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Kinetics and dynamics of azoalkane photofragmentation: Direct studies using transient CARS spectroscopy

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Rice University, 1990
RICE UNIVERSITY

KINETICS AND DYNAMICS OF AZOALKANE PHOTOFRAGMENTATION:
DIRECT STUDIES USING TRANSIENT CARS SPECTROSCOPY

by

KATHERINE ANN BURTON

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

DOCTOR OF PHILOSOPHY

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September, 1989
Abstract

Kinetics and Dynamics of Azoalkane Photofragmentation: Direct Studies Using Transient CARS Spectroscopy

by

Katherine Ann Burton

A fundamental and long-standing question surrounds the mechanism of primary bond cleavage in azoalkanes: do the two C-N bonds break in a synchronous or a stepwise manner? When a vapor phase azoalkane absorbs near ultraviolet light, it dissociates into two alkyl radicals and nitrogen. Transient CARS spectroscopy was used here as a time-resolved probe of the photoproducts formed from azoalkanes excited at 355 nm. In a detailed reinvestigation, azomethane was found to dissociate in a stepwise process involving a methyl diazenyl radical intermediate. The diazenyl intermediate was formed in less than 1 ns and lived for 5.3 ± 1 ns before fragmenting into a methyl radical and nitrogen. Kinetic studies on azoisopropene (AIP) also gave evidence for stepwise photodissociation with a similar diazenyl lifetime. The first methyl radical formed in azomethane photodissociation was found to have 0 to 4 quanta of \( v_2 \) excitation, whereas the second methyl radical was predominantly vibrationally unexcited. The nascent rotational temperature of \( N_2 \) from azomethane was found to be 2500 K, and its vibrational distribution was confirmed to be 84% in \( v=0 \) and 16% in \( v=1 \). These results seem consistent with predictions based on the transition state structure computed for methyl diazenyl dissociation. Internal energy distributions were also measured for the nitrogen formed from 3-(methylazo)-3-methyl-butene (MAMB), which was previously shown to undergo stepwise dissociation through a methyl diazenyl intermediate. The rotational and vibrational energy distributions from MAMB were almost identical to those from azomethane, consistent with a common dissociation mechanism. AIP also gave similar nitrogen rotational and vibrational distributions, suggesting that the
dissociative transition state of isopropyldiazenyl is similar to that of methyldiazenyl. In summary, direct kinetic measurements have demonstrated stepwise gas phase photodissociation in acyclic azoalkanes. Related measurements of product internal energy distributions should form the basis for a detailed dynamical understanding.
Acknowledgements

I would like to acknowledge all the people involved in this work. No project like this could be done alone, and I would like to thank my colleagues and friends who made this thesis possible. Without the scientific insight and wisdom of my advisor, Bruce Weisman, I could not have done this work, and I cannot thank him enough. I thank Jodye Selco for teaching me the ways of graduate school and for her friendship throughout the years. I thank Pat Holt for his patience, kindness and wit; I learned from him that graduate school and research could be exciting and fun. I also thank Keith McCurdy for his patience in teaching me the ways of CARS.

Steve Adams has been my good friend as well as my partner in a number of experiments. His companionship and scientific knowledge have made research enjoyable, and I look forward to working with him again at NRL. I would also like to thank Steve for preparing some of the azo samples. I would like to thank James Miller for his help in taking the azo-n-propane data as well as for his undying friendship. Meg Fraelich has been a wonderful friend, and I regret that I did not have a chance to work with her.

Kim Andrews has provided invaluable assistance. He has written many of the computer programs used to acquire and process the data. Without his hacking ability, the lab computers would still be in the dark ages. I would also like to thank him for performing quantum chemical calculations and preparing some of the azo samples. I thank Joe Stout for maintaining the lab computers. I thank Anne Culotta for preparation of azoalkane samples. I would like to thank Dr. Paul Engel for many helpful discussions.

Most of all, I would like to thank my family, and I dedicate this thesis to them. Without my parents’ continual love and support, graduate school would have been nearly impossible. Peg and Gord, I love you and thank you.
My final thanks go to my husband, Greg Lynn. I hope that throughout our marriage and careers that I can be as loving and supportive with you as you have been with me.
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Chapter 1

Introduction

Photochemistry is a unique and fascinating field of study dealing with chemical reactions that occur when light interacts with molecules. It is a broad discipline that covers topics as diverse as photosynthesis, which allows plants to harness the energy of the sun, and the critical problem of depletion of the ozone layer.

Observations on the nature of the interaction of light with molecules led scientists to formulate the two laws of photochemistry (Calvert and Pitts, 1966). The first law, put forth more than a century ago in the works of Grotthus in 1817 and Draper in 1843, states: Only the light which is absorbed by a molecule can be effective in producing photochemical change. This law and its consequences are now such a part of general chemical understanding that they are taken for granted by modern chemists. The second law of photochemistry was deduced by Einstein in 1913 and later refined by Stark and Bodenstein. It states: The absorption of light by a molecule is a one-quantum process, so that the sum of the primary process quantum yields must be unity. However, in the limit of very high light intensity, the second law breaks down and molecules can and do absorb more than one photon of light.

The nature of photochemistry has changed since the formulation of the two laws. The development of narrow-bandwidth and short pulse lasers has enabled chemists to prepare and study molecules in great detail. A class of organic molecules of particular interest to photochemists are the azoalkanes.
Azoalkanes are a class of compounds in which the nitrogens of the azo group (-N=N-) are bonded to saturated carbons.

\[ \text{cis} \quad \text{trans} \]

The alkyl group (R) may be unsaturated. Azoalkanes can be acyclic, such as the simplest azoalkane, azomethane, or cyclic such as 2,3-diazabicyclo(2.2.1)hept-2-ene (DBH). The work presented here is on acyclic azoalkanes.

Azomethane

\[ \text{DBH} \]

Azoalkanes have been known since the turn of the century (Thiele, 1909). They dissociate to lose N\(_2\) and the two R groups both thermally and photolytically under a wide variety of conditions. Azo compounds are probably the cleanest and most convenient source of radicals and biradicals with nearly any desired structure. Azo compounds have been studied extensively over the last 30 years, and a number of excellent reviews have been written concerning their thermal and photochemical behavior (Strausz et al., 1972; Engel and Steel, 1973; Patai, 1975; Engel, 1980). Only a brief discussion of their relevant properties will be presented here.
One of the key questions concerning the azoalkanes is the nature of the primary bond cleavage. Do the C-N bonds break synchronously to form $2R + N_2$ or stepwise, through a diazenyl intermediate?

**Synchronous**

$$ R \quad \text{N} = \text{N} \quad R' \quad \xrightarrow{\text{hv}} \quad N_2 + \cdot R + \cdot R' $$

**Stepwise**

$$ R \quad \text{N} = \text{N} \quad R' \quad \xrightarrow{\text{hv}} \quad \cdot N \quad \text{N} \quad R' \quad + \cdot R $$

$$ \cdot N \quad \text{N} \quad R' \quad \rightarrow \quad N_2 + \cdot R' $$

Whether this reaction proceeds through a diazenyl radical was asked early in azoalkane research (Ramsperger, 1929). Ramsperger compared the $E_a$ for the thermal dissociation of azomethane, 3-methylazo-2-methyl-propane and azoisopropane (AIP). He found that the $E_a$ of the unsymmetrical azo fell between that of the two symmetrical compounds and concluded that both C-N bonds break at once.

<table>
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<td>51.2</td>
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Unfortunately the $E_a$ used for AIP by Ramsperger was incorrect. The best value is 47.9 kcal/mol (Perona, *et al.*, 1973). Using Ramsperger's argument and assuming that the other $E_a$s are reliable, these results would indicate a sequential mechanism.

Since Ramsperger's work, much effort has been spent trying to decide between a synchronous and a sequential mechanism, particularly for the thermolysis of the azo compounds. The rate of thermolysis of azoalkanes is mainly determined by the stability of the first alkyl radical produced in the dissociation. The Ramsperger criterion has been applied to many azos. The free energies of activation have been determined for a number of symmetrical and unsymmetrical azoalkanes. The conclusion from this body of work is that an unsymmetrical azoalkane cleaves by a stepwise mechanism since the different R groups cause the two C-N bonds to be stretched unequally (Engel, 1980). The mechanism for the bond cleavage of a symmetric azoalkane has never been determined.

A variety of other techniques have been employed to determine the nature of the mechanism. These more recent efforts also support a sequential bond cleavage for an unsymmetrical azoalkane. The formation of "turnaround" photoproducts from allylic azos such as 3-(methylazo)-3-methyl-1-butene (MAMB) has been observed, which indicates the presence of the diazenyl intermediate in solution phase thermolysis (Engel and Gerth, 1983). The involvement

![Chemical Structure](image)

MAMB
of the diazenyl radical was also deduced from experiments of the thermal dissociation of unsymmetrical phenylazos (Tsolis et al., 1972; Green et al., 1977; Porter et al., 1978). The decomposition of N-cumyl-N'-1-norbornyl diazene was studied using $^{15}$N CIDNP (Chemically Induced Dynamic Nuclear Polarization). The presence of the transient intermediate 1-norbornyl diazenyl radical was suggested and this diazenyl radical was subsequently trapped using triphenylmethyl. Perhaps the most conclusive demonstration of a one bond cleavage was in the transient CARS study of the photodissociation of gas phase MAMB (Adams, 1989; Adams et al., 1986), in which the appearance rates of all three primary photoproducts were observed. The 1,1-dimethylallyl fragment was formed promptly whereas the N$_2$ and methyl radical were delayed following the decay of an intermediate having a lifetime of 12 ns. There is no direct evidence of a diazenyl intermediate in the dissociation of a symmetrical acyclic azoalkane.

The photolysis of azoalkanes in the gas phase has been known for at least 50 years as an efficient means of producing free radicals. The quantum yield for photodissociation is dependent on pressure. In the low pressure regime, the quantum yield is one. As the pressure is increased, either by adding more azo or an inert gas, the quantum yield decreases, and photoisomerization becomes the dominant channel. In the solution phase, isomerization is the primary result of irradiation, with the quantum yield for dissociation of acyclic azo compounds being usually falling below 0.1 (Fogel and Steel, 1976). In fact, the irradiation of acyclic azoalkanes at low temperature is a common method for generating the cis isomer. The cis isomer is inherently less stable than the trans isomer, and many cis azo compounds undergo thermolysis at low temperatures. If an $\alpha$ hydrogen is present tautomerization to the more stable hyrazone is much more pronounced with the cis than the trans isomer (Engel, 1980).
The absorption spectra of the azoalkanes are well known and have been analyzed in depth (Rau, 1973; Robins, 1974). Most azoalkanes exhibit a weak absorption in the near UV (300-400 nm) corresponding to an n→π* transition. The extinction coefficient for the cis isomer is generally 10 times larger than for the trans. This difference can be understood by considering the molecular orbitals of the isomers. The n→π* transition is of \(a_g\rightarrow b_g\) local symmetry, which is dipole forbidden. The corresponding transition in the cis isomer is of \(b_1\rightarrow a_2\) symmetry and is dipole allowed. It has been argued that the transition in the cis is not as strong as expected because of poor spatial overlap between the n and π* orbitals (Robin, 1974). Below 270 nm there is a more intense allowed transition whose nature has been the subject of some discussion and is thought to be a Rydberg transition (Robin, 1974).

While the mechanism for dissociation of azo compounds in solution has been studied in detail, most studies of the chemistry in gas phase have been primarily concerned with determining which excited states are involved. High pressure studies of the photodissociation of various azoalkanes have found curvatures in the Stern-Volmer plots (plots of \(\Phi_d^{-1}\) vs. concentration) implying that more than one excited state is involved in the dissociation (Worsham and Rice, 1967; Pritchard and Servedio, 1975). There is much controversy in the literature concerning which states are involved and a number of different mechanisms have been suggested (Chervinsky and Oref, 1977;
Pritchard et al., 1976; Collier et al., 1968). A model which adequately describes the gas and solution dissociation as well as isomerization has yet to be found (Engel, 1980).

The goal of the studies described here is to determine the mechanism for the gas phase, near UV photodissociation of selected symmetrical azoalkanes. This goal requires a technique that will excite the azoalkane samples and after a short delay, preferably in the nanosecond range, probe for the photofragments. Since neither fluorescence nor phosphorescence has ever been observed for a acyclic azoalkane, it is difficult to monitor directly the excited states involved in the photodissociation (Engel, 1980). A pump and probe technique that would allow direct observation of all of the photoproducts would be valuable for determining the mechanism.

