute force excitation would select anything but the lowest channel, but in a relatively small molecule such as HN$_3$ such an excitation apparently finds the reaction coordinate before dissipating into random energy.

An interesting extension of this work would be to incorporate the existence of the hose into an optimal control scheme for the design of active control pulses [50]. There may be advantages to specifying as a target a molecular state within the hose leading to the transition state, rather than the transition state itself. Certainly for HN$_3$ the hose is sufficiently well characterized that it is clear which local modes are constrained and which are not, so (in Rabitz’s terminology) both the target objective and the penalty costs are well defined. These quantities determine the nature of the optimal wavepacket which is the solution to the time dependent Schrödinger equation.
Appendix A
Pandora

This appendix gives an overview of the Pandora program package for calculation of classical trajectories. After a brief introduction comes a section summarizing the structure of Pandora. The final section deals with modifications that I have made.

A.1 Introduction

Pandora is a package of programs that can be easily modified to generate classical trajectories for specific molecules. Written in Fortran 77, it is the product of many people’s labor, with all the strengths and weaknesses inherent in such a collaborative effort. A detailed description of Pandora’s inner workings would comprise a thesis in itself, so in the interests of brevity this appendix will only summarize the main features of the package.

A.2 Pandora’s structure

The reusable code in Pandora is fundamentally nothing more than a numerical integration of Hamilton’s equations of motion, but many stages are necessary before reaching the heart of the matter. Pandora consists of more than twenty interlocking programs and subroutines which may conveniently be regarded as comprising the following subpackages, each of which will be discussed in the following subsections:

- External routines which are molecule specific
- Diagnostic routines
- Set up routines
- Initial conditions routines
• Numerical integration

To adapt Pandora for a specific molecule requires creation of a number of molecule specific routines, which is the subject of the following subsection.

A.2.1 Molecule specific routines

To function, Pandora must be supplied with a number of external routines whose purpose is to define the desired molecule. Principal among the external routines is the one that describes the potential function of the molecule. Pandora also requires routines that specify molecular geometry, masses, local modes, force constants and a whole host of conversion factors. The final external component is a routine which monitors the progress of a trajectory, terminating it when the reaction criteria are met, and writing out the desired values.

A.2.2 Diagnostic routines

Having specified the Hamiltonian for a given molecule in the external routines, a vital step before proceeding further is to verify that Hamiltonian. The diagnostic routines permit quality assurance of the external routines, allowing verification of the molecular descriptors and the potential energy function by calculating several values, including:

• the location and value of the potential minimum

• the corresponding equilibrium geometry

• the vibrational frequencies at the minimum

• the normal modes of vibration at the minimum
each of which can be compared to literature values. Pandora does not automate verification of another critical point of the PES, the transition state. This must be done separately, outside of Pandora.

A.2.3 Set up routines

While internal coordinates are convenient for specifying potential functions and molecular geometries, there are a host of problems with using them to propagate equations of motion, most of which arise because under some conditions internal coordinate angles are ill defined or even cease to exist. To finesse the shortcomings of internal angles Pandora propagates equations of motion in cartesian coordinates. This however requires frequent interconversions between internal and cartesian coordinates. I have grouped together as the “set up routines” those programs involved in these interconversions. Key amongst these routines is one which converts the molecular geometry, specified by bond lengths and bond angles, into the corresponding cartesian coordinates. The other critically important conversion uses the Wilson $B$ matrix to interconvert internal coordinates and momenta with their cartesian equivalents.

A.2.4 Initial conditions

Pandora provides a variety of means to assign initial conditions. A typical dynamic analysis requires examination of many trajectories whose initial excitations are similar, but also differ randomly. Choices of excitations include exciting a specified local mode, a specified normal mode, or orthant sampling. To insure that trajectories are semiclassical, prior to excitation each normal mode is allocated a half quantum of energy. While assigning initial conditions Pandora typically converts from cartesians into internal coordinates, calculates normal modes, calculates excitations, reconverts
from internal to cartesian coordinate, adjusts to remove any bulk translation or rotation, and finally scales values to achieve the target energy. Each step involves a routine of some complexity, so assigning initial conditions is one of the more difficult steps in Pandora.

Please see the appendix on initial conditions for a detailed discussion of the types of initial conditions used most frequently in this work.

A.2.5 Numerical integration

Having successfully generated a set of initial conditions Pandora is now ready to propagate a trajectory. The cycle involved in every integral step is relatively simple, or the process of running a trajectory (with up to $10^6$ cycles of integration) would be impractical. A typical integration cycle involves generating the equations of motion by calculating coordinate and momentum derivatives of the Hamiltonian followed by a numerical time integration the equations of motion. The outcome of the propagation step is checked against the termination criteria (i.e. reaction occurring or exceeding the maximum allowed time or number of cycles) and then the cycle repeats. Details of the numerical integrator are given in a separate appendix.

Most of the customization of Pandora to a particular molecule resides in designing the output routine. The potential function defines the system to be studied, but the output routine controls when a trajectory terminates, and what quantities are saved for later analysis. The nature of the investigation governs which properties of the trajectory are important to capture.

A.3 Modifications to Pandora

Despite Pandora's maturity as a program package I made a number of changes while studying the dynamics of HFCO. Some changes were a matter of convenience
and some were a consequence of formyl fluoride's planar geometry.

A.3.1 Minor modifications

The following modifications were made to fix problems, or for aesthetic reasons.

- Time steps from the numerical integrator can differ in size. Many of my post trajectory analyses are based upon evenly sampled data. For convenience, rather than output data at an arbitrary number of integration steps, I found it desirable to output values at specified time intervals. To do so accurately I interpolated actual integration cycle data points. Since in most Pandora trajectories the saved data are only a small subset of the generated values the interpolated output values are more than sufficiently accurate.

- In the initial conditions routine for exciting a local mode I fixed a bug that tended to make the energy distribution algorithm unstable when the oscillator in question involved both a light and a heavy mass.

A.3.2 Planar geometry modifications

Other modifications were a consequence of planar geometry, which had not previously been used in Pandora.

- I had to modify the routine which converts cartesian coordinates into internal coordinates to include calculation of an out of plane bending angle.

- In the routine which calculates the Wilson $G$ matrix elements I added code to do so for the out of plane bend.

- I updated the routine for calculating local mode energy to include calculation of out of plane bending local mode energy.
Appendix B
Calculation of initial conditions

This appendix discusses the three major algorithms used in this work for selection of initial conditions.

B.1 Introduction

In many respects information gathered from classical trajectories constitutes an experiment, where the relevant instrument happens to be a computer. As in any experiment, the results are only as meaningful as the experimental design allows. The choice of initial conditions for trajectories defines the scope of these computational experiments. When initial conditions bear no relation to the physics of the problem the results are generally so complex as to be uninterpretable. However, if one is careful (and fortunate in the choice of problem to be studied) properly designed initial conditions restrict degrees of freedom of a problem to a manageable level, and the results are sufficiently simple to be interpreted, sometimes even unambiguously.

In the course of this research I ran trajectories in both Pandora and MATLAB. Irrespective of the program package, data sets came from three basic forms of initial conditions, depending upon the type of information desired. The three basic initial conditions sets were:

- Microcanonical
- Transition state
- Normal mode

and each will be discussed in a separate section.
B.2 Microcanonically sampled initial conditions

Microcanonically sampled initial conditions imply a random sampling of a specified isoenergy hypersurface of a given Hamiltonian. These are the conditions required to determine a $k(E)$ value from trajectory data that is suitable to compare with a calculated microcanonical RRKM rate constant. To satisfy these requirements the selected initial conditions must be both unbiased and monoenergetic. Strict compliance with these criteria is not easily accomplished, but the systems I studied were apparently insensitive to small biases in the distribution of initial conditions.

The approach I took to microcanonical sampling of initial conditions is as follows. At the desired energy I found the limits in both coordinates and momenta if all available energy were in each single mode. These limits form the range over which random initial conditions are selected. After each oscillator $q$ and $p$ is selected the total energy is calculated. Usually (but not always) the total energy is greater than the desired energy. Whether larger or smaller, all $q$ and $p$ values are scaled until the energy is within the specified tolerances for the desired energy (usually within a half a percent). This sampling algorithm is fully classical, disregarding the zero point energy, in order to completely sample the classical Hamiltonian isoenergy hypersurface.

A weakness of the preceding algorithm is that $q$ and $p$ are scaled by the same factor although $p$ usually has a much greater range. This results in most of the energy scaling occurring in the coordinates, which introduces some degree of bias into the selection of initial conditions. A refinement to the preceding algorithm which addresses this deficiency is suggested by Topper [51]. In the refined algorithm I discard any randomly selected initial conditions that are not within five percent of the target energy. Remaining $q$ and $p$ values are scaled not by a constant factor, but rather by a factor related to the local normal of the Hamiltonian. This modified
scaling alters $q$ and $p$ differently, but in proportion to their actual contributions to the Hamiltonian. Scaling ceases when conditions are within the specified tolerance of the desired energy.

The preceding refinement to the selection algorithm is more nearly unbiased than the original, but in practical terms the refinement makes no difference. Given sufficient numbers of trajectories, decay curves generated by either the original or the modified algorithm were substantially the same.

**B.3 Transition state initial conditions**

To study reaction dynamics, one must have trajectories that react, which can be accomplished in a number of ways. One can select random initial conditions and propagate them until reaction occurs (which was the approach I took in the early stages of this study), or one can begin with reaction, and propagate trajectories backwards in time, back to bound configurations. The first approach is inefficient, since much of the trajectory is irrelevant to the final process of reaction, so most of the computational effort is discarded. The second approach, while more efficient, is somewhat more perilous. When looking for correlations in the motions of prereaction dynamics, one must be very careful that any observed bias in the distribution of prereactive states is not a consequence of bias in the selection of the initial conditions.

My approach to selection of transition state initial conditions is as follows. I desired a random distribution of initial conditions over the subspace that is the transition state, so the method is rather similar to that for selecting microcanonical initial conditions. At the transition state I find the limits for each oscillator if all available energy were in each successive oscillator. In this case the available energy is only that which is in excess of the barrier. I select random initial conditions for all modes save the reactive one, whose coordinate corresponds to the transition state, and whose
momentum is constrained to be negative, thereby returning the trajectory to bound states. The $q$ and $p$ values of the orthogonal modes are scaled until the total energy is within the specified tolerances of the target energy, and propagation commences.

In the larger systems studied, commencing at the transition state was vital, since the computational effort was close to the limits of the available computational capacity. Under these circumstances it is particularly desirable to verify that the observed results are not an artifact of the selected initial conditions. For HN$_3$ the correlated motion exhibited by the N-N stretching mode is particularly striking. Phase convergence in this mode is dramatic, so it is very important to assure oneself that the observed phase convergence is not a consequence of bias in the selection of initial conditions. Fig. B.1 shows the distribution of initial conditions for one hundred trajectories begun at the transition state. The solid line marks the limit of the available energy. The distribution of initial conditions is reasonably random, and certainly lacks the strong phase convergence that is evident in trajectories leading to the transition state. I can conclude that the observed phase convergence is not an artifact of the initial conditions.

