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The photoexcitation spectra of transition region species in reactions of $K + NaX$ ($X = Cl, Br, I$)

Barnes, Michael Dean, Ph.D.

Rice University, 1991
RICE UNIVERSITY

THE PHOTOEXCITATION SPECTRA OF TRANSITION REGION SPECIES
IN REACTIONS OF K + NaX (X = Cl, Br, I)

by

MICHAEL DEAN BARNES

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

DOCTOR OF PHILOSOPHY

APPROVED, THESIS COMMITTEE

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ABSTRACT

The Photoexcitation Spectra of Transition Region Species
in Reactions of K + NaX (X = Cl, Br, I)

by

Michael Dean Barnes

The photoexcitation spectra of transition region species formed in bimolecular reactions of K + NaX (X = Cl, Br, I) have been observed by measuring the intensity of sodium D line emission at 589.0 nm as a function of excitation wavelengths between 595 and 640 nm. The portion of the spectrum measured for the K + NaCl system is qualitatively similar to that previously observed by Magurie, et al (MAG86). The spectra obtained for the K + NaBr and NaI systems are significantly different than that of the K + NaCl system, and show a distinct feature centered at approximately 610 nm, and indicate that the reaction dynamics are quite different for the heavier sodium halide systems. The results of classical trajectory calculations performed using K + NaCl potential energy surfaces suggest that the structure in the K + NaBr and K + NaI spectra is not due to a mass effect; but rather from unique features of the potential energy surfaces for these reactions which are, as yet, unknown. Because of insufficient theoretical and experimental information, interpretation of these results in terms of the dynamical processes in these reactions is not yet possible. However, several different possible mechanisms of this structure are discussed which can be experimentally tested. Results of proposed future experiments should be able to provide the necessary information to understand the nature of these spectra.
ACKNOWLEDGEMENTS

There are many people to whom I am deeply indebted for providing the support which was essential for the work reported in this thesis. I would first like to thank my advisors, Professors Philip Brooks and Robert Curl, for their support and commitment to this project in the face of some very long odds. My past colleagues in this laboratory, Syd Ulvick and Jim Spence deserve special thanks for enduring my many questions, and teaching me the skills required for survival in the lab. More importantly, their friendship made it possible to endure the hard times and prevented me from completely losing my sanity during some of the more particularly 'difficult' periods. I would also like to thank Bruce Johnson for all the help with the classical trajectory calculations. Without his generous contributions of time and effort, these calculations would not have been possible (at least not in time for the thesis deadline).

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Chapter 1

Introduction

The ability to predict and control the outcome of a particular chemical reaction depends upon having a complete understanding of the underlying dynamical processes which are involved. Therefore, an understanding of how matter is transformed from one substance into another is of fundamental importance. The goal of chemical dynamics is to learn precisely how old bonds are broken and how new ones are formed during the course of a chemical reaction.

The reaction between reagent molecules to form products must, at some point, involve some transient intermediate species which is neither reagents or products. In general, these intermediates formed in a chemical reaction have many different nuclear configurations which change continuously throughout the collision. It is therefore convenient to define "transition region species" , or TRS, as the set of all configurations intermediate between reagents and products (BRO88). The primary goal in studies of these dynamical systems is to obtain experimental information on the TRS which could lead to insight into the motions of nuclei during a chemical reaction. From such information, it may be possible to infer properties, such as intermolecular forces, of the potential energy surfaces (PES) involved; leading, in principle, to improvements in
theory which would increase our understanding of the dynamics of these systems and provide greater predictive capabilities.

The experimental difficulties in probing systems as they undergo reactions lie primarily in the fact that the duration of the reaction event is extremely short, typically between $10^{-14}$ and $10^{-12}$ seconds. The development of spectroscopic probes of these transition region species requires that they interact with a radiation field and that the interaction is manifested in some experimental observable. To maximize chances for success, it is desirable to select a chemical reaction for study which is known, or assumed, to proceed through a long lived reaction complex. The choice of chemical system must also be such that interferences from uninteresting processes, which may obscure the signal of interest or complicate interpretation of experimental results, are minimized. Assuming that a chemical system is found which satisfies the above criteria, the goal of spectroscopy of transition region species is to obtain a spectrum of the TRS from which information can be extracted regarding the dynamics of the reaction event.

How information on the nuclear motions during a chemical reaction be obtained from a spectrum of the TRS? In the vibrational spectrum of a polyatomic molecule, features are observed in a spectrum which can be assigned to the normal vibrational modes corresponding to identification of different types of nuclear motion. In simple cases, the correlation between nuclear motion and spectral features is usually straightforward since the normal vibrational modes and associated transition energies can be predicted (WIL55). In the case of transition region species, however, there will be many different types of motion in the transition region which might result in a broad, featureless spectrum because of the variety of initial conditions and nuclear configurations which are explored. Nevertheless, the observation of structure in the TRS spectrum is not precluded by the large extent of averaging over collision parameters and configurations. Such features could arise as a result of an aspect of the collision kinematics, or from features of the potential energy surfaces which could result in an
increase in absorption strength at certain wavelengths. However, if features are observed, identifying the underlying dynamics presents a problem since fairly accurate potential energy surfaces must already exist in order to correlate nuclear motion with observed spectral information.

A fundamental limitation to the study of dynamics of reactive bimolecular collisions experimentally is our inability to restrict the range of initial conditions. Even in molecular beam studies, where often the distributions of speeds, and internal energies can be controlled, the collisions are still averaged over a range of impact parameters and relative orientations - resulting in blurring of spectral features in the TRS spectrum. This problem can be avoided or at least reduced by studying the photodissociation of stable species instead of transition region species in bimolecular collisions. Photodissociation, or 'half-collision', experiments avoid averaging over a broad range of initial conditions by choosing a stable species as the initial state and exciting to a dissociative state. These experiments probing the dynamics of the dissociation event can reveal detailed information on the nuclear motion as the molecule breaks apart.

In the landmark experiments of Kinsey and co-workers (IMR84), photodissociation experiments of CH₃I and O₃ were carried out, and weak fluorescence from the dissociating molecule onto ground vibrational states was observed. This process can be viewed as the propagation of a wavepacket which evolves in time on the excited state surface. The upper surface is strongly repulsive in the case of CH₃I and O₃, and the molecule breaks apart on a femtosecond time scale. Consequently, as the wavepacket evolves, it develops Franck-Condon overlap with a variety of ground vibrational state wavefunctions, resulting in transitions from the repulsive state to these ground vibrational levels. This is a Raman process, and the intensities of these transitions can be shown to contain information about the dynamics of the dissociation event (LEE82). The projection of the ground vibrational wavefunction (φᵢ) onto the time varying
excited state wavefunction \( \phi_1(t) \), called the "correlation function", is related to the Raman amplitude as \( \text{(IMR84)} \),

\[
\alpha_{1f}(\omega) = \int_0^\infty \exp(i\Delta \omega) < \phi_1 | \phi_1(t) > \, dt
\]

where \( \alpha_{1f}(\omega) \) is the Raman amplitude, \( \omega \) is the frequency of transition, \( \exp(i\Delta \omega) \) is a detuning factor, and the quantity \( < \phi_1 | \phi_1(t) > \) is the correlation function - the projection of the ground vibrational state, \( \phi_f \) onto \( \phi_1(t) \) which contains the dynamical information.

In the case of \( \text{O}_3 \), a long progression in the symmetric stretch \( (\nu_1) \) vibration was observed along with only even numbered levels in the asymmetric stretch \( (\nu_3) \). No emission corresponding to the bending mode \( (\nu_2) \) was observed. The conclusions made were that the initial motion of the dissociating \( \text{O}_3 \) molecule is primarily along the symmetric stretch coordinate \( (q_1) \). Since the wavepacket remains symmetrical during this motion, there is no overlap with the odd numbered \( \nu_3 \) wavefunctions which are antisymmetric. As the wavepacket moves along \( q_1 \), it also spreads into the asymmetric stretch coordinate \( (q_3) \). Eventually, more of the motion becomes directed along the \( q_3 \) coordinate and dissociation into \( \text{O} + \text{O}_2 \) takes place. The absence of any emission corresponding to the \( \nu_2 \) bending mode indicates that the bond angle does not change appreciably during the dissociation process. These results for the photodissociation of \( \text{O}_3 \) illustrate how, with the aid of well defined initial conditions, detailed information on the nuclear motions during the process of dissociation can be obtained by Raman measurements made in the frequency domain.

Another probe of nuclear motion in the transition region of a potential energy surface using a half-collision technique was developed by Neumark and co-workers (BRA90). In these experiments, a stable \( \text{XHY}^- \) (where \( X \) and \( Y \) are halogen atoms) anion is produced in a pulsed molecular beam and the electron is then photodetached to form the unstable neutral \( \text{XHY} \) species which can be thought of as transition region species in the
reaction $X + HY$. Information regarding the potential energy surfaces and nuclear motions is obtained by analyzing the kinetic energy distribution of the photodetached electrons. The electron photodetachment process involves excitation from the lower lying anionic state to the higher energy neutral state. Peaks are observed in the electron kinetic energy distribution, corresponding to transitions between the ground vibrational state of the anion with bound vibrational states on the neutral surface.

In the study of the IHI$^-$ spectra (WEA88), peaks corresponding to both the antisymmetric stretch (H atom motion) and symmetric stretch (I atoms) in the neutral species were observed although no potential energy wells exist in the calculated surfaces for the neutral system. These bound states in the transition region are believed to be supported by minima in the "effective potential" - calculated by adiabatic separation of symmetric and asymmetric stretch motions (BAB81). The photodetachment method is an excellent probe of the transition region in neutral reactions. Its fundamental limitation is that only the Franck-Condon region is probed where the geometry of the neutral species is similar to that of the ion and may not be representative of TRS geometries in bimolecular collisions.

In an extension of these photodissociation and photodetachment experiments, Bernstein, Zewail, and co-workers developed time domain probes of the dynamics of the $H + CO_2$ reaction (SCH87). By forming the HI-CO$_2$ van der Waals molecule in a supersonic jet using the method developed by Wittig and co-workers (BUE85), they were able to constrain the impact parameter and initial orientation of the H and CO$_2$ reagents. The reaction was initiated with a photolysis pulse, dissociating the HI to form a 'hot' H atom (speed about 200 Å/ps), and the rate of formation of OH was monitored using laser induced fluorescence (LIF) with a probe pulse fired at some specified time following the photolysis pulse. It was found that the rise time of the OH LIF signal was about 5 picoseconds, indicating a long lived complex. Although this method does yield
information on the time scale required for the reacting system to evolve into products, the details of the nuclear motion during this relatively long time scale remain unclear.

Each of the methods described here has the distinct advantage of limiting the range of initial conditions. As a result, meaningful information regarding details of the dynamics of unimolecular dissociation could be obtained. The disadvantage of this type of method is that the geometry of the system is constrained in ways which may not be representative of bimolecular reactions in free space which have a range of impact parameters and orientations. Since most chemical reactions involve full bimolecular collisions, it is important to investigate transition region species which are formed in these systems despite the problem of averaging over collision parameters.

In a recent study of transition region species formed in the bimolecular reaction, H + para-H$_2$ (KLI91), the presence of dynamic scattering resonances, or, *Feshbach* resonances, were investigated. These resonances have been predicted to occur when the collision energy is equal to the energy of an excited vibrational state in the reaction complex (TRU81) and results in an increase in the reaction cross section for that collision energy. Therefore, measurements of reaction cross sections as a function of collision energy can be thought of as a vibrational spectrum of the TRS in this system, even though the TRS itself does not interact with a radiation field, and could display structure corresponding to these dynamical resonances. In choosing the H + para-H$_2$ system, these workers were able to distinguish between elastically and reactively scattered H$_2$ since elastic collisions cannot interconvert the para and ortho forms but reactive ones can. Integral rate constants for the formation of ortho-H$_2$ were measured for different collision energies using (2+1) resonance-enhanced multiphoton ionization. No structure was observed which could be attributed to the presence of Feshbach resonances - in excellent agreement with more accurate theoretical predictions (ZHA88). These calculations suggest that, although resonances should appear in the partial scattering waves which would be observed in differential cross section
measurements, averaging over all partial waves results in a blurring of this structure so that only weak undulations are present in the integral cross sections as a function of collision energy. These results have provided perhaps the best detailed comparison of experiment and theory to date.

Each of the methods and results thus far described have provided a great deal of important information on the details of the dynamical processes involved with chemical reaction. However, in order to complement this information, it is desirable to devise a method which directly probes transition region species formed in an actual chemical reaction requiring a full bimolecular collision. One possible method for directly probing these transition region species involves detecting the absorption of light by the TRS by the emission of a product in an excited state.

Consider a reactive system which has an excited electronic state which correlates in the product asymptote to an excited product, shown schematically in Figure 1.1. The reactive collision can be thought of as a classical trajectory (see Chapter 4) initially being propagated on a ground state potential energy surface. At some point along the trajectory where the difference in potential energies is equal to the energy of a probe photon, \( h\nu_{\text{probe}} \), it is possible for the reacting system to absorb a photon and be promoted to an excited state surface. As the trajectory now progresses on the excited surface, it may eventually go on to react to produce an excited product. In general, these excited products will fluoresce at characteristic wavelengths which are different from the probe wavelength and can serve as an indication that light absorption by the reacting system has taken place.
Figure 1.1. Fixed angle potential energy surfaces for the generic A + BC system. Orientation of axes and asymptotic energies shown with arrows. A reactive trajectory is drawn on the surface for illustration.
There are three major requirements on the chemical system chosen for this type of 'absorption spectroscopy' of the TRS. The first is that the reaction proceed through a relatively long lived complex so that there is higher probability for light absorption. Secondly, the system must possess a low lying excited electronic state (e.g., accessible with conventional wavelengths) which correlates with an excited product which has an allowed optical transition back to the ground state. Finally, the chemical system should be exoergic so that the emission of the excited product will be blue-shifted with respect to the probe wavelength. This is important since the energy of the probe would be insufficient to excite the product, thus eliminating possible artifactual sources of signal.

In the first experiments of their kind, Brooks, Curl, and co-workers, observed photoexcitation of transition region species in the exoergic reaction \( K + HgBr_2 \) (HER80). Beams of \( K \) and \( HgBr_2 \) were crossed inside the cavity of a flash pumped dye laser tuned to 595 nm, and blue-shifted fluorescence from the \( B^2 \Sigma \) state of \( HgBr \) at 500 nm was observed. It was determined that all three beams were required to produce the signal and no absorptions were known for reagents or products at the probe wavelengths used. The "three-beam signal" observed for this system was ascribed to the absorption of light by the reacting system followed by emission of the \( HgBr^* \) excited state product.

In an extension of this work, transition region species in the reaction \( K + NaCl \rightarrow KCl + Na \), which has many similarities to the \( K + HgBr_2 \) system, has been successfully investigated using this technique (MAG83, MAG84, MAG86). The \( K + NaCl \) reactions on the ground state PES are exoergic by about 0.2 eV and are known to have large cross sections. Angular distribution measurements of reactively scattered \( KX \) by Herschbach and co-workers (MIL67), showed that these reactions proceed through a long-lived complex with a lifetime of at least one rotational period. Ab initio potential energy surfaces have been calculated (ROA68, YAM88) for the \( K + NaCl \) system, and two low lying excited state surfaces have been predicted. These excited state surfaces should
be accessible with visible wavelengths, and correlate in the product asymptote with excited \( (2P_{3/2}, 1/2 ) \) Na atoms, with the \( 2P \rightarrow 2S \) transitions occurring at 589.0 and 589.6 nm for the 3/2 and 1/2 states respectively. The exoergicity of the reaction, coupled with the energy of collision, makes it possible to produce excited Na atoms by exciting the complex with photon energies less than the energy required to excite \( 2P \) sodium atoms. Thus, emission at the Na D lines (589.0, 589.6 nm) may serve as the signature of light absorption by the reacting system.

In those experiments, continuous effusive beams of potassium and sodium chloride were crossed inside the resonating cavity of a cw dye laser tuned to wavelengths between 595 and 740 nm. Emission from the three beam intersection region was filtered with a narrow band pass (4.7 Å fwhm) interference filter centered at one of the Na D lines (589.0 nm) and detected with a cooled photomultiplier tube operating in single photon counting mode. Counts were accumulated in all eight beam-on/beam-off combinations so that contributions from all two-beam and single-beam processes could be accounted for. The "three-beam signal" was obtained by subtracting the count rate for these single and two beam processes from that obtained when all three beams cross (see Chapter 2). The observed three beam signals were positive and statistically significant (signal/noise ratio = 20) at all probe wavelengths, and determined to be linear with respect to all three beam intensities.

Several possible artifact sources of the three beam signal were investigated, and it was shown that there was no correlation between the three beam signal and potassium photoluminescence (due to laser induced fluorescence of \( K_2 \)) and that sodium atom impurities, present in both beams, were not responsible for the signal. It was concluded that the three beam signal arises from the reactive decomposition of electronically excited transition region species, written in a stepwise fashion as:
\begin{align}
(1.2) \quad & K + \text{NaCl} \rightarrow [\text{KClNa}]^+ \\
& [\text{KClNa}]^+ + \text{hv} \rightarrow [\text{KClNa}]^{+*} \\
& [\text{KClNa}]^{+*} \rightarrow \text{KCl} + \text{Na}^* (^{2}P_{3/2,1/2}) \\
& \text{Na}^* \rightarrow \text{Na} + \text{hv} (589.0, 589.6 \text{ nm}) 
\end{align}

where $[\text{KClNa}]^+$ represents transition region species formed at the intersection of the K and NaCl beams, and $[\text{KClNa}]^{+*}$ represents the electronically excited TRS following photon absorption.

The three beam signals obtained for the $K + \text{NaCl} + \text{hv}$ system were plotted as a function of probe wavelength to obtain a photoexcitation spectrum of the KClNa TRS, shown in Figure 1.2. Because the excited TRS may decompose either reactively ($\text{Na}^*$) or nonreactively ($K^*$), this spectrum cannot truly be considered an absorption spectrum because the nonreactive pathway of the excited TRS is not monitored. Copious emission has been observed at 766 nm, corresponding to the $K$ ($4p \rightarrow 4s$) transition. However, because the emission is no longer blue-shifted with respect to the probe wavelengths and laser-excited $K_2$ is present, it is difficult to be certain that all the signal observed arises from excitation of the TRS.

The photoexcitation spectrum shows a steep rise at laser wavelengths between 600 and 595 nm, and a threshold at about 735 nm. The position of the threshold was shown to be consistent with energy conservation considerations which predict that the threshold for the formation of $\text{Na}^*$ should occur at a wavelength shorter than 842 nm. The signals between about 610 and 680 nm are essentially constant with perhaps a broad maximum at about 645 nm. The cause of the large increase in signal as the probe wavelength approaches the Na D line has not yet been ascertained but it is likely that the feature is due to a combination of higher TRS excitation probability and energy transfer processes not associated with photoexcitation of the TRS. The spectrum observed for the $K + \text{NaCl}$ system demonstrated that photoexcitation of transition region species in
Figure 1.2. Photoexcitation spectrum for K + NaCl + hv from Maguire, et al (MAG86). Each three beam signal, representing intensity of Na D line emission, is normalized by the product of all three beam intensities.
bimolecular collisions was possible. However, due to the lack of prominent spectral features, it was difficult to come to any conclusions regarding the nature of the TRS in this reaction or of the potential energy surfaces involved.

The spectrum shown in Figure 1.2 is just what one might expect for a photoexcitation spectrum of transition region species formed in a bimolecular reaction. Averaging over the range of impact parameters, orientations, and the broad distributions of speeds and internal energies determined by the temperatures of the source nozzles (1100 °K for NaCl, and 550 °K for K), should tend to 'wash out' any structure which might be present.

In an attempt to limit the range of initial conditions, seeded supersonic beam sources were developed to reduce the spread of velocities and internal energies (ULV88). Beam characterization studies showed that these new sources were indeed successful in reducing the distribution of speeds for both beams. Small, but positive three beam signals were observed using seeded reagent beams, however attempts to obtain TRS spectra were largely unsuccessful because of poor signal/noise ratios and unexpected background signals involving the seeded K beam. In the final chapter, the reasons for the low signal levels and the nature of this background signal are discussed in detail.

The inability to limit the range of initial conditions, along with the lack of accurate potential energy surfaces, makes it difficult to interpret the spectrum shown in Figure 1.2 in terms of the nuclear motion during chemical reaction. However, some insight may be gained into the dynamics of this class of reactions by substituting NaBr and NaI for NaCl. In changing only the halogen atom, all the advantages of the K + NaCl system previously described are still retained - with the notable exception that there are no calculated potential energy surfaces for the K + NaBr and K + NaI systems. The physical and chemical differences between the different sodium halides, such as vibrational frequencies, rotational constants, and halogen atom size, electronegativities and polarizabilities, may result in differences in the TRS photoexcitation spectra. These
possible differences in the spectra may lead to insight into the dynamics of this class of reactions which could ultimately be used in developing potential energy surfaces for the K + NaBr and K + NaI reactions.

In this thesis, results of crossed beam experiments performed on the K + NaBr and K + NaI systems are presented which show that the TRS photoexcitation spectra for these systems are indeed different from that observed for the K + NaCl system. The experimental apparatus used to obtain these results is described first, and, in the final chapter, possible mechanisms are discussed for the observed differences in the TRS spectra for the K + NaCl, NaBr, and NaI systems.
Chapter 2

Experimental

As described in Chapter 1, the K + NaX system has several properties which make it well suited for study of transition region species formed in bimolecular reactions. In this chapter, a description of the experimental method used to investigate these species and details of the apparatus are provided. Transition region species are formed at the intersection of continuous beams of K and NaX which are made as intense as possible. The beams cross inside the extended cavity of a cw dye laser where the high circulating power makes it possible for the TRS to absorb a photon and become electronically excited. Once the TRS has become excited, it may decompose reactively to give an excited (\(^2P\)) sodium atom which may emit at the sodium D lines. Thus, the emission at the Na D lines may serve as an indication that light absorption by the TRS has taken place provided that care has been taken to account for emission due to single and double beam processes.

The apparatus which is used to investigate these transition region species is composed of several different systems which function as a single unit. The basic components of this apparatus are the molecular beam sources, laser, and light collection and detection systems. This chapter begins with a description of the molecular beam
sources and the laser, including preparation procedures and operating parameters. A
description of light collection and detection system is provided next, followed by a
discussion of how the three beam signal is measured and normalized.

A schematic of the experimental setup is shown in Figure 2.1. The apparatus used
for the experiments described in this thesis is a hybrid of that used by Maguire
(MAG84) and that used by Ulvick (ULV88) which combines advantages from each
configuration. In addition several minor changes have been made which have improved
the beam and signal stability and the run-to-run reproducibility. For most details
regarding construction, dimensions, etc., the reader is referred to one of the two above
mentioned references.