The technique of "flash photolysis" was first developed by Norrish and Porter (1949), and later refined by other scientists including Herzberg and Ramsay (1952). In flash photolysis, an intense pulse of light is passed into an absorbing sample medium to form a high concentration of intermediates. The nature of these intermediate species is then probed using a rapid spectroscopic method. In its conventional form, flash photolysis utilizes a broad band visible and ultraviolet flash to excite the sample, and after a delay of microseconds, a second flash to interrogate the excited sample. The utilization of laser and computer technologies has, over the years, changed the face of flash photolysis, and now time resolution in the femtosecond range is attainable. In using flash photolysis to determine the mechanism for the gas phase photolysis of symmetric azoalkanes, it would be desirable to study the photoproducts and precursors.

For detecting the nitrogen and alkyl radical photoproducts of azoalkanes, an electronic absorption spectroscopy would be very inconvenient because of the inconveniently short wavelengths required. The first absorption band of the methyl radical occurs at 216 nm (Herzberg, 1961) and nitrogen does not absorb wavelengths
greater than 150 nm (Okabe, 1978). Because of this a time-resolved vibrational probe of the product species was chosen. Transient CARS (coherent anti-Stokes Raman spectroscopy), a nonlinear form of Raman spectroscopy, in principle allows detection of nitrogen, the diazenyl intermediate, and alkyl radicals.
Chapter 2
Experimental

Introduction

In order to determine the mechanism for the gas phase photodissociation of symmetricalazoalkanes, an apparatus is needed that will probe the for the photoproducts with nanosecond time resolution. A high performance transient absorption apparatus had been built in this lab to study photophysical processes on the nanosecond scale (Weisman et al., 1983). This apparatus was modified by previous workers to perform coherent anti-Stokes Raman spectroscopy experiments (Holt, 1984). The purpose of this apparatus was to allow the study of transient species both in collisional and precollisional environments.

This apparatus is based on two Nd:YAG laser systems that operate at 10 Hz with a computer controlled delay between the firing of the two lasers. This system uses one laser system to excite the sample, and then, after a delay of 0 to 1000 ns, probes the excited sample with the second laser system. This pump and probe system allows direct time-resolved CARS observation of photochemical processes.

A brief description of CARS theory will be presented here, followed by a description of the apparatus and the computer controlled data acquisition and analysis systems.

CARS Theory

In 1928, C. V. Raman first observed that when dust-free samples were irradiated with light of a single frequency, they scattered light not only of the incident frequency (Rayleigh scattering), but also of different frequencies (Raman, 1928). This Raman process is an inelastic photon-scattering phenomenon in which the medium absorbs a photon while simultaneously emitting one of higher or lower frequency. This difference
in frequency usually corresponds to the energy difference between rotational or vibrational levels in the sample molecule. The importance of this effect was immediately recognized by early investigators, and Raman spectroscopy has for many years been an important spectroscopic tool in the study of molecular structures. The Raman effect is particularly useful in that it allows observation of transitions in which the dipole matrix element vanishes, such as for totally symmetric vibrations or molecules with inversion symmetry. As a result, Raman spectroscopy has proven to be a valuable complement to traditional Infrared spectroscopy.

Unfortunately, the inelastic light scattering process is extremely inefficient, and even with laser sources, low Raman intensities have remained problematic. The Raman output is frequently masked by sample fluorescence, and Raman studies of transient phenomenon are particularly difficult. CARS is a relatively new form of Raman spectroscopy that overcomes some of the problems associated with the low efficiency of spontaneous Raman scattering.

CARS is a nonlinear form of Raman spectroscopy. Consider a sample with Raman-active vibrational mode $\omega_v$. If two collinear beams of frequencies $\omega_1$ and $\omega_2$ (hereafter called "laser" and "Stokes" beams respectively) such that $\omega_1 - \omega_2 = \omega_v$, are passed through the sample, a new wave is generated at the frequency $\omega_3$. This anti-Stokes frequency, where $\omega_3 = \omega_1 + (\omega_1 - \omega_2) = 2\omega_1 - \omega_2$ is generated in the forward direction and is collinear with the two pump beams. This new wave results from the inelastic scattering of the wave at $\omega_1$ by the molecular vibrations coherently driven by the waves $\omega_1$ and $\omega_2$ (Druet and Taran, 1979). For reasons of symmetry, this same mechanism creates a similar wave at $2\omega_2 - \omega_1$, CSRS (coherent Stokes Raman scattering). CSRS has been observed and is sometimes used for spectroscopic purposes.
despite experimental difficulties involving poor detector efficiencies for the induced signal and difficulties in separating the signal from the background light.

CARS was first observed by Terhune (1963) as a by-product of stimulated Raman scattering. The three wave mixing process that was responsible for the observed effect was later described by Bloembergen and Shen (1965) and experimentally verified by Maker and Terhune (1965). The first CARS experiments were carried out using ruby lasers. One ruby laser would produce the "laser" frequency and the Stokes frequency would be generated by stimulated Raman scattering using a second ruby laser. This arrangement made scanning over various Raman modes impossible, and it was not until the development of the tunable dye laser that the field of CARS spectroscopy blossomed.

In a more general description, CARS is a three-wave mixing of electric fields, $\omega_1$, $\omega_j$, and $\omega_k$, such that $\omega_3 = \omega_1 - \omega_j + \omega_k$. In most CARS experiments $\omega_1 = \omega_k$, and $\omega_1$ is held fixed while $\omega_j$ is scanned over the Raman resonance and $\omega_3$ is detected to measure the CARS spectrum. A brief discussion of the theory behind CARS will be given here. A more complete account can be found elsewhere (Valentini, 1985; Nibler and Knighten, 1979; Tolles et al., 1977; Druet and Taran, 1981).

The conversion of the two input beams into the coherent anti-Stokes component at $2\omega_1 - \omega_2$ is a direct consequence of the nonlinear dielectric properties of materials. The polarization of a medium in an electric field can be expanded in a power series

$$P(\omega) = \chi^{(1)}(\omega)E(\omega) + \chi^{(2)}(\omega)E^2(\omega) + \chi^{(3)}(\omega)E^3(\omega) + \cdots \quad (1)$$

where $P(\omega)$ is the macroscopic polarization vector, $\chi^{(i)}$ is the dielectric susceptibility tensor of rank $i + 1$ associated with the $i^{th}$ order electric field, and $E$ is the applied electric field. In the limit of low field intensity, only the first term is important and it is the basis of linear optical response. The higher terms of the polarization become important only in the regime of high field intensities, which explains why the entire area of nonlinear optics
boomed after the advent of the laser. The second term, which depends of the square of
the field strength, is responsible for second harmonic generation, the hyper-Raman effect,
and other effects. Because this term is identically zero for an isotropic medium, these
second-order effects cannot exist in a liquid or a gas. The third-order term is responsible
for a number of effects including third harmonic generation and CARS.

The electric dipole moment, $\mu$, induced in a molecule or an atom by an electric
field can be expanded as a power series

$$\mu = \alpha E + \beta E^2 + \gamma E^3 + \ldots.$$  \hspace{1cm} (2)

The coefficients $\alpha$, $\beta$ and $\gamma$ etc. are tensor quantities, corresponding to the fact that the
induced dipole vector may point in a different direction from that of the applied field.
The polarizability $\alpha$ and the hyperpolarizabilities $\beta$ and $\gamma$ are tensors of the order $i + 1$
associated with the $i$th order electric field. The polarization $P$ is related to the induced
dipole by

$$P = N\mu$$  \hspace{1cm} (3)

where $N$ is the particle density. The dielectric susceptibilities are related to the molecular
polarizabilities by

$$\chi^{(1)} = N\alpha \quad \chi^{(2)} = N\beta \quad \chi^{(3)} = N\gamma.$$  \hspace{1cm} (4)

It is important to recognize how the dielectric susceptibility tensors and the molecular
polarizabilities are related, since the theoretical description of the effect of an intense
electric field of a molecule deals with the molecular properties, while experimental
observations are by necessity macroscopic. Only the $\chi^{(3)}$ term will be considered for the
rest of this discussion.
Assuming that the applied electric field is made up of harmonic components that are plane waves, an electric field can be written

$$E(r,t) = (1/2) \sum [E(\omega_j,r)\exp(iK_j r - \omega_j t) + \text{c.c.}]$$

(5)

where $|K_j| = \omega_j n_j/c$ with $n_j$ the index of refraction at $\omega_j$ and $c$ the speed of light. Since coherent anti-Stokes Raman scattering involves up to three distinct frequencies $j$, the sum is over $j = 1 - 3$. Rewriting equation 5 for all three different frequencies and inserting it into equation 1 yields

$$P^{(3)}(r,t) = (1/8) \sum \chi^{(3)} E(\omega_1,r)E(\omega_2,r)E(\omega_3,r)$$

$$\times \exp[i(K_i + K_j + K_k)r]\exp[-i(\omega_i + \omega_j + \omega_k)t]$$

(6)

It is now obvious that the polarization will have frequency components at $\omega_2 = \omega_i + \omega_j + \omega_k$. $\omega_i$, $\omega_j$, and $\omega_k$ can be either positive or negative. Thus $P^{(3)}$ can have many frequency combinations; $3\omega_i$, $3\omega_j$, and $3\omega_k$ correspond to third harmonic generation, $\omega_i + \omega_j + \omega_k$ gives frequency summation, and $\omega_i + \omega_j + \omega_k$ ($\omega_i > \omega_j$) yields the CARS process.

To determine the magnitude of the generated CARS signal, the amplitude of the electromagnetic wave generated at $\omega_3$ needs to be determined. Using Maxwell’s equations, assuming no dispersion in the sample and recognizing that the intensity is related to the electric field amplitude by

$$I(\omega) = (c/8\pi) |E|^2$$

(7)

one can deduce that

$$I_3(L) = (12\pi^2\omega_2/c^2)^2(I_1)^2(I_2)|\chi^{(3)}|^2 L^2$$

(8)

where $L$ is the length of the sample and $I_1$ is the intensity of the beam at frequency $\omega_1$.

This result illustrates some important characteristic features of CARS. The signal intensity scales as the square of the intensity of the $\omega_1$ beam and is directly proportional to the intensity of $\omega_1$. It is easy to see how the efficiency of CARS would be greatly enhanced.
by using pulsed, high peak power lasers. This equation, unfortunately, gives an unrealistic relationship between the sample length L and the intensity $I_3(L)$. It would appear that the intensity of the CARS beam increases indefinitely with sample length. This error is due to the neglect of the dispersive properties of the medium. In fact the intensity varies with the path length according to the following relation:

$$I_3(L) = \frac{(12\pi^2\omega_2/c^2)^2\Omega_1^2\Omega_2^2|\chi^{(3)}|^2}{2L^2} \times \left(\frac{\sin(\Delta kL/2)}{(\Delta kL/2)}\right)^2$$

(9)

where $\Delta k = 2k_1 - k_2 - k_3$. $\Delta k = 0$ is the so called phase matching condition for which the signal is a maximum. In low pressure gases, where the dispersion is negligible, the phase matching condition may be satisfied by more than one configuration of the input beams, but the signal is at a maximum when the beams are collinear. In samples with non-negligible dispersion, the phase matching condition occurs when the beams are crossed at a specific angle. If the beams are assumed to be gaussian rather than plane waves, a more reasonable dependence on sample length can be determined. It can be shown (Valentini, 1985) that equation 9 will be valid if the sample length is smaller than the beam confocal parameter $b$, given by

$$b = \frac{2\pi(d_0)^2}{\lambda}$$

(10)

where $\lambda$ is the wavelength and $d_0$ is given by

$$d_0 = 4\lambda f/\pi d$$

(11)

where $f$ is the focal length, and $d$ is the beam diameter at the focusing lens. Although more rigorous theoretical analyses have been carried out on third order processes (Bjorklund, 1975; Shaub et at., 1977), this description is adequate for understanding CARS at an experimental level. To determine how the CARS signal is dependent on the sample being studied, the magnitude and nature of $\chi^{(3)}$ needs to be determined.
The effect of an intense electric field on a medium is to polarize that medium in a nonlinear fashion. The magnitude of the third-order susceptibility is a measure of the conversion efficiency of the CARS process at \(2\omega_1 - \omega_2\). This partial conversion of the laser and Stokes beams into the anti-Stokes component takes place in any material, including the noble gases. However, this conversion efficiency increases greatly when the difference between the laser and Stokes frequencies corresponds to a Raman resonance of the medium.