### B.4 Normal mode initial conditions

Mode specific decay curves arising from normal mode selection of initial conditions proved to be very informative. Results could be interpreted based on viewing normal modes as discrete subsets of the full Hamiltonian. All trajectories with initial conditions specified by normal mode selection were run within Pandora, whose sampling algorithm is as follows. Initial phase angles are generated randomly for each normal mode. The magnitude of the vector is determined by the number of quanta in each mode, which is always at least a half. The initial conditions vector is transformed from polar coordinate amplitude and angle values to internal coordinates and
Figure B.1  Distribution of initial conditions for one hundred HN$_3$ trajectories with total energy of 1.1E$_B$. Although these points are distributed evenly with respect to phase angle this mode shows very strong phase convergence preceding reaction.
momenta. These in turn are transformed into cartesians for subsequent propagation. As usual, allowances must be made for rotation and translation of the center of mass, and the values must be scaled to yield exactly the desired energy.

Since zero point energy was explicitly included, all trajectories arising from normal mode sampled initial conditions are semiclassical. Theses trajectories were utilized in two fashions. First, mode specific decay curves shed light on the structure of the Hamiltonian. Some modes are on average closer to the transition state than are others, and so react more rapidly. Second, when the initially selected phase angle is saved to be compared to time to reaction for a given trajectory, interesting patterns emerge. For many modes there is a systematic and explainable relationship between the initial phase angle and the time to reaction.
Appendix C
Wilson G matrices

This appendix shows by example how and why the Wilson G matrix is constructed, and in a final section shows one application.

C.1 Introduction

The principal beauty of the cartesian coordinate system lies in its orthogonality. Since no axis projects onto any other each dimension is independent. Despite this clear advantage, there are many occasions when problems are more tractable when posed in other coordinate systems. However, to properly frame the problem one must take into account the nonorthogonality of the coordinate system in question. Within chemistry a nonorthogonal basis that is of great utility is that of local mode coordinates. Wilson was first to demonstrate how to properly account for the nonorthogonality of local modes when calculating the kinetic component of the Hamiltonian. The following discussion is based on the development given by Wilson, Decius and Cross in the bible of dynamics, "Molecular Vibrations" [6].

In cartesian coordinates the kinetic energy contribution to the Hamiltonian is:

\[ 2T = \sum_{\alpha}^N m_\alpha \left( \dot{x}_\alpha^2 + \dot{y}_\alpha^2 + \dot{z}_\alpha^2 \right) \]  

(C.1)

where \( m_\alpha \) is the mass of the \( \alpha \)th atom, and \( x_\alpha, y_\alpha \) and \( z_\alpha \) give the displacement of the \( \alpha \)th atom from the origin in terms of cartesian coordinates. Another coordinate system related to cartesians (that can be even more convenient) is that of mass weighted cartesians. In this system the kinetic energy of a molecule reduces to

\[ 2T = \sum_{i=1}^{3N} \dot{q}_i^2 \]  

(C.2)
where $q_i$ is the displacement from the origin along one cartesian axis of an atom, but the axis has been rescaled such that

$$q_1 = \sqrt{m_1} x_1 \quad q_2 = \sqrt{m_1} y_1 \quad q_3 = \sqrt{m_1} z_1$$ (C.3)

$$q_4 = \sqrt{m_2} x_2$$ (C.4)

Note that the summation limit in Eq. C.2 is over $3N$, where $N$ is the number of atoms in the molecule.

Each of the preceding coordinate systems yields a simple expression for kinetic energy because in both systems the axes are orthogonal. However, neither is a particularly auspicious framework for formulating an expression for the molecular potential. Potential energy surfaces are usually most conveniently framed in terms of a basis that relates atoms to each other structurally. The so called “bond” or “local” modes (defined in terms of diatomic stretches, triatomic bends, and tetraatomic torsions and out of plane bends) form a basis for internal coordinates. While this framework facilitates intuitive consideration of the effects of potential functions on molecular motions, it suffers a major liability. Bond modes do not form an orthogonal basis, so the kinetic energy term is no longer as simple as those of the preceding equations.

C.2 $G$ matrix elements for out of plane motion

How do we formulate an expression for kinetic energy that is appropriate for internal coordinates? In this section I describe the steps necessary to compensate for the nonorthogonality of the internal coordinate basis, and illustrate the steps with an example. When using the program package Pandora to study the dynamics of formyl fluoride I had to modify it to accommodate planar molecules. The following summarizes the steps necessary to calculate the Wilson $G$ matrix terms for out of plane motion.
Let $S_t$ be one of the $3N$-6 internal coordinates (for a nonlinear molecule), and $c_t$ be one of the $3N$ cartesian coordinates. We can then express internal coordinates in terms of cartesians as follows:

$$S_t = \sum_{i=1}^{3N} B_{ti} c_t \quad t = 1, 2, ..., 3N - 6 \quad (C.5)$$

where $B_{ti}$ are the transformation coefficients, which depend upon the instantaneous molecular geometry. For convenience $B_{ti}$ are often grouped into triples, corresponding to the coefficients for a single atom. To compensate for nonorthogonality of the $S_t$ coordinates it is necessary to be able to calculate their projection onto one and other by forming unit vectors corresponding to unit motion of $S_t$ resolved into a cartesian basis, as follows:

$$\vec{e}_{12} = \left( \frac{\Delta x_{12}}{r_{12}}, \frac{\Delta y_{12}}{r_{12}}, \frac{\Delta z_{12}}{r_{12}} \right) \quad (C.6)$$

where $\vec{e}_{12}$ is the unit vector along the bond connecting atoms 1 and 2, $x_{12}$ is the separation between the two bonded atoms in the x direction, and $r_{12}$ is the distance between the atoms. In addition to unit vectors for the stretches we also need to characterize triatomic bond angles, which is most easily done by taking the dot products of the unit vectors for the two bonds involved:

$$\cos \phi = \vec{e}_{12} \cdot \vec{e}_{23} \quad (C.7)$$

Finally, to characterize out of plane motion, one must first define the plane. Let the plane be defined by bonds 1 and 2, with bond 3 corresponding to out of plane motion. Recalling (painfully) elementary calculus there is a convenient relationship amongst vectors which defines the angle out of the plane [52]:

$$\vec{v}_1 \cdot \vec{v}_2 \times \vec{v}_3 = v_1 v_2 v_3 \cos \phi \sin \theta \quad (C.8)$$

where $\phi$ is the in plane angle between $v_1$ and $v_2$, and $\theta$ is the out of plane angle. I believe Eq. 18 in Chapter 4-1 of Wilson Decius and Cross (WDC) to be in error. The
relationship for the sine of the out of plane angle should be

\[ \sin \theta = \frac{\hat{e}_{42} \times \hat{e}_{43} \cdot \hat{e}_{41}}{\cos \phi_1} \]  

(C.9)

Having now defined all elements of internal coordinates (i.e. bond lengths and bond angles) in terms of an orthogonal basis (i.e. cartesians) we are now able to determine the values for \( B_{ii} \) in Eq. C.5.

![Diagram](image)

**Figure C.1** HFCO out of plane motion.

Consider HFCO as an example of a molecule which can exhibit out of the plane motion. Any three atoms can define a plane, leaving the fourth to define the out of plane component. I chose to define the plane using the three massive atoms, C, O and F, leaving the highly mobile H atom to define the out of plane motion. In conformance with WDC conventions I have labelled H as atom 1, F as atom 2, O as atom 3 and C as atom 4, and also defined the angles between them in accordance
with WDC. The $B$ coefficients simply resolve unit motion for each of the internal coordinates into cartesian components. The internal coordinate component for out of plane motion for atom 1, which defines the bending angle, is

$$s_{t1} = \frac{1}{r_{41}} \left[ \frac{\bar{e}_{42} \times \bar{e}_{43}}{\cos \theta \sin \phi_1} - \frac{\tan \theta}{\sin^2 \phi_1} (\bar{e}_{42} - \cos \phi_1 \bar{e}_{43}) \right]$$  (C.10)

where $t$ specifies the out of plane bending mode. Atoms 2 and 3, along with the central atom, define the plane. The internal coordinate component for atom 2 is

$$s_{t2} = \frac{1}{r_{42}} \left[ \frac{\bar{e}_{43} \times \bar{e}_{41}}{\cos \theta \sin \phi_1} - \frac{\tan \theta}{\sin^2 \phi_1} (\bar{e}_{42} - \cos \phi_1 \bar{e}_{43}) \right]$$  (C.11)

and that for atom 3 is very similar, since they serve similar purposes in our scheme of definitions

$$s_{t3} = \frac{1}{r_{43}} \left[ \frac{\bar{e}_{41} \times \bar{e}_{42}}{\cos \theta \sin \phi_1} - \frac{\tan \theta}{\sin^2 \phi_1} (\bar{e}_{43} - \cos \phi_1 \bar{e}_{42}) \right]$$  (C.12)

Finally, since the out of plane bend is an internal coordinate, no net motion can result. Therefore the component for the central atom (4) compensates for all others, as follows

$$s_{t4} = -s_{t1} - s_{t2} - s_{t3}$$  (C.13)

Each of the above $s_{tj}$ expressions gives rise to three $B_{ti}$ terms, corresponding to sequentially specifying each cartesian component of the $\bar{e}$ unit vectors. When all $B$ coefficients are formulated for out of plane local mode motion they form a row within the greater $B$ matrix, whose columns each correspond to a cartesian coordinate of a specific atom. The $B$ matrix is thus a (3N-6,3N) construct, and is the stepping stone to the desired $G$ matrix

$$G = \frac{1}{m} B B^\dagger$$  (C.14)

Inspection of Eq. C.14 shows that the $G$ matrix is of dimension (3N,3N). This large $G$ matrix block diagonalizes into a smaller (3N-6,3N-6) matrix which relates the internal
coordinates, and another (6,6) matrix which relates to the translation and rotation of the center of mass. It is the (3N-6,3N-6) matrix which is usually referred to as the Wilson $G$ matrix, and is the one required in the following expression for kinetic energy in terms of internal coordinates:

\[ 2T = P^\dagger GP \]  

(C.15)

where $P$ is a column matrix of the momenta conjugate to internal coordinates $S$.

The $G$ matrix may be interpreted physically as follows. The $G$ matrix arises because internal coordinates are not orthogonal. Off diagonal elements within the $G$ matrix arise as a consequence of the projection of one local mode motion onto another, while diagonal elements represent the projection of a local mode motion onto itself. Beyond a certain point, when two local mode motions no longer share common atoms, their interaction must be zero, and can also be zero despite having atoms in common. (For example, the torsional local mode has zero projection onto the stretching mode of its central atoms, so by coincidence these two local modes are orthogonal.) For this reason, although $G$ must be of dimension $(\ell,\ell)$ where $\ell$ is the number of local modes, as $\ell$ becomes large many of the off diagonal elements of $G$ will be zero.