2.1 Vacuum System

The two molecular beam source chambers are pumped by 10" diffusion pumps
backed by Leybold-Hereaus D90-A high-throughput direct drive mechanical pumps
(ULV88). Although this fast pumping speed is not required for the kinds of particle flow
rates used in these experiments, it greatly reduces the pump-down time in between
experiments (a). The reaction zone and buffer chambers are pumped by three 6"
diffusion pumps which are backed by a single Leybold-Hereaus D8-A mechanical pump.
Liquid nitrogen cryoplates are added for increased pumping speed, and a lower base
pressure - typically about 2 x 10^{-7} torr, and about 4.5 x 10^{-7} torr in the main
chamber with beams at full intensity.

(a) The pump down time is dependent on what tasks are required for the turn around (i.e.,
extensive use of water and other solvents to remove deposits of beam material), and is
typically between 12 and 24 hours.
Figure 2.1. Schematic of Experimental Setup.
2.2 Potassium Beam Source

The potassium beam source used for the experiments described here is the same as that used in previous studies (MAG84, ULV88). It is a two-chamber (body and nozzle) differentially heated monel oven which can hold a 25 gram charge of potassium. A conflat type seal is made with a monel lid machined with a 0.010" wide by 0.020" knife edge and three 0.010" copper gaskets. The lid is held down firmly with a screw-clamp which bears on a ball bearing mounted on the center of the lid. The oven is heated using tantalum heater coils spot-welded to tantalum bus wires. Three independent heating circuits are used (skimmer, nozzle, and body) with chromel-alumel thermocouples to monitor the temperatures. The operating temperatures used for these three components are given in Table 2.1.

One of the most important requirements of these experiments is alignment of the nozzle and skimmer. When the source and skimmer are at full temperature, the nozzle and skimmer orifices must be coaxial so that maximum beam intensity can be obtained. In addition, the beam must be positioned correctly to avoid reducing the intersection volume of the three beams, and to maximize detection efficiency. If the center of the three-beam intersection region is not located on the optical axis of the collection optic, the image of the intersection region will also be located off the optical axis, consequently not all the light collected will reach the photodetector. If the intersection is located above or below the focal point of the collection lens, the image will be blurred at the detector also resulting in a loss of signal. Moreover, each of these effects results in interference filter rejection of light which becomes no longer normal in incidence on the filter. It is therefore not surprising that the most common experiment failure mode; a low or non-existent three beam signal, is often attributable to faulty beam alignment.

The description of the alignment procedure which follows is only required when the skimmer has been bumped, rewired, or moved out of position due to repeated thermal cycling. The procedure described here is performed on the optical table outside of the
vacuum chamber. Other alignment methods have been tried, however, this method was found to be the easiest and most precise.

The fact that the beam sources operate at high temperatures and that the source and skimmer operate at different temperatures, require compensation for thermal expansion. This means intentionally misaligning the nozzle and skimmer at room temperature so that they become aligned at full operating temperature. The first step of the alignment procedure is to set up a target aperture whose vertical position (5.000") corresponds to the height of the beam axis with respect to the bottom of the hexagonal chamber. Next, the beam of a low power helium-neon laser is directed through the target aperture. The baseplate, designed for kinematic mounting of the potassium oven, is placed on the support blocks (see Figure 2.2) and oriented so that, viewing from directly above, the beam and the center groove of the baseplate are superimposed.

To account for the vertical thermal expansion of the skimmer (approximately .015"), shims are placed between the baseplate support blocks and optics table to bring the nozzle orifice up to the level of the HeNe beam. The baseplate is secured on the optics table, and the oven is placed on the baseplate. The HeNe beam is then adjusted to pass through the center of the target aperture and the nozzle orifice. The skimmer is then mounted on the baseplate and positioned using the adjustment screws so that the HeNe beam passes directly through the center of the skimmer orifice. The positioning may be checked by inspecting the diffraction pattern formed on a target downstream of the skimmer; when the beam is centered on the skimmer orifice, a clear circular diffraction pattern should be observed. After the skimmer has been positioned, a 0.005" shim (corresponding to the difference of vertical thermal expansion between oven body and skimmer) must be inserted between the foot of the skimmer mount and the baseplate. Being careful to maintain side-to-side alignment (by inspection of the diffraction pattern), the foot mounting screws are loosened and the shim inserted, then all mounting screws are tightened and secured. The diffraction pattern which results after the
procedure has been successfully performed should be symmetrical with respect to a vertical axis and slightly fuzzy at the bottom.

A check is required to ensure that the beam is indeed delivered to the proper location. Judging the quality of the beam alignment by inspection of beam traces left on partitions and cold plates is difficult and often misleading. Intensity measurements do not give a good indication of the beam alignment since the beam detectors are so far away from the source (≈ 50 cm). A target experiment was devised to check the alignment and to give exact information about the location of the beam with respect to the desired beam intersection point. A copper target was machined with a dowel pin hole in the base designed to mount in the precise center of the hexagonal chamber with cross-hairs etched on the face designating the exact desired vertical and horizontal location of the beam. With the target in place, the chamber is evacuated and a test beam is run with the source at full temperature for about an hour. The source is then cooled, and the chamber is vented and the beam trace deposited on the target is inspected. Any fine adjustments, if required, are made and the target experiment is repeated until the center of the beam trace is located on the desired point.

An important component of the K beam source is the set of liquid nitrogen cryoplates which collect the skimmed potassium during operation. The arrangement of cryoplates can be seen in Figure 2.2. One purpose of the cryotrap is to localize potassium condensation making cleanup much easier. The more important function of the K-source cryotrap, specifically the plate inserted between the nozzle and skimmer, is the significant reduction of "potassium photoluminescence" - a background signal due to the interaction between the K beam and laser beam. The exact nature of the potassium photoluminescence signal is not known, but it is presumably some process which involves potassium dimer (K₂), or the mixed alkali dimer NaK. Both of these species are known to exist in small concentrations in the K beam and both have well known absorptions in the wavelength region used in these experiments. Without the nozzle-
Figure 2.2. Potassium beam source chamber. Nozzle-skimmer distance is 1.1 cm, nozzle-crossing region distance is 6.0 cm.
skimmer cryoplate installed, the potassium photoluminescence signal can be as high as several thousand counts per second. With this plate in place, the photoluminescence signal is reduced to levels of around 20 - 50 counts per second. Regular maintenance of the cryotrap is required to maintain optimum performance. In addition to the regular cleaning, a light sanding of the plate surfaces, especially where two plates are joined, enhances the thermal contact which improves the condensation of the skimmed beam material and keeps the photoluminescence signals down to a minimum.

The intensity of the K beam was measured using a surface ionization detector (SID). The SID is composed of a hot tungsten filament which is positively biased with respect to a collector plate. The 0.002" diameter filament is heated resistively with a d.c. current of 0.27 amperes. Positive ions are formed on the hot tungsten surface which are then accelerated to the collector. The collector acts as a current source and the beam intensity may be measured as a small current - typically on the order of about 100 - 300 nanoamperes. Because signal normalization requires dividing by the product of the beam intensities, normalized signal reproducibility depends on the reproducibility of intensity measurements. Small changes in the position of the detector can result in large changes in the intensity measurement because of the long distance between source and detector and the small small viewing window of the detector. It was found that a significant improvement in the run-to-run reproducibility of normalized signals could be obtained if the detectors were not touched until replacement of the filament was required.

The optimum K beam intensity was determined from consideration of many competing factors. Since the three-beam signal is known to be linear with K beam intensity (MAG84), the maximum possible beam intensity is desired. However, it is also known (ULV88) that the K photoluminescence signal scales nonlinearly with beam intensity. The three-beam signal stability also becomes poorer at extremely high K beam intensities. The K beam intensity used therefore is a compromise which gives a
large enough stable three-beam signal, and minimizes the size of the K-
photoluminescence signal. Figure 2.3 shows the variation of K beam intensity and K-
photoluminescence with oven temperature.

![Graph showing variation of K beam intensity and photoluminescence with oven temperature.](image)

**Figure 2.3.** Variation of measured K beam intensity and potassium
photoluminescence at 600 nm with oven temperature.

2.3 Sodium Halide Source

Many different factors must be considered in the design of a sodium halide beam
source which can reliably produce salt beams of high intensity. The source must be able
to maintain temperatures close to the melting point of stainless steel, and be resistant to
corrosion from gas phase NaX molecules. The source must have a reliable lid seal that
permits addition and removal of salt which does not depend on gaskets or clamps which
often fail at high temperatures. Corrosion of the nozzle orifice can enlarge the orifice to
an unusable size in a matter of several weeks of use (ULV88). Therefore, the nozzle
construction of the source should be so that the nozzle itself may be replaced if necessary without rebuilding the entire source. A sodium halide beam source was developed which satisfied all of the above design criteria, and was designed to be used with the top-hat and baseplate for the supersonic alkali-halide source described by Ulvick (ULV88). This new source can easily be used as either an effusive or supersonic beam source with virtually any size nozzle orifice. An assembly diagram is shown in Figure 2.4.

Each component of the beam source was machined from 316 stainless steel, with the lid and nozzle chamber attached to the body chamber with vacuum welds. The salt is added (and removed) from a metal-gasket VCR fitting in the back (Cajon 316 1/4" I.D. weld stub) and a VCR blank-off gasket forms a reliable gas tight seal. The body chamber is large enough to hold 200 grams of salt so that several experiments can be run without removing the source. The nozzle head is also a VCR fitting (Cajon 316 modified male connector) and the actual nozzle, a circular disc of 0.005" thick stainless steel with a 500 micron hole in the center, serves as the metal VCR gasket. The nozzle disc is held in place by the nozzle nut whose threads are coated with MoS₂ and a Nickel anti-seize coating to prevent the seizing of the nut to the nozzle head. A gas tight seal can be made on the nozzle head with the nozzle nut applied with only finger tightness. If the nut is screwed on any tighter, it makes it extremely difficult to remove the nut (after use) with the threads still intact. When a nozzle replacement is required due to a clog or corrosion, the nut is taken off and the old nozzle disc removed and a new one put back in its place. Typically, some light machining is required for a nozzle replacement which usually entails retapping the nozzle nut and cleaning the threads on the head. In the worst case, where the threads on the nozzle head have been completely stripped, the nozzle head is cut off and a new one is welded on. Since the nozzle head is a commercially available inexpensive VCR component, no new fabrication is required and replacement of the nozzle head usually requires no more than about 2 hours of shop time.
Figure 2.4. Assembly diagram of NaX source. All materials are 316 Stainless.
The nozzle and body are heated with two sets of coiled tantalum heaters. As with the K beam source, temperatures are monitored with chromel-alumel thermocouples which are mounted in ports shown in Figure 2.4. The individual body heaters are made from about 3 feet of 10 ml tantalum wire, which when coiled has a length of about 3 inches and a resistance of about 5 ohms. The body heating circuit consists of four sets of six parallel heaters in series, giving a total load of about 3.3 ohms. The nozzle is heated with a similar circuit with the nozzle typically heated about 200 degrees higher than the oven body. The operating temperatures for the different sodium halides are given in Table 2.1.

Several different types of skimmers were tried in order to achieve the best collimation with the closest nozzle-to-reaction zone distance. It was found by performing target experiments similar to that described for the K-beam, that every skimmer which met the geometry requirements failed to produce a well collimated beam. Even at very low oven temperatures and fairly large nozzle-skimmer distances, the diameter of the beam traces showed that the skimmer was acting as a secondary source. It was possible to achieve and sustain satisfactory beam intensities in spite of the poor collimation. However, as illustrated by the intensity vs. temperature profile for NaCl in Figure 2.6, there is a substantial intensity limitation imposed by this problem. The variation of beam intensity as a function of oven temperature behaves similarly for NaBr and NaI, with the peak shifted to lower temperatures.

The NaX source-skimmer configuration, shown in Figure 2.5, which seemed to allow the shortest nozzle-beam intersection distance and the best beam quality involved mounting the collimator directly on the partition. Because of the relatively poor collimation, the type of alignment procedure such as described for the K source was not required since the beam diameter is so large. A level HeNe beam was directed through the
Figure 2.5. NaX source - skimmer configuration.
collimator orifice, and both the beam and collimator position are adjusted until the beam passing through the orifice is centered side-to-side with respect to the nozzle orifice, and approximately 1/2 nozzle diameter (.25 mm) high to account for the difference in vertical thermal expansion between oven and skimmer. The cold plates were water cooled and trap only on the sides of the collimator because of spatial constraints. It is very likely that introduction of a nozzle-skimmer cold plate similar to that used for the potassium beam could greatly improve the collimation.

The intensity measurements of the sodium halide beams were also made with a surface ionization detector. However, the surface ionization of sodium halides is not quite as straightforward as surface ionization of potassium. When a sodium halide molecule
hits the tungsten surface, it must first dissociate and the free sodium atom then surface
ionizes to form a positive ion. The ratio of positive ions formed on the surface to neutral
atoms is given by the Saha-Langmuir equation (LAN25)

$$\beta = \frac{i_+}{i_a} = \frac{\omega_+(1-r_+)}{\omega_a(1-r_a)} \exp \left[ \frac{(\Phi_W - I.P.)}{kT} \right],$$

where $\omega_+$ and $\omega_a$ are the statistical weights of ions and atoms respectively, $r_+$ and $r_a$
are the reflection coefficients (assumed to be negligibly small), $\Phi_W$ is the work function
of the tungsten surface, I.P. represents the ionization potential of the atom, $k$ is the
Boltzmann constant, and $T$ is the absolute temperature of the filament. Since the
ionization potential of the sodium atom (5.14 eV) is greater than the work function of
tungsten (4.54 eV), the probability of ion formation is small for sodium compared with
that of potassium.

Equation 2.1 suggests that the degree of ionization on the tungsten surface is the
same for sodium and all sodium halides, however it is found that the surface ionization
efficiency differs for different sodium halides (JOH39). The presence of adsorbed
halogen atoms, even at temperatures as high as 2600 °K, increases the work function of
the filament. For example, it is known that the work function of a W-I filament is about
5.5 volts (JOH39). Thus, the surface ionization efficiency of different sodium halides
depends also on the number of adsorbed halogen atoms. Johnson, et al, determined
relative ionization efficiencies for NaCl, NaBr, and NaI on hot tungsten filaments and
showed that the ionization efficiencies for NaCl, NaBr and NaI could be expressed in
terms of the filament temperature, $T_f$, as

(2.2a) \quad NaCl: \quad \log_{10}(i_+/i_a) = -1616/T_f - 0.670

(2.2b) \quad NaBr: \quad \log_{10}(i_+/i_a) = -1514/T_f - 0.670

(2.2c) \quad NaI: \quad \log_{10}(i_+/i_a) = -1309/T_f - 0.670.
The temperature of the filament used for surface ionization detection of the sodium halides can be estimated from a knowledge of the cross sectional area of the filament and the current used (SU60). For a current of 0.32 amperes (the filament current used for each sodium halide) and a filament diameter of 0.002", the temperature is approximately 1850 °K. Substituting this value for \( T_f \) in equations 2.2a,b, and c, the ionization efficiency \( \left( \frac{i_e}{i_a} \right) \) for NaCl is 0.028; for NaBr is 0.032; and for NaI is 0.042. Thus, for equal beam flux, the measured beam intensity for NaBr and NaI will be larger, relative to NaCl, by factors of 1.14 and 1.50 respectively. These intensity correction factors are used later for comparison of normalized signals between the different sodium halides.

Table 2.1. Typical Operating Conditions for Molecular Beam Sources

<table>
<thead>
<tr>
<th></th>
<th>K</th>
<th>NaCl</th>
<th>NaBr</th>
<th>NaI</th>
</tr>
</thead>
<tbody>
<tr>
<td>nozzle temp (°C)</td>
<td>520</td>
<td>1300</td>
<td>1150</td>
<td>1000</td>
</tr>
<tr>
<td>skimmer temp (°C)</td>
<td>300</td>
<td>550</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>body temp (°C)</td>
<td>280</td>
<td>900</td>
<td>840</td>
<td>780</td>
</tr>
<tr>
<td>intensity ((10^{-9} \text{ Amp})^a)</td>
<td>300</td>
<td>7</td>
<td>6</td>
<td>6</td>
</tr>
</tbody>
</table>

\(^a\) Intensities not corrected for surface ionization efficiencies.

Each different sodium halide beam was run under conditions of roughly equal vapor pressure inside the oven, so that the SID signals were approximately the same. The vapor pressure inside the oven at these temperatures is about 3 torr (COG48). When a new charge of salt has been added, the oven is preheated 24 hours prior to the experiment at temperatures just past the melting temperature of the salt. The melting and resolidification process outgasses the beam material and prevents 'spitting' which
can result in a clog. In order to produce a stable beam, it is important to have the nozzle and skimmer at about full temperature before bringing up the temperature of the body. It was found that the best performance was achieved by warming the oven slowly over a period of about 4 hours in order to minimize thermal gradients.

2.4 Laser

The dye laser configuration is basically unchanged from the previous setup (MAG84, ULV88). The resonating cavity of a Spectra-Physics 375 dye laser, pumped by a Coherent Innova 20 Argon Ion laser, was extended by replacing the standard output coupler with a spherical high-reflector 150 cm downstream of the beam waist. This modification allows the vacuum chamber to be inserted into the resonating cavity of the dye laser. Quartz windows are mounted at Brewster's angle to allow light to pass back and forth without serious reflectance losses. The windows, which also form a vacuum seal, are 1 cm thick to prevent lensing and strain-induced birefringence due to the pressure differential when the chamber is evacuated. They are also slightly wedged ($\approx 1^\circ$) to prevent etalon effects. Wavelength tuning is accomplished with a three-plate birefringent filter driven by a stepper motor (ULV88), and one 'step' changes the wavelength by approximately 0.1 Å. A counter keeps track of the number of steps from some arbitrary origin which allows for reproducible wavelength selection. The wavelength is measured with a mini-monochromator (resolution of $\approx 1$ nm) using a brewster window reflection, and a second brewster window reflection is steered into a power meter for laser power measurements.

The alignment of the dye laser cavity is a critical task in the preparation of a three-beam experiment. If the cavity is not aligned properly, laser performance suffers and the decrease in power can easily reduce the signal to unusable levels. If the beam is not positioned properly, then the volume of beam intersection decreases and little or no signal will be obtained. In addition, improper alignment of the cavity results in a large
increase in scattered light which causes a reduction of the signal to noise ratio. A method of alignment was developed which ensures the accurate and reproducible positioning of the dye laser beam which is discussed in the following paragraphs.

A schematic of the dye laser cavity geometry is shown in Figure 2.7. The presence of the wedged vacuum windows causes the angle of the beam axis with respect to the horizontal to change as the beam passes through the window. To ensure that the beam passes through the center of the hexagonal chamber, the cavity is aligned so that the beam is horizontal inside the chamber. First, apertures (≈ 1mm diameter) are placed on the inside center of each brewster window flange thus defining the optical axis inside the chamber. The beam of a helium neon laser is positioned so that the beam passes cleanly through each aperture. The vacuum chamber is then evacuated and the position of the HeNe is adjusted slightly so that the beam again passes cleanly through each internal aperture, thereby compensating for the change in index of refraction resulting from the evacuation. Now, the position of the external irises are adjusted so that the beam is located on the center of each iris. As long as these external irises remain in place, they serve as external reference points which can be used for future alignments without the need for the internal apertures.

Now that the optical path of the laser has been defined, the dye laser head must be positioned. The vertical and side-to-side position of the dye laser head is adjusted so that the HeNe beam is slightly high with respect to the center of standard output coupler aperture (see Figure 2.8) and is perfectly centered on the folding mirror aperture. The latter step is usually best performed by removing the folding mirror and holder, and inspecting the beam as it passes through the aperture. Finally, the dye laser head is secured by tightening the mounting clamps and the alignment is double checked. The dye laser can now be tuned and optimized. The tune-up procedure is described in detail elsewhere (SPE75) and will not be discussed here. After lasing with the extended cavity is established, the power and
Figure 2.7. Schematic of dye laser cavity geometry. Birefringent filter and heat pipe oven are not shown.

The wedge angles and beam refraction are exaggerated for illustration.
stability are optimized using adjustments on the high reflector and the thumbwheels on the dye laser head. Once this is done, the sodium heat pipe oven (MAG84), is inserted into the cavity and positioned to give the best power and stability. The sodium heat pipe oven is heated to produce a small amount of sodium vapor which absorbs the spontaneous fluorescence of the dye at the sodium D lines. Without the heat pipe in place, the sodium atom impurities in each beam absorb the spontaneous dye emission at 589.0 nm and extremely intense background signals are observed - typically on the order of several thousand counts per second. With the heat pipe oven installed and operating at a temperature of about 300 C, these background signals are completely eliminated.

The presence of small amounts of dust particles and irregularities at the surfaces of the brewster windows cause some of the laser light to become incoherently scattered which can give rise to a significant scattered light background signal. Even though most of the scattered light is rejected by the interference filter, approximately 1 scattered light photon in 10^6 is passed. In previous experiments, a "light tube" (MAG84) was used to reduce the scattered light inside the chamber. Although it was quite effective in reducing scattered laser light, it had the disadvantage of having many surfaces which could scatter beam particles, which could change the single collision environment of the beam intersection region.
A replacement for the light tube was designed which was just as effective in reducing the scattered light signal as the light tube, while eliminating any scattering surface in the beam intersection region. The new design, shown in cross section in Figure 2.1 and 2.7, consists of two 8" long tubes which screw into the center of each brewster window flange, so that the center of each tube is located on the optical axis. The ends which face the crossing region are tapered at 20° with the edges as sharp as possible. The inside diameter of each tube is reamed at 0.750" and a set of three 'light skimmers' slip fit, with a tolerance of 0.002", into each tube. These light skimmers consist of a 2" long stainless steel casing, whose outside diameter is turned to 0.748", and a brass cone press-fit into one end. A 30° taper is cut into the press-fitted plug which gives a sharp, clean edge, and a hole about 7 mm in diameter. The close tolerance between the outside diameter of the casing and the inside diameter of the tube ensures that the center of the skimmer holes will be located on the optical axis. Before use, each of the skimmers are coated with soot from an acetylene flame, which has excellent light absorbing and vacuum properties.

2.5 Light Collection and Detection

The ability to observe the emission from excited sodium atoms produced from dissociation of electronically excited transition region species depends on high collection and detection efficiency. A schematic of the fluorescence collection and detection system is shown in Figure 2.9. The fluorescence from the three-beam intersection region is collimated by an f1.5 achromatic triplet (Melles-Griot # 01-LAT-007), passed through a flat quartz vacuum window (= 1 cm thick) and filtered by a narrow bandwidth (2.9 Å fwhm) interference filter centered at 589.0 nm (Pomfret Research Optics #8829) with peak transmission about 30 percent. The light at the Na D line passed by the interference filter is then focussed onto the GaAs photocathode of a cooled RCA-C31034A photomultiplier tube.
Figure 2.9. Schematic of light collection and detection apparatus.
The vertical position of the collection optic with respect to the three beam intersection point must be adjusted to optimize the light collection efficiency. The focal point of the collection optic relative to the inside of the supporting flange is determined by passing the expanded beam of a HeNe laser 'in reverse' through the achromat. The position of the focus is adjusted using the threaded collection optic holder so that the focal point is exactly 6.50" (the lid thickness + distance from top of hexagonal chamber to the beam intersection point) from the inside edge of the collection optic flange. When positioned in this way, the focal point of the collection optic will be at the exact center of the hexagonal vacuum center.