The simplest approach to determining the relationship between \(\chi^{(3)}\) and the spectral properties of spontaneous Raman scattering is given by Tolles et al. (1977). The resonant frequency \(\omega_o\) is treated as a damped harmonic oscillator, and following Placzek's treatment, Tolles relates the linear polarizability tensor \(\alpha\) of the molecule to the harmonic oscillator coordinate \(q\):

\[
\alpha = \alpha_0 + (d\alpha/dq)_0 q + \ldots
\]

If this oscillator is put in the presence of an electric field it can be shown (Valentini, 1985) that the polarization of the medium is related to the square of \(d\alpha/dq\). The differential Raman cross section \(d\sigma/d\Omega\) is related to \((d\alpha/dq)_0^2\) by

\[
(d\alpha / dq)_0^2 = (2 m \omega_o c^4 \pi^2 / h(\omega_o)^4) (d\sigma/d\Omega)
\]

Recalling that the intensity of the CARS signal is related to \(|\chi^{(3)}|^2\), the following expression can be derived (Tolles et al., 1977) for a signal at a Raman resonance:

\[
|\chi^{(3)}|^2 = (N \Delta_o c^4 \pi^2 / h(\omega_o)^4)^2 (d\sigma/d\Omega)^2 (1/\Gamma_o)^2.
\]

Thus the magnitude of the CARS signal depends on the square of the spontaneous Raman cross section, the square of the difference in population between the two states involved \((\Delta_o)\), and the square of the linewidth of the Raman transition \((\Gamma_o)\).

As was mentioned earlier, the coherent anti-Stokes process which generates the anti-Stokes signal at \(\omega_3 = 2\omega_1 - \omega_2\) is greatly enhanced when \(\omega_1 - \omega_2 = \omega_o\), a Raman
active transition. The total susceptibility is therefore composed of resonant
(corresponding to the enhancement at \(\omega_c\)) and frequency-independent nonresonant
components:

\[
\chi^{(3)} = \chi^{\text{res}} + \chi^{\text{NR}}.
\]  
(15)

For simplicity, the (3) superscript will be omitted from future discussion. It is important
to realize that off-resonance, or if the number of species with a resonant signal is small,
the magnitude of the susceptibility is governed by the nonresonant term, which usually
arises from a solvent or a buffer gas. Because of this, CARS can be used not only for
measuring Raman transitions, but also for detecting bulk properties of a medium.
Unfortunately, this nonresonant component can also limit the sensitivity of the CARS

The resonant portion of the third-order susceptibility is composed of a real and an
imaginary part:

\[
\chi^{\text{res}} = \chi' + i\chi''
\]  
(16)

For a simple resonance, the imaginary and real components have the form where the real
component of the susceptibility has a derivative shape centered on the lorentzian that
describes the imaginary component. If the square of \(\chi^{\text{res}}\) is plotted, a simple lorentzian
line shape, similar to that of the spontaneous Raman line shape, is obtained. However, if
there is also present a large amount of material that possesses broad nonresonant
component (\(\chi^{\text{NR}}\), a significantly distorted line shape results. This distortion occurs
because the nonresonant portion of the signal can couple with the real part if the resonant
component as seen below:

\[
|\chi^{(3)}|^2 = (\chi' + \chi^{\text{NR}})^2 + (\chi'')^2
= (\chi')^2 + 2\chi'\chi^{\text{NR}} + (\chi^{\text{NR}})^2 + (\chi'')^2.
\]  
(17)
The mixing term $2\chi'\chi^{NR}$ adds an asymmetric shape to the CARS spectrum. This term also has the interesting effect that if the nonresonant component becomes large in comparison to the resonant terms, equation 17 becomes

$$\left|\chi^{(3)}\right|^2 = (\chi^{NR})^2 + 2\chi'\chi^{NR}. \quad (18)$$

In this limit, the CARS signal no longer depends on the square of the population difference in the resonant species.

It is important at this stage to clarify the nature of the CARS process. Consideration of a quantum-mechanical description of the hyperpolarizability $\gamma$ (the molecular description of $\chi^{(3)}$) by Valentini (1985), gives unrealistic behavior for the CARS process exactly on resonance. This phenomenon was explained by Druet and Taran (1981). They stated that CARS is actually two distinct processes interfering with each other. The first is a "parametric" process wherein two photons at $\omega_1$ are converted into one at $\omega_2$ and one at $\omega_3$ without exchanging any energy with the sample. This "parametric" process has been erroneously cited in the past as the only CARS process. The second process has been described by Bloembergen (1965) as the "Raman-like" process. This may be viewed as the interference between two separate Raman processes. One photon at $\omega_3$ is destroyed to produce a photon at $\omega_2$ and two vibrational quanta (Figure 1). This Raman-like process is the only one responsible for the anti-Stokes signal exactly at the peak of a Raman resonance.

There was debate in the early CARS literature as to the selection rules for the process. Even though CARS is related to the spontaneous Raman cross section, the fact that it is a nonlinear three-wave mixing process might lead one to suspect that there would be different selection rules for CARS and spontaneous Raman scattering. Hudson (1974) argued that slightly relaxed Raman selection rules applied, but an exact analysis
Figure 1. Energy level diagrams describing the CARS process. The illustrations show the difference between energy levels as compared with photon energies. Diagrams (a) and (b) describe the CARS process at the peak of a Raman resonance, whereas (c) describes the process off resonance. Note that $\omega_3$ in the text is denoted as $\omega_0$ in this figure.
by Yuratich and Hanna (1977) proved that the selection rules for CARS are exactly the same as those for ordinary Raman scattering.

While all molecular vibrations that are Raman active are also CARS active, there are several differences between ordinary Raman scattering and CARS that should be discussed. Combining equations 8 and 14, the power of the anti-Stokes beam is

$$P_3 = \left(96\pi^2 \omega_3^2 c/\hbar \omega_2^4\right)^2 (P_1)^2 (P_2)^2 (N\Delta v)^2 (d\sigma/d\Omega)^2 (1/\Gamma_v)^2.$$  \hspace{1cm} (19)

In ordinary Raman scattering, the power of the Raman signal is given by

$$P_{\text{raman}} = NL\Omega (d\sigma/d\Omega) P_1$$  \hspace{1cm} (20)

where $N$ is the number density, $L$ is the length of the focal region, and $\Omega$ is the solid angle collected (the output is scattered into $4\pi$ steradians). These equations demonstrate that the CARS signal increases rapidly with laser power, and since the output of the CARS is laser-like, collection efficiencies can be much greater for CARS than for normal Raman. These equations also indicate a disadvantage of CARS. The CARS output drops rapidly with number density and sensitivity is frequently a problem. Another advantage to CARS is that the bandwidth of the anti-Stokes signal is determined by the bandwidths of the input beams, and thus, a monochromator is not required to obtain spectral resolution.

The preceding discussion assumes that the two input beams are collinear, and that the coherent anti-Stokes beam emerge collinear with these two beams. This "collinear" CARS has the largest signal of any possible geometry which satisfies the phase matching condition, but it is not the only geometry that satisfies this condition. Another optical alignment of the beams that satisfies the phase matching condition is a technique known as folded BOXCARS (Shirley et al., 1980). In folded BOXCARS, the "laser" pulse is separated into 2 equal components in a plane, and the Stokes pulse is centered in a plane above the $\omega_1$ beams. When these beams are focused into the cell, they overlap, and the
resulting CARS signal is spatially separated from the input beams (Figure 2). This technique has a number of advantages over collinear CARS.

There are two major difficulties with collinear CARS. One is that the two beams produce a signal over the entire path of their overlap. To remove the background CARS signal that is generated before and after the sample cell, a number of filters are needed. These filters have the unfortunate inherent characteristic that they inhibit scanning to low Raman shifts, where the frequency of $\omega_1$ approaches that of $\omega_3$. The second problem is that since $\omega_3$ is collinear with the two inputs, a great deal of filtering is needed to remove the exclude light at $\omega_1$ and $\omega_2$. The CARS signal can be as much as 14 orders of spectral magnitude below the $\omega_1$ intensity, so this is no small feat. Folded BOXCARS gets around both of these problems by having the beams spatially separated. Very few special filters are needed to separate the scattered input beams from the CARS signal, and small Raman shifts can be studied. Unfortunately, because of its crossed-beam nature, the anti-Stokes power is lower than in collinear CARS. Calculations predict a loss of a factor of eight between collinear and BOXCARS, but in practice, a loss factor of 20 to 100 is more common (Valentini, 1985).

The experiments reported in this thesis were performed using a folded BOXCARS phase matching geometry with the transient CARS apparatus described in the following section.

APPARATUS

The backbone of our apparatus is two homemade Nd:YAG laser systems that generate the pump and probe pulses. The delay between the firing of the excitation pulse and the interrogating probe pulse is electronically controlled and can be varied between 0 and 1000 ns. The Stokes laser wavelength is varied independently of the delay, so each laser shot corresponds to a selected time delay and Raman frequency. The lasers and
Figure 2. Geometry that describes the optical paths for the probe beams in a folded BOXCARS alignment (A) and the resulting phase matching diagram (B). The subscripts denote beams: 1, "laser"; 2, Stokes; 3, CARS.
optics necessary for this apparatus will be described first, followed by a description of the photometry, sample handling and computerization.

**Lasers**

The two one meter long Nd:YAG oscillators operate at 1064 nm and were built following a Molecron design using Quantel laser heads. The excitation oscillator contains a Quantel model 411 head while the probe cavity has an older SF-410 head. All laser optics, CARS optics and the sample cell are rigidly fastened to a 5 x 10 foot Newport Corporation research grade optical table. The excitation cavity is an unstable resonator built for high energy extraction. The probe cavity is designed to operate TEM$_{00}$ because the CARS sensitivity and noise are critically dependent on the spatial quality of the "laser" and Stokes beams.

Both oscillators use polarization output coupling. The unstable resonator polarization-coupled design allows full utilization of the laser rod volume without producing the "doughnut mode" beam shape characteristic of diffraction-coupled resonators. The excitation and probe oscillators are equivalent except for their focusing optics and apertures. The excitation cavity has a planar front mirror and a 4 meter radius (convex) back mirror (nearest to the Pockels cells). Output coupling is controlled by an AR/AR coated quarter wave retardation plate and a thin film polarizer that reflects only vertically polarized light. Q-switching is achieved through a second AR/AR coated one-quarter wave plate adjacent to a Pockels cell (Inrad model 202-090). When there is no voltage on the Pockels cell, it behaves like a window and the polarization plane of the light which passing through the thin film polarizer is rotated 90 degrees by two passes through the quarter-wave plate and it is then rejected by the polarizer. When a suitably high voltage is applied to the Pockels cell, it behaves like a quarter-wave plate, and Q-switching is enabled. This optically biased Q-switch extends the lifetime of the
Pockels cell significantly since the quarter-wave voltage is applied only briefly to initiate lasing. The cavity also contains a weak converging lens (about 0.2 diopters) to compensate for the effects of the back cavity mirror plus thermal lensing in the rod. A 6 mm steel aperture centered along the beam axis defines the beam diameter and protects the optics from off-axis rays.

The probe oscillator has different cavity focusing since it is a stable TEM$_{00}$ resonator. The back mirror has a 8 meter (concave) radius of curvature, and the cavity is apertured to 3 mm to generate a high quality gaussian beam. The probe oscillator was found to be temperature sensitive, so that if the temperature fluctuated, the beam would not remain be TEM$_{00}$. This problem was traced to the thin film polarizer, the cavity's output coupler, which was humidity sensitive. When the temperature varied, the relative humidity in the lab also changed, and the polarizer angle for maximum discrimination between p and s polarized light also changed. This problem was solved by replacing the thin film polarizer with a Karl Lambrecht Glan-laser calcite prism polarizer. This prism polarizer solved the instability problem in the cavity. In the future, the thin film polarizer in the excitation oscillator should also be replaced with a temperature and humidity insensitive prism polarizer.