C.3 Verification of the $G$ matrix

The preceding discussion shows how to formulate the $G$ matrix from cartesian coordinates. WDC also give expressions for the $G$ matrix elements in terms of local mode coordinates. In my work I have used both methods, depending upon whether the equations of motion are being propagated in cartesians or in internal coordinates. Whichever method is used requires verification of the $G$ matrix. The HFCO appendix contains a section which discusses how the Hamiltonian may be verified by calculating
normal mode vibrational frequencies. The $G$ matrix is an integral component of that calculation, and correct frequency values are a good indication that the $G$ matrix has been properly formulated.

### C.4 Coordinate and momentum scaling

In analyzing trajectories circumstances frequently arise where it is desirable to compare the values of oscillator coordinates and momenta. (One such case involves calculating the phase space separation of adjacent trajectories.) In the atomic units framework, and in most systems, the values associated with momenta are typically much larger than those for coordinates. Consider a phase space ellipse for a harmonic oscillator:

![Figure C.2 Harmonic oscillator phase space ellipse.](image)

To compare $p$ and $q$ on an equal footing we need conversion factors which will render the phase space ellipse of the harmonic oscillator circular, so that the con-
tributions of scaled coordinates and momenta are equal at any phase angle. One approach is to scale $p$ and $q$ so their maxima are equal.

The Hamiltonian is

$$H(p, q) = \frac{1}{2} G p^2 + \frac{1}{2} F q^2 = E$$  \hspace{1cm} (C.16)

The maximal values of $p$ occur when $q$ is zero, so

$$p_{\text{max}} = \pm \sqrt{\frac{2E}{G(q = 0)}}$$  \hspace{1cm} (C.17)

Similarly for $q$

$$q_{\text{max}} = \pm \sqrt{\frac{2E}{F}}$$  \hspace{1cm} (C.18)

So we need a conversion factor $c$ which makes the maximal values equal

$$p_{\text{max}} = c q_{\text{max}}$$  \hspace{1cm} (C.19)

$$\sqrt{\frac{2E}{G}} = c \sqrt{\frac{2E}{F}}$$  \hspace{1cm} (C.20)

$$c = \sqrt{\frac{F}{G}}$$  \hspace{1cm} (C.21)

Within our group it is customary to scale both axes, reducing $p$ and increasing $q$, to make the ellipse circular. Let $c'$ be the scaling factor by which to increase $q$, and $\frac{1}{c'}$ be the factor by which to decrease $p$. The total scaling must be $\sqrt{\frac{F}{G}}$, as was shown above, so

$$c'^2 = \left(\frac{F}{G}\right)^\frac{1}{4}$$  \hspace{1cm} (C.22)

$$c' = \left(\frac{F}{G}\right)^\frac{1}{4}$$  \hspace{1cm} (C.23)

$$\frac{1}{c'} = \left(\frac{G}{F}\right)^\frac{1}{4}$$  \hspace{1cm} (C.24)

Therefore

$$q' = \left(\frac{F}{G}\right)^\frac{1}{4} q$$  \hspace{1cm} (C.25)
and

\[ p' = \left( \frac{G}{F} \right)^{1/4} p \]  \hspace{1cm} (C.26)

where \( q' \) and \( p' \) are now scaled in a manner to allow direct comparison between them.
Appendix D
Numerical integrators

This appendix gives a brief overview of numerical integrators used in this research. Following the introduction comes a section which reviews Pandora’s numerical integrators. The final section discusses MATLAB’s numerical integrator.

D.1 Introduction

Numerical integration of the equations of motion is the heart of the process of generating a trajectory. Hamilton’s equations of motion are paired first order differential equations

\[ \dot{q} = \frac{\partial H}{\partial p} \]  \hspace{1cm} (D.1)

\[ \dot{p} = -\frac{\partial H}{\partial q} \]  \hspace{1cm} (D.2)

whose (numerical) integration generates new values of $q$ and $p$

\[ q = \int \frac{\partial H}{\partial p} \, dt \]  \hspace{1cm} (D.3)

\[ p = -\int \frac{\partial H}{\partial q} \, dt \]  \hspace{1cm} (D.4)

In the course of this research I have generated trajectories within the program package Pandora, and within the scientific computing package MATLAB. The details of each numerical integrator are slightly different, so each will be discussed in a separate section.

D.2 Pandora’s numerical integrators

Pandora propagates trajectories using cartesian coordinates. The advantages of this system lie in the simplicity of the kinetic energy term and in the unambiguous
definition of coordinates. The disadvantages are that there is some degree of inconvenience in transforming back and forth between internal and cartesian coordinates and that in cartesian coordinates there are more equations of motion than in internal coordinates.

Much of the heavy computational work in generating a trajectory is done by the numerical integrator, so a more efficient integration algorithm can allow one to attack larger problems with the same computer resources. In the interests of efficiency, Pandora uses a two stage process. Numerical integration is instigated using a fourth order Runge-Kutta integrator, which is a technique that is reliable and does not require extrapolation of prior data points, but is rather slow. After three cycles of Runge-Kutta integration sufficient data points have accrued to begin using predictor-corrector integration. This algorithm is both reliable and fast, but requires prior data on which to base its predictions. If the predictor-corrector integration fails to converge Pandora decreases the integration time step, orders three more cycles of Runge-Kutta integration and then resumes predictor-corrector integration.

The following discussion of both Runge-Kutta and predictor-corrector integrators is based on Chapter 16 of “Numerical Recipes” [53].

D.2.1 Runge-Kutta integrators

Runge-Kutta integration is an adaptation of Euler’s method, whereby the slope (i.e. derivative) at one point is projected, to yield the next point in the integration. Higher orders of Runge-Kutta integration simply correspond to evaluating the derivatives at a number of intermediate points within an integration step, and projecting the next point as a weighted average of the intermediate results.

Fourth order Runge-Kutta integration is the norm in numerical integration. Press et.al. note that fourth order integration is very efficient, requiring only four function
evaluations, while for orders higher than four the number of function evaluations is greater than the order of the procedure [53]. These authors also note that higher order Runge-Kutta solutions are not necessarily more accurate than lower order ones, they simply permit the possibility of larger integration step sizes.

D.2.2 Predictor-corrector integrators

The work horse of Pandora's numerical integration is a predictor-corrector routine. This algorithm requires four previous integration points. The prediction stage of the algorithm uses polynomial extrapolation of the previous data to predict the next data point. The corrector extrapolates the next point by integrating the previous slopes. If the predictor and the corrector are within the desired tolerance the point is accepted. If they are not, Pandora retreats to Runge-Kutta integration with a smaller time step to prime the pump, and predictor-corrector integration resumes.

When an unusually small time step is required (less than 0.1 au) it is often an indication that there is a problem with the potential. One of the coordinates may be becoming singular, and the integrator is dutifully attempting to climb the pole, in which case the potential, not the integrator, needs to be fixed. Pandora's numerical integrators are quite robust. Early on I played with an adaptive step size Runge-Kutta algorithm as an alternative to the predictor-corrector. The change was never implemented in Pandora because the time savings were marginal, but in the course of testing each method I ran very long trajectories (of more than $10^6$ cycles) both forwards and backwards. After this lengthy round trip I compared the starting and the ending points and found them to be substantially the same.
D.3 MATLAB integrator

Both HN$_3$ and HONO were studied using data generated sometimes in Pandora, and sometimes in MATLAB. The MATLAB numerical integrator is ODE45, a fourth/fifth order Runge-Kutta-Fehlberg integrator. From discussion by Press et.al., I infer that this mixed order denotes that the procedure is accurate to the fifth order, but that the error can only be estimated to the fourth order. (MATLAB’s documentation is incomplete in this regard, nor is the code itself clear.) With this routine the user has no control over the step size, but has the ability to specify a tolerance for the solution. The tolerance default value (which I used) is $10^{-6}$, and resulted in energy conservation in the fourth place for most systems. Because MATLAB is slower than Pandora, and runs on less powerful computers, the MATLAB trajectories were usually fairly short, involving between $10^3$ and $10^5$ integration cycles, so extreme accuracy for the integrator was less of a concern.
Appendix E
Phase analysis of trajectories and the Hilbert transform.

This appendix gives more background for phase analysis of trajectories and the Hilbert transform, addressing a number of details overlooked in the Hilbert transform chapter. Early sections show the formulation of the action-angle transform for harmonic and Morse oscillators. Later sections elaborate on technical details for implementation of the numerical Hilbert transform, and compare the Hilbert transform amplitude to the action from the action-angle transform.

E.1 Introduction

Much of my research involves aspects of examining trajectories in terms of phase of the oscillators. Coherent comparison of trajectories sidesteps problems inherent in aligning trajectories in time, and avoids distortions in trajectory comparisons caused by differing energies in the oscillators. It also allows comparison of trajectories while the reaction coordinates are in similar regions of phase space. Beyond these benefits, phase is a natural framework in which to examine molecular motions, since molecules are frequently modeled as collections of coupled oscillators. In much the same way that a center of mass frame can be more informative than a laboratory frame, I believe that an oscillator phase based frame can be more more informative than a time frame.

E.2 The harmonic oscillator action-angle transform

The preceding presupposes that a means exists to transform trajectories from time to phase. A familiar technique from classical mechanics involves transforming $H(x, p)$ where coordinates $x$ and momenta $p$ are functions of time, to $H(J, \theta)$ where
$J$ is related to the energy of the oscillator, and $\theta$ is the oscillator phase angle. The following derivation (based on notes from JSH and Chapters 8 and 10 of Goldstein's "Classical Mechanics"[5]) shows the action-angle transform for a harmonic oscillator, our usual starting point.

Following the development in Goldstein, Chapter 8, the generating function of the transform is $F_2$, so that

$$\theta = \frac{\partial F_2}{\partial J} \quad (E.1)$$

$$p = \frac{\partial F_2}{\partial x} \quad (E.2)$$

where $J$ is the classical action:

$$J = \frac{1}{2\pi} \int p \, dq \quad (E.3)$$

which for the harmonic oscillator is

$$J = \frac{E}{\omega} \quad (E.4)$$

where $E$ is the energy of the oscillator, and $\omega$ is the frequency. The Hamiltonian can be expressed as

$$H \left( x, \frac{\partial F_2}{\partial x} \right) = E \quad (E.5)$$

which for a harmonic oscillator becomes

$$\frac{1}{2} G \left( \frac{\partial F_2}{\partial x} \right)^2 + \frac{1}{2} F x^2 = E \quad (E.6)$$
where \( G = \frac{1}{\mu} \) and \( F = \frac{\partial^2 V}{\partial x^2} \). \( V \) is the potential and \( \mu \) is the reduced mass. Solving for the generating function:

\[
\frac{\partial F_2}{\partial x} = \left[ \frac{1}{G} \left( 2E - F \, x^2 \right) \right]^\frac{1}{2}
\]  \hspace{1cm} (E.7)

\[
F_2 = \int_0^x \left[ \frac{1}{G} \left( 2E - F \, x^2 \right) \right]^\frac{1}{2} \, dx
\]  \hspace{1cm} (E.8)