The position of the interference filter is also optimized for the best percent transmission at 589.0 nm. A reproduction of the % transmission vs. wavelength scan which was taken by Pomfret Research Optics, Inc. is shown in Figure 2.10. The measured fwhm bandpass was 3.5 Å, which after calibration with the 597.55 Neon line, was calculated to be 2.85 Å. The wavelength which is transmitted by the filter is extremely sensitive to the angle of incidence, and shifts to the blue approximately by 0.2 Å per degree from normal. In order to ensure that the optimum filter position has been obtained, a potassium beam is run and the Na impurity is excited with the short cavity output of the dye laser tuned to 589.0 nm. The filter position is then adjusted to give the maximum photomultiplier signal and the filter holder is marked to record the position.

The photomultiplier tube used is the RCA-C31034A; a low dark noise variant of the C31034. It is housed in a thermoelectric cooler (Products for Research #TE206) which keeps the temperature of the tube at about -30° C. This low temperature is required to keep the dark counts, which arise from thermionic emission, to a minimum. Approximately once every six weeks, the cooler must be dried to remove the condensation which accumulates in the chamber. If the chamber is not kept dry, a large increase in dark counts will be observed.
Figure 2.10. Transmission curve of Na D line interference filter provided by Pomfret Research Optics, Inc. Measured half-bandwidth is 3.5 Å and after calibration with 597.55 Ne line gives half-bandwidth of 2.9 Å.

2.6 Data Acquisition

Photomultiplier counts are accumulated for each of the eight possible beam on/beam off combinations so that contributions from all two beam and single beam processes may be accounted for. Each of the three beams is blocked and unblocked using solenoid driven flags, whose status (up or down) is determined by an optical switch. Flags are also used to block the incandescent light from the hot tungsten filaments of the SID’s. Without these detector flags, the all-beams off signal can be as high as several hundred counts per second. When a measurement is made, the detector flags are raised (which blocks the light) and a particular beam combination is selected using the beam flags. Counts are then accumulated for a specified amount of time, typically 30 seconds, with an Ortec 770 pulse counter/timer for each of the eight beam combinations.
Table 2.2. Beam Combinations and Short-Hand Designations

<table>
<thead>
<tr>
<th>Beam Combination</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Laser + K + NaX</td>
<td>111</td>
</tr>
<tr>
<td>(2) Laser + K</td>
<td>110</td>
</tr>
<tr>
<td>(3) Laser + NaX</td>
<td>101</td>
</tr>
<tr>
<td>(4) Laser</td>
<td>110</td>
</tr>
<tr>
<td>(5) K + NaX</td>
<td>011</td>
</tr>
<tr>
<td>(6) K</td>
<td>010</td>
</tr>
<tr>
<td>(7) NaX</td>
<td>001</td>
</tr>
<tr>
<td>(8) all beams off</td>
<td>000</td>
</tr>
</tbody>
</table>

Table 2.3. Calculation of Elementary Processes

<table>
<thead>
<tr>
<th>Signal</th>
<th>Elementary Process</th>
<th>Combination of Measured Sums</th>
</tr>
</thead>
<tbody>
<tr>
<td>R000</td>
<td>PMT Dark Current</td>
<td>000</td>
</tr>
<tr>
<td>R100</td>
<td>Scattered Light</td>
<td>100 - 000</td>
</tr>
<tr>
<td>R010</td>
<td>K Background</td>
<td>010 - 000</td>
</tr>
<tr>
<td>R001</td>
<td>NaX Background</td>
<td>001 - 000</td>
</tr>
<tr>
<td>R110</td>
<td>K Photoluminescence</td>
<td>110 - 010 - 100 + 000</td>
</tr>
<tr>
<td>R101</td>
<td>NaX Photoluminescence</td>
<td>101 - 001 - 100 + 000</td>
</tr>
<tr>
<td>R011</td>
<td>Chemiluminescence</td>
<td>011 - 001 - 010 + 000</td>
</tr>
<tr>
<td>R111</td>
<td>Three-Beam Signal</td>
<td>111 - 011 - 101 - 110 + 100 + 010 + 001 - 000</td>
</tr>
</tbody>
</table>
The eight beam combinations and their short-hand designations are listed in Table 2.2. Each individual measurement represents a sum of contributions from elementary processes (MAG84). Thus, the elementary processes can be expressed as sums and differences of the individual measurements, and are given in Table 2.3. The error associated with each measurement is assumed to be the square root of the total number of counts, so the error in each elementary rate (counts/second) is given by the square root of the sum of all counts associated with that process divided by the acquisition time. For example, the error associated with the three-beam signal would be given by

\[(2.2) \quad \sigma(3BS) = \sqrt{111 + 101 + 110 + 011 + 100 + 010 + 001 + 000} / t,\]

where \(t\) is the length of the data acquisition time. The error in the three beam signal is obviously minimized with long integration times, and when all background signals are made as small as possible.

After all eight measurements have been made, the detector flags are lowered (opened) and the beam intensities are measured after the signals from the SID's have reached a constant value. After the beam intensities are recorded, a new wavelength is selected with the stepper motor controller and measurements begin for the next data point. For most experiments, a reference signal was arbitrarily chosen to serve as an indication of the relative stability and reproducibility of the signal within a run. In an experiment, the wavelengths for the first several data points are usually selected randomly to get some idea of the stability of the signal. Typically, the beams are at full intensity for a period of about 30 - 60 minutes before the signals become sufficiently stable to begin scanning measurements. When the signals appear to have stabilized (usually within 10-15%), a wavelength region is selected and is scanned at regular step intervals. The experiment is continued until either the charge of potassium or salt has been used up, or the beam intensities drop to a level which makes the signal unusable.
Chapter 3

Results

The K + NaX reactive system was shown in Chapter 1 to be particularly well suited for study of transition region species, and the apparatus constructed for that purpose was described in the previous chapter. The results of the previous K + NaCl studies (MAG84) showed that observation of the photoexcitation of transition region species was possible, and a spectrum (Figure 1.2) was obtained that was interpreted to be a photoexcitation spectrum of the [KClNa] reaction complex. However, because the spectrum was basically featureless, it was difficult to make any conclusions regarding details of the reaction dynamics or potential energy surfaces involved. By performing experiments with different sodium halides, it was hoped that differences in the TRS spectra might lead to some insight into the dynamics of the K + NaX reactions. In the first section of this chapter, the results of a comparative study of the K + NaCl, K + NaBr, and K + NaI systems are presented. In the second section, the results of several artifact tests are discussed which indicate that the experimental signal does indeed originate from the reactive decay of electronically excited transition region species.
3.1 Results of K + NaX (X = Cl, Br, I) + hv

The first experiments were performed on the K + NaCl system in order to establish that the previously observed spectrum shown in Figure 1.2 was reproducible under similar conditions and to serve as a benchmark for future measurements with other sodium halides. Three separate experiments were performed on the K + NaCl system, however only a relatively small amount of data was collected during these first runs due to some initial stability problems encountered with the salt beam source. These problems were eventually solved, and, in later experiments, the amount of data which could be collected in a single run was basically limited by the size of the potassium charge.

Figure 3.1 shows a plot of the normalized three beam signals as a function of laser wavelength for K + NaCl. The spectrum (in this wavelength range) is qualitatively similar to that previously observed with the exception that a minimum seems to be present at about 607 nm. The three beam signal count rates, given in Table 3.1, are also qualitatively the same as previously observed. It can be seen in Table 3.1 that the NaX Background signal is quite large for NaCl and decreases for NaBr and NaI. The origin of this background signal is a combination of the glow from the salt skimmer heater wires and blackbody radiation from the nozzle. The decrease in count rates is due to both improvements in shielding and a decrease in nozzle and skimmer temperatures for the heavier sodium halides.

These results obtained for the K + NaCl system established that the spectrum previously obtained was reproducible and served as a check that the apparatus was functioning properly. Experiments on the K + NaBr system were then performed to see what differences in the spectrum might be observed. Eleven separate runs on the K + NaBr system were made, and the normalized three beam signals for laser wavelengths between 595 and 640 nm for the K + NaBr system are shown in Figure 3.2a. These
<table>
<thead>
<tr>
<th>Signal</th>
<th>Origin</th>
<th>$X = \text{Cl}$</th>
<th>$X = \text{Br}$</th>
<th>$X = \text{I}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R000</td>
<td>Dark Current</td>
<td>$55 \pm 1$</td>
<td>$21 \pm 1$</td>
<td>$21 \pm 1$</td>
</tr>
<tr>
<td>R100</td>
<td>Scattered Light</td>
<td>$21 \pm 2$</td>
<td>$29 \pm 2$</td>
<td>$57 \pm 2$</td>
</tr>
<tr>
<td>R010</td>
<td>K Background</td>
<td>$5 \pm 2$</td>
<td>$3 \pm 1$</td>
<td>$1 \pm 1$</td>
</tr>
<tr>
<td>R001</td>
<td>NaX Background</td>
<td>$581 \pm 4$</td>
<td>$336 \pm 4$</td>
<td>$29 \pm 2$</td>
</tr>
<tr>
<td>R110</td>
<td>K Photoluminescence</td>
<td>$42 \pm 3$</td>
<td>$16 \pm 2$</td>
<td>$61 \pm 3$</td>
</tr>
<tr>
<td>R101</td>
<td>NaX Photoluminescence</td>
<td>$-11 \pm 6$</td>
<td>$4 \pm 5$</td>
<td>$-3 \pm 3$</td>
</tr>
<tr>
<td>R011</td>
<td>Chemiluminescence</td>
<td>$4 \pm 5$</td>
<td>$1 \pm 5$</td>
<td>$-2 \pm 2$</td>
</tr>
<tr>
<td>R111</td>
<td>Three Beam Signal</td>
<td>$114 \pm 8$</td>
<td>$237 \pm 8$</td>
<td>$234 \pm 5$</td>
</tr>
</tbody>
</table>
Figure 3.1. Normalized three beam signals vs. wavelength for K + NaCl + hv. Error bars are +/- 1 sigma.
Figure 3.2a. Normalized three beam signals vs. wavelength for $K + NaBr + hv$. Signals are corrected for surface ionization efficiency and photon energies in cm$^{-1}$ are given in parentheses. Curve is for illustration only.
Figure 3.2b. Long wavelength portion of K + NaBr + hv spectrum. The dye used for these measurements was DCM.
Figure 3.3: Normalized three beam signals vs. wavelength for K + NaI + hv. Signals are corrected for ionization efficiency. Curve is for illustration only.
signals are normalized by dividing the raw three beam signal by the product of the three beam intensities and then multiplying by the surface ionization efficiency relative to NaCl. In the short wavelength region between 600 and 595 nm, the signal shows similar behavior to that of the K + NaCl system. However, unlike the K + NaCl system, the signal increases dramatically as the laser is tuned from 600 to 610 nm. Past 610 nm, the signal shows an approximately exponential decline, and positive signals were observed out to about 690 nm. The three beam signals for wavelengths between 630 and 690 nm are shown in Figure 3.2b. Although there is a good deal of scatter in the data, the spectrum obtained for K + NaBr displays a clear feature with a maximum at about 610 nm, and a minimum at around 600 nm.

The results obtained from five separate runs for the K + NaI system, shown in Figure 3.3, are strikingly similar to that of K + NaBr, with the exception that the normalized signals are slightly larger. The same feature is apparent in the K + NaI spectrum as was observed for K + NaBr, although the minimum does not appear quite as deep for the K + NaI spectrum. The feature in the K + NaI spectrum also seems to appear somewhat sharper than that of NaBr, however, the scatter in the data makes it difficult to make any conclusion regarding relative widths of these features. As yet, no measurements have been made for the K + NaI system at wavelengths longer than 640 nm.

3.2. Artifact Investigations

Emission at 589.0 nm which requires the presence of all three beams has been observed for each of the three K + NaX systems. However, the existence of a positive three beam signal at this wavelength does not necessarily mean that the signal originates from Na* produced from reactive decomposition of an excited reaction complex. In order to verify that the signal does indeed originate from this process, several tests were
performed to examine possible sources of artifactual three beam signals which could arise from other processes.

Several tests have already been performed on the K + NaCl system (MAG84). It was previously verified by different filter tests, that the fluorescence at 589.0 nm originated from excited sodium atoms. The three beam signal was shown to be linear with respect to all three beam intensities and to have no correlation with potassium photoluminescence. Energy transfer processes involving sodium atom impurities were investigated by crossing sodium atom beams with potassium and sodium chloride. No three beam signal was observed in either case, and it was concluded that sodium atoms are not responsible for the three beam signal. Even though the three beam signal showed no correlation with K photoluminescence, there still existed the possibility that excited K$_2^+$ could give rise to a three beam signal by a collisional energy transfer process. An experiment was performed in which the potassium beam was passed through an inhomogeneous magnetic field (KAE86). One half of the potassium atoms (those with m = -1/2) are focused by the field, while the dimers are unaffected. It was found that the three beam signal increased by a factor of two when the magnet was energized, thus correlating an increase of signal with an increase in K atom particle density. It was concluded from these experiments that K atoms are required for production of the three beam signal. The results of these artifact investigations into the nature of the three beam signal for the K + NaCl system indicated that the signal does indeed arise from sodium atoms produced from the reactive dissociation of excited transition region species.

The experimental results reported here for the K + NaCl, NaBr, and NaI systems were all obtained under virtually identical K beam conditions. Therefore, it is highly unlikely that the feature observed in the spectra for the K + NaBr and K + NaI systems is caused by some artifact associated with the K beam. The possibility remains, however, that the signals in the NaBr and NaI systems may be an artifact which involves some (unknown) species in the salt beams. Several tests were performed on both the NaBr and
Nal systems to verify that the signal is not a result of an artifact associated with these salt beams.

The first step in this verification process was to determine the origin of the emission at 589.0 nm in the K + NaBr case. Filter tests were performed in order to determine whether this emission is actually from \( ^2P \) Na atoms or from some broad band fluorescence. The complete absence of any significant NaX photoluminescence signals (see Table 3.1) at the Na D line suggests that the possibility of fluorescing species in the salt beam is remote. However, a test is still required since any fluorescence would likely be red-shifted, and therefore not observed through the standard interference filter. In a standard three beam experiment, beams of K and NaBr were brought up to full intensity, and several measurements at 615 nm were made until a stable three beam signal (≈ 150 cps) was obtained. The interference filter was then rotated approximately 15° which caused the peak wavelength transmitted by the filter to shift by about 3 Å (see section 2.8), and a measurement was made in the standard way. No significant three beam signal was observed with this filter orientation. The filter was then rotated back to the original position and another measurement was made, and the three beam signal observed was basically the same as in the first measurement. As an additional test, the standard Na D line interference filter was replaced with a bandpass filter centered at 597 nm with a fwhm bandwidth of 4.3 nm (Optical Filter Corporation, #1089). As with the rotated filter measurement, no significant signal was observed with this (597nm) filter. The standard interference filter was replaced and, again, the three beam signal returned. It was concluded from these tests, that the emission observed at 589.0 nm is not part of a broad band fluorescence. The filter rotation test showed that the bandwidth of the emission must be less than at least 4 Å (at the base), and it was concluded that the emission at 589.0 nm most likely originates from excited sodium atoms.
The presence of free sodium atoms in each beam creates the possibility of energy transfer processes which could result in the formation of \(^2P\) atoms without any chemical reaction taking place. Results of previous tests showed that sodium atoms, when crossed with either K or NaCl, did not produce a three beam signal. However, it was thought that the NaBr beam may contain a significantly higher concentration of sodium atoms which might give rise to a spurious three beam signal. The concentration of sodium atoms in both the NaCl and NaBr beams was probed using the spontaneous emission of the (nonlasing) dye. It was determined that the sodium atom concentration in the NaBr beam was actually less (by a factor of about 2) than that of the NaCl beam. From the results of this test, any artifactual signal which could arise from processes such as Na + [K \]+ \(\text{hv}\) (where [K] represents any species in the K beam) can be ruled out.

Although the same K beam conditions were used throughout these experiments, the possibility still exists that sodium atom impurities in the K beam could give rise to a spurious three beam signal through a collisional energy transfer process involving some unknown excited species in the NaBr or NaI beams. In order to investigate this possibility, an experiment was devised to examine the dependence of the three beam signal on sodium atom concentration in the K beam. Four experiments were run on the K + NaI system to see what affect, if any, is observed on the magnitude of the three beam signal at various wavelengths when extra sodium is deliberately added to the K source. In the first experiment, a 'neat' (no extra sodium added) potassium beam was used and measurements were made at several different wavelengths. The Na impurity in the potassium samples used is typically about 50 ppm - corresponding to about .5 milligram in a 25 gram charge. The second experiment was run using a 'spiked' K charge with 25 mg of sodium added, and three beam signal measurements were made at the same wavelengths as in the first experiment. The third experiment was similar to the second, was performed adding 50 mg of sodium to the potassium charge. Finally, a fourth
Figure 3.4. Normalized three beam signals for K + NaI + hv at 595, 597, 605, 610, and 620 nm. Different symbols denote amount of sodium added to potassium charge prior to run. Error bars are ± 1 σ.

An experiment was run with a neat K beam to check the reproducibility of results obtained in the first run. No significant difference was observed at any wavelength between the neat and sodium-added runs. A comparison of signals at several different wavelengths is given in Figure 3.4. It was concluded that sodium atom impurities are not responsible for the three beam signals observed in these experiments.

The results of the artifact tests performed on the K + NaBr and K + NaI systems demonstrated that the emission at 589.0 nm originates from excited sodium atoms. The amount of free sodium atoms in the NaBr beam was observed to be less than in the NaCl beam. The three beam signal for K + NaI showed no correlation with the amount of sodium impurity in the K beam, and no NaX photoluminescence was observed for any of
the sodium halides at any wavelength. These tests, combined with the exhaustive artifact tests previously performed on the K + NaCl system lead to the conclusion that the three beam signal is attributable to photoexcitation of the [KXNa] transition region species.

A distinct feature has been observed in the plot of normalized three beam signals as a function of laser wavelength which is similar for both the K + NaBr and K + NaI systems and not observed for the K + NaCl system. It is possible that a much broader maximum (than that of NaBr and NaI) also exists for the K + NaCl system, however more data is required before that conclusion can be made. Assuming that these signals do indeed arise from the process of photoexcitation of transition region species, there remains the task of understanding the origin of this structure. One possibility is that the mass of the halogen atom significantly influences the probability of light absorption in this wavelength region. It may also be that this feature arises from differences between the potential energy surfaces involved in the different chemical systems. In the next chapter, the question of whether the feature is a result of a mass effect or of differences in the potential energy surfaces is addressed. Further discussion on these spectra and the nature of this feature for these K + NaX systems will be deferred until the final chapter.
Chapter 4

Classical Trajectory Calculations

The motions of nuclei during chemical reaction can often be investigated using classical mechanical methods provided that the potential energy surfaces are known for the chemical system of interest. Classical trajectory studies, such as periodic orbit analysis (JOH89, HAH91), have been successfully used to establish a correspondence between spectral features and the classical motions involved. Since potential energy surfaces have been calculated for the K + NaCl system (YAM88), it is possible to investigate the classical nuclear motions for that system. Because the potential energy surfaces for the K + NaBr system are, as yet, unknown, direct comparison of the two systems is not possible. However, by using the same (K + NaCl) potential energy surfaces, the effect of halogen mass on the dynamics of reaction may investigated by substituting the mass of Br for that of Cl.

Two different types of calculations were performed in order to understand the effect of halogen atom substitution. The effect on the dynamics of the ground state reaction was examined by calculating TRS lifetime distributions for the different sodium halides. In addition, "surface hopping" trajectory calculations were performed to investigate the possible differences in light absorption probability and upper state dynamics between K + NaCl and K + NaBr as a result of increased halogen mass. The first
several sections of this chapter discuss the procedure for performing the calculation. The final sections are devoted to the actual calculations which were performed and a presentation of the results.

4.1 Hamilton's Equations of Motion and Jacobi Coordinates

Hamilton's equations of motion for a system described by the coordinates $q(1,\ldots,3n)$ and conjugate momenta $p(1,\ldots,3n)$, are written as

$$
\dot{q}_i = \frac{\partial q_i}{\partial t} = \frac{\partial H}{\partial p_i} ; \quad \dot{p}_i = -\frac{\partial H}{\partial q_i} = -\frac{\partial V}{\partial q_i}
$$

where, for a system of $n$ particles in three dimensional space,

$$
H = \sum_{i=1}^{n} \frac{1}{2m_i} \left( \sum_{j=1}^{3} p_j^2 \right) + V(q_1,\ldots,q_{3n})
$$

$H$ is the classical Hamiltonian expressing the sum of kinetic and potential energy, and $V$ is the potential energy function of the coordinates $q(1,\ldots,3n)$. The time evolution of coordinates and momenta of the system is computed by first specifying initial values for each $q_i$ and conjugate $p_i$, as well as the potential energy function, $V$. The differential equations of motion are then integrated to give new values for $q$ and $p$. In principle, the equations of motion may be solved for a system with any number of particles. However, in a three-dimensional space fixed coordinate system, the number of simultaneous differential equations which must be solved is $6n$ (where $n$ is the number of particles in the system), since there are 3 components for the position and momentum vector of each particle. In most cases, the classical trajectory method is practically limited to systems containing only three particles - although simplifications may often be made to allow
investigation of systems with more than three bodies. For the rest of this chapter, the discussion pertains only to a three-body system.

The canonical atom + diatom (A + BC → AB + C) reactive system in the laboratory frame is shown in Figure 4.1. The position and momentum vectors in this space fixed coordinate system for A, B, and C are denoted \( q_A, p_A, q_B, p_B, q_C, \) and \( p_C \). If

![Diagram of particles A, B, and C with coordinates](image)

**Figure 4.1.** Position and momentum vectors of particles A, B, and C in the space-fixed laboratory coordinate system.

the components of these vectors were specified, one could proceed with the computation of the time evolution of these quantities. There are two major disadvantages to this approach. First, some (arbitrary) origin must be chosen for the coordinate system and the position vectors specified relative to that origin. Secondly, the calculation would result in the time evolution of these vectors relative to the origin when what is really
desired is a knowledge of the motions of the nuclei relative to each other. Thus, a coordinate transformation is desired which removes the dependence on a fixed laboratory origin and expresses the coordinates and momenta relative to some internal origin. Many different such transformations exist, but by far the most common is the transformation to "Jacobi Coordinates" which is used in the calculations presented here.

The transformation from laboratory to Jacobi coordinates involves exchange of the three position vectors in the lab frame for three new position vectors which describe (1) the position of the center of mass of the three-body system; (2) the position of A relative to the center of mass of BC; and (3) the position of B relative to C. The three new position vectors which result from this transformation are shown in Figure 4.2.