The capacitor banks and charging power supplies needed to drive the flashlamps in the heads are supplied by Quantel. A simple transistor-transistor logic (TTL) circuit delays the firing of the Pockels cell for Q-switching until maximum inversion in the laser rod has been obtained, about 100 μsec after the flashlamps fire. An analog delay generator (Evans Associates Model 4141) under computer control is triggered to produce reference and delayed TTL output pulses. The reference pulse triggers a 30-stage avalanche transistor Marx bank (Pulsar Associates) to generate the 3kV pulse needed to
drive the Pockels cell of the excitation laser. A second Marx bank is triggered from the
delayed output to fire the probe Pockels cell.

The output of the probe oscillator is usually about 110 mJ in a 10 ns pulse. The
spectral bandwidth of both resonators is about 1 cm⁻¹. The bandwidth of the probe laser
can be narrowed to less than .1 cm⁻¹ by inserting an intracavity etalon (1 cm⁻¹ free
spectral range, 50% reflecting at 1064 nm). The energy of the excitation oscillator is
approximately 250 mJ. In the past this cavity operated at closer to 350 mJ per pulse.
Recent alignments have shown that high energy is sacrificed when the cavity is adjusted
for the best beam quality. There are single-pass Nd:YAG amplifiers (Quantel model SF
410) for both the excitation and probe pulses. To generate the 10 mJ of third harmonic
light needed for excitation in these experiments, an amplifier was not needed. The
355 nm third harmonic light is obtained by frequency doubling the 1064 nm with a Type
II KD*P crystal (θ_m = 57°30'). The 532 nm second harmonic light is then frequency
summed with the remaining 1064 nm in a similar Type II crystal to generate the third
harmonic. Since the intensity of CARS signal depends quadratically on the "laser" pulse
and linearly on the energy of the Stokes pulse, maximum energy is preferable for these
beams, and the output of the probe oscillator is always amplified.

The 1064 nm probe oscillator output is sent along an optical path of 5 meters
which allows the beam to expand due to its natural divergence from approximately 3 to 6
mm. This beam is passed through an AR/AR coated one-half wave retarding plate that
rotates the polarization by 45 degrees, and then into the amplifier. The amplified
1064 nm beam is frequency doubled using another Type II KD*P crystal to obtain about
90 mJ of 532 nm light. The half waveplate is used so that the second harmonic will be
horizontally polarized. Horizontally polarized light is needed to pump the dye laser to
obtain the Stokes beam. 40% of the 532 nm light is split off after the doubling crystal to
generate the "laser" beam. Usually between 30 and 35 mJ of ω₁ light is generated, and
the remaining 45 mJ pumps the dye laser. The three Quantel SF-410 laser heads are
about 10 years old, and the cladding on all three is badly crazed. If more efficient
operation is desired, this cladding needs to be replaced.

The probe dye laser has been described in detail elsewhere (Selco, 1983), and
only a short description will be given here. This Littman-type dye laser has three stages,
the oscillator, pre-amplifier and amplifier. The oscillator and pre-amplifier contain NSG
Precision Model T-524 flowing dye laser cells. These cells are mounted on translation
stages that are controlled with 80-pitch screws to allow for fine transverse adjustment.
The dye lasers cells are a relatively recent change in the design and have improved the
beam quality dramatically over the previous version (Holt, 1984). The rest of the
oscillator cavity consists of the pumping optics, a AR coated output coupler, a Fresnel
rhomb, a 2400-line/mm holographic grating and a 2" X 2" aluminum mirror. The
retroreflecting aluminum mirror is mounted on a rotary table, and tuning is accomplished
by rotating this mirror about the stationary holographic grating. A computer controlled
stepping motor, recently improved by Joe Stout, provides reproducible scanning without
occupying much of the lab computer's time.

The oscillator and preamplifier cells are side-pumped, while the amplifier is
longitudinally pumped to generate the best beam shape. The dye is circulated through
the cells from a reservoir which is a reconstructed glass wash-bottle. A small tube that
can be fitted with a septum was blown into the side of the reservoir to permit easy
adjustment of the dye concentration. The oscillator and pre-amplifier run at a fairly high
concentration and share a single reservoir. The amplifier operates with a lower
concentration and has its own reservoir. Twenty percent of the pump beam is put into
each of the oscillator and the pre-amp stages. Since the dye is flowed through the dye
laser cells with a slow sheeting action, a magnet drive gear pump (Micropump 182-361) with a flow rate of 15 to 40 ml/min was recently installed. This pump, which flows at a faster rate than previous pumps, provides smooth and reliable flow. The amplifier dye is flowed rapidly through a cuvette cell with a Micropump 370-140 pump. The spectral bandwidth of the dye laser is about 0.2 cm\(^{-1}\).

The two dyes used for theazoalkane experiments were DCM and Rhodamine 640. Output energies varied from 7 to 10 mJ. This is at least twice the energy reported by workers in this group (Adams, 1989). This increase was due to very careful alignment and concentration adjustment. As the concentration increases, the amplified spontaneous emission (ASE) from the pre-amp stage also increases. Fine tuning the alignment of the oscillator and the pre-amp can remove a large portion of the ASE, and the usable energy then increases dramatically. It has been found that most of the ASE comes from a fluorescence spot on the fresnel rhomb that is amplified in the pre-amp stage. This ASE can be removed by tilting the rhomb so the front face is no longer perpendicular to the beam axis. Further improvements are possible by changing the focusing in the pre-amp. If the focusing cylindrical lens is tilted so that the 532 pump light is not uniform in intensity when it hits the flowing dye cell, the ASE is substantially reduced. This ASE problem is much worse in high gain dyes such as R640 and R610 than it is in DCM.

Another problem encountered was that R640 did not lase efficiently at the wavelength desired in the nitrogen region. To force R640 to lase at a Raman shift of 2330 cm\(^{-1}\), the dye was base shifted by adding small amounts of NaOH in methanol. Adding base shifts a Rhodamine perchlorate dye to the blue and adding acid shifts the same dye to the red. This lab has always found problems with R640 degrading and turning purple in a matter of days, and the problem was found only recently. Some brass swagelock fittings were present in the dye flow system, and the brass was dissolving in
the mildly acidic dye. When these fittings were replaced with stainless steel ones, the dye remained stable.

**CARS Geometries**

Once the "laser" and Stokes beams have been generated, they now have to be overlapped in a manner that satisfies the phase matching condition of the CARS process. Although only the BOXCARS geometry was used in the experiments described here, a short description of the collinear geometry and optics will be given first to clarify a normalization technique that will be described in the photometry section. In collinear CARS, the sample is first excited by the third harmonic excitation pulse. After the programmable delay, the two probe beams are collinearly combined and directed through the sample volume excited by the 355 nm light (Figure 3). Since a CARS signal is produced wherever the probe beams are overlapped, a nonresonant signal can be produced in the sample cell windows and the air outside the cell. It is easy to see that if the nitrogen photoproduct is to be studied, the air background will be intolerable. To eliminate this, the sample cell window was a Schott OG 515 filter that absorbed the unwanted blue CARS light. The exit window was a dielectric filter that blocked the Stokes beam and passed the "laser" and the 355 nm pulses. This suppressed CARS generation after the sample cell. The remaining "laser" light was removed with spectral filters, and the CARS signal from the sample was detected with a photomultiplier tube.

In BOXCARS, the alignment was more complicated (Figure 4). The setup for the folded BOXCARS which was designed by Tom Bevilacqua allows for probing at Raman shifts below < 1000 cm⁻¹. First both probe beams are reduced to 3 mm diameter through telescopes. The "laser" beam is split into 2 equal components in the horizontal plane, separated from each other by about 4 mm. This is accomplished by a specially designed optical element that is 1" in diameter with the back surface 100 % reflecting at 532 nm
Figure 3. Optical schematic for the transient collinear CARS apparatus which includes the reference cell used for normalization.
Figure 4. Optical schematic for transient BOXCARS apparatus. L = lens, P = prism, BS = beam splitter.
TRANSIENT BOXCARS OPTICAL SCHEMATIC
and the front surface 50% reflecting over one half and AR coated over the other half. When the light hits the element at 45°, half of the 532 light is reflected. The remaining light is reflected off the back surface and through the AR coated side parallel to the directly reflected beam. The Stokes beam is directed onto the bottom of a prism that is centered above the two "laser" beams. The three probe beams then pass through a 50 cm f.l. lens and are focused into the center of the sample cell (Figure 5). Since the probe beams are separated when they pass through the sample entrance and exit windows, no special filtering is needed, and uncoated suprasil flats are used for windows.

As a result of the phase matching, the CARS signal is produced in the same vertical plane as the Stokes beam, but the beam path is moving up away from the Stokes and the "laser" pulses. This ω3 beam is now spatially separated from the input beams. To excite the sample, the 355 nm pulse is directed into the cell from the opposite direction from the top of a prism along the path of the Stokes beam. The CARS signal beam passes directly over the excitation prism. The CARS beam is recollimated, focused through a 50 μm pinhole to remove any ultraviolet induced luminescence, and filtered to remove any scattered ω1 light before it is sent to the detector.

To align the beams initially, masks with the correct "laser" and Stokes beam positions are placed before and after the sample cell. After aligning the beams through their respective holes and removing the masks, a sample is introduced into the cell and the beams are adjusted until a signal is obtained. Both the BOXCARS ω1 splitter and the Stokes prism are mounted on Newport Corporation mirror mounts with 80 pitch screws that allow precise adjustments. The standard tune-up sample used with DCM (for probing in the C-H stretching region) is methane. Methane is ideal in that the frequency of its symmetric stretch is well known at 2914.2 cm⁻¹ (Herzberg, 1945); and if the misalignment is severe, an entire atmosphere of the gas can be added to the cell. As a
Figure 5. Expanded view of the overlap geometry for transient BOXCARS from Figure 3. Pump is the "laser" beam and the anti-Stokes is the CARS beam.
Folded BOXCARS
rough guide, the CARS process should generate blue $\omega_3$ light visible on a white card to
the naked eye using about 150 torr of methane. In the nitrogen region, air is used as the standard.

It is much more difficult to overlap the excitation and probe beams than it is to generate a ground state CARS signal. The 355 nm beam is first aligned manually along the path of the Stokes beam by using the phosphorescent spot seen when the third harmonic hits a standard business card. A sample that has an absorption at 355 nm is then put into the cell. When the excitation is overlapped with the probe beams, the amount of CARS signal will be reduced. This depletion allows us to set the temporal overlap between the excitation and probe beams. Temporal overlap occurs when the near-gaussian 10-ns wide pulses arrive at the center of the cell at the same time. This is the calibration for zero time delay. It is also possible to determine temporal overlap by using the photodiodes that monitor beam energies and checking that the beams arrive at the center of the sample cell simultaneously by looking at the overlap of the photodiode pulses on an oscilloscope. This method is only accurate to $\pm 2$ ns, while the ground state depletion method is accurate to about 1 ns. The oscilloscope technique should only be used as a last resort or if the sample has no ground state CARS features in the region of study.

Photometry

It is important not only to generate an optimal CARS signal, but also to detect the signal efficiently. Since the BOXCARS signal is spatially separated from the probe beams, collecting it is fairly simple. Only a single filter is needed to remove scattered "laser" light, usually an Omega Optical DF 475 or DF 480 whose optical density at 532 nm is greater than 5.3. The CARS light is passed through a PTR tunable grating filter onto a Hamamatsu R1477 PMT biased at -900 Volts. The R1477 has a much higher
quantum efficiency in the blue compared with more standard PMTs such as the RCA 1P28. Studies were undertaken to demonstrate that the output of the PMT is linear with respect the incoming light pulse energy at this voltage. The tunable grating filter and PMT are mounted together in a black, light-tight housing. To acquire the most useful data, it is also necessary to account for fluctuations in the probe and excitation beams and their effect on the CARS signal.

The energies of all three beams are monitored with silicon photodiodes (Silicon Detector Corporation Type SD-200-13-23-042). Less that 1% of each of the input beams is directed into a separate photodiode to monitor its energy. These photodiodes are sensitive in the UV and the visible and are biased by a 9 V battery. To remove time skew effects, the photodiodes and the PMT are collected for 3 \( \mu \)sec using Evans 4130 gated integrators that track the delay between the probe and excitation firings. The gate openings are synchronized with each laser firing. The outputs of the gated integrators are digitized by a 12 bit analog to digital converter mounted in the lab computer. At every selected time delay, the lab computer program switches on alternate laser shots between a fixed delay of -25 ns (the sample is probed prior to excitation) and the selected delay. With this technique, the background CARS signal as well as the excitation-induced CARS signal can be obtained. Using the readouts obtained from the photodiodes, the CARS signal is normalized by the data acquisition program to account for energy fluctuations in the probe and excitation beams. CARS is also sensitive to spatial fluctuations in the probe beams, and to account for these a spatially sensitive normalization technique was developed.