Eq E.1 and Eq E.4 in combination with Eq E.8 yield

\[
\theta = \frac{\partial F_2 \partial E}{\partial E \, \partial J} = \omega \int_0^x \frac{1}{2} \left[ \frac{2E}{G} - \frac{F}{G} \, x^2 \right]^{-\frac{1}{2}} \left( \frac{2}{G} \right) \, dx
\]  \hspace{1cm} (E.9)

\[
= \left( \frac{\omega}{G} \right) \left( \frac{G}{F} \right)^{\frac{1}{2}} \int_0^x \left[ \frac{2E}{F} - x^2 \right]^{-\frac{1}{2}} \, dx
\]  \hspace{1cm} (E.10)

\[
= \frac{\omega}{(FG)^{\frac{1}{2}}} \sin^{-1} \left[ \left( \frac{F}{2E} \right)^{\frac{1}{2}} \frac{x}{x} \right] \bigg|_0^x
\]  \hspace{1cm} (E.11)

\[
\omega = \left( \frac{k}{\mu} \right)^{\frac{1}{2}}, \text{ } F = k \text{ and } G = \frac{1}{\mu}, \text{ so}
\]

\[
\omega = (FG)^{\frac{1}{2}}
\]  \hspace{1cm} (E.12)

\[
\theta = \sin^{-1} \left( \frac{F}{2E} \right)^{\frac{1}{2}} \, x
\]  \hspace{1cm} (E.13)

or

\[
x = \left( \frac{2E}{F} \right)^{\frac{1}{2}} \sin \theta
\]  \hspace{1cm} (E.14)

but by Eq E.4 and Eq E.13
\[ x = \left(\frac{2JG}{\omega}\right)^{\frac{1}{2}} \sin \theta \]  
(E.16)

For a harmonic oscillator

\[ E_{HO} = \omega J \]  
(E.17)

\[ = \frac{1}{2} G p^2 + \frac{1}{2} F \left(\frac{2JG}{\omega}\right) \sin^2 \omega \]  
(E.18)

Rearranging

\[ G p^2 = 2\omega J - \frac{2FGJ}{\omega} \sin^2 \theta \]  
(E.19)

\[ = 2\omega J \cos^2 \theta \]  
(E.20)

we get an expression for momentum

\[ p = \left(\frac{2E}{G}\right) \cos \theta \]  
(E.21)

A final check comes from substituting for \( x \) and \( p \) in the Hamiltonian

\[ H(J, \omega) = \omega J \cos^2 \theta + \omega J \sin^2 \theta \]  
(E.22)

which as expected yields

\[ E = \omega J \]  
(E.23)

The purpose of this lengthy procedure is to demonstrate that the Hamiltonian can be expressed as a function of \( J \) only. Therefore the energy of the system can be expressed as a function of \( J \). It also implies that \( \theta \), the variable conjugate to \( J \) is cyclic, since the Hamiltonian is independent of \( \theta \). One beauty of the action-angle transform is that the frequency of periodic motion can be found without solving the equations of motion [5].
E.3 The Morse oscillator action-angle transform

As always, when one departs from the harmonic oscillator life becomes more complex. The following derivation is based on notes from JSH for the action-angle transform of the Morse oscillator.

Consider a Morse potential

\[ V(x) = D(1 - e^{-\alpha x})^2 \]  \hfill (E.24)

with turning points for energy \( E \) of

\[ x_{\text{lim}} = \frac{1}{\alpha} \ln \left( 1 \pm \left( \frac{E}{D} \right)^{\frac{1}{2}} \right) \]  \hfill (E.25)

where the \(-\) term is the upper limit and the \(+\) term is the lower one. The integral for the action is

\[ J = \frac{1}{\pi} \int_{x_i}^{x_u} p \, dx \]  \hfill (E.26)

For the Morse oscillator

\[ E = \frac{p^2}{2m} + D \left( 1 - e^{-\alpha x} \right)^2 \]  \hfill (E.27)

so

\[ p = \left[ 2m \left( E - D \left( 1 - e^{-\alpha x} \right)^2 \right) \right]^{\frac{1}{2}} \]  \hfill (E.28)

therefore

\[ J = \frac{1}{\pi} \int_{x_i}^{x_u} \left[ 2m \left( E - D \left( 1 - e^{-\alpha x} \right)^2 \right) \right]^{\frac{1}{2}} dx \]  \hfill (E.29)

For convenience we make the substitution

\[ u = \left( \frac{E}{D} \right)^{\frac{1}{2}} \left( 1 - e^{-\alpha x} \right) \]  \hfill (E.30)

so

\[ du = \left( \frac{E}{D} \right)^{\frac{1}{2}} \left( \alpha e^{-\alpha x} \right) dx \]  \hfill (E.31)
after which the integration limits for a single cycle become \( u = 1 \) for the upper limit and \( u = -1 \) for the lower one. The substituted expression for \( J \) is

\[
J = \frac{1}{\pi} \int_{-1}^{1} \left(2mE\right)^{\frac{1}{2}} \left(\frac{E}{D}\right)^{\frac{1}{2}} \frac{1}{\alpha} \frac{\left(1 - u^2\right)^{\frac{1}{2}}}{\left(1 - \left(\frac{E}{D}\right)^{\frac{1}{2}} u\right)} \, du
\]  

(E.32)

Making further substitutions \( \frac{1}{\alpha} = \frac{1}{\alpha} \left(\frac{m}{2D}\right)^{\frac{1}{2}} \) and \( q = \left(\frac{E}{D}\right)^{\frac{1}{2}} \) we get

\[
J = \frac{2E}{\pi\Omega} \int_{-1}^{1} \frac{\left(1 - u^2\right)^{\frac{1}{2}}}{1 - qu} \, du
\]  

(E.33)

and one last change of variables,

\[
u = \cos \theta
\]

(E.34)
\[du = -\sin \theta \, d\theta\]  

(E.35)

the new limits of integration become \( \pi \) to 0, and we get the following expression for the action of a Morse oscillator:

\[
J = \frac{2E}{\pi\Omega} \int_{\pi}^{0} \frac{\sin^2 \theta}{1 - q\cos \theta} \, d\theta
\]  

(E.36)

\[
= \frac{2E}{\pi\Omega} \int_{0}^{\pi} \frac{\sin^2 \theta}{1 - q\cos \theta} \, d\theta
\]  

(E.37)

Integrals of this form have the solution

\[
\int_{0}^{\pi} \frac{\sin^2 x \, dx}{a + b\cos x} = \frac{\pi}{a + (a^2 - b^2)^{\frac{1}{2}}}
\]  

(E.38)

In this case \( a = 1 \) and \( b = (-q)^2 = \frac{E}{D} \), so

\[
J = \frac{2E}{\pi\Omega} \frac{\pi}{1 + (1 - \frac{E}{D})^{\frac{1}{2}}}
\]  

(E.39)

\[
J(E) = \frac{2E}{\Omega} \frac{1}{1 + \left(1 - \frac{E}{D}\right)^{\frac{1}{2}}}
\]  

(E.40)
Eq E.40 can be rearranged to yield $E(J)$

$$E(J) = \Omega J - \frac{\Omega^2 J^2}{4D}$$  \hspace{1cm} (E.41)

The final useful information to be gleaned from this change of variables comes from applying Hamilton's equations of motion to determine $\omega$, the time derivative of $\theta$, the variable conjugate to $J$.

$$\omega \equiv \frac{\theta}{J} = \frac{\partial H}{\partial J}$$  \hspace{1cm} (E.42)

$$= \Omega - \frac{\Omega^2 J}{2D}$$  \hspace{1cm} (E.43)

or alternatively

$$\omega = \Omega \left(1 - \frac{E}{D}\right)^{\frac{1}{2}}$$  \hspace{1cm} (E.44)

I wish to thank Professor Hutchinson for his notes covering this derivation. Without several nonobvious changes of variable an analytic solution would not be possible. As it stands, Morse oscillators mark the limit of problems for which the action-angle transform is tractable, yet Morse oscillators are one of the simplest building blocks of a realistic PES. As soon as the potential involves coupling, then in general trajectories will not close on themselves. When this occurs the action-angle transform fails, because it is not possible to integrate over a full cycle of motion. How then may we go about assigning a phase to the complex motions that can result from oscillations governed by a realistic Hamiltonian?

**E.4 Mechanics of the Hilbert Transform**

Applied physics is replete with examples of problems that are intractible analytically but yield readily to numerical solutions. One that springs to mind is numerical integration of equations of motion, the means by which I generate trajectories. I therefore propose as an alternative to the action-angle transform a numerical method
which is capable of yielding a phase angle for oscillator motions arising from an arbitrarily complex Hamiltonian. The method involves applying the Hilbert transform [33] to the time series of local mode coordinates. (For technical reasons to be addressed shortly, momenta are easier to transform than position, but as both are cyclic and so have an associated phase, either will do.)

E.4.1 Hilbert transform phase

The steps involved in generating a numerical phase value via the Hilbert transform are as follows:

1. Select the time series to be transformed. As trivial as this sounds, this step is actually crucial to the ultimate success of the method. Subsequent steps involve concerns related to periodicity and Fourier transform edge effects, so proper selection and preparation of the time series is critical. Factors to keep in mind are:

   - The act of crossing the transition state to react is intrinsically nonperiodic, so no phase $\theta$ (which is the integral of the frequency $\omega$) may reasonably be defined for a nonrecurring motion. (By definition, only recurring motions have a frequency.) The Hilbert transform fails near the transition state, but so also does the action-angle transform. However, with some experimentation one can quickly learn how much of the final reactive motion can be included in the time series to be transformed.

   - Characterizing local mode motion using momentum rather than position is valid (since the phases of coordinate and momenta differ only by a $\frac{\pi}{2}$ lag) and is preferrable for the following reasons:
- Momenta vary about zero rather than an equilibrium position, so there are fewer problems with the dc level in a Fourier transform, and dc removal is easier.

- At the transition state the momentum is tending towards zero. The other end of the time series can be truncated at a similar zero crossing to help limit Fourier transform edge effects.

- Other useful means of suppressing edge effects include:

  - Include as many full cycles of oscillation as is practical. A longer data set helps to minimize edge effects and anomalies, such as the anharmonicity of reaction. In addition, the numerical Hilbert transform is an approximation of the analytic Hilbert transform, which involves integration from $-\infty$ to $+\infty$. A larger data set is a better approximation to the infinite integral.

  - Any dc level in the data should be removed.

  - The edge corresponding to reaction may be gently ramped so that at the edge its value is zero, rather than simply approaching zero.

  - The Fourier transform presupposes periodicity and continuity across the edges of the data set to be transformed. Proper preparation of the data to conform with these requirements gives better results. I package the data to be transformed by selecting a transform length at least twice as long as the selected time series. The time series is truncated so that it ends in zeros. The truncated time series is copied into the vector to be transformed beginning at the first sample. The mirror image of the time series is copied into the transform vector beginning from the last sample. The center of the vector is a short range of
zeros that keep the ends from interacting. In this way the data to be transformed is periodic and continuous across all boundaries. The extra zeros and mirror image series requires a larger transform, but are otherwise benign. They insures a better behaved transform, and upon inverse transforming may simply be discarded.

2. For a vector as specified above take the forward Fourier transform and multiply the frequency series by \( i \text{ sgn}(s) \). This step results in all frequencies from - Nyquist to zero being multiplied by \(-i\), and all positive frequencies being multiplied by \(+i\).