![Diagram showing the position vectors of A, B, and C in the Jacobi coordinate system.](image)

**Figure 4.2.** Position vectors of A, B, and C in the Jacobi coordinate system.
In order to express the coordinates of one system in terms of the other, some basic definitions are first required. First, let $m_a$, $m_b$, and $m_c$ represent the mass of particles A, B, and C respectively. Next, let \{$q_1,q_2,q_3$\}, \{$q_4,q_5,q_6$\}, and \{$q_7,q_8,q_9$\} be the components of the position vectors of A, B, and C respectively in the lab frame. Now, let \{$Q_1,Q_2,Q_3$\}, \{$Q_4,Q_5,Q_6$\}, and \{$Q_7,Q_8,Q_9$\} represent components of vectors $\mathbf{R}$, $\mathbf{r}$, and $\mathbf{p}$ respectively; where $\mathbf{R}$ is the position of B relative to C, $\mathbf{r}$ is the position of A relative to the center of mass of BC, and $\mathbf{p}$ is the position vector of the center of mass of the three-body system relative to the origin of the space-fixed coordinate system.

The equations which transform $q_i$ into $Q_i$ and their inverses may be written as

\begin{align}
Q_i &= q_i + 6 - q_i + 3 \\ 
Q_j &= q_j - (m_b q_j + m_c q_j + 3)/(m_b + m_c) \\ 
Q_k &= (1/M)(m_a q_k + 6 + m_b q_k + 3 + m_c q_k) \\
\end{align}

(for $i = 1,3$)

(for $j = 4,6$)

(for $k = 7,9$)

where $M = (m_a + m_b + m_c)$. The expressions for the inverse transformation are

\begin{align}
q_i &= [(m_b + m_c)/M]Q_i + 3 + Q_i + 6 \\
q_j &= -[m_c/(m_b + m_c)]Q_j + 3 - (m_a/M)Q_j + + Q_j + 3 \\
q_k &= [m_b/(m_b + m_c)]Q_k + 6 - (m_a/M)Q_k + 3 + Q_k \\
\end{align}

(for $i = 1,3$)

(for $j = 4,6$)

(for $k = 7,9$).

Now, let $p_i$ represent the momentum conjugate to $q_i$, and $P_i$ the momentum conjugate to $Q_i$. To find the transformed expressions for $p_i$ and $P_i$, one starts with the relation ($WHI37$),

\begin{align}
p_i = \sum_j P_j (\partial Q_j / \partial q_i) .
\end{align}

The expressions for $p_i$ in terms of $P_i$ can then be written as

\begin{align}
p_i &= m_a (\partial q_i / \partial t) = P_i + 3 + (m_a/M)P_i + 6 \\
p_j &= m_b (\partial q_j / \partial t) = -P_j + 3 -[m_b/(m_b + m_c)]P_j + (m_b/M)P_j + 3 \\
p_k &= m_c (\partial q_k / \partial t) = P_k + 6 - [m_c/(m_b + m_c)]P_k - 3 + (m_c/M)P_k \\
\end{align}

(for $i = 1,3$)

(for $j = 4,6$)

(for $k = 7,9$).
The Hamiltonian expressed in terms of the Jacobi coordinates and conjugate momenta becomes

\[
H = \frac{1}{2\mu_{bc}} \sum P_i^2 + \frac{1}{2\mu_{a, bc}} \sum P_j^2 + \frac{1}{2M} \sum P_k^2 \\
+ V(Q_1, \ldots, Q_6) \quad (i = 1, 3 \ ; \ j = 4, 6 \ ; \ k = 7, 9),
\]

where \( \frac{1}{\mu_{bc}} = \frac{1}{m_b} + \frac{1}{m_c} \ ; \ \frac{1}{\mu_{a, bc}} = \frac{1}{m_a} + \frac{1}{(m_b + m_c)}. \) The first kinetic energy term in this Hamiltonian represents vibrational and rotational energy of the diatom, the second term gives the translational energy associated with the relative motion of A with respect to the center of mass of BC, and the third term is the translational energy of the center of mass. It should also be noted that in the Jacobi coordinate system, the potential energy function, \( V \), is explicitly independent of the coordinates of the center of mass. In general, most potential energy functions are explicit functions of internuclear separations, so it is convenient to write the relations between the internuclear distances, \( R_1, R_2, \) and \( R_3 \) in terms of the Jacobi coordinates \( \{Q_1, \ldots, Q_6\}. \) Let \( R_1 \) be the distance between A and B; \( R_2 \) the distance between B and C; and \( R_3 \) the distance between C and A. The functions \( R(Q) \) are then

\[
R_1 = \left[ (m_{c'} Q_1 + Q_4)^2 + (m_{c'} Q_2 + Q_5)^2 + (m_{c'} Q_3 + Q_6)^2 \right]^{1/2} \\
R_2 = \left[ Q_1^2 + Q_2^2 + Q_3^2 \right]^{1/2} \\
R_3 = \left[ (m_{b'} Q_1 - Q_4)^2 + (m_{b'} Q_2 - Q_5)^2 + (m_{b'} Q_3 - Q_6)^2 \right]^{1/2}
\]

where \( m_{c'} = m_c/(m_b + m_c) \) and \( m_{b'} = m_b/(m_b + m_c). \)

With the preceding expressions, it is now possible to write the differential equations of motion using the Jacobi coordinates and conjugate momenta. The time derivatives of \( Q_i \) are, using equations (1) and (6),

\[
\begin{align*}
\frac{\partial Q_i}{\partial t} & = (1/\mu_{bc}) P_i \quad \text{(for } i = 1, 3) \\
\frac{\partial Q_j}{\partial t} & = (1/\mu_{a, bc}) P_j \quad \text{(for } j = 4, 6) \\
\frac{\partial Q_k}{\partial t} & = (1/M) P_k \quad \text{(for } k = 7, 9)
\end{align*}
\]
Writing the differential equations for $P$ require use of the chain rule, that is

\begin{equation}
(10) \quad (\partial V/\partial Q_i) = \sum (\partial V/\partial R_k)(\partial R_k/\partial Q_i) \quad \text{(for } k = 1,3). \end{equation}

The time derivatives of $P$ are then

\begin{equation}
(11) \quad -(\partial P_i/\partial t) = (m_0'/R_1)(m_c' Q_i + Q_{i+3})(\partial V/\partial R_1) + (Q_i/R_2)(\partial V/\partial R_2) \\
+ (m_b'/R_3)(m_b' Q_i - Q_{i+3})(\partial V/\partial R_3) \quad \text{(for } i = 1,3) \end{equation}

\begin{equation}
\quad -(\partial P_j/\partial t) = (1/R_1)(m_c' Q_{j-3} + Q_j)(\partial V/\partial R_1) \\
- (1/R_3)(m_b' Q_{j-3} + Q_j)(\partial V/\partial R_3) \quad \text{(for } j = 4,6) \end{equation}

\begin{equation}
\quad -(\partial P_k/\partial t) = 0 \quad \text{(for } k = 7,9). \end{equation}

From equations (10) and (11) it can be seen that, under transformation to Jacobi coordinates, the motion of the center of mass has been separated from the relative motions of $A$ and $BC$. Also, since $P_7$, $P_8$, and $P_9$ are constants of the motion, the six equations describing the motion of the center of mass may be ignored. This leaves 12 remaining equations which describe the motion of $A$ relative to the center of mass of $BC$, and the motion of $B$ relative to $C$. In addition, the kinetic energy term in equation (7) containing the momentum components of the center of mass of the system can be ignored giving an effective Hamiltonian,

\begin{equation}
(12) \quad H = 1/2\mu_{bc} \sum P_i^2 + 1/2\mu_{ab,bc} \sum P_j^2 + V(R_1,R_2,R_3). \end{equation}

The total angular momentum can also be easily expressed in terms of the Jacobi coordinates and momenta. The total angular momentum $L$, is the vector sum

\begin{equation}
(13) \quad L = L_A + L_B. \end{equation}

The first vector, $L_A$, is the cross product $r \times P_A$; and the second vector, $L_B$ is the cross product $R \times P_B$. Evaluation of these two cross products gives the components of the total angular momentum vector as
\[ (1.4) \quad L = \{ (Q_2P_3 - Q_3P_2 + Q_5P_6 - Q_6P_5) ; \\
( Q_3P_1 - Q_1P_3 + Q_6P_4 - Q_4P_6) ; \\
( Q_1P_2 - Q_2P_1 + Q_4P_5 - Q_5P_4) \} , \]

with the magnitude of \( L \) given as
\[ (1.5) \quad L = \left[ L_x^2 + L_y^2 + L_z^2 \right]^{1/2} . \]

Since the magnitude of total angular momentum and total energy are quantities which must be conserved throughout the trajectory, their values are checked periodically throughout the calculation to ensure numerical accuracy. Typically, the magnitude of error between initial and final values of total energy and angular momentum was less than one part per million.

4.2 Specification of Initial Values for Dynamical Variables

Now that the coordinate system has been transformed and the equations of motion relating to the center of mass have been removed, it is necessary to specify initial values for the six Jacobi coordinates \((Q_i)\) and the conjugate momenta \((P_i)\). Starting with atom A, a Cartesian system is oriented and aligned in such a way as to simplify the problem of specification of \(Q_{4,5,6}\) and \(P_{4,5,6}\) as much as possible without loss of generality. The orientation and alignment of this Cartesian system is shown in Figure 4.3. First, the \(y\) - \(z\) plane is chosen to contain A, the relative velocity vector \((v_A - v_{BC})\), and the center of mass of BC. Next, the \(z\) axis is oriented such that it is parallel with the relative velocity vector with the origin at the center of mass of BC. In this way, there is no component of momentum in the \(x\) or \(y\) direction. The assignment of the momentum components is then
\[ (1.6) \quad P_{4}^0 = 0 ; \quad P_{5}^0 = 0 ; \quad P_{6}^0 = \mu_{a,bc}v_{r} <v_r> \]

where \(<v_r>\) is the magnitude of the relative velocity vector. The assignment of coordinates is seen to be,
\[(17) \quad Q_4^0 = 0; \quad Q_5^0 = b; \quad Q_6^0 = -(s^2 - b^2)^{1/2},\]

where \(b\) is the impact parameter and \(s\) is the initial separation.

\[\begin{align*}
P_4 &= 0 \\
P_5 &= 0 \\
P_6 &= \mu_{A,BC} \langle v_r \rangle \\
S_0 &= \langle r \rangle
\end{align*}\]

\[\begin{align*}
Q_4 &= 0 \\
Q_5 &= b \\
Q_6 &= -(s_0^2 - b^2)^{1/2}
\end{align*}\]

\[\begin{align*}
+ z' &\quad \text{center of mass of B-C} \\
+ y' &\quad B \\
- y' &\quad C \\
- z' &\quad - (S_0^2 - b^2)^{1/2}
\end{align*}\]

**Figure 4.3.** Specification of Jacobi coordinates and momenta of particle A. Particles B and C are, in general, not in the \(y' - z'\) plane.

In order to specify the initial coordinates and momenta of the diatom, it is necessary only to define the vibrational and rotational state of the molecule. Figure 4.4 shows the position of B relative to C defined by the spherical coordinates \(R, \Theta,\) and \(\Phi;\) where the orientation of the spherical coordinate system is chosen such that \(z''\) is parallel to \(z'.\) The values of the first three Jacobi coordinates are

\[(31) \quad Q_1^0 = R \sin \Theta \cos \Phi; \quad Q_2^0 = R \sin \Theta \sin \Phi; \quad Q_3^0 = R \cos \Theta\]

where \(R\) is the internuclear separation between B and C.
Figure 4.4. Specification of Jacobi coordinates for B-C using spherical coordinate system. The z'' - axis here is parallel to z' - axis shown in Figure 4.3.

The task now is to specify the total momentum of the diatom, again in as simple terms as possible without loss of generality. The first simplification is to choose the internuclear separation, R, to be either the maximum or minimum classical turning points of vibration; R⁺ or R⁻. With the choice of R as a turning point, there is no momentum component along the bond axis. No generality is lost with this choice of initial diatomic separation since averaging over the vibrational phase is accomplished by an alternative device which is discussed in the next section. All that remains is to specify the momentum perpendicular to the bond axis, which is simply the momentum associated with rotation of the diatom.
Figure 4.5 shows a vector diagram which describes the specification of momentum perpendicular to the bond axis. First, $\vec{\kappa}$ is defined to be a unit vector in the $z''$ direction. Two other unit vectors $\vec{\lambda}$ and $\vec{\nu}$ are defined such that

\[ \vec{\lambda} = \frac{\vec{R} \times \vec{\kappa}}{|R| \sin \Theta} \quad \text{and} \quad \vec{\nu} = \frac{\vec{R} \times \vec{\lambda}}{|R|} . \]

Now, let $\eta$ be the angle formed between $\lambda$ and the momentum vector perpendicular to the bond axis, $\vec{P}$. The vector $\vec{P}$ can now be expressed as the sum of components which are parallel and perpendicular to the vector $\kappa$. These components are written as

\[ (20a) \quad \vec{p}_\parallel = p \sin \eta \, \vec{\nu} ; \quad \vec{p}_\perp = p \cos \eta \, \vec{\lambda} \]
where \( p \) is the magnitude of the rotational momentum vector given by

\[
(20b) \quad p = \sqrt{ \frac{i(j+1)\hbar^2}{R^2} }.
\]

From (32) and (33) the components of \( \vec{P} \) can be written in terms of the orientation angle \( \eta \), the polar angle \( \phi \), the azimuthal angle \( \Theta \), and the magnitude of the momentum vector, \( p \) as

\[
(21) \quad P_1^o = -p (\sin \phi \cos \eta + \cos \phi \cos \Theta \sin \eta) \\
P_2^o = p (\cos \phi \cos \eta - \sin \phi \cos \Theta \sin \eta) \\
P_3^o = p (\sin \Theta \sin \eta).
\]

Each of the twelve dynamical variables \( Q_1, \ldots, 6 \) and \( P_1, \ldots, 6 \) have now been specified in terms of following quantities: the magnitude of the relative velocity vector, \( <v_1> \); the impact parameter, \( b \); the initial separation between the atom and c.m. of the diatom, \( s \); the diatomic internuclear separation, \( R \); and the angles \( \eta, \phi, \) and \( \Theta \). Values for each of these quantities are selected randomly according to probability distributions appropriate for each parameter. The procedure for selection of these values is described in the following section.

4.3 Monte-Carlo Selection of Input Parameters

For the results of classical trajectory calculations to more accurately reflect properties of the real chemical system, it is necessary to integrate over the distribution of speeds and internal states of the reactants. The Monte-Carlo method of integration over initial states consists of random selections of values weighted by an appropriate probability distribution. The FORTRAN subroutines used to generate input parameters by the Monte-Carlo method are given in Appendix 1.
If the probability distribution for a particular quantity is known (or can be estimated) the random selection may be accomplished in the following way. Let \( P(x) \) represent the probability distribution function for the quantity 'x', so that \( P(x) = \frac{dn_x}{dx} \), where \( n_x \) is the number of points for a given value of \( x \), and normalized so that
\[
\int_0^\infty P(x)dx = 1 \quad (22)
\]
It is desired to determine a function, \( C(x) \), so that the distribution of \( n_x \) in the space of \( C(x) \) is uniform - that is, \( \frac{dn_x}{dC(x)} = k \) (\( k \) is a constant). According to the chain rule:
\[
P(x) = \frac{dn_x}{dx} = \left( \frac{dn_x}{dC(x)} \right) \left( \frac{dC(x)}{dx} \right) = k \left( \frac{dC(x)}{dx} \right) \quad (23a)
\]
which means that the function \( C(x) \) is related to the indefinite integral of \( P(x) \) as
\[
C(x) = \frac{1}{k} \int P(x)dx \quad (23b)
\]
If \( P(x) \) is normalized, it can be seen from (23a) that the value of \( k \) is unity. Since the function \( C(x) \) is uniformly distributed, a random selection of the value of \( x \) can be made by solving the equation
\[
C(x) = \xi \quad (24)
\]
for \( x \) in terms of a random number, \( \xi \), whose value is between 0 and 1.

For those functions whose indefinite integrals do not exist, an alternative method is used (BUN71). This method involves first specifying the most probable value, \( a_{mp} \), of a particular distribution function. Then a maximum value, \( a_{max} \), is specified which truncates the distribution function at that value. Two new random numbers, \( \xi_1 \) and \( \xi_2 \), are selected and the test value for \( a_t \) is
\[
a_t = a_{max} \xi_1 \quad (25)
\]
If the quotient, \( P(a_t)/P(a_{mp}) \), is greater than \( \xi_2 \), then the selected value is \( a_t \). If this test fails, then two new random numbers are generated and the process repeated until a
successful selection has been made. This method insures that most of the selected values will be close to the most probable value where \( \frac{P(a_t)}{P(a_{\text{mp}})} = 1 \).

### 4.3.1 Impact Parameter

The probability distribution of impact parameters is given as (BUN71)

\[
(26) \quad P(b) = \frac{2b}{b_{\text{max}}^2},
\]

so

\[
(27) \quad C(b) = \int \frac{2b}{b_{\text{max}}^2} \, db = \frac{-b^2}{b_{\text{max}}^2}.
\]

From equation (24), the selection of \( b \) is made by generating a random number \( \xi \), and solving for \( b \)

\[
(28) \quad b = b_{\text{max}} \sqrt{\xi}.
\]

The choice of \( b_{\text{max}} \) is made by trial and error so as to be large enough to include all interesting trajectories without being so large that many trajectories occur without particle interaction.

### 4.3.2 Initial Separation

In principle, all trajectories could be started with the same initial separation, however, this would require explicitly averaging over the vibrational phase. It is much simpler to keep the vibrational phase fixed, and average over a range of initial separations which effectively averages over the phase of vibration. One starts by specifying some arbitrary fixed value for the initial separation, \( S_0 \). The Jacobi coordinate, \( Q_\theta^0 \), is then selected from a distribution uniform between \(-\left(S_0^2 - b^2\right)\) and \(-\left(S_0^2 - b^2\right) + \Delta \) (KAR65), where \( \Delta \) is given by
\[(29) \quad \Delta = \frac{1}{2} \tau \langle v_r \rangle \]

where \( \tau \) is the vibrational period, and \( \langle v_r \rangle \) is the magnitude of the relative velocity vector. The choice of \( Q_6^0 \) is determined by

\[(30) \quad Q_6^0 = s_z = -(s_0^2 - b^2) + \Delta \xi \]

where \( \xi \) is a new random number. In cases where more than one vibrational state is important, the vibrational quantum number, \( v \), should be chosen first and \( \tau \) calculated as a function of \( v \).

### 4.3.3 Magnitude of Relative Velocity Vector

The distribution of speeds was assumed to be Maxwellian, and of the form

\[(31) \quad P(v_r) = \lambda_v, v_r^2 \exp\left\{- \frac{\mu_{a,b,c} v_r^2}{2kT} \right\} \]

where \( \mu_{a,b,c} \) is the reduced mass of the three body system expressed as

\[(32) \quad \frac{1}{\mu_{a,b,c}} = \frac{1}{m_a} + \frac{1}{m_b} + \frac{1}{m_c}, \]

\( k \) is the Boltzmann constant, \( T \) is the temperature in degrees Kelvin, and \( \lambda_v \) is a normalization constant. Since equation (31) does not have a simple functional form for its indefinite integral, the second selection procedure is used to obtain an initial value for \( v_r \). The most probable value of \( v_r \) is obtained by setting the first derivative of (31) with respect to \( v_r \) equal to zero and solving for \( v_{r_{\text{mp}}} \), and the maximum values are chosen such that \( P(v_{r_{\text{max}}}) \) is equal to 0.0001. The most probable relative speeds and maximum speeds for the chloride and bromide cases along with respective source temperatures are shown in Table 4.1.
4.3.4 Vibrational and Rotational Quantum Numbers

The determination of the internuclear separation and magnitude of rotational momentum require a knowledge of the rotational and vibrational state of the molecule. The vibrational and rotational states are selected from Boltzmann distributions characterized by the source temperature, $T$. The probability distribution of vibrational energies is

$$P(E_v) = A_v \exp\left(-\frac{E_v}{kT}\right),$$

with the normalization constant $A_v = 1/kT$. The integral of equation (33) is easily evaluated as

$$C(E_v) = \int P(E_v) dE_v = 1 - \exp\left(-\frac{E_v}{kT}\right) = \xi.$$

The selection of $E_v$ is easily made by solving equation (34) in terms of the random number $\xi$. Since the distribution of vibrational energies is not continuous, the selected value of $E_v$ does not, in general, correspond to a real vibrational state. Thus, an additional step is needed to assign the vibrational energy level. The vibrational energy of a diatomic molecule is approximately equal to $\omega_e(v + 1/2)$, so the vibrational quantum number may be determined by an integer conversion of the argument $(E_v/\omega_e - 1/2)$.

The selection of the rotational quantum number $j$ is made in a similar way, with the distribution of rotational energies given as

$$P(E_r) = A_r E_r^{-1/2} \exp\left(-\frac{E_r}{kT}\right).$$

However, the presence of the $E^{-1/2}$ term requires that the selection of $E_r$ be made according to the same procedure used to select the relative speed. The most probable values of $j$ for each sodium halide along with $j_{\text{max}}$ are given in Table 4.1.
4.3.5 Calculation of Turning Point Internuclear Distances

The diatomic internuclear distances which represent classical turning points, \( R_+ \) and \( R_- \), are determined by finding the roots of the equation (KAR65)

\[
D_0 [1 - \exp\{-a(R - R_0)\}]^2 + \frac{j(j+1)\hbar}{2\mu_{bc}R^2} = \omega_0(v+\frac{1}{2}) - \omega_0\chi_0(v+\frac{1}{2})^2 + B_0 j(j+1) - \alpha_0(v+\frac{1}{2})(j+1).
\]

On the right side of this expression, \( D_0 \) is the bond dissociation energy, \( a \) is the Morse parameter, \( R_0 \) is the equilibrium bond length, and \( \mu_{bc} \) is the reduced mass of the diatom. On the left is the internal energy of the diatom expressed as a function of \( v \) and \( j \) and the spectroscopic constants \( \omega_0 \), \( \omega_0\chi_0 \), \( B_0 \), and \( \alpha_0 \). These spectroscopic constants for NaCl, NaBr, and NaI are given in Table 4.1. Once \( R_+ \) and \( R_- \) have been determined, one of the two is selected by generating a new random number; if \( \xi \) is less than .5, \( R_- \) is chosen; if \( \xi \) is greater than .5, the choice is \( R_+ \).

4.3.6 The Orientation, Polar, and Azimuthal angles

All that remains to be specified are the orientation of the rotational momentum vector, and the polar angles which specify the position of B relative to C. The orientation angle \( \eta \) should have a uniform distribution between 0 and \( 2\pi \), so \( \eta \) is selected according to

\[
\eta = 2\pi \xi.
\]

The polar angle \( \phi \) is also uniformly distributed between 0 and \( 2\pi \), and is also selected according to equation (37). The azimuthal angle \( \Theta \) is weighted as \( \sin\Theta \) so the selection of \( \Theta \) is made according to

\[
\Theta = \cos^{-1}(2\xi - 1).
\]

That is, \( \cos\Theta \) has a uniform distribution between -1 and 1.
Table 4.1 Spectroscopic Constants, Source Temperatures, and most-probable speeds for the alkali-halides NaCl, NaBr, and Nal.