To compensate correctly for both energy and spatial fluctuations, the induced CARS signal was normalized to a reference CARS beam produced in a reference cell containing a nonresonant material. This reference cell was utilized in conjunction with
the collinear CARS geometry used for previous azoalkane studies. To obtain a reference
CARS signal that would directly track the sample cell CARS, 15% of the overlapped
"laser" and Stokes beams were split off before entering the sample cell. These beams
were diverted away from the sample cell using a porro prism and focused into the
reference cell, which was an 8" long 1-1/2" O.D. aluminum tube. Each end of the tube,
which had a 5/8" I.D., is machined with an O-ring groove to fit 1" diameter windows and
six tapped 8-32 screw holes. Each end had a aluminum retaining plate to fasten the
windows to the cell. The optics were the same as described earlier for the sample cell
except for the PMT, an RCA 1P28-A. An NPT pipe fitting on the side of the cell allowed
the cell to be connected with the vacuum line and an argon lecture bottle. The gas
handling system was comprised of copper tubing and Swagelock fittings and was fitted
with a 160 psi pressure gauge and a Whitey ball valve. With this, the reference cell could
be filled with to up to 11 atm of argon (a frequency-independent nonresonant CARS
scatterer). By dividing the sample signal by the reference signal on a shot-to-shot basis,
both energy and spatial fluctuations of the probe beams could be accounted for.
Unfortunately, aligning the "laser" and Stokes beams for maximum signal in both the
sample and reference cells proved to be very difficult. Normalizing the sample signal to
the reference signal proved to be no more effective in reducing noise than normalizing to
the probe beam energies from the photodiodes. The best way to normalize the sample
signal would be to put a reference cell in series with the sample cell. The probe beams
would then be directed through the reference cell and the resulting \( \omega_3 \) could be split off
and detected, and the probe beams would continue through the sample cell. This would
guarantee that the alignment for the maximum reference signal would be the same as for
the maximum sample signal. The reference cell was permanently removed when the
apparatus was set up for BOXCARS because of alignment obstacles.
Sample Handling

The Pyrex sample cell is 50 cm long with a 25 mm I.D. and was specially designed for BOXCARS. It has 4 Ace 25 mm I.D. O-ring joints; one at each end and two facing each other across the center. The two end joints hold the suprasil sample windows with O-ring compression seals. Teflon stopcocks and FETFE O-rings are used throughout the sample cell. The 2 side joints were sealed with aluminum disks. The sample cell is also attached to the vacuum line, the gas manifold and two capacitance manometers. The manometers (MKS Instruments Type 221 A and Datametric # 660A-1000T-R12-41X-4) measure sample pressures from .001 to 1000 torr.

The sample cell is attached to the gas manifold and the vacuum pumps through stainless steel bellows to protect the cell from mechanical stress. The vacuum system consists of a mechanical rotary pump (Precision Scientific # 10422-15) and a 2" Varian oil diffusion pump that can obtain a background pressure of less than 10^{-5} torr. The pressure in the diffusion pump forearm is measured with a thermocouple gauge. An ion gauge is available for pressures less than 1 millitorr but is used only to test the effectiveness of the diffusion pump. The sample cell is also attached to a three port sample manifold through a Whitey needle valve through which the scarce azo samples are carefully added. The gas manifold is constructed from copper tubing and Swagelock fittings. The entire sample, vacuum and gas manifolds are designed so that either the sample cell or the gas manifold can be isolated and pumped out by the vacuum line.

Computerization

The laboratory computer is a vital component of the apparatus and is responsible for all aspects of data acquisition. The computer system consists of a DEC LSI-11/73 with 1.25 Mbytes of memory, serial interfaces, and two hard disk drives (a 30 Mbyte DSD-880 and a 70 Mbyte Fujitsu 2312). Analog control voltages are supplied by a 4
channel digital to analog converter (Andromeda DAC-11). These voltages are used to set the Evans programmable delay generators and drive an analog meters used as alignment aids. A 16 channel, 12-bit ADC board (Andromeda ADC-11) digitizes the voltages from all of the gated integrators. Programming is done almost totally in Fortran 77. The 11/73 is operated under the TSX-plus, multitasking, multiuser operating system. Three connected graphics terminals can be used for data acquisition or analysis. Hard copies of data files can be obtained by screen dumping the data graphed on one of the terminals to a NEC P6 pinwriter. Publication quality figures are generated using a digital plotter (Hewlett-Packard 7470A) controlled by a custom plotting program.

A number of excellent computer programs have been written by Patrick Holt and modified by Kim Andrews. These enable the operator to tune up the lasers and alignment as well as acquire data. CARSET displays a continually updated ten shot average of all of the beam energies as well as the CARS signal. Simple keyboard commands can be used to adjust the delay, retake backgrounds and other options. Photodiode readings or the CARS signal can be displayed on analog meters, so that tuning up the laser energies, obtaining a CARS signal or getting a ground state depletion is very convenient.

The versatile CARS data acquisition program allows the Stokes wavelength to be fixed at a Raman transition of interest and the delay scanned to generate a kinetic scan, or the delay can be fixed and the dye laser scanned for a spectral data slice. The CARS signal induced by the excitation is separated from the background signal by subtracting the signal generated at -25 ns from the positive-delay signal. This gives the "transient" or "induced" CARS signal.

Data are acquired in a number of different modes that allow accurate separation of the induced signal from the ground state signal. All of the modes described normalize
the CARS signal to the probe and, if necessary, excitation energy. Mode 31 is used to generate a ground state spectrum. In Mode 31, no excitation is used; the probe frequency is scanned and the signal is square rooted to obtain a $|\chi^{(3)}|$ spectrum. All other modes described generate the induced CARS spectrum.

Mode 52 takes the positive-delay signal and subtracts the negative delay signal from it. Mode 52 data is not square rooted and a "fixup" routine is used to obtain concentrations of the transient photoproduct. Mode 51 takes the square root of the signal at positive time and subtracts the square root of the signal at negative time. Mode 51 is a valid description of the population difference in a vibrational transition only when the transient species being studied is a permanent photoproduct (nitrogen for example). Since ground state nitrogen is being built in during a scan, this signal from the ground state nitrogen must be properly removed to generate the transient signal. Mode 51 is used to accomplish this. It has been shown (Druet and Taran, 1981, Tolles et al., 1977) that the difference between the square root of the CARS signal at the band maximum and the square root of the CARS signal at the band minimum varies linearly with number density. This allows us to obtain meaningful kinetics for the nitrogen photoproduct. A kinetics scan (Mode 51) is taken at the band minimum and subtracted from a kinetic scan (Mode 51) taken at the band maximum. The resulting data file is accurately proportional to the change in nitrogen concentration induced by the excitation pulse.

The majority of data discussed in this thesis were taken with Mode 53. In Mode 53, the CARS signal at negative time is subtracted from the CARS signal at positive time, and then the square root is taken to generate an induced $|\chi^{(3)}|$ spectrum. Mode 53 is valid only when the transient species is not a permanent photoproduct.

In conclusion, an apparatus is available that allows time-resolved photodissociation studies of various species. The transients are observed through their
Raman active vibrations, and both kinetic and spectral data can be obtained to investigate the mechanism and dynamics of the photodissociation.
Chapter 3

Azomethane

Introduction

Although azoalkanes have been known since 1909, there has been a resurgence of interest in their chemistry in the last 30 years. The majority of work on the azos has centered on the dissociation mechanism and the excited states involved in dissociation and isomerization. Previous thermolysis and recent photolysis studies have demonstrated that unsymmetrical azoalkanes dissociate through a stepwise mechanism involving a diazenyl intermediate R-N=N (Engel, 1980; Adams et al., 1986).

\[ \text{R-N=N-R} \rightarrow \text{R-N=N + R} \rightarrow 2\text{R + N}_2 \]

Some investigators believe that symmetric azoalkanes dissociate synchronously, although this has never been demonstrated (Engel, 1980).

\[ \text{R-N=N-R} \rightarrow 2\text{R + N}_2 \]

Azomethane is the prototypical symmetric azoalkane and has been the object of many experimental and theoretical studies. The involvement of a number of different excited states in the photolysis of azomethane has been suggested, but none has been experimentally detected. Gas phase azomethane dissociates into two methyl radicals and nitrogen with a quantum yield of one at pressures of up to 45 atm of CO₂ (Chervinsky and Oref, 1977). This would indicate that if the dissociative state were \( S_0 \), its lifetime would be less that 25 ps to avoid collisional quenching. The dissociation of azomethane into 2CH₃ and N₂ is endothermic by 11400 cm⁻¹ (Engel, 1980). Previous transient CARS studies of the photodissociation of azomethane yielded significant data, but were not able to determine the mechanism (Holt et al., JACS 1984).

Holt et al. suggested that because the vibrational distribution of the nitrogen photoproduct was found to be relatively cold, the dissociation proceeded through a
diazanenyl intermediate in which the N-N bond distance was similar to that in \( \text{N}_2 \). The photodissociation of azomethane with 355 nm excitation has now been extensively reinvestigated to better determine the kinetics and dynamics of photodissociation. The results of this investigation will be described in this chapter.

One expects all three possible photoproducts, methyl, methylidiazanenyl, and nitrogen can be studied using transient CARS. The methyl radical was first observed by Herzberg and Shoosmith (1956) in UV absorption following photodissociation of \( \text{Hg(CH}_3\text{)}_2 \). They determined from a rotational analysis of the of the first excited state at 216.0 nm that methyl is planar in the ground state with \( D_{3h} \) symmetry. A number of different spectroscopic techniques have been used to determine the fundamental vibrational frequencies of the methyl radical as well as some of its molecular constants. Tan et al. (1972) developed a rapid scan infrared spectrometer for gas phase detection of the methyl radical. Snelson (1970) used infrared spectroscopy in an argon matrix to observe \( \nu_2 \), the out-of-plane deformation or "umbrella" mode; \( \nu_3 \), the degenerate asymmetric stretch; and \( \nu_4 \), the degenerate in-plane C-H deformation (1396 cm\(^{-1}\)). Using gas phase high resolution infrared tunable diode laser spectroscopy, Yamada et al. (1981) studied the \( \nu_2 \) 1-0 (606.5 cm\(^{-1}\)), 2-1, and 3-2 bands of the methyl radical. Amano et al. (1982) accurately measured the band origin of \( \nu_3 \) to be 3160.8 cm\(^{-1}\) using difference frequency laser spectroscopy. Holt et al. (JCP, 1984) used transient CARS spectroscopy to detect the previously unobserved totally symmetric \( \nu_1 \) stretch at 3004.8 cm\(^{-1}\). Spirko and Bunker (1982) used Yamada's data to determine equilibrium bond lengths and calculated vibrational field parameters for the methyl radical.

Holt (1984) observed a methyl hot band red shifted from the ground state methyl origin by about 7 cm\(^{-1}\). He assigned this to the symmetric stretch with 1 quantum excitation in the \( \nu_2 \) mode. This is in reasonable agreement with the recently reported
anharmonic coupling constant of -9.8 cm\(^{-1}\) (Kelly and Westre, 1988), and it is also within tolerable agreement with a theoretical calculation by Botschwina et al. (1983) that predicts \(X_{12}\) to be -13 cm\(^{-1}\). Analogous \((0,2) \rightarrow (1,2)\), as well as \((0,1) \rightarrow (1,1)\) transitions were also observed in the photodissociation of deuterated azomethane (Miller, 1989). It seemed possible from the data of Holt (1984) that the hot methyl might show different appearance kinetics than the cold methyl. This possibility was the basis for reinvestigating the photolysis of azomethane.