3. Take the inverse transform of the frequency series in step 2. The net effect of steps 2 and 3 is to produce a new time series which has a phase shift of \( \frac{\pi}{2} \) with respect to the original data. Note that except for a scale factor the Hilbert transform of momentum is the same as coordinate data centered about zero.

4. Construct the function \( Q \)

\[
Q = f(t) - i F_{H_1}(t) \tag{E.45}
\]

where \( f(t) \) is the original time series, and \( i F_{H_1}(t) \) is the \( \frac{\pi}{2} \) phase shifted time series, multiplied by \( i \).

5. Transform the function \( Q \) from complex cartesians coordinates \( (a + ib) \) into complex polar coordinates \( (re^{i\theta}) \) by the following relationships [34]:

\[
r = (a^2 + b^2)^{\frac{1}{2}} \tag{E.46}
\]

\[
\theta = \tan^{-1} \frac{a}{b} \tag{E.47}
\]

6. Unwrap the phase so that \( \theta \) increases monotonically.
Despite the apparent intricacy of the Hilbert transform, it is relatively easy to insure that the results are free from artifacts and are physically meaningful. The simplest diagnostic is to superimpose the original data (with dc removed) and the derived phase $\theta$. The phase plot should be well behaved at the edges, and should track the oscillations of the time series properly. Critical points of the assigned phase (i.e. $0, \frac{\pi}{2}, \pi, \frac{3\pi}{2}$ and $2\pi$) should coincide with critical points of the momentum waveform (i.e. extrema and zero crossings). If the derived phases fail to track critical points then the time series has not been properly conditioned. Possible problems include:

- Too few cycles are being transformed.
- The dc level has not been fully removed.
- Too much of the final aperiodic motion is being included.
- Fourier transform edge effects.

The Hilbert transform does not permit assigning a phase angle to motion all the way to the transition state. The final reactive motion must be both truncated and tapered. However, aside from the final quarter cycle of activity (from roughly equilibrium to the transition state), the Hilbert transform assigns physically reasonable phase angles to motions arising from arbitrarily complex Hamiltonians. The Hilbert transform deals only with the time series of oscillations and never interacts directly with the Hamiltonian that generates the trajectories.

E.4.2 Hilbert transform amplitude

The Hilbert transform is a tool which characterizes both the phase $\theta$, and the amplitude $r$ of an oscillator. The action-angle transformation specifies oscillator phase, $\theta$
and also its conjugate variable $J$, which is related to oscillator energy. Both measures of phase are functionally equivalent. What is the relationship between $r$ and $J$? For the harmonic oscillator we have previously derived the following:

$$p = \left( \frac{2E}{G} \right)^{\frac{1}{2}} \cos \theta$$

(E.48)

In a manner analogous to the numerical approach, I now take the Hilbert transform of the momentum relationship. Recall that the Hilbert transform of $\cos \theta$ is $-\sin \theta$ [33]. Let $P_{Hi}$ be the transformed momentum.

$$P_{Hi} = -\left( \frac{2E}{G} \right)^{\frac{1}{2}} \sin \theta$$

(E.49)

The function $Q$ becomes

$$p(\theta) - iP_{Hi}(\theta) = \left( \frac{2E}{G} \right)^{\frac{1}{2}} \cos \theta + i \left( \frac{2E}{G} \right)^{\frac{1}{2}} \sin \theta$$

(E.50)

Expressing $Q$ is complex polar coordinates we find

$$r = \left( \frac{2E}{G} \right)^{\frac{1}{2}}$$

(E.51)

Recalling that

$$\omega = (FG)^{\frac{1}{2}}$$

(E.52)

We find relationship between the momentum Hilbert transform amplitude $r$ and the action-angle transform action $J$ is

$$J = \frac{1}{2} \left( \frac{G}{F} \right)^{\frac{1}{2}} r^2$$

(E.53)

Had we instead elected to take the coordinate Hilbert transform we would find the following relationship:

$$J = \frac{1}{2} \left( \frac{F}{G} \right)^{\frac{1}{2}} r^2$$

(E.54)
The difference between the two expressions arises because coordinates and momenta have intrinsically different units. However, in either case for the harmonic oscillator $J$ is proportional to $r^2$. This implies that energy is proportional to the square of oscillator amplitude, an entirely reasonable result.
Appendix F
Calculations of rate constants

This appendix is a more detailed look at RRKM theory, focussing on means of calculating RRKM rate constants. Of particular importance to the previous chapter devoted to RRKM theory is a derivation showing the relationship between the area of the Hamiltonian isoenergy hypersurface and the \( N(E) \) term in the fundamental RRKM equation.

F.1 Introduction

This appendix addresses calculation of rate constants. The first section covers the assumptions of RRKM theory. The next section derives a classical RRKM rate constant appropriate for comparison to trajectories. Subsections delineate various levels of approximation in the calculation of RRKM rate constants. The following section covers determination of a rate constant from classical trajectories, and the final section gives conclusions.

The principle focus of this work is to reconcile the existence of correlated motion with RRKM kinetics. To do so requires detailed understanding of RRKM kinetics, and the ability to characterize a given molecule as either RRKM or not. In the next section I look in detail at the basic assumptions of RRKM.

F.2 RRKM assumptions

RRKM (Rice-Ramsperger-Kassel-Marcus) theory is one of the most elegant in chemistry, allowing calculation of unimolecular rate constants of remarkably good accuracy [42] from relatively few parameters. This theory has proven to be an extremely useful for prediction of approximate rate constants. Few other theories can
match the accuracy of its results for such a wide range of systems. Molecules that are exceptions to RRKM theory are sufficiently rare as to merit individual study.

RRKM theory is a microcanonical transition state theory [54], and as such is based upon relatively few assumptions, namely:

1. There exists a state with reaction coordinate $R^*$ which separates reactants from products [42]. (This simply postulates the existence of the transition state.)

2. The full phase space of the activated molecule is equally available for decay [42].
   (This excludes the possibility of trapped or constrained trajectories.)

3. Reactions correspond to a single crossing of the transition state [8]. (This excludes the possibility of back reactive trajectories, so that the flux across the transition state corresponds to the actual number of reactions.)

Assumption 2 is of critical importance to the phenomenon of correlated motion. Reconciling the second assumption with the existence of correlated motion is the subject of Chap. 4. The purpose of this appendix is to explore RRKM theory in greater depth, and show several methods of calculating microcanonical RRKM rate constants. The ultimate objective is to have a value to compare with trajectory derived rate constants. Those trajectories were generated using classical mechanics, a single total energy value and Hamiltonians without rotation. To be comparable, all subsequent derivations will be for microcanonical classical systems with $\ell = 0$.

**F.3 Derivation of a classical RRKM rate constant**

The following derivation for a classical rotationless microcanonical transition state theory is based on that of Steinfeld et. al. [8]. The fundamental assumptions in this derivation are:
• All states are at a single energy.

• \( q_1^\dagger \in \{ q_1^\dagger, q_1^\dagger + dq_1^\dagger \} \), where \( q_1^\dagger \) is the reaction coordinate value at the transition state.

• The reaction coordinate is separable form all other degrees of freedom.

Molecules at the transition state, poised to react, are those with \( q_1^\dagger \in \{ q_1^\dagger, q_1^\dagger + dq_1^\dagger \} \) and \( p_1^\dagger \in \{ p_1^\dagger, p_1^\dagger + dp_1^\dagger \} \) where \( p_1^\dagger > 0 \). Relative to all molecules, the fraction of reactive ones is given by:

\[
\frac{dN \left( q_1^\dagger, p_1^\dagger \right)}{N} = \frac{\int_{H=0}^{H=E-E_1^\dagger+E_0} dq_2^\dagger \cdots dq_{3n}^\dagger dp_2^\dagger \cdots dp_{3n}^\dagger}{\int_{H=E} dq_1 \cdots dq_{3n} dp_1 \cdots dp_{3n}} \ dq_1^\dagger \ dp_1^\dagger \quad (F.1)
\]

\( E_1^\dagger \) is the translational energy in the reaction coordinate, and \( E_0 \) is the transition state energy, so \( E - E_1^\dagger - E_0 \) is the energy available to all other modes when the system is at the transition state. Therefore the numerator of Eq. F.1 (which will hereafter be abbreviated as \( a \)) corresponds to all states accessible to systems at the transition state. Likewise, the denominator (designated as \( b \)) corresponds to all bound states available at the specific energy of the calculation, which is the area of the \( H = E \) hypersurface of the Hamiltonian.

All molecules with \( q_1^\dagger \in \{ q_1^\dagger, q_1^\dagger + dq_1^\dagger \} \) and \( p_1^\dagger > 0 \) will cross the transition state and react within a time interval \( dt = \mu_1 \frac{dq_1^\dagger}{dp_1^\dagger} \), where \( \mu_1 \) is the reduced mass corresponding to \( q_1 \). Therefore, the fractional reactive flux corresponding to reactive momentum \( p_1^\dagger \) is:

\[
\frac{1}{dt} \frac{dN \left( q_1^\dagger, p_1^\dagger \right)}{N} = \frac{a}{b} \frac{p_1^\dagger}{\mu_1} dp_1^\dagger \quad (F.2)
\]
since \( \frac{d q_i^\dagger}{dt} = \frac{d p_i^\dagger}{\mu_i} \). By a beneficent quirk of nature \( \frac{d p_i^\dagger}{\mu_i} = dE_i^\dagger \), the differential translational energy along the reaction coordinate. Thus

\[
\frac{dN(q_1^\dagger, p_1^\dagger)}{N\,dt} = dE_i^\dagger \frac{a}{b}
\]  

(F.3)

To find the total reactive flux we must evaluate all \( E_i^\dagger \in \{0, E^\dagger\} \)

\[
\frac{1}{N} \frac{dN}{dt} = \int_0^{E^\dagger} dE_i^\dagger \frac{a}{b}
\]

(F.4)

Note that the numerator in Eq. F.4 corresponds to determining all states available at the transition state, which is an \( N - 1 \) dimensional space (since the reaction coordinate is not included). This is roughly equivalent to \( G(E^\dagger) \), the sum of states at the transition state. The numerator in Eq. F.4 is a surface integral for \( H = E \) over an \( N \) dimensional phase space, which is roughly equivalent to the density of states \( N(E) \). Therefore:

\[
\frac{1}{N} \frac{dN}{dt} \approx \frac{G(E^\dagger)}{N(E)}
\]

(F.5)

The right hand side of Eq. F.5 is the change in the fraction of reactive molecules with time, which is the rate constant, \( k \). We see that for a rotationless microcanonical system a classical RRKM rate constant can be evaluated by finding the number of states at the transition state, and the density of states for all bound states at the specified energy.

\[
k(E) \approx \frac{G(E^\dagger)}{N(E)}
\]

(F.6)

The preceding expression is given as an approximate equality because strictly \( G(E^\dagger) \) and \( N(E) \) are quantum mechanical in nature, and we have not accounted in this classical calculation for the quantization of phase space. While Eq. F.6 is conceptually simple, in almost all systems \( G(E^\dagger) \) and \( N(E) \) are difficult to calculate directly.
For this reason there is a great divide between "theoretical" and "practical" RRKM calculations, centered upon what approximations are made when calculating $G(E^\dagger)$ and $N(E)$. In its most fundamental form a microcanonical RRKM rate constant is simply the ratio of all states capable of reacting within a time $dt$ (i.e. $G(E^\dagger)$) i.e. the flux across the transition state, to all bound states at energy $E$ (i.e. $N(E)$). The many formulae that are variations on this calculation reflect a range of approximations for estimating these quantities.