<table>
<thead>
<tr>
<th></th>
<th>NaCl</th>
<th>NaBr</th>
<th>Nal</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu$ (amu)$^a$</td>
<td>13.870687</td>
<td>17.803436</td>
<td>19.463754</td>
</tr>
<tr>
<td>$D_e$ (cm$^{-1}$)$^a$</td>
<td>34116.9</td>
<td>30164.9</td>
<td>24196.4</td>
</tr>
<tr>
<td>$a$ (Å$^{-1}$)$^b$</td>
<td>0.902445</td>
<td>0.897485</td>
<td>0.894815</td>
</tr>
<tr>
<td>$R_0$ (Å)$^a$</td>
<td>2.36079</td>
<td>2.50203</td>
<td>2.71145</td>
</tr>
<tr>
<td>$\omega_e$(cm$^{-1}$)$^a$</td>
<td>366.0</td>
<td>302.1</td>
<td>258.0</td>
</tr>
<tr>
<td>$\omega_e\chi_e$(cm$^{-1}$)$^a$</td>
<td>2.05</td>
<td>1.50</td>
<td>1.08</td>
</tr>
<tr>
<td>$B_e$(cm$^{-1}$)$^a$</td>
<td>0.21806309</td>
<td>0.15125331</td>
<td>0.11780561</td>
</tr>
<tr>
<td>$\alpha_e$(cm$^{-1}$)$^a$</td>
<td>0.00162482</td>
<td>0.00094095</td>
<td>0.00064777</td>
</tr>
<tr>
<td>$T_S$(°K)</td>
<td>1300</td>
<td>1150</td>
<td>1000</td>
</tr>
<tr>
<td>$j_{mp}$</td>
<td>45</td>
<td>51</td>
<td>54</td>
</tr>
<tr>
<td>$j_{max}$</td>
<td>110</td>
<td>115</td>
<td>-</td>
</tr>
<tr>
<td>$v_{rmp}$(cm/s)</td>
<td>1.24388 x 10$^5$</td>
<td>1.031212 x 10$^5$</td>
<td>9.209650 x 10$^4$</td>
</tr>
<tr>
<td>$v_{rmax}$(cm/s)</td>
<td>3.7316 x 10$^5$</td>
<td>3.09363 x 10$^5$</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ (HUB79)

$^b$ The Morse parameter is calculated (STR89) from $a = \omega_e (D_e \hbar / \pi \mu)^{-1/2}$
4.4 Computing the Trajectory

Once values for each of the input parameters have been selected, the final requirements for computing the trajectory are the specification of a potential energy function, and some method of numerically integrating the differential equations of motion. All the calculations discussed in this chapter used a version of a "hybrid-gear" numerical integration algorithm (GEA64). The hybrid-gear algorithm contains a combination of 4th-order Runge-Kutta and 'predictor-corrector' algorithms. The more efficient predictor-corrector routine is used for the main part of the calculation. However, this routine is not self-starting and therefore requires the less efficient Runge-Kutta for calculating the first few steps of the trajectory. The FORTRAN subroutines used for the numerical integration are given in Appendix 2.

The potential energy functions used are the $^1\text{2}^A'$ ground state surface and the $^3\text{2}^A'$ excited state surface for K + NaCl (YAM89). Yamashita, et al, parameterized these potential energy functions by fitting 241 points, calculated for different nuclear configurations, by the *ab initio* configuration-interaction (CI) method to a Murrel-Sorbie type analytical function which has the form

$V_{\text{ABC}}(R_1, R_2, R_3) = V_A^{(1)} + V_B^{(1)} + V_C^{(1)}$

$+ V_{AB}^{(2)}(R_1) + V_{BC}^{(2)}(R_2) + V_{CA}^{(2)}(R_3)$

$+ V_{\text{ABC}}^{(3)}(R_1, R_2, R_3)$

This function is a sum of single body terms (which are zero in the case of the ground state), two body terms which are Morse type functions, and the three-body term whose form is given as (MUR84)

$V_{\text{ABC}}^{(3)}(R_1, R_2, R_3) = V_0 \prod_{i=1}^{3} \left[ 1 - \tanh \left( \frac{\gamma_i R_i}{2} \right) \right]$
where $\rho_i = R_i - R_i^0$, $P(R_1, R_2, R_3)$ is a fourth order polynomial of $R_1$, $R_2$, and $R_3$, and $V_0$, $R_i^0$, and $\gamma_i$ are fitting parameters. These parameterized potential energy functions are given in Appendix 3. The ($\partial V/\partial r_i$) terms were evaluated by finite difference with the differentiation spacing optimized to give the best trajectory stability - that is, to minimize the errors in total energy and angular momentum. Finally, a choice must be made for a system of units whose dimensions fall within the 'dynamic range' of the computer. For example, if the cgs system of units were used, representation of the values of the dynamical variables would require exponentiation which reduces the numerical accuracy of the calculations. For the calculations discussed here, the unit of length was taken to be the angstrom (Å); the unit of mass as the amu, and the unit of time taken to be the femtosecond.

4.5 Distributions of TRS Lifetimes

The effect of mass and velocity on the lifetime of the transition region species formed in collisions of $K + NaX$ was examined for both reactive and non-reactive encounters. The method used to calculate the time spent in the complex region is similar to that employed by Kwei, et al (KWE73). Basically, a counter is incremented after every time step in which all internuclear distances ($R_1$, $R_2$, and $R_3$) are less than some pre-set value; the value used here was 8 angstroms. At the end of the trajectory, the counter is multiplied by the time step (1 femtosecond), which gives the total time spent in this region of configuration space. After a large number of trajectories have been run, the lifetimes are 'binned' (with each bin being 250 femtoseconds wide), and a frequency distribution plot is made.

Two types of lifetime distribution calculations were performed. First, the distribution of TRS lifetimes for all collisions (reactive + non-reactive) was determined for $K + NaCl$ and $K + NaBr$ trajectories on the same ($K + NaCl$) ground
state PES. In the second set of calculations, only the lifetimes of reactive collisions were considered. Before presenting the results of these studies, however, it is useful to examine the properties of some representative trajectories to demonstrate the sensitivity of these properties (such as lifetime) on the initial conditions of the trajectory.

In Figure 4.6, plots of $R_1$ and $R_2$ as a function of time are shown, with the third degree of freedom not displayed. The three plots (figures 4.6a, 4.6b, and 4.6c) represent reactive trajectories whose set of initial conditions differ only in the magnitude of the relative velocity vector - with $\langle v_r \rangle$ increasing from 12.92 Å/ps in Figure 4.6a to 14.10 Å/ps in Figure 4.6b to 15.28 Å/ps in Figure 4.6c. It is immediately apparent that the lifetime of the TRS is not a simple function of the relative speed. Even with the impact parameter, initial orientation and separation, and vibrational and rotational energy fixed, the TRS lifetime can vary by as much as a factor of 20 or more with only a 10 percent change in the value of $\langle v_r \rangle$. It is also important to note the extreme longevity of the trajectories depicted in figures 4.6a and 4.6b. The duration of the collision represented by Figure 4.6c is only about 400 femtoseconds - a value fairly typical of most collisions; while the lifetime of the first trajectory is over 6 picoseconds and the second lasting at least 9 picoseconds. This finding is consistent with results obtained from other trajectory studies (KWE73,YAM88) which clearly showed the predominance of a direct reactive mechanism at larger collision energies, while at smaller collision energies the reaction complex becomes much longer lived. It is believed that these long-lived, or "snarled", trajectories contribute most to the experimental signal owing to a higher probability of light absorption. Thus, the distribution of TRS lifetimes may give some insight into ways in which the experimental signals may differ between the two chemical systems.
Figure 4.6. Sample K + NaCl trajectories showing variation of rK-Cl and rCl-Na as a function of time for 3 different collision energies. All other input parameters are held constant.
For both sets of calculations the maximum impact parameter used was 5 angstroms, and the initial separation ($S_0$) set at 15 angstroms. Comparison of results between 3000 and 4000 trajectory samples indicated that the Monte-Carlo integration over the range of initial conditions was converged after 4000 trajectories. All trajectories for the lifetime distribution calculations were run on the $1\ 2A'$ ground state potential energy surface for K + NaCl. Thus, the trajectories for K + NaCl and K + NaBr differed only in the mass of the halogen atom, and the distribution of kinetic, vibrational, and rotational energies for the two sodium halides.

Figure 4.7 shows the normalized TRS lifetime distributions for all (reactive + nonreactive) K + NaX collisions. It is seen that the peak of both distributions occurs at 750 femtoseconds, with a somewhat broad shoulder extending out to about six picoseconds. There is only a slight difference between the two distributions, mainly that the shoulder for the K + NaBr system is somewhat more pronounced. Figure 4.7b shows an expanded view in the lifetime region between one and four picoseconds.

The distribution of lifetimes for reactive trajectories, shown in Figure 4.8, is similar to that observed for all K + NaX collisions with the peak shifted to slightly longer times. The reaction 'probability' can be estimated from the ratio of reactive trajectories to the total number of trajectories run and it was seen that the K + NaBr system had a slightly larger percentage (31.2%) than K + NaCl (29.6%). Comparison of the distribution of TRS lifetimes for reactive trajectories with that of the all-collision distribution shows that the peak in the all-collision lifetime distribution arises mainly from non-reactive collisions in which the K atom is elastically scattered. In contrast, most of the long-lived trajectories are reactive, with the outcome being determined primarily by the exoergicity of the reaction. This accounts for the difference in the percentage of reactive trajectories between the two systems, as with a reduced mean speed, fewer K atoms are elastically scattered and more trajectories may go on to react. The main peak
Figure 4.7. Normalized lifetime distributions for 4000 reactive + non-reactive K + NaCl and NaBr trajectories. Figure 4.7b is an expanded view in the 1 to 4 picosecond region.
Figure 4.8. Normalized distribution of lifetimes for 4000 reactive $K + NaCl$ and $NaBr$ trajectories. Each point represents the fraction of the total number of trajectories having a certain lifetime.

$\tau_{\text{avg} \ Br} = 3.10$ picoseconds

$\tau_{\text{avg} \ Cl} = 2.74$ picoseconds
in the reactive trajectory lifetime distribution at about 1 picosecond correspond to reactions proceeding via a direct mechanism with trajectories similar to that shown in Figure 4.6c. It is apparent that the K + NaBr reactive trajectories have a significantly smaller direct component and slightly larger long-lived (4-8 ps) component that its K + NaCl counterpart and the peak is shifted to a slightly longer time.

These lifetime distributions were calculated in an attempt to understand the effect of the mass of the halogen atom and differences in kinetic, vibrational, and rotational energy on the dynamics of the ground state reaction of K + NaCl and NaBr. While no really striking difference is observed in the distribution of lifetimes of collisions on the ground state for these two systems, the differences in translational and internal energies between the sodium halides may affect the probability of light absorption and subsequent dynamics on the excited state. In the next section, the process of light absorption by the reacting system is modeled using 'surface hopping' techniques in order to determine the effect of halogen atom substitution on the probability of forming Na⁺.

4.6 Surface Intersections and Adiabatic Transitions

The process of light absorption by a chemical system (either static or dynamic) is usually thought of in terms of a vertical 'arrow', whose length is proportional to the energy of the photon, which connects the two states. Physically, this picture represents a coupling of the dipole moment of the system with the electric field vector of the radiation field followed by a 'vertical' transition to the upper state in which the position of the nuclei are unchanged during the transition (see Figure 1.1). An alternative way of viewing this process involves adding the energy of the photon to the ground state potential energy to create a so-called "laser dressed" potential energy function (YAM89). For a certain range of photon energies, there will be an n-1 dimensional
surface of intersection between the laser dressed ground state and the excited state, where \( n \) is the dimensionality of the potential energy surfaces. As the system moves through a point of surface intersection, it may either remain on the same surface or cross over to the other potential energy surface. A transition in which the system remains on the same surface is called \textit{diabatic}; if the system crosses over to the excited state potential energy surface, the transition is said to be \textit{adiabatic}. Thus, the absorption of light corresponds to an adiabatic transition from the laser dressed ground state to the excited state PES.

Surface crossing calculations were performed which model the absorption of radiation by the reacting system. One goal of these calculations was to establish a correlation between nuclear configurations at the point of surface intersection, and reactive trajectories on the excited surface as a function of photon energy. Comparison of results between the two sodium halides should give some insight into the contribution of a 'kinetic effect' on the formation of Na*. The second goal was to investigate the mechanism of the steeply rising feature present in all three photoexcitation spectra. Because this feature is common to all three spectra, it seems likely that the potential energy surfaces are similar in the region where this absorption occurs. Therefore, a comparative study using the same surfaces for different chemical systems ought to lead to some insight into the mechanism of this feature. The method used for these calculations is similar to that employed by Yamashita, et al (YAM89), and consists of basically three components. First, a set of initial conditions is selected and a trajectory is propagated on the ground state PES. When a point of surface intersection is encountered, the adiabatic transition probability is evaluated according to the Landau-Zener formula. If the transition probability is greater than a random number generated, the trajectory is then propagated on the excited surface, and the outcome (reactive or nonreactive) is determined.
For an adiabatic transition to occur, there must be some way for the wavefunction of the system to change continuously as it evolves from an eigenfunction on the ground state to an eigenfunction on the excited state. This is facilitated by constructing adiabatic potential energy surfaces from the two diabatic surfaces which intersect. These adiabatic surfaces are obtained (PRE70, STI76) by diagonalizing the \(2\times2\) matrix
\[
H_{ad} = \begin{bmatrix}
    w_1' & d_{12} \\
    d_{12} & w_2
\end{bmatrix},
\]
where \(w_1'\) is the diabatic potential energy of the laser dressed ground state \((w_1'=w_1+\hbar\nu)\), \(w_2\) is the diabatic potential energy of the upper surface and \(d_{12}\) is the matrix element which couples the two diabatic states. In the case in which the coupling of the two states is due to the radiation field, the coupling term \(d_{12}\) is equal to \(\mu \cdot \vec{E}\) where \(\mu\) is the dipole moment, and \(\vec{E}\) is the electric field vector. The two eigenvalues of \(H_{ad}\) are
\[
W_{\pm} = \frac{1}{2}(w_1' - w_2) \pm \frac{1}{2}\sqrt{(w_1' - w_2)^2 + 4d_{12}^2},
\]
and the eigenvectors are
\[
|\psi_{+}\rangle = \cos\left(\frac{\Theta}{2}\right)|\phi_1\rangle + \sin\left(\frac{\Theta}{2}\right)|\phi_2\rangle; \quad |\psi_{-}\rangle = -\sin\left(\frac{\Theta}{2}\right)|\phi_1\rangle + \cos\left(\frac{\Theta}{2}\right)|\phi_2\rangle
\]
where \(\phi_1\) and \(\phi_2\) are the diabatic wavefunctions, and \(\Theta\) is given by
\[
\Theta = \cos^{-1}\left(\frac{w_1' - w_2}{\sqrt{(w_1' - w_2)^2 + 4d_{12}^2}}\right).
\]
The potential curves and wavefunctions in the diabatic and adiabatic representation are shown schematically in Figure 4.9.
Figure 4.9. Transition through a point of diabatic curve intersection. If an adiabatic transition is made, the wavefunction $|\psi_+\rangle$ (initially $|\psi_1\rangle$) is transformed smoothly along $W_+$ to $|\psi_2\rangle$.

The probability of making an adiabatic or diabatic transition as the system passes through the point of intersection can be estimated by the Landau-Zener formula (STI76). The Landau-Zener probability for a diabatic transition is given by

$$P_d = \exp \left( -\frac{2\pi d_{12}^2}{\hbar |(\partial \Delta w/\partial t)|} \right);$$

where

$$\frac{\partial \Delta w}{\partial t} = \sum_{i=1}^{3} \frac{\partial \Delta w}{\partial r_i} \cdot \sum_{j=1}^{6} \frac{\partial r_j}{\partial Q_l} \cdot \frac{\partial Q_l}{\partial t}$$
and \( \Delta w = w_1' - w_2 \). Since \( (\partial w/\partial \eta) \), \( (\partial \eta/\partial Q_j) \), and \( (\partial Q_j/\partial t) \) are quantities which are known at each step in a trajectory, it is a simple matter to calculate the Landau-Zener transition probability once the point of surface intersection has been located. The sum of adiabatic and diabatic probabilities is one, so the adiabatic transition probability, \( P_{ad} \), is \( 1 - P_d \). In case where the argument of the exponent is much less than one, the exponential can be expanded, and keeping only the first two terms gives

\[
(46) \quad P_{ad} = 1 - \exp \left( -\frac{2\pi d_{12}^2}{\hbar |(\partial \Delta w/\partial t)|} \right) \approx \frac{2\pi d_{12}^2}{\hbar |(\partial \Delta w/\partial t)|} .
\]

It is apparent from equation (46) that adiabatic transitions are most favored when \( d_{12} \) is large, or when \( \partial \Delta w/\partial t \) becomes small. For cases in which the diabatic states are coupled by a radiation field, the value of \( d_{12} \) is usually quite small unless extraordinarily large electric fields are used. For most cases, the coupling is extremely weak and most transitions through the crossing are diabatic, which is to say no photon is absorbed. The value of \( d_{12} \) (0.004336 eV) used for these calculations was the same as that used by Yamashita, et al (YAM89) and corresponds to laser power density of 14 MW/cm\(^2\), while the experimental power density is on the order of KW/cm\(^2\). This artificially large value of \( d_{12} \) is necessary for the calculations to improve the yield of trajectories which make an adiabatic transition. The factors which influence the magnitude of the \( (\partial \Delta w/\partial t) \) term, seen from inspection of equation (44), are the nuclear velocities \( (\partial Q_j/\partial t) \), and the difference in slopes of the two diabatic potential energy surfaces \( (\partial \Delta w/\partial \eta) \). Thus, an adiabatic transition is favored in a case of small nuclear velocities, or at a crossing in which the two surfaces are close to being parallel.

The surface-hopping program was designed to provide several pieces of information. For every adiabatic transition, the nuclear configuration (at the crossing), the Landau-Zener transition probability, and the time required to make the crossing \( (t_1) \) was recorded. Once on the adiabatic surface, the trajectory is continued until either
the K-X or X-Na distance exceeded 15 Å. The trajectory is then terminated and identified as to either nonreactive or reactive respectively. Every trajectory on the excited state thus has a record of the time required to make the crossing, the nuclear configuration at the crossing, the time required for completion of the trajectory, and the outcome - reactive, or nonreactive. In Figure 4.10, a flow chart is given for the surface hopping program which gives a basic description of how the calculation is made.
Figure 4.10. Program format for surface-hopping trajectory calculations.
4.7 Results of Surface Hopping Trajectory Calculations

Surface hopping trajectory calculations were carried out at five different wavelengths (590, 595, 600, 615, and 650 nm) for both the K + NaCl and K + NaBr systems on the same (K + NaCl) potential energy surfaces in order to examine the effect of halogen atom mass on the probability of light absorption and the formation of Na⁺. The energy of the photon is added to the the ground state potential energy and the the trajectory is propagated on the laser-dressed ground state until a point of curve intersection is reached. For each trajectory which is allowed to make an adiabatic transition, a record is kept of the nuclear configuration at the point of transition, the Landau-Zener transition probability, and the time required to reach the crossing seam. Once on the excited state surface, the trajectory is continued until either the K - X or Na - X distance exceeds 15 Å; corresponding to nonreactive or reactive trajectories respectively. The calculations were continued until 500 excited state reactive (ER) trajectories were accumulated to investigate trends in the transition probabilities, configurations, and the relative number of ER trajectories as a function of the halogen atom mass.

To examine the effect of halogen mass and photon energy on the probability of light absorption, average Landau-Zener transition probabilities were calculated at each wavelength for reactive and nonreactive trajectories for both chemical systems. Figure 4.11 shows a plot of the average transition probabilities as a function of wavelength. For all wavelengths, the transition probabilities were calculated to be highest for nonreactive trajectories. This is due to the velocity term in equation (44) and the fact that there is a significant barrier to formation of products on the excited state surface. Trajectories which have low relative velocities have favorable transition probabilities
but insufficient energy to cross the barrier to formation of products. The transition probabilities are highest at 650 nm and decrease toward 600, and, except for the nonreactive Cl case, show a slight maximum at 595nm. At longer wavelengths, the crossing seam is shifted further back in the reactant channel where the surfaces are more parallel which increases the transition probability (YAM89). The cause of the slight increase at 595 nm is not known exactly but it may be that, for this wavelength, the crossing seam is located in a region where the two surfaces become more parallel. The decrease in transition probability at 590 nm contradicts the intuitive notion that, as the excitation wavelength approaches the Na D line, there should be a large increase in the probability of light absorption as the two surfaces become parallel out in the product channel. The reasons for the failure of this model to predict such "exit-channel excitation" near the Na D line will be discussed in the final chapter. Another somewhat
surprising result is that lower average transition probabilities were calculated for the Br system than for the Cl system. Because of the lower mean speed, it might be expected that the transition probability should be greater for the Br case. It may be that most of the configurations at the crossing seam for the Br system may be at a point where there surfaces are less parallel than for the Cl system.

Figure 4.12 shows the configurations at the point of transition for each of the 500 ER trajectories for the Cl and Br systems at three different wavelengths and it can be seen that there is a significant difference in the set of configurations between the two chemical systems. Most of the configurations look quite similar with included angles about 75 degrees, however the (ER) K + NaCl trajectories show a number of configurations which have angles greater than 90 degrees with relatively long Cl-Na distances. Almost none of these large angle configurations are present in the Br case. For the Cl system, the number of these large angle configurations seems to decrease slightly with increasing wavelength and the Cl-Na distance becomes shorter.