In the studies of Holt et al. (JACS, 1984), the rise of the methyl radical was only investigated using only SF\(_6\) as a vibrational relaxer. It was found that for an SF\(_6\) pressure of 400 torr, the rise time was approximately 4 ns. The appearance time of nitrogen in the presence of He as a rotational relaxer was found to be less than 2 ns. It was deduced that the methyl was not promptly vibrationally relaxed with 400 torr of SF\(_6\), and that the precursor of the photoproducts lived for less than 2 ns. In retrospect, the difference in the rise times between the N\(_2\) and the methyl fragments might also be explained by uncertainty in the zero time delay settings.

**Experimental Details**

Trans-azomethane was synthesized by Steve Adams. All measurements were made at 295 ± 1 K. Static vapor pressures of 1 to 8 torr of azomethane were used with He or SF\(_6\) added as buffer gases. Azomethane was photolyzed using ca. 5 ns pulses at 355 nm. After a variable time delay, the CARS probing beams passed through the sample to detect excitation-induced changes. The sample volume was replenished through diffusion with fresh azomethane during the 100 ms between shots. When a large amount of the sample had been destroyed or when considerable N\(_2\) had built up, a fresh charge of azomethane and buffer (if needed) was put into the cell. Approximately 15% of the azomethane in the probed volume was dissociated with each shot.
In the present work, the photolysis was first probed in the C-H stretching region using DCM dye giving Raman shifts from 2750 to 3550 cm⁻¹. To tune up the lasers and correctly overlap the Stokes and the "laser" beams in the center of the cell, small amounts of methane were added. The overlap could be set and the frequency calibrated using methane's well known 2914.5 cm⁻¹ symmetric stretch. The methane was then pumped out of the cell, and usually 5 torr of azomethane was added. The Raman spectrum of azomethane is well known (Durig et al., 1970; Craig et al., 1978). The spatial as well as temporal overlap of the excitation and probe beams was obtained by monitoring the ground state depletion of the strong azomethane band at 2926 cm⁻¹. In the photodissociation of azoalkanes, a large amount of translational energy is imparted to the photofragments, causing them to leave the probe volume at rates much faster than diffusional. Moderate pressures of helium (200-400 torr) were added to the sample to contain the photofragments. These translationally hot molecules could also collide with the unexcited sample molecules and cause a decrease in the sample density. The result of this heating effect is a collisionally-induced depletion. To help moderate this heating effect, helium was added to samples when the temporal overlap was being checked, so that the ground state depletion occurred only from 355 nm absorption and not from collisional-induced effects.

Results

With the temporal overlap set so that the excitation and probe beams could be adjusted to arrive at the center of the sample cell at the same time with an uncertainty of approximately 1 ns, the behavior of the hot and cold methyls was investigated. In a series of spectral scans under rotationally relaxed conditions, the relative amounts of the hot band (1 quantum in the ν₂ mode) and the cold band (0 quanta in the ν₂ mode) were studied. At a delay of 5 ns, the intensities of the two are similar, but at a delay of 255 ns,
the hot band was completely relaxed, probably through collisions with the parent molecule (Figure 6). When the same spectrum was scanned at early times with no buffer, there was much more intensity in the hot than in the cold band. This might indicate that the cold methyl is more rotationally excited than the hot one. At 50 ns delay, the cold band has built up significantly (Figure 7).

The relative intensities of the hot and cold bands were measured while varying the excitation energy to check for multiphoton effects. If the hot methyl is produced through a multiphoton absorption of the parent molecule, then as the energy of the excitation is increased there should be a systematic increase in the ratio of the intensity of the hot band to that of the cold band. Figure 8 shows the effect of increased excitation energy on the two bands. No multiphoton processes are observed.

From its frequency, it was assumed that the hot band corresponded to a methyl with one quantum of excitation in the umbrella mode (Botschwina, 1983). There was also a lack of reasonable alternatives to this assignment. The band is too long-lived to be a diazenyl intermediate or an excited state precursor to the cold methyl radical. Holt et al. (JCP, 1984) found not only the origin frequency of the symmetric stretch, but also the change in rotational constants in the $v_1 0\rightarrow 1$ vibrational transition. It should be possible to unequivocally assign the hot band from its high resolution rotational contour. To obtain this contour the etalon is placed in the Nd:YAG probe cavity to narrow the bandwidth from approximately 1 cm$^{-1}$ to < 0.2 cm$^{-1}$. Figure 9 shows a high resolution scan of the two bands at early time with moderate rotational relaxation.

For calibration purposes, a high resolution spectrum of the cold band was studied first (Figure 10). This averaged spectrum was obtained in the presence of 700 torr of He added for rotational relaxation. The probe delay was 25 ns. The top spectrum is experimental and the bottom is the simulated fit. To simulate CARS data, the real and
Figure 6. Low resolution scan of the rotationally relaxed "hot" and "cold" bands from azomethane. The sample contained 5 torr azomethane and 700 torr He.
Figure 7. Low resolution scan of the "hot" and "cold" bands from azomethane with no buffer gas present. The sample contained 5 torr of azomethane.
Figure 8. Low resolution scan of the "hot" and "cold" bands from azomethane using different excitation energies. The dash-dot line corresponds to 5.5 mJ excitation, the dashed line corresponds to 11 mJ, and the solid line corresponds to 20.5 mJ. The sample contained 5 torr of azomethane and 270 torr of helium.
Figure 9. High resolution scan of the "hot" and "cold" bands from azomethane. The sample contained 5 torr of azomethane and 270 torr He. The scan was taken at a delay of 25 ns. The sample contained 5 torr of azomethane and 700 torr He.
Figure 10. High resolution scan of the "cold" band of the totally symmetric stretch of the methyl radical and a computer simulation of the rotationally unresolved spectrum. The simulation and its parameters are discussed in the text.
imaginary parts of $\chi^{(3)}$ are modeled separately to account for interference effects. After the $\chi^{(3)}$ spectrum was computed with a 0.22 cm$^{-1}$ resonant linewidth and a small nonresonant contribution, the spectrum was convolved with a 0.18 cm$^{-1}$ Gaussian instrumental bandwidth to yield the final fit.

The methyl radical is planar oblate symmetric top in its $^2A_2^*$ (D$_{3h}$) electronic ground state. The spectral modulation in the simulated spectrum originates from incompletely resolved rotational structure in the $\Delta J = 0, \Delta K = 0$ Q branch of the radicals. The simulated spectrum is calculated using the well known rotational constants, $B_0 = 9.57789$ cm$^{-1}$ and $C_0 = 4.74202$ cm$^{-1}$ (Yamada et al., 1981), a rotational temperature of 375 K and appropriate spin statistical factors (Herzberg, 1945). Based on Herzberg's treatment of D$_{3h}$ symmetric top, the spin weight is 2 for $K = 0$ and J even. The spin weight is also 2 for $K = 3q$, for all integers $q$ not equal to zero. The spin weight is 0 when $K = 0$ and J is odd; the spin weight is 1 for $K = 3q \pm 1$. The best agreement between the data and the simulation was obtained by starting with the values of Holt et al. (JCP, 1984) for $v_0, B_1, C_1$ and making fine adjustments in the values of $B_1$ and $C_1$. Holt et al. found that $B_1 - B_0 = -0.085 \pm 0.002$ cm$^{-1}$ and $C_1 - C_0 = -0.048 \pm 0.002$ cm$^{-1}$.

From adjusting the values for $\Delta B$ and $\Delta C$, as well as the temperature and nonresonant contribution, the best agreement between the reduced data and the simulation was obtained with $B_1 - B_0 = -0.086 \pm 0.001$ cm$^{-1}$ and $C_1 - C_0 = -0.051 \pm 0.001$ cm$^{-1}$, very similar to the previous results. The new numbers are probably more reliable because the data are of higher quality.

To verify that the hot band is in fact that of a methyl radical, a high resolution scan was taken of it after rotational relaxation (Figure 11). Since a methyl hot band is presumed to have excitation in the out-of-plane stretching mode, $v_2$, which has $A_2^*$ symmetry, the intensities of the rotationally unresolved features will be different than for
Figure 11. High resolution scan of the "hot" band of the totally symmetric stretch of the methyl radical and a computer simulation of the rotationally unresolved spectrum. The simulation and its parameters are discussed in the text.
the cold band. Again using Herzberg's (1945) discussion of the spin statistics for an oblate top with $D_{3h}$ symmetry and a vibrational species of $A_2'$, the spin weight is 2 for $K = 0$ and odd $J$, or when $K = 3q$, for all $q$ not equal to zero. The spin weight is 0 for $K = 0$ and even $J$, and the spin weight is 1 for $K = 3q \pm 1$. It would also be reasonable to expect that excitation in the umbrella mode would change the values of $\Delta B$ and $\Delta C$. Using the new spin weights and varying the temperature, Raman line width, nonresonant contribution, origin frequency, and $\Delta B$ and $\Delta C$, the simulation in bottom of Figure 11 was generated. Good agreement was obtained using a temperature of 450 K, a Raman linewidth of 0.30 cm$^{-1}$, and a small nonresonant contribution. The following results were obtained: vibrational origin frequency $\nu_0 = 2998.0 \pm 0.4$ cm$^{-1}$; $B_1 - B_0 = -0.070 \pm 0.002$ cm$^{-1}$, and $C_1 - C_0 = -0.060 \pm 0.002$ cm$^{-1}$. The rotational contour of the hot band could not be simulated using spin statistics for the cold band. This would confirm that the hot band indeed arises from methyl radicals with 1 quantum of excitation in the $\nu_2$ umbrella mode.

A scan from 2970 to 3010 cm$^{-1}$ at early time with 100 torr of He showed small features that might originate from further excitation in the $\nu_2$ mode (Figure 12). The negative going feature at 2990 cm$^{-1}$ is a small azomethane ground state depletion. A high resolution scan at early time over the same region proved interesting (Figure 13). A total of five partially resolved rotational contours are seen. No further features were detected in scans to lower frequencies. To determine the assignment of these bands, their rotational contours were studied. The bottom of Figure 13 shows the most probable rotational contour for each hot band. Methyl radicals with 0, 2, or 4 quanta in the $\nu_2$ mode will have the same ground state ro-vibrational symmetry and therefore the same spin statistics, whereas the bands with an odd number of quanta in the umbrella mode will all have the spin statistics described above for the hot band. From a rough analysis
Figure 12. Low resolution scan of the rotationally relaxed methyl radicals that shows lower frequency features. The negative-going feature at 2989 cm\(^{-1}\) is a ground state depletion. The scan was obtained at a delay of 20 ns. The sample contained 5 torr azomethane and 700 torr He.
Figure 13. High resolution scan of the $v_2$ sequence bands of the methyl radicals and computer simulations of their rotationally unresolved contours. The number of quanta of excitation in the $v_2$ mode is shown in the simulation figure. The scan was taken at a delay of 25 ns. The sample contains 5 torr azomethane and 270 torr He.
of the rotational structure of the five bands, they seem to be a sequence with 0 to 4 quanta of excitation in the \( v_2 \) mode. These bands are separated by an average of 7.5 cm\(^{-1} \). (See Table 1 for details) The cross-sections of the hot band transitions should be the same as that of the cold band. Under vibrationally nascent conditions, the measured intensity of the cold band is about equal to the sum of the intensities in the other four bands. Unfortunately, only the cold and the first hot band (1 quantum in the \( v_2 \) mode) are intense enough to permit reliable studies of their kinetic behavior.