F.3.1 The harmonic oscillator approximation

As usual when physics becomes ugly, we can retreat to the comfort of a solvable problem, the harmonic oscillator. Treating oscillators in the Hamiltonian as harmonic results in a very elegant and practical approximation to Eq. F.6. The following derivation follows that of Steinfeld et. al. [8].

Recalling our starting point, Eq. F.1, we wish to find a simple way to evaluate the volume of phase space contained by the Hamiltonian at a given energy. Separating the Hamiltonian into individual harmonic oscillators, in mass reduced coordinates we get

$$H(q, p) = \sum_{i=1}^{n} \frac{p_i^2}{2} + \frac{\lambda_i q_i^2}{2}$$  \hspace{1cm} (F.7)

where $\lambda_i = 4\pi^2 \nu_i^2$. One can calculate the volume for each oscillator as follows:

$$V_i = \int_{H=0}^{H=E} \int dp_i \ dq_i$$  \hspace{1cm} (F.8)

For the harmonic oscillator this is simply the area of an ellipse, $\pi ab$, where $a = \sqrt{2E}$ and $b = \sqrt{\frac{2E}{\lambda}}$, resulting in

$$V_i = \frac{E_i}{\nu_i}$$  \hspace{1cm} (F.9)

where $E_i$ is the energy of the oscillator and $\nu_i$ is the (energy independent) harmonic frequency of oscillation. The volume of phase space for $s$ harmonic oscillators is
simply:

\[ V_s = \frac{E^s}{s! \prod_{i=1}^{s} \nu_i} \]  

where the \( s! \) term arises because in Eq. F.1 the integrals are iterated \([53]\). The denominator in Eq. F.6 corresponds to evaluating the area of the hypersurface \( H = E \).

This can be determined by differentiating successive volume calculations \( V(E) \), with respect to energy. The numerator in Eq. F.6 can be determined by calculating the volume of the \( s - 1 \) dimensional volume of the Hamiltonian at the transition state.

Because the preceding development for the harmonic oscillator approximation is to be applied to classical systems I have evaded the issue of quantization of phase space. However, to formally equate volume of phase space with number of states, one needs to quantize phase space with Planck’s constant, so in one dimension:

\[ G(E) = \frac{V}{\hbar} \]  

For a molecule with \( s \) oscillators, \( G(E^\dagger) \) spans an \( s - 1 \) dimensional space:

\[ G(E^\dagger) = \frac{(E^\dagger)^{s-1}}{(s - 1)! \hbar^{s-1} \prod_{i=1}^{s-1} \nu_i^\dagger} \]  

\( N(E) \) is \( \frac{\partial G(E)}{\partial E} \), so for a system with \( s \) oscillators

\[ N(E) = \frac{E^{s-1}}{(s - 1)! \hbar^{s} \prod_{i=1}^{s} \nu_i} \]  

The result is a familiar expression for an RRKM rate constant:

\[ k(E) = \frac{G(E^\dagger)}{h \ N(E)} \]  

\[ = \left( \frac{E^\dagger}{E} \right)^{s-1} \frac{\prod_{i=1}^{s} \nu_i}{h \prod_{i=1}^{s-1} \nu_i^\dagger} \]  

To arrive at the simple and convenient formulation of Eq. F.15 we had to make some large assumptions, namely:
• The Hamiltonian is separable. This approximation neglects all couplings.

• The oscillators are harmonic. In reality at least the reaction coordinate, if not others, is anharmonic.

The harmonic rate constant, obtained from Eq. F.15, is fairly direct to calculate. Frequencies in the numerator correspond to behaviour at the transition state, so for \( \nu(E^\dagger) \) I used values obtained from one dimensional trajectories at energy \( E^\dagger \). Denominator frequencies reflect behaviour near equilibrium. As part of the process of verifying each potential I determined vibrational frequencies from the eigenvalues of the Hamiltonian. Since these eigenvalues are calculated at the potential minimum, and the process involves an harmonic approximation, I chose these frequencies to represent harmonic frequencies at equilibrium. Note that if all oscillators were truly harmonic the equilibrium and the transition state frequencies would be the same, since harmonic frequencies are energy independent.

F.3.2 The anharmonic oscillator approximation

The next level of approximation in evaluating Eq. F.6 is to preserve the anharmonicity of the Hamiltonian. This is done by recognizing that in an anharmonic system \( \nu = \nu(E) \). The following derivation is after C. Hynes (private communication to J. S. Hutchinson.)

The density of states for a one dimensional oscillator is

\[
N(E) = \frac{\partial}{\partial E} \int \frac{dq \, dp}{\hbar} \Theta(E - H) \tag{F.16}
\]

where \( \Theta(E - H) \) is a step function.

\[
N(E) = \int \frac{dq \, dp}{\hbar} \delta(E - H) \tag{F.17}
\]
\[
= \frac{1}{\hbar \omega}
\]  
\text{(F.18)}

Extending this to two oscillators, but neglecting coupling

\[
N(E) = \int \frac{dq_1}{h} \int \frac{dp_1}{h} \int \frac{dq_2}{h} \int \frac{dp_2}{h} \delta(E - (H_1 + H_2))
\]  
\text{(F.19)}

\[= \int_0^E d\varepsilon \int \frac{dq_1}{h} \int \frac{dp_1}{h} \int \frac{dq_2}{h} \int \frac{dp_2}{h} \delta(E - H_1 - \varepsilon) \delta(\varepsilon - H_2)
\]  
\text{(F.20)}

\[= \int_0^E d\varepsilon \int \frac{dq_1}{h} \delta(E - H_1 - \varepsilon) \int \frac{dq_2}{h} \delta(\varepsilon - H_2)
\]  
\text{(F.21)}

\[= \int_0^E d\varepsilon \frac{N_1(E - \varepsilon)N_2(\varepsilon)}{\hbar \omega_1(\varepsilon)}
\]  
\text{(F.22)}

where \(N(E) = \frac{1}{\hbar \omega(\varepsilon)}\). For a harmonic oscillator \(\omega(\varepsilon)\) is constant, but in the anharmonic case

\[
N(E) = \int_0^E d\varepsilon \frac{1}{\hbar \omega_1(E - \varepsilon)} \frac{1}{\hbar \omega_2(\varepsilon)}
\]  
\text{(F.23)}

This technique can be extended to as many dimensions as the system requires. Once \(N(E)\) is known \(G(E)\) may be simply calculated by

\[
G(E) = \int_0^E N(\varepsilon)d\varepsilon
\]  
\text{(F.24)}

For modes other than the reactive coordinate determining \(\omega(E)\) is relatively straightforward. One simple procedure is to form one dimensional Hamiltonians for each oscillator in the system, then run a series of trajectories spanning energies 0 to \(E\), and a second series spanning 0 to \(E^\dagger\), to be sure each span is adequately sampled. For each energy I determined a value for the period of the oscillation, which can be inverted to yield frequency. For harmonic oscillators the period is independent of energy. For Morse oscillators the period increases with energy. Torsional modes are particularly complex, with the period increasing with energy, rising to a pole when the oscillator energy is equal to the torsional barrier height, and then decreasing rapidly again as the torsional mode becomes capable of free rotation. In the freely rotating
case the coordinate \( \theta \) increases without bound, but periodicity remains in momentum because the potential is cyclic.

The most difficult mode is the reaction coordinate. This motion is clearly anharmonic, and when energy in the reaction coordinate exceeds \( E_0 \) (as it must do to react) \( \omega(E) \) is not defined, because after reaction unbounded motion has no periodicity. Recall that the reason for finding \( \omega(E) \) was to use it to calculate \( N(E) \). When one considers the phase space energy contours of an anharmonic oscillator both the nature of the problem and a solution to it become evident.

Fig. F.1 shows isoenergy contours for an anharmonic oscillator. When energy in the oscillator exceeds the barrier energy the isoenergy curves open and lose any

\[ \text{Figure F.1 Isoenergy contours for an anharmonic oscillator.} \]
resemblance to the harmonic phase space ellipse. However, there continues to be new bound states accessible as energy increases. To calculate $N(E)$ when the phase space curve does not close I again created a one dimensional Hamiltonian for the reaction coordinate. I then used Monte Carlo integration to evaluate the areas of the isoenergy curves lying within the bound region of phase space, i.e. $G(E)$. $N(E)$ is then obtained by differentiating $G(E)$ with respect to energy. (Monte Carlo integration will be discussed in greater length shortly.)

Using a number of techniques I have characterized either $N(E)$ or $\omega(E)$ for each oscillator, and now have the necessary tools with which to calculate an anharmonic rate constant. Using numerical integration I find $N(E)$ by evaluating Eq. F.22 for energies from 0 to $E$. $G(E^\dagger)$ is found stepwise, by first evaluating Eq. F.22 for energies from $E_0$ to $E$, followed by integration of Eq. F.24. Finally the anharmonic rate constant is obtained from Eq. F.6.

F.3.3 Full RRKM calculation by Monte Carlo integration

Both the harmonic and the anharmonic oscillator approximations to the RRKM rate constant share the characteristic of neglecting couplings in the Hamiltonian. To retain coupling in the rate constant calculation I needed a way to evaluate Eq. F.6 directly. The denominator corresponds to the volume of an $s - 1$ dimensional phase space of the reduced Hamiltonian (i.e. all modes except the reaction coordinate) at energy $E^\dagger$. The numerator may be calculated as the numerical derivative with respect to energy of the volumes of phase space enclosed by $H(E)$ and by $H(E + \delta E)$. Each of these phase space volumes may be determined by Monte Carlo integration.

Monte Carlo integration is a numerical technique for evaluating multidimensional integrals [53]. While conceptually simple, Monte Carlo integration must be applied with some care to ensure valid results. Consider the arbitrary volume to be inte-
grated to be enclosed by a box. The surrounding box must be simple enough to permit easy calculation of its volume. The essence of Monte Carlo integration is to fill the box with random points, and then to compare the number of points lying within the integration volume to the total number of points. If a point lies within the integration boundary, a counter is incremented. After an appropriate number of points the volume of the integral is determined by multiplying the volume of the box by the ratio of "hits" to total points. A question naturally arises regarding what is an "appropriate" number of points. A standard part of Monte Carlo integration code is to calculate both the volume and its standard deviation. This gives an estimate of the error in the measurement. Since Monte Carlo integration is a random number technique, improvement in the error grows only as $N^{\frac{1}{2}}$. A second factor influencing accuracy of the results is how frequently points lie inside the integration boundary. Accuracy is diminished if the "hits" constitute a small fraction of the total attempts. For this reason the confining box should be as small as possible. With these considerations in mind, my approach to solving for an RRKM rate constant using Monte Carlo integration was as follows:

1. Determine for each oscillator the limiting values of $p$ and $q$ corresponding to all available energy (either $E$ or $E^\dagger$) being in that mode. These aggregate limits allow calculation of the volume of the confining box, which is $s$ dimensional for the full space, and $s - 1$ dimensional for the reduced space circa the transition state.