Transition point configurations which led to nonreactive trajectories on the excited state (ENR), shown in Figure 4.13, are similar to the ER configurations but have a smaller large angle component. For the Br system, the ENR data show virtually no configuration with an angle larger than 90 degrees. The ER and ENR data for the two chemical systems seems to suggest that these large angle configurations arise from higher energy collisions which displace the sodium atom farther on initial impact. This result is consistent with conclusions made from the distribution of lifetimes for reactive K + NaX trajectories which clearly showed an enhanced 'direct mechanism' component for the K + NaCl system.
Figure 14.12 a, b, c, d, e, f. Configurations at the point of transition for reactive trajectories on the excited state surface at 595, 615, and 650 nm. The origin of the horizontal axis represents the position of the K atom. The position of the halogen atom is located at the position where the line segment (denoting the X-Na bond) intersects the horizontal axis, and the endpoint of the line segment represents the position of the Na atom. Average values of r(K-X), r(X-Na), and theta are given in brackets.
Figure 4.12 a. $\lambda = 595$ nm, $X = \text{Cl}$

$\langle r_{K-\text{Cl}} \rangle = 4.41$ Å, $\langle r_{\text{Cl}-\text{Na}} \rangle = 2.66$ Å, $\langle \Theta \rangle = 74.3^\circ$

Reactive

Figure 4.12 b. $\lambda = 595$ nm, $X = \text{Br}$

$\langle r_{K-\text{Br}} \rangle = 4.32$ Å, $\langle r_{\text{Br}-\text{Na}} \rangle = 2.63$ Å, $\Theta = 71.1^\circ$
Figure 4.12 c. $\lambda = 615$ nm, $X = Cl$

$<r_{K-Cl}> = 4.26 \text{ Å}, <r_{Cl-Na}> = 2.79 \text{ Å}, \Theta = 79.0^\circ$

Reactive

Figure 4.12 d. $\lambda = 615$ nm, $X = Br$

$<r_{K-Br}> = 4.45 \text{ Å}, <r_{Br-Na}> = 2.63 \text{ Å}, \Theta = 72.2^\circ$
Figure 4.12 e. $\lambda = 650$ nm, $X = Cl$

$<r_{K-Cl}> = 4.50$ Å, $<r_{Cl-Na}> = 2.89$ Å, $\psi = 83.1^\circ$

Reactive

Figure 4.12 f. $\lambda = 650$ nm, $X = Br$

$<r_{K-Br}> = 4.75$ Å, $<r_{Br-Na}> = 2.61$ Å, $\psi = 75.3^\circ$
Figure 14.13 a, b. Configurations at the point of transition for nonreactive trajectories on the excited state surface at 615 nm. The axis convention is the same as in the previous diagram. Average values of r(K-X), r(X-Na), and theta are given in brackets.
Figure 4.13 a. \( \lambda = 615 \text{ nm, } X = \text{Cl} \)
\\[<r_{\text{K-Cl}}> = 4.41\text{Å}, <r_{\text{Cl-Na}}> = 2.66\text{Å}, <\Theta> = 74.3^\circ]\\

Nonreactive

Figure 4.13 b. \( \lambda = 615 \text{ nm, } X = \text{Br} \)
\\[<r_{\text{K-Br}}> = 4.57\text{Å}, <r_{\text{Br-Na}}> = 2.62\text{Å}, <\Theta> = 72.2^\circ]\\
The ratio of ER trajectories to the total number of trajectories run was used to approximate the intensity of Na D line emission as a function of wavelength for the two chemical systems. Since the magnitude of the experimental signal is determined by the number of transition region species which absorb a photon and go on to react on the excited state surface, the number of ER trajectories can be used to calculate a model spectrum. A schematic of the process of light absorption with approximate potential energy curves for the $1^2A'$ ground state and the $3^2A'$ lowest excited states is shown in Figure 4.14.

![Potential Energy Curve](image)

**Figure 4.14.** Schematic of curve crossing treatment of light absorption process with approximate potential energy curves for the K + NaCl system. The ground state is shown with the photon energy added to it and a Landau-Zener probability is evaluated at the curve intersection which determines whether absorption takes place.
Figure 4.15 shows the percentages of the total number of trajectories which are reactive on the excited state as a function of excitation wavelength for the Cl and Br systems. It can be seen from Figure 4.15 that only a small difference in the probability of Na* formation is predicted between the K + NaCl and K + NaBr systems. The calculated signal trends appear to be basically identical for the two systems, with the calculated Br signals slightly lower than those of the Cl system, and the results obtained for wavelengths between 600 and 650 are agree with the previous calculations of Yamashita, et al (YAM89). The shorter wavelengths (595, and 590 nm) were chosen to see if this model could predict the same sort of signal behavior in this wavelength range as is experimentally observed. The results of these calculations show that no such large

![Graph showing ratio of ER trajectories to total number of trajectories as a function of laser wavelength. The two Br points at 595 nm illustrate relative error in the calculations.](image)
signal increase is predicted by this model. The reasons for these calculated signal trends will be discussed in detail in the final chapter. It seems likely that the discrepancy between theory and experiment is due to inaccuracies in the calculated potential energy surfaces, however, it is unknown what modifications, if any, could be made in these surfaces which could improve the agreement.

The results of these surface hopping trajectory calculations performed on the K + NaCl potential energy surfaces indicate that the mass of the halogen atom does have some affect the transition probability and the types of configurations which make a transition. The calculated spectrum shows basically no mass effect, however these calculated spectra do not display the same signal trend in the 600 to 650 nm range which is experimentally observed for the K + NaCl system. This makes it uncertain as to whether a mass effect exists or not. From the results of these calculations, it must be concluded that the structure observed in the photoexcitation spectra for the K + NaBr and K + NaI systems arises from details of the (unknown) potential energy surfaces unique to those chemical systems. In the final chapter, possible mechanisms for both these features are discussed, as well as plans for future experiments which may help to understand the nature of these spectra.
Chapter 5

Discussion and Conclusions

Transition region species formed in the bimolecular reactions of \( K + NaX \) (\( X = Cl, Br, I \)) were investigated by crossing the reagent beams inside the cavity of a cw dye laser and measuring the intensity of Na D line emission at 589.0 nm as a function of dye laser wavelength. Positive signals requiring the presence of all three (laser, potassium, and sodium-halide) beams have been observed using probe wavelengths between 595 and 640 nm. Artifact tests performed on these systems indicate that the three beam signal originates from reactive decomposition of electronically excited transition region species formed in the bimolecular reaction as described by (1.2). The variation of three beam signal with excitation wavelength can then be interpreted as a photoexcitation spectrum of the transition region species formed in these reactions.

The purpose of this investigation was to see if reactions with different sodium-halides would result in differences in the TRS spectra which could lead to a more detailed understanding of the dynamics of these reactions. The spectrum obtained for the \( K + NaCl \) system was shown to be qualitatively similar to that previously observed (MAG84), and all three TRS spectra share a common 'blue' feature where the three beam signal rises steeply between 600 and 595 nm. The spectra for the \( K + NaBr \) and \( NaI \) systems,
however, each show an additional 'red' feature which is clearly not present in the K + NaCl spectrum, about 900 cm\(^{-1}\) wide at the base with a peak at approximately 610 nm. This red feature has survived in spite of averaging over initial orientations, thermal energy distributions, and impact parameters and suggests that there is a significant difference in the reaction dynamics among the different chemical systems.

Classical trajectory calculations using the K + NaCl potential energy surfaces suggest that the red feature is not due to a mass effect but rather to unique features of the K + NaBr and K + NaI potential energy surfaces which are as yet unknown. The results of these trajectory calculations also showed that no distinct blue feature should appear in these spectra. In this chapter, the discrepancy between experiment and theory regarding the blue feature is examined and several possible reasons given as to why they differ. Possible mechanisms of the red feature observed in the K + NaBr and NaI systems are also discussed, along with a description of proposed future experiments which may provide some clues as to the nature of these features and hopefully some insight into the details of chemical reaction in these systems.

5.1. The Blue Feature

As a chemical reaction is proceeding, the system may absorb a photon if the laser is tuned to a frequency corresponding to the potential energy difference between the ground (\(V_1\)) and an excited state (\(V_2\)) for a given instantaneous nuclear configuration (\(R_i\)); that is, where \(V_2(R_i) - V_1(R_i) = \nu\). An increase in intensity of absorption of light by the TRS may result from either a large number of similar configurations, or from regions where the ground and excited state are relatively parallel allowing many different configurations to absorb at the same frequency. Thus, there are three principal ways in which features may arise in this type of spectrum. In the first case, there may be a region of the lower PES where the system remains trapped for a period of time.
resulting in a "persistent" configuration which will increase the probability of absorption at the wavelength corresponding to the spacing between the potential energy surfaces. In the second case, there may be certain configurations that are explored by all trajectories en route from reactants to products; for example, as a result of a 'bottleneck' in the ground state surface which forces trajectories with widely different initial conditions through a narrow region of phase space. In the third case, there may be regions of the ground and excited PES's traversed by the system which are relatively parallel which allow many different configurations to absorb, or by greatly increasing the adiabatic transition probability where $\partial \Delta \omega / \partial t$ approaches zero.

It has been suggested that the blue feature near the Na D line arises from excitation in the product channel from the ground state PES where the two surfaces are presumed to be relatively parallel (BAR91). The concept of 'exit channel excitation' is intuitively appealing since the large number of sodium atoms formed in the ground state reaction could be perturbed at long range by the newly formed KX molecule, thus differing only slightly between chemical systems as is experimentally observed. This could result in increasing absorption probability as the wavelength approaches the D line. However, it was shown in section 4.7, contrary to what is observed experimentally for the three chemical systems studied, that the surface hopping classical trajectory model failed to predict a large increase in the number of Na* atoms formed as the excitation wavelength approached the Na D line (see Figure 4.16). In order to understand why this model does not predict a steep increase in the production of Na*, it is necessary to examine some of the details of the potential energy surfaces that were used in the calculation.

The method of calculation of ab initio energies and the functional form of the parameterized $1\,^2A'$ and $3\,^2A'$ surfaces were discussed in Chapter 4. It is useful to examine the state correlation diagram shown in Figure 5.1, in order to understand from which reactant and product states these surfaces are formed and how the features in
Figure 5.1. State correlation diagram for the $K + NaCl \rightarrow KCl + Na$ reaction reproduced from Yamashita, et al (YAM88). The zero of energy (in eV) is defined as ground state reactants.
these surfaces arise. First, consider the reaction between K(4s) and Na\(^+\)Cl\(^-\) without rearrangement of the electrons. This reaction would follow a diabatic path leading to Na\(^+\) + K(4s)Cl\(^-\) which is much higher in energy than the ground state Na(3s) + K\(^+\)Cl\(^-\) products. Since the evolution from ground state reactants to ground state products must involve a transition between neutral and ionic states of the alkali atoms, the path which joins these two lowest lying states is an adiabatic curve constructed from the diabatic curves which correlate with the higher energy states K\(^+\) + Na(3s)Cl\(^-\) and Na\(^+\) + K(4s)Cl\(^-\). The reaction between a neutral K(4s) atom to the ionic NaCl molecule thus involves an adiabatic transition in which the electron jumps from the K atom to the NaCl molecule. At this point, the potential energy drops steeply and the system then evolves into the neutral Na(3s) and ionic KCl products. The minimum energy path along the \(1\ 2^A'\) surface, shown in Figure 5.2, indicates that the electron jump occurs at a K-Cl distance of about 4 Å. The K-Cl-Na angle along the minimum energy path changes abruptly from 180° to about 90° at the point of electron transfer, and, as the sodium atom leaves, the angle changes abruptly again, from about 90° back to a collinear geometry. The minimum energy configuration is lower in energy by about 0.8 eV with respect to ground state reactants, and has a K-Cl distance of 2.91 Å, a Cl-Na distance of 2.64 Å, and a K-Cl-Na angle of 85° (YAM88).

The excited state potential surfaces are constructed in a similar way as the ground state, except that the reactants and products correlate adiabatically with excited atomic states. The first excited state, the \(2\ 2^A'\) state, is predicted to have a deep well with a minimum energy of about 1.6 eV lower than excited state reactants and correlates with K(4p) and Na(3p) in the reactant and product asymptotes respectively. The \(3\ 2^A'\) and \(1\ 2^A''\) are basically parallel (YAM88), with the exception that the \(1\ 2^A''\) states should be less repulsive at smaller angles, and the \(3\ 2^A'\) state is calculated to have a potential energy minimum of about 0.7 eV with respect to excited state reactants.
Figure 5.2. Calculated minimum potential energy paths (eV) for the $1^2A'$ and $3^2A'$ state in which the angle is not restricted. The path shown for the $2^2A'$ state is approximated from Yamashita, et al (YAM89).
(YAM88). The minimum energy configuration of the $3^2A'$ state has a K-Cl-Na angle of about $135^\circ$, a K-Cl distance of 2.91 Å, and a Cl-Na distance of 2.75 Å.

Both the $2^2A'$ and $3^2A'$ states correlate adiabatically with the 3p state of the sodium atom. Since emission from only one of the fine structure states of the 3p sodium atom is observed, it is necessary to consider how the $3^2A'$ and $2^2A'$ state correlate with these fine-structure states. First ignoring the effect of spin-orbit coupling, the interaction of the dipolar electric field of the K$^+\text{Cl}^-$ with a $2p$ Na atom will give rise to three different potential energy curves corresponding to the placement of the electron in one of three ($p_x$, $p_y$, $p_z$) p-orbitals, shown schematically in Figure 5.3.

Let the x-z plane be defined to contain the three nuclei and the negative end of the KCl dipole oriented toward the Na(3p) atom. The lowest energy curve will correspond to placement of the electron in the $p_z$ orbital, and the second with occupation of the $p_x$ orbital. Since these two states will have electronic wavefunctions which are symmetric with respect to reflection through the x-z plane, they will be of A' symmetry. The third state, corresponding to the electron occupying the $p_y$ orbital will have a wavefunction which is antisymmetric with respect to reflection through the x-z plane, and will therefore be of A'' symmetry. The three curves shown in Figure 5.3 can then be identified, from lowest to highest, as the 2 A', 3 A', and 1 A'' respectively (the doublet designation will be omitted for the rest of the discussion). The coupling of the electron spin with the p-orbital angular momentum mixes these states and splits the single asymptotic product state into the 3/2 and 1/2 levels, where the magnitude of the splitting is about 17 cm$^{-1}$(WEA83). As shown in the insert of Figure 5.3, the spin-orbit splitting will cause the 2 A' and 3 A' states to separate near the asymptote, and, because these states are of the same symmetry, they cannot cross. Therefore, the 2 A' and 3 A' states correlate adiabatically with the $^2p_{1/2}$ and $^2p_{3/2}$ levels, and only transitions to the 3 A' and 1 A'' states should be observed in the experiments reported here.
Figure 5.3. Origin of potential curves from placement of electron in $p_x$, $p_y$, or $p_z$ orbital of excited sodium atom (the x-z plane is defined to contain the three nuclei). The effect of spin-orbit splitting of the $3^2p$ level is shown in the insert.
The variation of potential energy along fixed angle paths, given in Figure 5.4, shows that both the 1 A' and 3 A' states are quite repulsive at K-Cl-Na angles less than 50°. A closer look at the product asymptotic region of the 3 A' state, shown in Figure 5.5, demonstrates that the potential energy does not drop below the asymptotic value until the Cl-Na distance is less than 6 Å. The consequence of this feature of the upper surface is that there is little probability for a curve intersection between the laser dressed ground and excited states at long Cl-Na distances which would correspond to product channel excitation, even at wavelengths very near the Na D line. Figure 5.6 shows that only configurations which have a K-Cl-Na angle larger than 120° are able to make a transition in the product channel. However, because these large angle configurations are higher in energy on the ground state, very few transitions are made in this region. Moreover, most of these exit channel curve crossings occur on a fairly steep potential barrier. Since the adiabatic transition probability increases with lower speeds, most of the trajectories which do make a transition in this region will have insufficient energy to be overcome the barrier and will be nonreactive on the excited state surface. The combination of these factors explain the results of the surface hopping trajectory calculations shown in Figure 4.15, which showed that the number of Na⁺ atoms formed was not highly sensitive to excitation wavelengths near the Na D line.

The disagreement between the classical trajectory model and experimental results at wavelengths near the Na D line seems to cast some doubt as to the validity of the proposed product channel excitation mechanism for the blue feature. In order to understand exactly how this feature arises, several different possibilities are examined which may account for the discrepancy between theory and experiment.
Figure 5.4. Variation of potential energy along fixed angle paths on the $3^2A'$ state (A), and $1^2A'$ state (B). All energies are referenced to ground state reactants, and the vertical energy scale is the same for both plots.
Figure 5.5. Exit channel region of the $3 \, \text{A}'$ surface for fixed angles. The K-Cl distance is allowed to vary so that, for a specified angle and Cl-Na distance, the potential energy is minimized. Curves reach asymptotic value of 2.105 eV (Na D line) at a Cl - Na distance of about 20 Å.
Figure 5.6. Exit channel curve crossings for excitation wavelengths of 595 nm (A), and 590 nm (B). Ground state curve has angle fixed at 180°, different fixed angle curves for the excited state shown with dashed lines.
The first possibility is that the asymptotic properties of the 3 A' surface are poor. It is difficult to assess this possibility since the number of ab initio points calculated in this region and the residuals associated with the parameterized fit are unavailable. It may be that a second shallow well exists far out in the product channel (CI-Na distances > 9 Å), which might allow for curve crossings that give rise to the kind of Na* production which is experimentally observed in this region. The depth of this well would have to be at least 0.3 eV lower than the Na D line corresponding to the sum of the exoergicity of the ground state reaction and the energy difference between the Na D line and the onset of the blue feature (600 nm). Such a secondary feature in the product channel of the the 3 A' surface would be difficult to calculate, but the number of states and curves in the product asymptote region seen in the correlation diagram indicate that it could be possible.

A second possibility is that the large increase in the three beam signal in this wavelength range is due, in part, to an experimental artifact. The combination of Na atom impurities in the molecular beams and excitation wavelengths close to the Na D line allow for the possibility of collisional energy transfer or line broadening which might appear as a three beam signal. It is possible that the laser has a weak satellite mode at or very near the Na D line which could cause an artifact signal, however no evidence of these satellites are seen with the monochromator. Estimates of the magnitude of a three beam signal due to collisional broadening of the Na D line suggest that, even at 595 nm, this process does not significantly contribute to the observed experimental signal (HED72). It is also unlikely that there is a significant contribution to the three beam signal by collisionally dissociated NaK, since no real difference in signals were observed in this wavelength range when Na was added to the K beam.

The vibrational → electronic energy transfer process,

\[(5.1) \quad K_2 + h\nu \rightarrow K_2^\dagger \]
\[K_2^\dagger + Na \rightarrow Na^* + K_2\]
where $K_2^+$ is some vibronically excited species, has been previously investigated in the K + NaCl system (MAG84), and it was shown that no three beam signal exists for Na + K + hv at 600 nm. However, there could be a significant contribution to the signal from this process at shorter wavelengths. The electronic $\rightarrow$ vibrational energy transfer process, in which Na$^+$ is quenched by collisions with either rare gas atoms or diatomics, is well known and characterized (SIL74), however little is known about the process of electronic excitation arising from collisions with vibrationally excited species.

The contribution of this process could be investigated in two ways. Measuring the dependence of the three beam signal on K beam intensity on this wavelength range will show whether the signal is first or second order in K beam intensity. If this feature is a result of an artifact involving potassium dimer, the three beam signal should be nonlinear with K beam intensity in this wavelength region. The Na + K + hv crossed beam experiments should also be repeated at wavelengths in the region of this blue feature. Measurements of three beam signals in this system will indicate whether energy transfer processes are responsible for the large signal increase.

A third possibility is that the blue feature arises from contributions of the 2 A' state which is predicted to act at longer Cl-Na distances and could provide a mechanism for product channel excitation. However, any contribution from the 2 A' state must also involve a non-adiabatic transition to the 3 A' state, since only emission from the $^2p_{3/2}$ level is experimentally observed. The non-adiabatic transition probability from the 2 A' to 3 A' state might be expected to be significant, since the energy difference between the two p levels is small and these excited state electronic wavefunctions should change rapidly over a short distance (along the 'reaction coordinate') as the Na atom moves away from the newly formed KCl molecule. Because of the different states involved, the emission intensity at 589.6 nm (corresponding to the lower of the two p states) as a function of probe wavelength may be quite different than that observed at 589.0 nm. Therefore, some insight into the possible contribution of the 2 A' state, and
the mechanism of the blue feature, might be gained by observing 589.6 nm emission from the 1/2 fine structure state.

Several different possibilities have been discussed which may explain the nature of the steeply rising feature near the Na D line observed in all three photoexcitation spectra. At present, there is insufficient data to ascertain the true mechanism of this feature, however several different future experiments have been described which could provide some clues. The first priority should be to establish that this feature is not due to an experimental artifact. Assuming that it is not, the next task should be to examine the intensity of emission at the lower of the two D lines (589.6 nm). Comparison of the emission intensities from the two p states may provide some insight into contributions of the 2 A' state and the mechanism of the blue feature.

5.2 The Red Feature

In contrast with the photoexcitation spectra obtained for K + NaCl, the spectra for the K + NaBr and NaI systems show a well defined second (red) feature with a maximum at about 610 nm. However, the absence of potential energy surfaces for these reactions makes interpretation of these spectra in terms of the dynamics of the reaction event quite difficult. At best, it is presently possible only to discuss several different possibilities for the origin of such structure and what dynamical information might be gained from such an interpretation.

The existence of the fairly deep well in the ground state PES for the K + NaCl system makes it logical to assume that similar wells also exist in the K + NaBr and K + NaI surfaces. If the well depth for the heavier halide systems was significantly lower than that of K + NaCl, it might be possible for quasi-bound states to be formed during the chemical reaction which could give rise to the observed structure. Roach and Child (ROA68) suggested that the reason that the KCINa complex is lower in energy than the
reaction products, is an attraction between the NaK+ (dissociation energy 0.5 eV) and Cl- ions. This explanation accounts nicely for the small K-Cl-Na angle predicted for the minimum energy configuration, and the additional (0.2 - 0.3 eV) stabilization energy comes from the interaction with Cl-. On this basis, it might be expected that the KBrNa and KINa complexes may be slightly more stable than that of KClNa, however, it seems unlikely that there would be a difference of such magnitude as to account for the structure in the photoexcitation spectrum.

A different mechanism can be imagined in which the structure in these spectra arises not from a feature of the ground state; but rather from some difference in the upper state surface. For the K + NaCl system, there is a significant geometry change from the minimum energy configuration on the ground state ($\Theta_{\text{min}}^\text{g} = 90^\circ$) to that of the excited state ($\Theta_{\text{min}}^\text{e} = 140^\circ$). Thus, for K + NaCl, transitions from the bottom of the ground state well may be weak due poor Franck-Condon factors, or may lead primarily to non-reactive trajectories on the excited state surface which would not be detected. In the K + NaBr and NaI case, the upper state surface may be more attractive at smaller angles - that is, become more parallel to the ground state surface, which might produce an increase in signal intensity. It is difficult to predict how the substitution of Br and I for Cl should affect the properties of the upper state surface, although it may be possible to test this idea experimentally by measuring the K*/Na* branching ratios as a function of wavelength for the different sodium halides. Since the branching ratios would be sensitive to features of the excited state surface, these measurements may give some indication as to the relative differences of the 3 A' state for the different chemical systems.

Another interesting possible that the transitions responsible for the structure in the KBrNa and KINa spectra do not originate from the ground state PES; but rather from the first excited state. Figure 5.1 shows that there is an avoided intersection between the 1 A' and 2 A' states, and the minimum energy separation between these adiabatic states in
the K + NaCl system is predicted to be about 0.16 eV (ROA68, YAM88). Thus, it may be possible for non-adiabatic transitions to occur from the 1 A' to the 2 A' state upon collision. Estimates of the non-adiabatic transition probability for the K + NaCl system are small, however - on the order of 0.1 (KWE73). The 2 A' state is strongly bound by about 1.7 eV, and the system could remain trapped in this deep well for a significant amount of time since it would have insufficient energy to react on this excited state. These trapped species would, in principle, have very similar configurations, and excitation to the 3 A' state upon absorption of a photon could then result in a feature in the photoexcitation spectrum.