The kinetics of both the cold and the first hot band (known simply as the hot band) were studied extensively under a variety of conditions. To obtain kinetics of the hot band, the Raman frequency was held constant at 2995.5 cm\(^{-1} \), and the delay was varied. The probe laser was operated in its lower resolution mode for all kinetic studies. Although the hot methyl showed prompt appearance components, the kinetics could only be fit if He or He plus SF\(_6\) were added as buffer gases. The complex nature of the rotational relaxation could not be modeled with a simple phenomenological collisional decay process. In the presence of large enough He pressures (providing for rapid rotational relaxation) the hot methyl kinetic data could be fit with the following model:

\[
\begin{align*}
\text{CH}_3\text{NNCH}_3^* & \rightarrow \text{CH}_3^{**} + \text{NNCH}_3 & k_1 \\
\text{CH}_3\text{NNCH}_3^* & \rightarrow \text{CH}_3^* + \text{NNCH}_3 & k_2 \\
\text{CH}_3^{**} + M & \rightarrow \text{CH}_3^* + M & k_3 \\
\text{CH}_3^* + M & \rightarrow \text{CH}_3 + M & k_4
\end{align*}
\]

where M is a buffer gas and \( \text{CH}_3^* \), \( \text{CH}_3 \), and \( \text{CH}_3^{**} \) are methyl radicals with 0, 1 and 2 or more quanta in the \( v_2 \) mode respectively. \( \text{CH}_3\text{NNCH}_3^* \) is the dissociative state of azomethane that is promptly prepared by absorption at 355 nm. To obtain the fit to the data at 2995.5 cm\(^{-1} \), the kinetic equations in the above model were integrated to find the concentration of the species being probed (\( \text{CH}_3^* \)) as a function of time, convolved with
Table 1. Tabulation of data and computed parameters for the $v_2$ sequence bands.
**Methyl Symmetric Stretches Shifted by Excitation in the out-of-plane Deformation Mode**

<table>
<thead>
<tr>
<th>Number of Quanta in Deformation Mode</th>
<th>Band origin (wavenumbers)</th>
<th>Shift From Cold Band</th>
<th>Interval</th>
<th>Relative Populations</th>
<th>Spin Weight Type</th>
<th>Calculated Rotational Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3004.8</td>
<td>0</td>
<td>0</td>
<td>44%</td>
<td>A</td>
<td>Delta B: -0.086</td>
</tr>
<tr>
<td>1</td>
<td>2998.8</td>
<td>6.8</td>
<td>6.8</td>
<td>17%</td>
<td>B</td>
<td>Delta C: -0.051</td>
</tr>
<tr>
<td>2</td>
<td>2989.8</td>
<td>15.0</td>
<td>8.2</td>
<td>15%</td>
<td>A</td>
<td>Delta B: -0.070</td>
</tr>
<tr>
<td>3</td>
<td>2980.8</td>
<td>24.0</td>
<td>9.0</td>
<td>13%</td>
<td>B</td>
<td>Delta C: -0.060</td>
</tr>
<tr>
<td>4</td>
<td>2974.8</td>
<td>30.0</td>
<td>6.0</td>
<td>11%</td>
<td>A</td>
<td></td>
</tr>
</tbody>
</table>

**Average = 7.5**

**Spin Weights Type A**
- 2 for \( K \) equal to 0, \( J \) even
- 0 for \( K \) equal to 0, \( J \) odd
- 2 for \( K \) equal to 3q
- 1 for \( K \) equal to 3q +/- 1

**Spin weights Type B**
- 0 for \( K \) equal to 0, \( J \) even
- 2 for \( K \) equal to 0, \( J \) odd
- 2 for \( K \) equal to 3q
- 1 for \( K \) equal to 3q +/- 1

(where \( q \) is an integer)
the Gaussian instrumental response function (8 ns FWHM, limited by the pulse widths of
the laser), and the rates were adjusted for the best fit to the data. Figure 14 displays the
hot and cold rises and fits with 400 torr of He to rotationally relax the radicals. From the
fit, \((K_1 + K_2) = 6.8 \times 10^9 \text{ s}^{-1}\). The ratio of \(K_1\) to \(K_2\) describes concentration ratios of the
hot methyls with more than one quantum in \(v_2\), \(\text{CH}_3^{**}\), to those with only one quantum.
From the average of a number of computed fits with buffer pressures ranging from 400 to
700 torr of He with 0 to 100 torr of \(\text{SF}_6\), this ratio \([\text{CH}_3^{**}] / [\text{CH}_3^*]\) was found to equal 2.3.
The rise of the hot band was also found to be prompt in the presence of He plus \(\text{SF}_6\), a
vibrational relaxer (Figure 15).

The kinetics of the cold band was studied by fixing the Stokes frequency and
measuring the CARS signal as a function of delay at 3002.5 cm\(^{-1}\). The cold band
appearance was delayed under all conditions studied here. With only azomethane in the
cell, a long, slow, unfittable rise was observed (Figure 16). If rotational relaxers were
added, the methyl rise could be fit with the following model:

\[
\begin{align*}
\text{CH}_3\text{NNCH}_3^* & \rightarrow \text{CH}_3^* + \text{NNCH}_3 \quad \text{at} \quad k_1 \\
\text{CH}_3\text{NN} & \rightarrow \text{CH}_3 + \text{N}_2 \quad \text{at} \quad k_2 \\
\text{CH}_3^* + \text{M} & \rightarrow \text{CH}_3 + \text{M} \quad \text{at} \quad k_3 \\
\text{CH}_3^* & \rightarrow \text{Products} \quad \text{at} \quad k_4 \\
\text{CH}_3 & \rightarrow \text{Products} \quad \text{at} \quad k_5
\end{align*}
\]

where \(\text{M}\) is an inert collisional partner. The model described above includes no step for
rotational relaxation, and kinetic data files with He pressures of less than 400 torr could
not be fit successfully. The value of \(k_2\) was found to be insensitive to collisional
relaxation with He pressures above 400 torr or with He and \(\text{SF}_6\) mixes (Figures 14 and
15). The value of \(k_2\) was found to equal \(2.0 \pm 0.3 \times 10^8 \text{ s}^{-1}\), indicating a dissociative
lifetime of 5 ns for the methylidiazemyl intermediate. If the hot methyl is actually formed
Figure 14. Appearance kinetics for the rotationally relaxed "hot" and "cold" methyl radicals. The solid lines through the data are computed fits. The kinetics of the "hot" and "cold" bands were taken at 2995 and 3002.5 cm⁻¹ respectively. The parameters for the fit are discussed in the text. The sample contained 5 torr azomethane and 400 torr He.
Figure 15. Appearance kinetics for the "hot" and "cold" methyl radicals in the presence of He and SF₆. The solid lines through the data are computed fits. The kinetics of the "hot" and "cold" bands were taken at 2995 and 3002.5 cm⁻¹ respectively. The parameters for the fit are discussed in the text. The sample contained 5 torr azomethane, 50 torr SF₆, and 650 torr He.
Figure 16. Appearance kinetics of the methyl cold band from azomethane with and without of He. The kinetics were taken at 3002.5 cm\(^{-1}\). The samples contained 5 torr of azomethane.
in the first step in the dissociation and the cold methyl arises from the dissociation of the methylidiazenyl intermediate, then the appearance of the nitrogen photoproduct will also be delayed.

The nitrogen photoproduct was studied by probing the Q-branch of its fundamental vibrational transition at 2330 cm\(^{-1}\). Since nitrogen accumulates as a permanent photoproduct, it is vital to separate the newly formed nitrogen from the background. In measuring spectral data, the background nitrogen signal is simply subtracted out, but kinetic scans are more complex. Following the analysis of Tolles et al. (1977), kinetics were taken at the maximum and minimum of the dispersive-shaped nitrogen band. The difference between the \(|\chi^{(3)}|\) at the minimum and at the maximum is proportional to the nitrogen number density.

To generate the needed Stokes frequency, R640 dye was used. Probe overlap is obtained by adding air or carbon monoxide to the sample cell and aligning for the maximum ground state signal. Azomethane does not have any ground state features in this region (2000 to 2500 cm\(^{-1}\)), so overlapping the excitation with the probe pulses is much more difficult than in the C-H stretching region. Azomethane had a larger nonresonant background in the nitrogen region than in the C-H stretching region, probably from a strong or broad ground state feature to the blue of the dye range. Since this nonresonant signal originates from ground state azomethane, it will be partially depleted when the azo sample absorbs the excitation light. Excitation overlap was generated by aligning the 355 nm beam in the center of the cell for maximum depletion of this background. The depletion of this nonresonant background was not as strong as the depletion of an azomethane ground state, so a different method for obtaining accurate temporal overlap is needed. There is a manual procedure for determining temporal overlap using the photodiodes, which has been described in detail elsewhere (Adams,
1989). However, this method is not accurate enough for the present purposes. Fully deuterated azomethane has a very strong ground state feature at 2127 cm\(^{-1}\). Temporal overlap was verified by measuring the kinetics of this ground state depletion in the presence of moderate pressures of He. Using azomethane-d\(_6\) as the standard in the nitrogen region provided a temporal overlap that was as accurate as that used in the C-H stretching region.

The nonresonant contribution from the azomethane limited the amount of sample that could be used to a maximum of 2.5 torr. Early time scans over the nitrogen Q-branch with no added buffer gases showed no appreciable amount of nascent nitrogen. This suggests that the nitrogen is delayed in appearance or is rotationally or vibrationally excited. When moderate amounts of He were added (300-600 torr), a transient \(\text{N}_2\) signal was seen (Figure 17). Appearance kinetics were measured with He as a rotational relaxer (Figure 18). The data were fit using the following kinetic model:

\[
\text{CH}_3\text{NCH}_3^* \rightarrow \text{CH}_3 + \text{NNCH}_3 \quad k_1 \\
\text{NNCH}_3 \rightarrow \text{N}_2 + \text{CH}_3 \quad k_2 \\
\text{N}_2 \rightarrow \text{Products} \quad k_3
\]

The rate coefficient \(k_2\) was found to equal \(2.2 \pm 0.3 \times 10^8\) s\(^{-1}\) in the regime of rapid rotational relaxation (He pressure > 400 torr). The third step in the model describes the heating (change in nitrogen density) that occurs as the translational energy of the photoproducts is removed by the sample. The rotationally unrelaxed nitrogen kinetics could not be modeled successfully.

Nitrogen's vibrational anharmonicity of 14.5 cm\(^{-1}\) \(\omega_k\) is large enough at for the different vibrational transitions to be well separated. The nascent vibrational distribution for the nitrogen photoproduct had previously been determined (Holt \textit{et al.}, JACS, 1984) and was only confirmed in this study (Figure 17). Taking into account the v + 1
Figure 17. Vibrational distribution of nitrogen from azomethane. The populations in each vibrational level are discussed in the text. The sample contained 2 torr of azomethane and 400 torr of helium. The scans were taken at a delay of 15 ns.
Figure 18. Appearance kinetics of the nitrogen photoproduct from azomethane. The solid line through the data points is a computer fit. The parameters for the fit are discussed in the text. The sample contained 2 torr of azomethane and 400 torr He.
dependence in Raman cross-sections and recalling that the CARS signal at each band is proportional to the square of the population difference, it was determined that $84 \pm 2\%$ of the nascent nitrogen was in $v = 0$, $14 \pm 2\%$ in $v = 1$ and $0 + 2\%$ in $v > 1$. This result confirms that of Holt et al. (JACS 1984) where the following distribution was obtained: $86 \pm 3\%$ of the nascent nitrogen was in $v = 0$, $16 \pm 2\%$ in $v = 1$ and $< 3\%$ in $v > 1$.

To understand the dynamics of the dissociation, a complete product state distribution would be valuable. Holt et al. (JACS, 1984) reported the $N_2$ nascent rotational temperature to be 425 K at a delay of 10 ns with an azomethane pressure of 12 torr. Given the possible large amount of translational excitation in the photofragments, the above conditions are not necessarily pre-collisional. To assess the nascent distribution more carefully, high resolution spectra were obtained of the nitrogen photofragment. Figure 19 shows a much averaged spectrum of the nascent nitrogen from 2 torr of azomethane at a delay of 5 ns. The negative-going feature at small $J$ values is from collisional depletion of previously formed nitrogen. Since there are no observable changes in the nature of the spectrum when the azomethane pressure is halved to 1 torr or when a delay of 3 or 8 ns is used, it is assumed that this recoil effect does not change the nascent rotational temperature. The 2:1 modulation in the intensities for even to odd $J$ values result from the nuclear spin statistics of $^{14}N_2$, a homonuclear diatomic with $I = 1$. The presence of this modulation was utilized in obtaining the averaged spectrum shown in Figure 19. The data were offset in such a manner that the ratio between even and odd $J$ values remained constant at 2:1.

In order to assign a rotational temperature, it is necessary that the nitrogen data be describable by a Boltzmann distribution. The data were processed so that the population in each $J$ level, $N_J$, could be determined. The relative intensities at each $J$ level were
Figure 19. High resolution spectrum of the nascent rotational distribution of the nitrogen photoproduct from azomethane. The spectrum was obtained at a delay of 5 ns. The sample contained 2 torr of azomethane.
measured, and the distribution peaked at approximately \( J = 25 \). A Boltzmann distribution is given by:

\[
N_J = (2J + 1) \exp(-E_J/kT)
\]

(1)

where \( 2J + 1 \) is the degeneracy and \( E_J \) is the energy of the rotational state. This equation can be rewritten in terms of the rotational constant, \( B \):

\[
\ln(N_J/(2J + 1)) = (-Bhc/kT)(J(J + 1)).
\]

(2)

If the left hand side is plotted against \( J(J + 1) \), the temperature can be calculated from the slope. This plot is shown in Figure 20; the line through the data points is a least-squares fit. The calculated rotational temperature is \( 2500 \text{ K} \pm 300 \text{K} \). The correlation coefficient for the least-squares fit is 0.97. The correlation coefficient probably reflects experimental scatter in the data rather than a deviation from Boltzmann behavior.