2. Calculate via Monte Carlo integration the volume of the reduced Hamiltonian at the transition state.

3. Calculate via Monte Carlo integration and subsequent differentiation the density of bound states $N(E)$. This is done by finding the volume of the full Hamiltonian
at $E$, and again at $E + \delta E$. The density of states is the numerical derivative \( \frac{V_2 - V_1}{\delta E} \). This quantity is error prone, involving small differences in large numbers.

I guarantee the validity of the Monte Carlo integrations in the following ways:

- In each integration $V_1$ and $V_2$ must be separated sufficiently so that there is no overlap between their standard deviations at the $2\sigma$ level.

- When the previous condition is satisfied, I repeat the full integration with the same number of points and a different random seed, to establish the degree of repeatability of the results.

The number of points required to guarantee convergence of the integrals grows by roughly an order of magnitude per dimension of the integral. With the available computational capacity I was able to calculate Monte Carlo RRKM rate constants for systems with up to six dimensions, which limits this technique to triatomic molecules.

**F.4 Calculation of rate constants from trajectory lifetimes.**

Since RRKM theory is a microcanonical transition state theory, to be directly comparable to an RRKM rate constant, a kinetically determined rate constant must be based on trajectories that have a microcanonical distribution of initial conditions. But what constitutes a microcanonical distribution? According to Steinfeld et.al. [8] "RRKM theory assumes that initially, when $\tau = 0$, there is a statistical population of reactant internal states at a fixed total energy." For further details of the mechanics of achieving a microcanonical distribution of initial conditions please see the initial conditions appendix.

To determine a rate constant from trajectory lifetimes, for each case studied I ran up to two thousand trajectories with microcanonically sampled initial conditions. For every trajectory, reactive or not, I recorded the final time value. For reactive
trajectories the final time value occurs when the reaction coordinate exceeds its transition state value. For nonreactive trajectories the final time value corresponds to the allowed maximum time. In general maximum time values were selected to keep the fraction of nonreactive trajectories low.

I determined rate constants for each system by reordering the trajectory final times from least to greatest, and then by plotting $\ln \frac{A}{A_0}$ versus time, where $A$ is the number of trajectories as yet unreacted, and $A_0$ is the total number of trajectories (including nonreactive ones). This plot will hereafter be referred to as the decay curve because it shows the decay in population as a function of time. Because at a specified energy RRKM theory yields a single rate constant for a unimolecular reaction, it presupposes first order kinetics. Therefore the decay curve should be linear for RRKM molecules. RRKM theory also presupposes (by disallowing trapped trajectories) that given sufficient time (or a big enough computer) all trajectories will react, so there is no inherent difference between reactive and nonreactive trajectories. However, when generating trajectories in a finite capacity computer one encounters nonreactive trajectories. Even nonreactive trajectories contribute to the determination of the rate constant, through their inclusion in the $A_0$ value. However it is not appropriate to include points for nonreactive trajectories at the maximum time while fitting the decay curve for rate constant determination. As expected, the rate constant is the negative of the slope of the decay curve.

A few remarks are in order regarding sources of error in determining rate constants from trajectories. Error sources will be discussed and analyzed.

Selection of microcanonical initial conditions is nontrivial. Each system studied has only approximately the nominal total energy. In the worst case trajectory energies may differ in by up to one percent. The variation in frequency arising from this energy difference for well behaved Hamiltonians is negligible, but errors will arise as
a consequence of the fluctuation in the total energy in the system. Adapting the rate
constant expression for the harmonic oscillator approximation, we get:

\[ k(E) \propto \left( \frac{E}{E} \right)^{s-1} \]  \hspace{1cm} (F.25)

The magnitude for errors in the rate constant arising from fluctuations in the total
energy can be estimated from Eq. F.25 as follows:

\[ \frac{k(E + \Delta E)}{k(E)} = \left( \frac{\frac{E}{E + \Delta E}}{\frac{E}{E}} \right)^{s-1} \]  \hspace{1cm} (F.26)

\[ = \left( \frac{E}{E + \Delta E} \right)^{s-1} \]  \hspace{1cm} (F.27)

In the systems I have studied, I have selected the limits on \( \Delta E \) to be such that error
in the rate constant arising from this source is less than one percent.

Since rate constants are determined from trajectory lifetimes at first blush one
might assume that they are dependent upon the exact definition of the transition
state. What is the effect of redefining the values for \( q_i \rightarrow q_i + \delta q_i \)? In fact, since the
rate constant is found from the slope of the decay curve, there is no effect, since such
a redefinition of the transition state shifts the value of the time axis marginally, but
leaves the slope unchanged.

The final source of error considered is potentially the most troubling. Rate con-
stants are determined by a linear least squares recursive fit to the \( \ln \frac{A}{A_0} \) decay curve. If
the curve is perfectly linear then fitting any portion of it would give the same results.
Typically the portion available corresponds to those trajectories which react early.
If, because of computer limitations, the proportion of reactive trajectories is low, one
runs the risk that too short a segment of the decay curve is being fit, so beyond the
question of random errors in the rate constant resulting from least squares curve fit-
ing, one must address the issue of systematic errors in \( k \) arising from fitting too short
a range of values [42]. I have addressed this issue by choosing a maximum time for each system studied such that at least half of all trajectories react. The magnitude of this last error depends upon the degree to which the decay curve departs from linear.

F.5 Conclusion

The reason for calculating RRKM rate constants is to have values to compare to rate constants determined from trajectory lifetimes, and so to assess whether or not a given system is RRKM in behaviour. Good agreement between these two independent values would suggest that the system is RRKM, but this begs the question of what constitutes "good" agreement. In calculations for the H$_2^+$ system (which is RRKM) Berblinger and Schlier characterized agreement between the two rate constants in the range of twenty to sixty percent as good [42].

In the process of this analysis I discovered that the decay curves for HN$_3$ and HONO arising from trajectory lifetimes are intrinsically nonlinear. This nonlinearity prohibits assignment of a single meaningful microcanonical rate constant, so a direct comparison to calculated rate constants is impossible. However, linearity of the decay curve turns out to be perhaps the best diagnostic regarding the extent to which a system is RRKM in behaviour [14], so even without resorting to RRKM rate constant calculations it is possible to determine (via nonlinearity of the decay curve) that neither HN$_3$ nor HONO is RRKM. But what causes nonlinearity in their decay curves?

Recall that a key assumption of RRKM theory, (which limits it to systems with first order kinetics) is that all states are equally capable of reacting. Existence of phase space bottlenecks contradicts this assumption, and such systems no longer have first order kinetics. Such bottlenecks occur when one or more modes are isolated from the reaction coordinate. Isolation of a mode is a consequence of inadequate coupling between it and the other modes. The H-M stretching mode, where M is an atom which
is much heavier than hydrogen is a usual such example. Because of hydrogen’s small mass this frequency is often much higher than that of other molecular modes. The mismatch in vibrational frequencies makes energy transfer via resonances difficult, resulting in an isolated mode, and so in non RRKM behaviour. The systems studied in this work (HN₃ and HONO) both contain a H-M bond, so it comes as no great surprise that neither molecule is RRKM.

Although they proved to be irrelevent to the process of determining whether or not the systems studied are RRKM, for the sake of completeness the calculated RRKM rate constants are included in Tab. F.1. Not surprisingly, the rate constants for cis and trans HONO are very similar, although experimentally they differ greatly. This is one more confirmation that HONO is a non RRKM molecule. No values are listed in the table for rate constants determined by Monte Carlo integration, since (due to computational constraints) this technique is limited to triatomics.
<table>
<thead>
<tr>
<th></th>
<th>HN₃</th>
<th>HONO (cis)</th>
<th>HONO (trans)</th>
</tr>
</thead>
<tbody>
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<td>Energy (au)</td>
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<td>0.065</td>
<td>0.065</td>
</tr>
<tr>
<td>kₜₜO (au)</td>
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<tr>
<td>kₜₜO (au)</td>
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<td>6.8x10⁻⁵</td>
<td>5.8x10⁻⁵</td>
</tr>
</tbody>
</table>

**Table F.1** RRKM rate constants with different levels of approximation, where kₜₜO was calculated using the harmonic oscillator approximation and kₜₜO using the anharmonic oscillator approximation.
Appendix G
Development of the Formyl Fluoride PES.

This appendix uses formyl fluoride (HFCO) to illustrate the process of constructing and verifying a Hamiltonian, beginning with designing an analytic potential energy surface. Subsequent sections show techniques used to verify the Hamiltonian. The PES addresses the portion of phase space encompassing the dissociation of HFCO, in the following reaction.

\[ \text{HFCO} + h\nu \rightarrow \text{HF} + \text{CO} \]  \hspace{1cm} (G.1)

G.1 Introduction

HFCO was selected for study because its reaction coordinate involves severing the C-F and C-H bonds, and forming an H-F bond. Unlike previously studied isomerization and dissociation reactions and the HFCO reaction coordinate is not an extension of simple local mode motion. Unfortunately, the very complexity of the reaction coordinate which makes HFCO interesting to study also makes difficult the task of creating a suitable PES. An analytic PES was needed to construct the Hamiltonian with which to analyze the dynamics of the formyl fluoride system. Previous workers have performed ab initio calculations of varying degrees of exactness, but no analytical function existed. The following sections outline how I created and verified an analytical PES for HFCO.

G.2 PES construction

In a letter to the Journal of Chemical Physics [55] Morokuma and Kato outlined results of ab initio calculations for HFCO along its reaction coordinate. Two illustrations in this letter were invaluable to me in creating the PES, namely a figure showing
potential energy as a function of reaction coordinate (featuring barrier heights pre and post reaction), and a figure which demonstrated motions of the atoms as reaction progresses along the intrinsic reaction coordinate (IRC). Also vital was their calculation at the transition state of molecular geometry and PES curvature along the IRC. Other PES control points include experimentally determined values for the equilibrium geometry and frequencies of vibration. In constructing a PES for HFCO I created an analytical function which honors each of the preceding points of control while allowing rupture of the C-F and C-H bonds simultaneously with formation of the H-F bond.