The smaller mean thermal velocities for NaBr and NaI compared to NaCl would tend to favor adiabatic transitions through the avoided crossing. Thus, a non-adiabatic mechanism would require a significantly smaller separation between adiabatic states for the Br and I systems than for the Cl system. The results of chemiluminescence experiments performed on the KX + Na and NaX + K systems by Moulton and Herschbach (MOU66), and the interpretation by Struve (STR73) provide some clues as to the relative likelihood of non-adiabatic transitions for the Br and I vs. Cl systems. In these experiments, energy exchange processes were studied where highly vibrationally excited alkali halides (MX⁺) react with another alkali metal, M⁺ to form an electronically excited alkali metal product M⁺. The MX⁺ reagent was prepared by first reacting an alkali metal M with the dihalide X₂, and the MX⁺ product is formed in an extremely high vibrational state (ν = 40). The MX⁺ then goes on to react with a second alkali metal, and the intensity of fluorescence from the excited atomic products was measured. The specific reactions studied were:

\[(5.2)\]

\[\begin{align*}
\text{KBr}^+ + \text{Na} & \to \text{NaBr} + \text{K}^+ \\
\text{NaBr}^+ + \text{K} & \to \text{NaBr} + \text{K}^+ \\
\text{KCl}^+ + \text{Na} & \to \text{NaCl} + \text{K}^+ \\
\text{NaCl}^+ + \text{K} & \to \text{NaCl} + \text{K}^+ 
\end{align*}\]
Emission at 766.5 and 769.9 nm, corresponding to the $4^2 \mathrm{p} \rightarrow 4^2 \mathrm{s}$ transitions for potassium, was observed, and was found to be most intense for the reactive processes, $\text{KBr}^+ + \text{Na}$ and $\text{KCl}^+ + \text{Na}$. It was also found that the $\text{KBr}^+ + \text{Na}$ gave a greater yield of $K^*$ than $\text{KCl}^+ + \text{Na}$, by about a factor of 10, even though the $\text{KCl}^+$ has more vibrational energy than its $\text{KBr}^+$ counterpart. The yield of chemiluminescence from the nonreactive process, however, was much smaller than that of the reactive process and the cross section for $K^*$ formation in these nonreactive collisions was estimated to be at least one order of magnitude smaller than for the reactive process.

Struve's interpretation, based on pseudopotential calculations of the $\text{K} + \text{NaBr}$ surfaces, was that the $K^*$ emission is due to a non-adiabatic transition between the ground state and the first excited state. His estimate of the minimum energy separation between these two states for $\text{K} + \text{NaBr}$ was approximately 0.05 eV - or about a factor of 3 smaller than that of $\text{K} + \text{NaCl}$, thus accounting for the larger $K^*$ yield for the Br case. Unfortunately, no other details of these potential energy surfaces for the $\text{K} + \text{NaBr}$ reaction are available. It must be remembered that the alkali-halide reagents used in these chemiluminescence experiments possessed an enormous amount of vibrational energy - at least a factor of 10 larger than in the thermal beam experiments described in this thesis. Thus, extension of Struve's non-adiabatic mechanism to the thermal beam case may not be appropriate. However, the experimental results of these chemiluminescence experiments do seem to suggest that non-adiabatic transitions between the ground and first excited states may be more likely for $\text{K} + \text{NaBr}$ than for $\text{NaCl}$. At present, it remains uncertain as to whether a non-adiabatic mechanism is responsible for the observed feature in the KBrNa and KINa spectra, although there are several feasible experiments discussed in the next section which could test whether non-adiabatic transitions are indeed responsible for this structure.
5.3 Future Directions

Several different hypotheses have been presented to account for the features in the photoexcitation spectra for the K + NaCl, NaBr, and NaI systems. Presently, there is insufficient information to make a firm conclusion as to the mechanism of these features since the experimental data support many different possibilities. In order to understand the nature of these features and the underlying dynamics, additional theoretical and experimental information is required. The different possible mechanisms offered in this discussion are certainly not the only ones, however they seem to be the most plausible, and may be tested experimentally. In this section, several future experiments are detailed which may provide some insight into the dynamical processes of these reactions.

As previously discussed, any energy transfer artifact sources of the blue feature can be investigated by examining the linearity of the three beam signal with respect to K beam intensity and by re-running the Na + K + hv experiment in the 600 - 595 nm wavelength range. The results of these tests should indicate whether processes involving K$_2$ and/or Na impurities should be suspected. Should three beam signals exist for the Na + K + hv system in this wavelength range, or if the three beam signal is observed to be nonlinear with K beam intensity, the blue feature should probably be considered to be an artifact. It must be re-emphasized that these tests have already been performed on the K + NaCl system at other wavelengths, and the results clearly support the idea that the signal originates from photoexcitation of transition region species.

Relative differences in the excited state surfaces between the three chemical systems can be investigated by measuring the K$^+$/Na$^+$ branching ratio at different wavelengths. Large (several thousand counts per second) three beam signals have been previously observed at the K 4p $\rightarrow$ 4s transition at 766.5 nm, but the presence of even larger K photoluminescence signals, most likely due to multiphoton dissociation of K$_2$, makes it difficult to be certain that all of the three beam signal can be attributed to
photoexcitation of transition region species. Emission at 766.5 nm is also no longer blue shifted with respect to the probe wavelengths, and for these reasons the nonreactive pathway on the excited surface has not been thoroughly examined. A closer investigation may reveal ways in which K* emission can be measured that can be confidently assigned to processes involving only the TRS.

Experimental information which could supplement measurements of the reactive/nonreactive branching ratios for the K + NaX reactions could be obtained by studying the reverse reaction,

\[
(5.3) \quad \text{Na} + \text{KX} + \text{hv} \rightarrow \text{NaX} + \text{K}^*.
\]

This reaction has the disadvantage of no longer being able to provide blue shifted emission, but has the advantage that K* emission should not be obscured by processes involving K dimer. It has also been suggested (YAM89) that a measurement of K* emission as a function of probe wavelength from the reverse reaction will provide more information on the dynamics of the ground state.

Contributions from the 2 A' state can be examined for each of the chemical systems simply by replacing the interference filter (589.0 nm in these experiments) with one centered at 589.6 nm which would pass only the lower of the two Na D lines. Since emission at 589.6 nm would correspond to reactive dissociation on the 2 A' surface, the TRS spectra might be very different than those observed at 589.0 nm. For example, it has already been pointed out that the 2 A' state is predicted to have much different asymptotic properties than the 3 A' state (see figure 5.2), which could give rise to larger signals near the D line.

Insight into the possible non-adiabatic processes proposed to account for both the blue and red features could also be gained by experiments using a 589.6 nm interference filter in conjunction with seeded sodium halide beams. It was pointed out in the introduction that experimental difficulties were previously encountered in an attempt to use seeded NaX beams. In order to understand why experiments using seeded reagent
beams might be successful in probing non-adiabatic processes in the K + NaBr and K + NaI reactions, it is necessary to examine the reasons for the lack of success in the K + NaCl case.

Beam characterization studies showed that the seeded beams were indeed effective in reducing the distribution of speeds and internal energies. The translational temperature for the NaCl and K beams were determined to be about 250 K and 10 K respectively. The seeded K beam source was also effective in reducing the distribution of \( \nu \) and \( j \) states in the \( \text{K}_2 \ X(\Sigma_g^+) \) ground state. The vibrational and rotational temperature of the potassium dimer were estimated to be about 77 K and 10 K, respectively, from laser induced fluorescence measurements on the supersonic K beam.

Positive three beam signals were observed with crossed seeded beams. However, large K Photoluminescence (Laser + K beam) signals on the order of about 5000 counts per second were also seen. Although this large background signal, possibly due to multiphoton dissociation of higher potassium clusters formed in the supersonic expansion (ULV88), is subtracted out when calculating the three beam signal (see Chapter 2), it greatly reduced the signal/noise ratio and cast doubts as to whether the three beam signals observed were actually due to process described in (1.2).

Experiments performed with a seeded NaCl beam crossed with an effusive K beam also produced positive three beam signals, however, most of the signals obtained were too small to be useful. The poor signal resulted primarily from the the failure of the seeded NaCl beam source to produce a large enough particle density in the beam intersection region. In order to provide the differential pumping required for the seeded beam source, it was necessary to move the source back about 6 cm from its original position. For an effusive beam, this would result in a loss of particle density at the crossing region of approximately a factor of 4 due to the \( L^{-2} \) term in the expression for axial flux (CAR86, ULV88). However, that loss can be made up in the supersonic beam
since the axial flux for a supersonic beam is greater than that of an effusive beam by
approximately the square of the Mach number.

Results of time-of-flight experiments performed on the NaCl beam seeded in
Argon showed that, for a stagnation pressure of about 100 torr, the Mach number was
approximately 3. The NaCl vapor pressure, however, was only about 4-5 torr resulting
in a seeding ratio of ≈ 20. The net result was a reduction in NaCl particle density at the
crossing region, and three beam signal, of approximately a factor of 10. It was seen that
the three beam signal was maximized at low (20-40 torr) stagnation pressures,
however, at these low pressures, no significant reduction in the distribution of speeds is
expected to be obtained. Because of these experimental setbacks, attempts to gain
additional experimental information on the nature of transition region species in the K +
NaCl reaction by seeding the reagent beams have not yet succeeded.

However, it may be possible to overcome those problems since the signals for K
+ NaBr and NaI are at least a factor of 2 larger (in the peak region) than those of the K +
NaCl system. Since non-adiabatic transitions should be favored by an increase in
relative velocity, the increase in mean speed resulting from the supersonic expansion
should increase signal intensity if a non-adiabatic mechanism is responsible for these
features. On the other hand, if these features result from transitions between the 1 A'
and 3 A' states, the increase in mean speed could result in a decrease in signal due to a
shorter complex lifetime.

5.4 Summary and Conclusions

The goal of this study was to investigate the photoexcitation spectra of transition
region species in different potassium + sodium-halide systems with the hope that
differences in these spectra might lead to insight into the nuclear motion during
chemical reaction. The TRS spectra have been measured for the K + NaCl, NaBr, and NaI
systems for excitation wavelengths between 595 and 640 nm, and show that there are indeed major differences between the spectrum for the Cl system and the spectra for the Br and I systems. The experimental results show that there is a common blue feature in the TRS spectra for all the systems studied. In addition, the spectra obtained for the K + NaBr and NaI systems have a well defined second feature, which is not present in the K + NaCl TRS spectrum. However, due to insufficient theoretical and experimental information, interpretation of these results in terms of dynamical processes during reaction and features of the potential energy surfaces is not yet possible.

The results of classical trajectory calculations simulating the process of light absorption by the reacting system suggest that the differences in these spectra do not arise from a mass effect. However, the results of these calculations for K + NaCl and K + NaBr trajectories, performed on the same K + NaCl surfaces, do not even qualitatively predict the wavelength dependence of the three-beam signal for the K + NaCl system. It is therefore unlikely that the surfaces are sufficiently accurate to predict an effect of increased mass on the photoexcitation spectra. Thus, the experimental results suggest that either the potential energy surfaces or the model used to describe the photoexcitation process must be improved in order to accurately describe the variation of three beam signals with wavelength for these systems.

Several different possible mechanisms for the features in these spectra have been discussed which can be experimentally tested, and therefore would not depend on the results of theoretical calculations for affirmation. Several future experiments have been described which could aid in determining the mechanism of the features observed in these photoexcitation spectra. These possible mechanisms include differences in either the ground or excited state surfaces, or non-adiabatic processes in which the first excited state surface is involved. The results of these proposed experiments should be able to provide the information required to understand the nature of these spectra and extract information regarding the details of these chemical reactions.
It is hoped that the experimental results presented in this thesis will prompt the development of new theoretical and computational methods, which could facilitate the construction of accurate potential energy surfaces for these reactions - thus leading to a more detailed understanding of the dynamics of these reactions.
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Appendix 1

Fortran Subroutines to Generate Input Parameters by Monte-Carlo Method

```fortran
subroutine input(ksd,qp)
  implicit real*4 (a-h,q-z)
  real*8 xma,xmb,xmc,xmubc,xmuabc
  real*8 qp(12)
  dimension p(3)
  integer*4 ksd
  common/masses/xma,xmb,xmc,xmubc,xmuabc

  select magnitude of relative velocity vector vr (cm/sec)
  call vrmag(ksd,vr)

  select impact parameter b (Angstroms)
  call impar(ksd,b)

  select vibrational quantum number v
  call vqnum(ksd,v)

  select rotational quantum number qj
  call rqnum(ksd,qj)

  select z component of initial A - cmBC separation sz (Angstroms)
  call insep(ksd,vr,b,v,sz)
```

calculate turning-point B-C distances rplus,rminus by Newton's method

call rroot(1.0,qj,v,rplus)
call rroot(-1.0,qj,v,rminus)

c select either rplus or rminus
call rsel(ksd,rplus,rminus,r)

c select polar angle phi
call angle(ksd,phi)

c select momentum vector orientation angle eta
call angle(ksd,eta)

c select azimuthal angle theta
call azima(ksd,theta)

c calculate momentum components px,py,pz
call pvctr(ksd,qj,r,eta,phi,theta,p,rc)

Now convert to double precision, load Q's and P's into array 'qp'

Note: qp(1)=q1o,qp(2)=q2o .....qp(7)=p1o,..qp(12)=p6o

qp(1) = dfloat(r*sin(theta)*cos(phi))
qp(2) = dfloat(r*sin(theta)*sin(phi))
qp(3) = dfloat(r*cos(theta))
qp(4) = 0.d0
qp(5) = dfloat(b)
qp(6) = dfloat(sz)
qp(7) = dfloat(p(1))
qp(8) = dfloat(p(2))
qp(9) = dfloat(p(3))
qp(10) = 0.d0
qp(11) = 0.d0
qp(12) = dfloat(xmuabc*vr)      units of g*cm/sec
              return
              end

---------------------------------------------------------------------

c subroutine to calculate magnitude of relative velocity vector based on
  monte carlo sampling of a Boltzmann velocity distribution

subroutine vrmag(k,vr)
  implicit real*4 (a-h,q-z)
  real*8 xma,xmb,xmc,xmubc,xmuabc
  integer*4 k
  common/masses/xma,xmb,xmc,xmubc,xmuabc

  vmp = 0.0124388090     !specify most probable relative velocity (NaCl)
  vmax = 0.025000000    !specify maximum allowed value (m/sec)
  a = sngl(xmuabc)*(2.16175e-03)      !a = mu/2kT (amu A fs)

  do 10 i=1,9990
    e1 = ran(k)
    e2 = ran(k)
    vstar = vmax*e1

    q1=(vstar**2)*exp(-a*(vstar**2))
    q2=(vmp**2)*exp(-a*(vmp**2))
    q = q1/q2
    if (q.gt.e2) go to 101
    10    continue

  101  vr = vstar
               return
               end

---------------------------------------------------------------------

subroutine impar(k,b)
implicit real*4 (a-h,q-z)
integer*4 k

bmax = 5.000
e3 = ran(k)
b = bmax*(sqrt(e3))
return
end

subroutine insep (k,vr,b,v,sz)
implicit real*4(a-h,q-z)
integer*4 k

specify vibrational period (dependent on vibrational energy)
hpl = 33360.37250 !Planck's constant in cm^-1*fs
evib = 366.00*(v+0.50)
tau = hpl/evib !vib period in fs for NaCl

specify arbitrary reference separation s0
s0 = 10.000000 !Angstroms
q = (0.5)*(tau)*(vr)
e4 = ran(k)
delta = q*e4
sz = -sqrt((s0**2)-(b**2)) + delta
return
end

subroutine vqnum(k,v)
implicit real*4 (a-h,q-z)
real*4 kT
integer*4 k

we = 366.0000 !vibrational fundamental in cm^-1 NaCl
kT = 903.5000 !value is in cm^-1 source temp for NaCl
e5 = ran(k)
c
evib = kT*(-alog(1.0-e5))
c
gamma = evib/we
c
do 10 i=1,10
xl = float(i)
if(gamma.le.xl)go to 101
if(xl.eq.10)go to 102
10 continue
c
101 v = xl - 1.00
go to 103
c
102 v = 1.
c
103 return
c
end
c
c---------------------------------------------------------------
c
subroutine rqnum(k,qj)
implicit real*4(a-h,q-z)
integer*4 ksd,j
external erot,per
c
qjimp = 45.     !most probable rotational quantum # NaCl(1300K)
qjmax = 110.    !set truncation value
c
do 10 i=1,9990
e6 = ran(k)     !generate two new random numbers e6,e7
e7 = ran(k)
qj = qjmax*e6   !set trial value equal to qjmax*e6
ej = erot(qj)
ejimp = erot(qjimp)
pistar = per(ej)
pjimp = per(ejimp)
c
alpha = pistar/pjimp
c
if(alpha.gt.e7)go to 101  !compare relative probability to value
10 continue  !of e7 - this gives values centered at
              !most probable qj
c
101 continue  !selected value is (qjmax*e6)
return
c
c---------------------------------------------------------------

function erot(x)
implicit real*4 (a-h,q-z)

be = 0.21806309
erot = be*(x*(x+1))
return
end

function per(x)
implicit real*4 (a-h,q-z)
a = 1.10681e-03
la = 1/kT
per = (x**(-0.5))*(exp(-a*x))
return
end

subroutine root(ri,qj,v,rrt)
implicit real*4(a-h,q-z)
external fr,eint,rvib

ei = eint(qj,v)
rs = rvib(ri,ei)  !rplus for pure vibration - lower limit
rinc = 0.00020  !define starting increment
x = fr(qj,rs,ei)  !get initial value of fr - should be positive

if(x.lt.0)go to 101
rs = rs -(ri)*rinc  !keep reducing value of rs until x lt 0

101 if(abs(x).lt.(1.0e-02))go to 201  !if value of x is lt 1 ppm - exit
rs = rs + ri*(15.*rinc)  !back up 5 steps
rinc = rinc/10.0  !reduce increment by factor of 10

go to 6

201 rrt =rs
return
end
function eint(qj,v)
  implicit real*4 (a-h,q-z)

specify spectroscopic constants (all values are cm\(^{-1}\) unless specified)

  we = 366.0  ! vibrational fundamental
  wexe = 2.05  ! anharmonicity constant
  be = 0.21806309  ! rotational constant
  ae = 0.00162482  ! centrifugal distortion constant

calculate internal energy

eint = we*(v+0.50)-wexe*((v+0.5)**2)+
  1/2 be*(qj*(qj+1))-ae*(v+0.5)*(qj*(qj+1))

  return
end

---

function rvib(r1,eint)
  implicit real*4 (a-h,q-z)

ri is a control parameter - value = +1.0 for rplus, -1.0 for rminus

de = 34116.9
alpha = 0.902445
re = 2.36079000

rvib = re + ri*(-1./alpha)*log(1.-sqrt(eint/de)))

  return
end

---

function fr(qj,r,eint)
  implicit real*4 (a-h,q-z)

alpha = 0.9024450  ! morse exponential parameter (Ang\(^{-1}\))
beta = 1.214790  ! hbar/2mu (amu units)
de = 34116.90  

\text{ldissociation energy}

c
re = 2.360790  

\text{lequilibrium bond length (angstroms)}

c
fr = \beta((q_i(q_i+1))*r^{**}(2.)) + 
1 \text{ de}^*((1-\exp(-\alpha(r-re)))^2) - \text{elnt}

c
return
end

c
subroutine rsel(k,rp,rm,r)
implicit real*4  (a-h,q-z)

c
e1 = ran(k)

c
if(e1.lt.0.500000) go to 1
r = rp
go to 2
1 r = rm
2 return
end

c
subroutine angle(k,ang)
implicit real*4  (a-h,q-z)

c
e2 = ran(k)

c
choose angle from uniform distribution between 0 and 2\pi

c
ang = 2.0*3.141592653*(e2)

c
return
end

c
subroutine azima(k,azm)
implicit real*4  (a-h,q-z)

c
q1 = ran(k)

c
azm = \cos((2*q1)-1)

c
return
end

c
subroutine pvctr(k,qj,r,eta,phi,theta,p,rc)
implicit real*4  (a-h,q-z)
real*8 xma,xmb,xmc,xmubc,xmuabc
dimension p(3)
common/masses/xma,xmb,xmc,xmubc,xmuabc

c bea = 0.0000002822806   ! Rotational contant units of amu/ang/fs

c xmu = sngl(xmubc)

c pm = sqrt(2.00*xmu*bea*qj*(qj+1))

c px = -pm*((sin(phi)*cos(eta))+(cos(phi)*cos(theta)*sin(eta)))

c py = pm*((cos(phi)*cos(eta))-(sin(phi)*cos(theta)*sin(eta)))

c pz = pm*(sin(theta)*sin(eta))

c load values into array p

c p(1) = px
p(2) = py
p(3) = pz

c return
end

---------------------------------------------------------------

subroutine rint(y,rin)
implicit real*8 (a-h,q-z)
dimension y(12),rin(3),xr1(3),xr3(3)

c common/masses/xma,xmb,xmc,xmubc,xmuabc

c xm1 = xmc/(xmb+xmc)
xm2 = xmb/(xmb+xmc)

do 10 i=1,3
xrl(i) = (xm1*y(i)) + y(i+3)
10 continue

c rin(1) = dsqrt((xr1(1)**2)+(xr1(2)**2)+(xr1(3)**2))

c rin(2) = dsqrt((y(1)**2)+(y(2)**2)+(y(3)**2))

do 20 i=1,3
xr3(i) = (xm2*y(i)) - y(i+3)
20 continue

c rin(3) = dsqrt((xr3(1)**2)+(xr3(2)**2)+(xr3(3)**2))

c return
end
Appendix 2

Fortran Subroutines for Hybrid-Gear Numerical Integration of

Equations of Motion

---

```
subroutine hgear(y,icount,neq,deriv,energy,h,nstep,ifile)

sixth order hybrid gear routine
ref: j num anal, vol 2, 69 (1965)

implicit real*8 (a-h,o-z)
parameter(n2mx=12)
external energy,deriv,v1a

dimension y(n2mx),d1y(n2mx),d2y(n2mx),d3y(n2mx),d4y(n2mx),
   .zy(n2mx),y0(n2mx),y1(n2mx),y2(n2mx),y3(n2mx),yh(n2mx),y3p(n2mx),
   .f0(n2mx),f1(n2mx),f2(n2mx),f3(n2mx),fh(n2mx),zf(n2mx),rin(3),
   .ry1(3),ry2(3),ry0(3),ry(3),ryh(3),rz(3),ry3p(3),r0(3),yc(12),
   .r2z(3),zy2(12)
common/tstep,nstpwr
common/masses/xma,xmb,xmc,xmubc,xmuabc

c
this version of the hybrid gear code uses a subroutine deriv

to evaluate the derivative vector, rather than a function f(i,y)

c
erloc = 0.d0  !initialize errloc
call rint(y,rin)
ey=energy(y,rin)
am=angmom(y)
write(10,999)icount,(y(i),i=1,neq),ey,errloc,am
999 format(1x,i5,/,4(3(4x,g14.7),/),/2x,f14.12,3x,g14.7,3x,f14.12)
call spacef(8,icount,y)

c
data for runge kutta integration
b11 = 1.d0/3.d0
b21 = -1.d0/3.d0
```
b22 = 1.d0
b31 = 1.d0
b32 = -1.d0
b33 = 1.d0
w1 = 1.d0/8.d0
w2 = 3.d0/8.d0
w3 = 3.d0/8.d0
w4 = 1.d0/8.d0
c
data for hybrid gear routine
ga02 = 153.d0/128.d0
ga01 = 25.d0/16.d0
ga00 = -225.d0/128.d0
gb02 = 45.d0/128.d0
gb01 = 75.d0/32.d0
gb00 = 225.d0/128.d0
c
alpha1 = 0.5 for stability