Aside from its complicated reaction process, HFCO is challenging because in its equilibrium configuration the molecule is planar. This introduces a number of complications with Pandora (a program package for calculation of classical trajectories), and makes the task of creating a potential function more complex. The local mode motions of HFCO are three stretches (C-F, C=O and C-H), three in plane bends (OCF, FCH and HCO) and an out of plane bend. The alert reader will quickly recognize that the seven local modes specified are in excess of the $3N-6 = 6$ modes that are required. One of the in plane bends is redundant, but fortunately Pandora does not force an arbitrary selection. I am able to form a potential in terms of all local modes, and in Pandora's normal mode calculations routine the redundant mode is eliminated automatically by the mathematics of the process. For ease of implementation and also for greater physical insight, the analytical PES is composed of terms related to each of these local modes, or to linear combinations thereof. In the following subsections I examine the terms in the analytical PES local mode by local mode.
G.2.1 C=O stretch

The simplest local mode is that of the C=O stretch. Because this mode is basically unchanged during the reaction I modeled this term as a harmonic oscillator whose force constant was selected to optimize the match between the experimentally observed vibrational frequency and the frequency value obtained subsequent to normal mode analysis of the Hamiltonian. In reality, the force constant probably changes during the reaction as the CO bond goes from double to triple, but my HFCO potential was not this detailed.

G.2.2 Modes altered by reaction

All other local modes are profoundly altered as the reaction occurs, ceasing even to exist. For this reason, switching functions (whose values depend upon the reaction coordinate) modify several parameters controlling these terms in the potential function. In most of these switches the reaction coordinate is approximated by the value of the C-F stretch, although ideally the reaction coordinate would involve a linear combination of both the C-F stretch and the HCF bend. However, controlling switching functions based on a linear combination of local modes is a greater level of complexity than I was willing to incorporate into my analytical PES.

Out of plane bend

The out of plane bend is the next most simple term in the potential. Separated by symmetry from all other modes, it is well modeled as a harmonic oscillator whose force constant goes to zero as the reaction progresses.
OCF bend

The OCF bend is simply a harmonic oscillator whose force constant is turned off as the reaction occurs, and whose shape has been modified to have a local maximum when the OCF bending angle equals π. This detail insures that the potential is well behaved if the OCF bend passes through a linear configuration.

HCO bend

The HCO bending term is slightly more complex than the OCF term. This mode is basically a harmonic oscillator, but the center point of the oscillation is allowed to change value depending upon whether the molecule is near equilibrium or the transition state. The change in center point helps to insure that both configurations are planar, as ab initio calculations indicate that they should be. Lastly, just as with the OCF bend, I have modified the harmonic oscillator function so that when the HCO bending angle is π the potential is at a local maximum.

C-F dissociative mode

The C-F Morse function is modified (by a switching function) so that it has a local maximum at the transition state. This mode ceases to exist following reaction, but to prevent unilateral defection of the F atom the switching function is controlled by the value of the HCF bend.

Hydrogen motion

Morokuma and Kato's illustration of motion along the IRC shows the motion of H during reaction to be quite complex. From its initial (roughly equilateral) position at equilibrium H sweeps upwards in a broad arc, heading between C and F. Before it can
insert itself between these two atoms it is deflected, and swings around F, and reaction occurs as H and F depart together. The motion of hydrogen is complicated, and terms have been introduced into the C-H stretching potential solely for the purpose of bringing hydrogen motion into conformance with that proposed by Morokuma and Kato. Following reaction the C-H Morse oscillator is turned off as a function of C-F separation.

While the values for the Morse potential govern how easily the C-H bond breaks, it is dominantly the HCF bending motion which determines the path taken by hydrogen during reaction. Therefore the HCF bending motion term evolved into a complex expression. I chose to taper this mode so that near equilibrium it is the HCF bending motion, but post reaction it is the H-F stretching mode. The transition from bend to stretch is controlled by the true reaction coordinate, i.e. a linear combination of both the C-F stretch and the HCF bend. Both modes are modeled as harmonic oscillators. To create a saddlepoint at the transition state I included a gaussian "dam" to block the valley defined by the minimum of the two harmonic oscillators. The location and curvature of the gaussian were chosen to provide agreement with Morokuma and Kato's calculations for the transition state.

G.3 PES verification

The resulting analytical potential function (comprised of about seventy lines of code, with roughly thirty adjustable parameters) is subject to verification by comparing its attributes to the known physical control. This includes geometry comparisons at both equilibrium and the transition state, and comparisons of vibrational frequencies, as well as location, height and curvature of the transition state. Subsequent subsections discuss how these comparisons can be made, and give specific results for HFCO.
G.3.1 Control points

Validating a PES involves checking the response at certain critical points where results can be compared to external controls, such as spectroscopically determined data (usually frequencies, as well as some structural information) or results of ab initio calculations (such as frequencies and geometries). For surfaces existing in as many dimensions as does a PES (i.e. 3N-6), defining a location in a multidimensional space is often done with respect to a stationary point (i.e. a local minima which corresponds to an equilibrium value, or a saddlepoint such as the transition state.) Once a unique point on the PES can be identified, properties of the surface can be measured at that location. A local minimum is relatively easy to locate (several algorithms exist to automate the process), and is physically meaningful, corresponding to the equilibrium geometry. The saddlepoint of the transition state is harder to locate, involving a local maximum in one direction along with local minima in all others.

Equilibrium properties

A standard diagnostic for potential energy surfaces involves calculation of normal mode frequencies, usually at the equilibrium location. Having determined the minimum, one then evaluates both the $F$ and $G$ matrices, where the $F$ matrix is comprised of second derivatives of the potential, and the $G$ matrix is the matrix of the corresponding effective masses. (Please see the appendix on the Wilson $G$ matrix for a more complete discussion). The eigenvectors of the $FG$ product matrix are the normal modes of vibration at equilibrium, and the eigenvalues are related to the normal mode frequencies of vibration. The beauty of this particular diagnostic is that (barring the unlikely occurrence of cancelling errors) it permits verification of both the potential and the kinetic portions of the Hamiltonian.
Tab. G.1 shows the comparison between normal mode frequencies found for the PES, and those found experimentally [56]. Tab. G.2 shows the comparison between stationary point geometries for the PES and for those derived by ab initio calculations [55].

Transition state properties

Techniques exist for locating the transition state, but these tend to be cumbersome and far from foolproof. For the relatively low dimensionality of HFCO I elected to locate the transition state by searching phase space for zero slope locations in small regions near where I expected the transition state to be. This was sufficient to allow approximate location of the transition state. Once the transition state was located it was possible to determine the barrier height, curvature and local geometry.

At the transition state the barrier height is simply the difference between the value of the the potential at this location and at the minimum. Curvature of the transition state is related to vibrational frequencies at the saddlepoint. At this location there should be one negative eigenvalue, corresponding to negative curvature along the reaction coordinate, with all other eigenvalues positive, corresponding to positive curvature in all other modes. This distribution of eigenvalues does not guarantee that the specified location is exactly the transition state, only that the reaction coordinate now has negative curvature. However, if normal mode analysis turns up two negative eigenvalues then the location is clearly not a saddlepoint.

Tab. G.2 shows the comparison in transition state geometries between the PES and ab initio calculations [55], while Tab. G.3 compares transition state energy and frequencies for the PES and ab initio calculations [55].
G.4 Conclusion

As shown by the tabulated comparisons, the analytical potential function that I designed is in good agreement with all available physical control points. Beyond quantitative control I have also tried to instill qualitative features. Morokuma and Kato’s figure showing atomic motions along the IRC is striking because it shows that most of the motion along the reaction coordinate involves the hydrogen atom, which follows a distinctive sweep in the course of reaction. I have included terms in my potential that cause a local minimum in potential energy with much the same features as Morokuma and Kato’s hydrogen motion.

Despite the care with which it was constructed, I make no claims that this is a universally applicable PES. The switching functions which turn off terms in the potential are ad hoc. There are no control points with which to verify that the slopes of the potential energy function connecting the well specified equilibrium location and the well specified transition state are correct. Also, Morokuma and Kato include in their profile of reaction coordinate versus energy a further isomerization into a linear H-O=C-F molecule, which I have disallowed in my PES. Even given these limitations however, this analytical PES gave rise to some very interesting dynamics.

The OCF bending mode had two interesting features. In the last oscillation prior to reaction the motion of this mode correlated with that of the C-F stretch. Examination of the local mode energies shows that these two modes exchange energy cleanly for several oscillations until the amplitude is sufficient for reaction. This implies that the OCF bending mode is the driver that pumps energy into the C-F stretching reactive mode.

However, the C-F stretching local mode is only a portion of the reaction coordinate. What of the HCF bending mode? This motion is required to bring the
hydrogen into proximity with the fluorine atom, to allow reaction. When one examines the phases of oscillation for the both local mode components of the reaction coordinate (i.e. the C-F stretch and the HCF bend), one finds that for a short time the two modes are strongly correlated, sharing the same period, but oscillating exactly out of phase with each other. This motion makes sense physically, as this is a pattern of motion which brings the hydrogen atom into proximity with the fluorine atom at a time when the C-F bond is most extended, and both atoms of the departing H-F fragment have outwardly directed momentum vectors. This correlated motion permits a clean separation of the products.

I studied HFCO to determine if correlated motion can exist in a system where the reaction coordinate is a linear combination of local modes rather than just the extreme value of a single local mode. I found that correlated motion does exist in this system, and that reaction requires synchronization of several modes. These findings support the contention that correlated motion is not unusual, and can be found in systems with a wide range of reaction dynamics.
Frequency comparisons \(\text{cm}^{-1}\)

<table>
<thead>
<tr>
<th>normal mode</th>
<th>PES</th>
<th>control</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H stretch</td>
<td>2990.2</td>
<td>2981.0</td>
</tr>
<tr>
<td>C=O stretch</td>
<td>1836.4</td>
<td>1836.9</td>
</tr>
<tr>
<td>C-H bend</td>
<td>1338.0</td>
<td>1342.5</td>
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<tr>
<td>C-F stretch</td>
<td>1060.9</td>
<td>1064.8</td>
</tr>
<tr>
<td>out of plane bend</td>
<td>1012.0</td>
<td>1011.3</td>
</tr>
<tr>
<td>OCF bend</td>
<td>657.4</td>
<td>662.5</td>
</tr>
</tbody>
</table>

*Table G.1* Comparison of HFCO normal mode vibrational frequencies for the analytical PES and experimentally measured values.

Geometry comparisons (au)

<table>
<thead>
<tr>
<th>local mode</th>
<th>Equilibrium</th>
<th>Transition state</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>PES control</td>
<td>PES control</td>
</tr>
<tr>
<td>C=O stretch</td>
<td>2.228</td>
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<tr>
<td>C-F stretch</td>
<td>2.564</td>
<td>3.550</td>
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<tr>
<td>C-H stretch</td>
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<td>2.01</td>
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<tr>
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<td>2.12</td>
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<td>HCO bend</td>
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<td>3.21</td>
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<tr>
<td>out of plane bend</td>
<td>0.000</td>
<td>0.000</td>
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</tbody>
</table>

*Table G.2* Comparison of HFCO geometries for the analytical PES and for values derived from ab initio calculations.
### Transition state properties

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<thead>
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<th></th>
<th>PES</th>
<th>control</th>
</tr>
</thead>
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<tr>
<td>frequency (cm$^{-1}$)</td>
<td>1636i</td>
<td>1640i</td>
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<tr>
<td>barrier height (au)</td>
<td>0.095</td>
<td>0.097</td>
</tr>
</tbody>
</table>

**Table G.3** Comparison of HFCO transition state properties for the PES and for values derived from ab initio calculations.
Bibliography