ga12 = (15.d0/16.d0) -.5d0*(29.d0/32.d0)
ga11 = (-1.d0) -.5d0*(1.d0)
ga10 = (17.d0/16.d0) -.5d0*(-61.d0/32.d0)
gb12 = (5.d0/16.d0) -.5d0*(43.d0/160.d0)
gb11 = (11.d0/12.d0) -.5d0*(41.d0/24.d0)
gb10 = (-11.d0/16.d0) -.5d0*(31.d0/32.d0)
gg10 = (4.d0/3.d0) -.5d0*(-2.d0/15.d0)
c
alpha2 = 1.0, beta = 9/56

c
beta = 9.d0/56.d0
ga22 = 1.5d0*(29.d0/32.d0)+beta*(-45.d0/4.d0)
ga21 = 1.5d0*(1.d0)+beta*(0.d0)
ga20 = 1.5d0*(-61.d0/32.d0)+beta*(45.d0/4.d0)


gb22 = 1.5d0*(43.d0/160.d0)+beta*(-71.d0/20.d0)

gb21 = 1.5d0*(41.d0/24.d0)+beta*(-16.d0)

gb20 = 1.5d0*(31.d0/32.d0)+beta*(-3.d0/4.d0)

gg20 = 1.5d0*(-2.d0/15.d0)+beta*(-16.d0/5.d0)

gg21 = beta*1.d0
c


c

dh=h/8.d0
icount=0
do 99 i=1, neq
    y0(i)=y(i)
99 continue
c
call rint(y,ro)
call deriv(t0,y,ro)
c
do 1000 istep=1,16

c
icount=icount+1

    call rint(y,ry0)
call deriv(zf,y,ry0)

do 100 i=1,neq
d1y(l)=dh*zf(i)
100    continue

do 200 i=1,neq
    zy(l)=y(l)+b11*d1y(l)
200    continue

call rint(zy,rz)
call deriv(zf,zy,rz)

do 300 i=1,neq
d2y(l)=dh*zf(i)
300    continue

do 400 i=1,neq
    zy2(l)=y(l)+b21*d1y(l)+b22*d2y(l)
400    continue

call rint(zy2,r2z)
call deriv(zf,zy2,r2z)

do 500 i=1,neq
d3y(l)=dh*zf(i)
500    continue

do 600 i=1,neq
    zy(l)=y(l)+b31*d1y(l)+b32*d2y(l)+b33*d3y(l)
600    continue

call rint(zy,rz)
call deriv(zf,zy,rz)

do 700 i=1,neq
d4y(l)=dh*zf(i)
700    continue

do 800 i=1,neq
    y(l)=y(l)+w1*d1y(l)+w2*d2y(l)+w3*d3y(l)+w4*d4y(l)
800    continue

call rint(y,ry)
call deriv(f1,y,ry)
do 810 i=1,neq
    y1(l)=y(l)
810    continue
call rint(y1,ry1)
ey=energy(y1,ry1)
am=angmom(y1)
    write(10,999)1,(y1(i),i=1,neq),ey,errloc,am
    if(mod(1,nstepw).eq.0) then
      call spacef(8,1,y1)
    endif
    else if(icount.eq.16)then
      call rint(y,ry)
      call deriv(f2,y,ry)
    do 820 i=1,neq
        y2(i)=y(i)
    820 continue
    call rint(y2,ry2)
    ey=energy(y2,ry2)
    am=angmom(y2)
    write(10,999)2,(y2(i),i=1,neq),ey,errloc,am
    if(mod(2,nstepw).eq.0) then
      call spacef(8,2,y2)
    endif
    endif

1000 continue

c ------------------------------------------------------------------------
c enter main integration loop

lcount=2
    do 2000 istep=1,nstep
        lcount=lcount+1
        do 1100 i=1,neq
    yh(i)=ga02*y0(i)+ga01*y1(i)+ga00*y2(i)+
h*(gb02*f0(i)+gb01*f1(i)+gb00*f2(i))
    1100 continue
    call rint(yh,ryh)
    call deriv(fh,yh,ryh)

    calculate predicted array y3p
    do 1300 i=1,neq
        y3p(i)=ga12*y0(i)+ga11*y1(i)+ga10*y2(i)+
h*(gb12*f0(i)+gb11*f1(i)+gb10*f2(i))+
h*gg10*fh(i)
    1300 continue
    call rint(y3p,ry3p)
    call deriv(f3,y3p,ry3p)

    calculate corrected array y3
    set local truncation error errloc equal to zero
    errloc=0.d0
do 1500 i=1,neq
  q=ga22*y0(i)+ga21*y1(i)+ga20*y2(i)+
    .h*(gb22*f0(i)+gb21*f1(i)+gb20*f2(i))+
    .h*(gg20*fh(i)+gg21*f3(i))
  errloc=dmax1(dabs(q),errloc)
  y3(i)=y3p(i)+q
1500 continue

  c reset arrays for next step
  c note array f3 is not recalculated using corrected array y3
  c
do 1600 i=1,neq
  y0(i)=y1(i)
  y1(i)=y2(i)
  y2(i)=y3(i)
  f0(i)=f1(i)
  f1(i)=f2(i)
  f2(i)=f3(i)
1600 continue

  c print out new values of elements of y2
  c call rint(y2,ry2)
  c ey=energy(y2,ry2)
  c am=angmom(y2)
    write(10,999)icount,(y2(i),i=1,neq),ey,errloc,am
    if(mod(icount,nstpwr),eq,0) then
      call spacef(8,icount,y2)
    endif
2000 continue

do 2100 i=1,neq
  return
end

c return
end

subroutine deriv(f,y,r)
  implicit real*8 (a-h,o-z)
  common/masses/xma,xmb,xmc,xmubc,xmuabc
  common/au1/del
dimension f(12),y(12),r(3),dvd(3)
dimension qy1(3),qy2(3),qy3(3),qy4(3),qy5(3)
external energy, vd1a

  c xm1 = xmb/(xmb+xmc)
  c xm2 = xmc/(xmb+xmc)
c
g get gradient of potential dv/dr1 ,dv/dr2, dv/dr3
c  call dvdr(r,dvd)
c
dvdr1=dvd(1)
dvdr2=dvd(2)
dvdr3=dvd(3)
c
r1 = r(1)
r2 = r(2)
r3 = r(3)
c
set up differential equations for Q's (see Karplus, et al JCP 43,3259 (1965))
c
f(1)=y(7)/xmuabc
f(2)=y(8)/xmuabc
f(3)=y(9)/xmuabc
f(4)=y(10)/xmuabc
f(5)=y(11)/xmuabc
f(6)=y(12)/xmuabc
c
set up differential equations for P's
c
do 10 i=1,3
c
qy1(i) = (xm2/r1)*dvdr1*((xm2*y(i)) + y(i+3))
c
qy2(i) = dvdr2*y(i)/r2
c
qy3(i) = (xm1/r3)*dvdr3*((xm1*y(i)) - y(i+3))
c
f(i+6) = -1.0d0*(qy1(i) + qy2(i) + qy3(i))
c
10 continue
c
do 20 i=1,3
c
qy4(i) = (dvdr1/r1)*((xm2*y(i)) + y(i+3))
c
qy5(i) = (dvdr3/r3)*((xm1*y(i)) - y(i+3))
c
f(i+9) = -1.d0*(qy4(i) - qy5(i))
c
20 continue
c
return
cend
c
subroutine dvdr(r,dvd)
c
implicit real*8 (a-h,q-z)
external vdfa
dimension dvd(3),r(3)
common/dif/del

c
delh=del/2.d0
c
r1 = r(1)
r2 = r(2)
r3 = r(3)
c
get first derivatives of V w/ respect to r1, r2, r3
c
dvd(1)= (vd1a(r1+delh,r2,r3) - vd1a(r1-delh,r2,r3))/del
c
dvd(2)= (vd1a(r1,r2+delh,r3) - vd1a(r1,r2-delh,r3))/del
c
dvd(3)= (vd1a(r1,r2,r3+delh) - vd1a(r1,r2,r3-delh))/del
c
cuse five-point formula for first derivative
c
f(5)=(v(x1+del,y1,x2,y2)-v(x1-del,y1,x2,y2))
  1 -8.d0*v(x1+del,y1,x2,y2)+8.d0*v(x1-del,y1,x2,y2))/6.d0/del
c
f(6)=(v(x1,y1+del,x2,y2)-v(x1,y1-del,x2,y2))
  1 -8.d0*v(x1,y1+del,x2,y2)+8.d0*v(x1,y1-del,x2,y2))/6.d0/del
c
f(7)=(v(x1,y1,x2+del,y2)-v(x1,y1,x2-del,y2))
  1 -8.d0*v(x1,y1,x2+del,y2)+8.d0*v(x1,y1,x2-del,y2))/6.d0/del
c
f(8)=(v(x1,y1,x2,y2+del)-v(x1,y1,x2,y2-del))
  1 -8.d0*v(x1,y1,x2,y2+del)+8.d0*v(x1,y1,x2,y2-del))/6.d0/del

return
end
c
c
double precision function energy(y,rin)
implicit real*8 (a-h,o-z)
common/masses/xma,xmb,xmc,xmubc,xmuabc
common/tsip/tstep,nsantpwr
  dimension y(1),rin(3)
external vd1a

c
c1 = ((y(7)**2) + (y(8)**2) + (y(9)**2))/(2.d0*xmubc)
c2 = ((y(10)**2) + (y(11)**2) + (y(12)**2))/(2.d0*xmuabc)
v = vd1a(rin(1),rin(2),rin(3))
c
cenergy = (c1 + c2 + v)
return
end
c
csubroutine spacef(nsf,icount,y)
implicit real*8 (a-h,o-z)
common/masses/xma,xmb,xmc,xmubc,xmuabc
common/tstptstpnpswpwr
  dimension y(1),r(3)

write time t and space-fixed coordinates x1,y1,z1; x2,y2,z2; x3,y3,z3 to unit nsf
assume that cm = 0, then:

xmbc = xmb + xmc
xmt = xma + xmb + xmc

x1 = (xmbc/xmt)*y(4)
y1 = (xmbc/xmt)*y(5)
z1 = (xmbc/xmt)*y(6)

x2 = -(xmc/xmbc)*y(1) - (xma/xmt)*y(4)
y2 = -(xmc/xmbc)*y(2) - (xma/xmt)*y(5)
z2 = -(xmc/xmbc)*y(3) - (xma/xmt)*y(6)

x3 = (xmb/xmbc)*y(1) - (xma/xmt)*y(4)
y3 = (xmb/xmbc)*y(2) - (xma/xmt)*y(5)
z3 = (xmb/xmbc)*y(3) - (xma/xmt)*y(6)

xicount = dflot(iicount)
time = tstep*xicount
timep = time/1000.0
call rint(y,r)

write(nsf,1)timep,x1,y1,z1,x2,y2,z2,x3,y3,z3
  format((1x,f10.6,2x,'picoseconds',)//,3(5x,3(1x,e18.8)/))

rotate coordinates for computer animation
	xn1 = z1
txn2 = z2
txn3 = z3
yn1 = -x1
yn2 = -x2
yn3 = -x3
zn1 = -y1
zn2 = -y2
zn3 = -y3

write(100,2)time,xp1,yp1,zp1,xp2,yp2,zp2,xp3,yp3,zp3
  format(10(1x,f12.6))
write(3,3)(r(i),i=1,3)
write(4,4)(timep,(r(i),i=1,3)
  format(*'time(ps)',f10.6,5x,'r(K-X) = ',f12.8,3x,'r(X-Na) = '
         ,f12.8,3x,'r(Na-K) = ',f12.8,/)'
  return
end
c subroutine bond(nfile,icount,y)
  implicit real*8 (a-h,o-z)
  common/masses/xma,xmb,xmc,xmubc,xmuabc
  common/tstep/tstep,nstpwr
  dimension y(1)
  c write coordinates r12,r13, and theta to unit nfile, ...
  xm12=xm1+xm2
  xmt=xm3+xm12
    s1=dsqrt(y(1)**2+y(2)**2)
    s2=dsqrt(y(3)**2+y(4)**2)
    s12=y(1)*y(3)+y(2)*y(4)
  r12=s1
    r13=dsqrt((xm2*s1/xm12)**2+s2**2+2.d0*xm2/xm12*s12)
  ctheta12=(xm2/xm12*s1**2+s12)/r12/r13
  theta12=dacos(ctheta12)
  write(nfile,1)icount*tstep,r12,r13,theta12
  format(4(1x,g14.7))
  c c write coordinates R, alpha, and tau to file 11, where
  c xmu*R**2 = xmu1*s1**2 + xmu2*s2**2
  c dtan(alpha) = dsqrt(xmu2/xmu1)*s2/s1
  c dcos(tau) = s12/s1/s2
  c   xmu1 = x1*x2/(x1+x2)
  c   xmu2 = x3*(x1+x2)/(x1+x2+x3)
  c   xmu = dsqrt(xmu1*xmu2*xmu3/(x1+x2+x3))
  c   rmw1 = dsqrt(xmu1*xmu)*s1
  c   rmw2 = dsqrt(xmu2*xmu)*s2
  c   rhyp = dsqrt(rmw1**2+rmw2**2)
  c   alpha = datan(rmw2/rmw1)
  c   tau = dacos(s12/s1/s2)
  c write(11,*)sngl(icount*tstep),sngl(rhyp),sngl(alpha),sngl(tau)
  c return
  c end
  c-------------------------------------------------------------
  c double precision function angmom(y)
  implicit real*8 (a-h,o-z)
  common/masses/xma,xmb,xmc,xmubc,xmuabc
  common/tstep/tstep,nstpwr
  dimension y(1)
  c subroutine to calculate the magnitude of total angular momentum
  c first the x-component
  c amx = y(2)*y(9) - y(3)*y(8) + y(5)*y(12) - y(6)*y(11)
  c then the y-component
  c amy = y(3)*y(7) - y(1)*y(9) + y(6)*y(10) - y(4)*y(12)
and the z-component

\[ amz = y(1)y(8) - y(2)y(7) + y(4)y(11) - y(5)y(10) \]

finally the magnitude ...

\[ angmom = \text{dsqrt}(amx**2 + amy**2 + amz**2) \]

return
end
Appendix 3

Fortran Functions for Parameterized 1 A' and 3 A' K + NaCl Potential Energy Surfaces

c

double precision function v1a(r1,r2,r3)
implicit real*8 (a-h,o-z)
external vd1a, vd3a
here 'a' denotes electronic symmetry
c
c calculates the diagonalized potentials (adiabatic)
c
c yamashita and morokuma's parameters
c xlam = 700 nm
c hbar w = h c / xlam

c = 4.1356692e-15 eV*s * 2.99792458e10 cm/s / 7.e-5 cm

c = 1.2398424e-4 / 7.e-5 = 1.7712 eV

c xmu12 = 5 au elaser ~ 14 MW/cm**2
c d12 = 0.1 kcal/mol = 4.3364e-3 eV

d12 = .00004184d0
c

c = vd1a(r1,r2,r3)
c = vd3a(r1,r2,r3)
rt = dsqrt((vd3-vd1)**2 + 4.d0*d12**2)
c

c choose '+' combination
c
c = (vd3+vd1+rt)/2.d0
c

c return
c end

c

double precision function vd1a(r1,r2,r3)
implicit real*8 (a-h,o-z)
c

units: eV and Angstroms

diatomic ordering: 1 = KCl, 2 = NaCl, 3 = NaK

two-body coefficients

data re1,de1,bet1/2.666650d0,4.357d0,0.7842d0/
data re2,de2,bet2/2.360795d0,4.253d0,0.8969d0/
data re3,de3,bet3/3.5890d0,0.6277d0,0.8084d0/

three-body coefficients

data c1,c2,c3/0.198778d0,-0.036033d0,0.090965d0/
data c11,c22,c33,c12,c13,c23/0.076110d0,-0.036935d0, & -0.024975d0,-0.050197d0,0.022358d0,-0.041010d0/
data c111,c222,c333,c112,c113,c122,c223,c333,c123 & /-0.030233d0,0.012623d0,0.05095d0,0.082639d0,-0.000953d0, & 0.017681d0,-0.014992d0,-0.020310d0,-0.032535d0,0.046938d0/
data c1111,c2222,c3333,c1112,c1122,c1222,c1133,c1333,c2223, & c2233,c2333,c1233,c1233/0.008882d0,0.000315d0,-0.010586d0, & -0.081555d0,-0.034071d0,-0.010884d0,-0.023786d0,0.016267d0, & 0.002650d0,-0.001072d0,0.002806d0,0.009235d0,-0.033808d0, & -0.005758d0,0.010545d0/
data vd0/3.78405d0/
data gam1,gam2,gam3/0.953050d0,0.632566d0,0.304351d0/
data r10,r20,r30/2.91047d0,2.64589d0,3.75890d0/

initial definitions

rho1 = r1 - r10
rho2 = r2 - r20
rho3 = r3 - r30

monoatomic term energy

vd1a = 0.d0

add diatomic terms

x = dexp(-bet1*(r1-re1))
vd1a = vd1a + de1*(x*x-2.d0*x)
x = dexp(-bet2*(r2-re2))
vd1a = vd1a + de2*(x*x-2.d0*x)
x = dexp(-bet3*(r3-re3))
vd1a = vd1a + de3*(x*x-2.d0*x)

add triatomic terms (see p. 65 of Murrell, Carter, Farantos, ...)

\[ p = 1.d0 + c1*rho1 + c2*rho2 + c3*rho3 + c11*rho1**2 + c22*rho2**2 + c33*rho3**2 + c12*rho1*rho2 + c13*rho1*rho3 + c23*rho2*rho3 + c111*rho1**3 + c222*rho2**3 + c333*rho3**3 + c112*rho1**2*rho2 + c122*rho1*rho2**2 + c133*rho1*rho3**2 + c223*rho2**2*rho3 + c233*rho2*rho3**2 + c123*rho1*rho2*rho3 \]
& + c1111\*rho1**4 + c2222\*rho2**4 + c3333\*rho3**4
& + c1112\*rho1**3\*rho2 + c1122\*rho1**2\*rho2**2 +
c1222\*rho1\*rho2**3
& + c1113\*rho1**3\*rho3 + c1133\*rho1**2\*rho3**2 +
c1333\*rho1\*rho3**3
& + c2223\*rho2**3\*rho3 + c2233\*rho2**2\*rho3**2 +
c2333\*rho2\*rho3**3
& + c1123\*rho1**2\*rho2\*rho3
& + c1223\*rho1\*rho2**2\*rho3
& + c1233\*rho1\*rho2\*rho3**2
& 1-tanh(x) = 2/(1+exp(2x))
vd1a = vd1a + v0*p**8/(1.d0+dexp(gam1*rho1))
& /(1.d0+dexp(gam2*rho2))
& /(1.d0+dexp(gam3*rho3))

c
return
end

c
double precision function vd3a(r1,r2,r3)
implicit real*8 (a-h,o-z)

c
units: eV and Angstroms

c
diatomic ordering: 1 = KCl, 2 = NaCl, 3 = NaK

c
one-body coefficients
data v1,alp/0.49250d0,0.74092d0/

two-body coefficients
data re1,de1,bet1/2.666650d0,4.357d0,0.7842d0/
data re2,de2,bet2/2.360795d0,4.253d0,0.8969d0/
data re3,de3,bet3/4.06600d0,0.7628d0,0.4717d0/

c
three-body coefficients
data c1,c2,c3/0.205791d0,0.042534d0,-0.085309d0/
data c11,c22,c33,c12,c13,c23/0.10090d0,0.042503d0,
& 0.06007d0,0.026918d0,-0.098156d0,-0.127513d0/
data c111,c222,c333,c112,c122,c113,c133,c223,c233,c123
& -0.022723d0,-0.010684d0,0.004823d0,0.092104d0,-0.001266d0,
& -0.037563d0,0.025610d0,0.010948d0,-0.003532d0,0.000320d0/
data c1111,c2222,c3333,c1112,c1122,c1113,c1133,c1333,c2223,
& c2333,c2333,c1123,c1223,c1233,0.011983d0,0.005664d0,-0.002276d0,
& -0.044890d0,0.001567d0,-0.012746d0,-0.001327d0,-0.017369d0,
& 0.010997d0,-0.006059d0,0.000223d0,0.002648d0,-0.032377d0,
& -0.044707d0,0.003829d0/
data vo/0.37092d0/
data gam1,gam2,gam3/0.890710d0,0.736573d0,0.035073d0/
data r10,r20,r30/2.96339d0,2.69880d0,5.23217d0/

c

initial definitions

c
rho1 = r1 - r10
rho2 = r2 - r20
rho3 = r3 - r30

c
monatomic term energy

c 1-tanh(x) = 2/[1+exp(2x)]
c K* excitation energy is either 1.6104 eV or 1.6176 eV
   vd3a = 1.61040 + v1/(1.+dexp(all*(3.d0*rho1-rho2-rho3)))

c
add diatomic terms

x = dexp(-bet1*(r1-re1))
vd3a = vd3a + de1*(x*x-2.d0*x)
x = dexp(-bet2*(r2-re2))
vd3a = vd3a + de2*(x*x-2.d0*x)
x = dexp(-bet3*(r3-re3))
vd3a = vd3a + de3*(x*x-2.d0*x)

c
add triatomic terms (see p. 65 of Murrell, Carter, Farantos, ...)
rho1 = r1 - r10
rho2 = r2 - r20
rho3 = r3 - r30
p = 1.d0 + c1*rho1 + c2*rho2 + c3*rho3
   & + c11*rho1**2 + c22*rho2**2 + c33*rho3**2
   & + c12*rho1*rho2 + c13*rho1*rho3 + c23*rho2*rho3
   & + c111*rho1**3 + c222*rho2**3 + c333*rho3**3
   & + c112*rho1**2*rho2 + c122*rho1**2*rho2
   & + c113*rho1**2*rho3 + c133*rho1**2*rho3
   & + c233*rho2**2*rho3 + c233*rho2*rho3
   & + c123*rho1*rho2*rho3
   & + c1111*rho1**4 + c2222*rho2**4 + c3333*rho3**4
   & + c1112*rho1**3*rho2 + c1122*rho1**2*rho2**2 +
   c1222*rho1**2*rho2**3
   & + c1123*rho1**2*rho3 + c1133*rho1**2*rho3**2
   & + c1333*rho1**2*rho3
   & + c2233*rho2**2*rho3 + c2233*rho2*rho3
   & + c3333*rho2**2*rho3**2
   & + c1233*rho1**2*rho2**2*rho3
   & + c1123*rho1*rho2**2*rho3
   & + c1223*rho1*rho2*rho3**2
   & + c1233*rho1*rho2*rho3**2

1-tanh(x) = 2/[1+exp(2x)]
vd3a = vd3a + v0*p8/(1.d0+dexp(gam1*rho1))
   & /((1.d0+dexp(gam2*rho2))
   & /((1.d0+dexp(gam3*rho3))

return
end