To determine if the depletion of low \( J \) states effected the rotational distribution, the spectrum obtained using an azomethane pressure of 1 torr, for which much less depletion occurs, was compared with a spectrum taken using 2 torr of azomethane. The rotational distribution was virtually identical for the two sets of conditions, and the low \( J \) depletion does not appear to skew the rotational data. It is conceivable that the nascent nitrogen is formed with little rotational excitation, and that collisions with the translationally hot photoproducts rotationally excite the nitrogen. Assuming that the newly formed nitrogen is not translationally excited, the time between hard sphere collisions of nitrogen with azomethane is 35 ns. For the nitrogen to be rotationally excited in only 3 ns it must therefore have a collisional rate of 10 times gas kinetic. This would require more energy than the 16,800 cm\(^{-1}\) that is available from the photolysis. It therefore seems very unlikely that the rotational excitation is caused by collisional excitation.
Figure 20. Boltzmann plot of the nascent nitrogen rotational data from azomethane. The straight line through the data points is the least squares fit to the data. The rotational data can be described by a Boltzmann temperature of 2500 K.
$T = 2500 \text{ K}$

$J(J+1)$ vs. $\ln \left( \frac{(I+1)(I)}{I} \right)$
To complete the picture, the product state distributions of the methyl radicals
would be needed. A search for the methyl v=1→2 band was made at early times under
rotationally relaxed conditions. From Kelly and Westre's (1988) resonance Raman
studies, the v=1→2 transition should lie at 2957 cm⁻¹. No features were seen in this area.
Since there were no interfering ground states or transients at this frequency, the methyl v₁
mode is probably not vibrationally excited. The ratio of v=0 to v=1 levels was estimated
to be at least 10:1

High resolution spectra of the methyl radicals were taken to determine their
nascent rotational distribution. Spectra of all the bands were obtained at early times (3, 5
and 8 ns) with 5 torr of azomethane. In an attempt to assess the rotational distributions of
the bands, spectra were simulated at different rotational temperatures and compared with
the reduced data. Because of overlap between bands, only the cold band could be
accurately fit. The nascent methyl spectrum was simulated with a rotational temperature
of 1300 ± 200 K. A high resolution spectrum of the nascent cold methyl and its
simulation are shown in Figure 21. The first hot band also appears to be rotationally hot,
but its temperature could not be easily determined because of overlap with high J values
of the cold methyl. There were no noticeable changes in the shape of the rotational
contour as the delay was varied from 3 to 8 ns.

An extensive search was made for the pure rotational CARS spectrum of the
methyl radical at small Raman shifts (300-500 cm⁻¹), but no such signals were seen.
Transitions for J,K values of eight and greater would be expected to occur in the scanned
region. Since J,K values of at least 10 are evident in the high resolution C-H stretching
band, the lack of pure rotational signal at lower Raman shifts is attributed to low
sensitivity. Searches were also made for the methylidiazanyl radical in the C-H stretching
region and the N=N stretching region (1300-1800 cm⁻¹). These experiments were carried
Figure 21. High resolution scan of the nascent rotational distribution of the second methyl fragment from azomethane. The parameters for the simulation are discussed in the text. The spectrum was taken at a delay of 5 ns. The sample contained 5 torr of azomethane.
out at early times under rotationally relaxed conditions, but no methylidiazenyl features were observed. Since the partial pressure of the methylidiazenyl was approximately 300 millitorr, the inability to observe the radical was possibly due to an overlap with a ground state feature, a small Raman cross section or a broad rotational contour that is not uncommon for asymmetric tops.

Discussion

The solution phase thermolysis of azoalkanes has been studied in depth over a period of decades. Thermolysis proceeds from the vibrationally excited ground electronic state $S_0^*$. Isomerization has been found to be the major channel in solution phase photochemistry. Since photodissociation may proceed from a surface other than the $S_0^*$, the mechanisms of thermolysis and photolysis might be quite different.

Although the gas phase photolysis of azomethane is probably the most convenient source of methyl radicals, relatively few experiments have been performed to determine the gas phase photodissociation mechanism. Sleppy and Calvert (1959) studied the gas phase photolysis of azomethane and looked for the diazenyl intermediate using visible and ultraviolet transient absorption. Their apparatus operated on the millisecond time scale, and no sign of the methylidiazenyl was observed.

In the transient CARS studies described here, no methylidiazenyl radical was directly detected, but a stepwise mechanism can be inferred from the kinetics and product state distributions of the photofragments. The spectral scans in Figure 8 show no signs of multiphoton induced effects, which indicates that both the hot and cold methyl radicals are produced after single photon absorption. The appearance of the cold methyl is delayed under all conditions studied here (Figure 22) and described previously (Holt, 1984) using He, SF$_6$ and mixtures of the two as collisional partners. Appearance rates with buffer pressures below 400 torr He are not displayed because with the kinetic model
Figure 22. Pressure dependence of the appearance times of the second methyl radical and the nitrogen photoproduct. The open triangles denote the methyl appearance rates, while the circles represent that of the nitrogen. The filled in triangle denotes methyl appearance rates with 50 torr of SF$_6$ as well as 650 torr of He. The error bars reflect the error in the calculated appearance rates. A total of 51 data files are represented in this figure.
that had no step for rotational relaxation, these data could not be adequately fit. Since no pressure dependence of the appearance rate is seen in Figure 22, the delayed appearance of the cold methyl is attributed not to rotational or vibrational relaxation, but instead to a chemical precursor with a 5 ns lifetime. The appearance of the nitrogen photoproduct is also delayed, and its pressure dependence is also shown in Figure 22. The lack of proportional pressure dependence in the nitrogen rise also indicates that its delay is due to the methyl diazenyl intermediate rather than rate-limiting rotational relaxation. From this kinetics results, it appears that the following stepwise mechanism describes the photolysis of azomethane:

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{h} \nu \quad \text{CH}_3 \\
\text{N=}= \text{N} & \quad \text{N=}= \text{N} + \cdot \text{CH}_3^+ \\
\cdot \text{N}= & \quad \cdot \text{CH}_3 + \text{N}_2
\end{align*}
\]

\[k > 10^9 \text{ s}^{-1}\]
\[\kappa \sim 2 \times 10^8 \text{ s}^{-1}\]

A study of the stoichiometry of the dissociation also demonstrates that the first step is not multiphoton induced. In a different kinetic model, described below, the appearance of the cold band was fit with a mechanism that allows for a multiphoton step in the production of the hot methyl.

This model was designed to determine the initial ratio of hot methyl to cold methyl concentrations. In this model, the first step of dissociation of the azomethane into the hot methyl, CH$_3^+$, and the diazenyl radical was assumed to be prompt. The subsequent processes are:
$\text{CH}_3\text{NN} \rightarrow \text{CH}_3 + \text{N}_2 \quad k_1$

$\text{CH}_3^* + \text{M} \rightarrow \text{CH}_3 + \text{M} \quad k_2$

$\text{CH}_3^* \rightarrow \text{Products} \quad k_3$

$\text{CH}_3 \rightarrow \text{Products} \quad k_4$

where steps 3 and 4 allow the radicals to be removed from the sample volume either by reaction or translational motion. The appearance kinetics at the cold methyl band was fit by allowing the initial concentrations of the hot methyl and the methyldiazemyl to vary. The best fit was obtained when these concentrations were $1:1 \pm 15\%$, consistent with the proposed mechanism but not with an arbitrary mixture of single and multiphoton products.

It seems reasonable some fraction of the second-step methyl radicals could be formed with some excitation the $v_2$ mode during the dissociation; it also seems reasonable that some of the first-step methyl could be produced with no excitation in the $v_2$ mode. To test these hypotheses, the cold methyl appearance was fit with a model that included a prompt component. Most kinetic data could not be fit with this model, but some data files suggested a small ($<15\%$) prompt component. This result is consistent with the data of Figures 14 and 15, which show no significant prompt component to the rise. It appears therefore that few or none of the first methyl radicals are produced with no excitation in the $v_2$ mode. To determine if the second-step methyl radicals have any excitation in the $v_2$ mode, the first methyl rise was modeled with a delayed ($5\text{ ns}$) component included, and the relative amount of this component was allowed to vary. The best fit to the hot methyl data was obtained when the contribution from the delayed methyl was less than 20%. The above analyses combined with the kinetics of the photofragments confirm that the photolysis proceeds through a two-step mechanism that
produces methyl radicals having very different internal excitations. From the plot in Figure 22, the decay rate of the methylidazonyl was determined to be $1.9 \pm 0.3 \times 10^8$ s$^{-1}$.

An important goal in the spectroscopic studies of the methyl radical has been determination of spectroscopic constants that will provide more information about the potential energy surface of the radical. This information will help theoretical chemists test and verify their calculations. Central to the understanding of the potential energy surface is knowledge of the harmonic frequencies, $\omega_p$, that correspond to the curvatures at the radical's equilibrium geometry. Determining harmonic frequencies, $\omega_p$, from experimentally measured transition frequencies $\nu_i$, requires knowledge of the anharmonic coupling constants. For the $\nu_1$ totally symmetric stretch of the methyl radical (Herzberg, 1945):

$$\omega_1 = \nu_1 - 2X_{11} - \frac{1}{2}X_{12} - X_{13} - X_{14}$$

where $X_{11}$ is the anharmonic coupling constant between the totally symmetric stretch and one of the other vibrational modes. Kelly and Westre (1988) reported the $X_{11}$ value to be -22.7 cm$^{-1}$. The value for $X_{12}$ was found from our high resolution methyl spectra to be $-6.8 \pm (0.2)$ cm$^{-1}$. Kelley and Westre (1988) determined that $2X_{12}$ was equal to $-19.6 \pm 3$ cm$^{-1}$. $2X_{12}$ should equal the shift seen in our high resolution spectra between sequence bands with $\nu=2$ and $\nu=0$ quanta in the $\nu_2$ mode. This shift was determined from our data to be $-15.0 \pm 2$ cm$^{-1}$ which agrees within combined error limits with the Kelley and Westre value. The resolution in these transient CARS studies is greater than in the resonance Raman work of Kelley and Westre, and consequently the value of $-15.0 \pm 0.2$ cm$^{-1}$ is probably more reliable. Accurate knowledge of this and other coupling constants will provide additional information about the potential surface of the methyl radical.
Bauer (1969) suggested that an analysis of the product state distribution of the three photofragments might help in determining the dissociative mechanism. Information about the transition state geometry of the methyldiazenyl radical can be determined from the rotational and vibrational distribution of the nitrogen photofragment as well as that of the second methyl radical. Although the transition state structure for the first step in azomethane photodissociation is not known, it would seem reasonable for excitation to occur in the \( v_2 \) mode as the geometry of the methyl changes from a near tetrahedral to a planar species. From a rough analysis of the data shown in Figure 13, 19% of the first-step methyls have 4 quanta of excitation in \( v_2 \), 24% have 3 quanta in \( v_2 \), 27% have 2 quanta in \( v_2 \), 30% have 1 quantum in \( v_2 \), and less than 5% of the hot methyls have excitation in \( v>4 \). This analysis assumes that 20% of the population in the first hot band actually originates from the second methyl. No other hot bands were observed, but this could be due to low CARS sensitivity. An analysis of the \( v_2 \) manifold using IR spectroscopy could confirm these findings.

A number of calculations have been carried out on diazene (HNNH), the simplest azo compound and on its possible dissociative intermediate HNN (Baird, 1975; Jensen et al., 1987; Curtiss et al., 1984). Calculations have been made on the isomerization, thermolysis and photolysis pathways (Dannenberg and Rocklin, 1982; Osamura et al., 1979; Baird and Swenson, 1973; Olbrich, 1978). It is important to note that although diazene is the simplest azo compound, its chemistry is significantly different from that of azomethane (Vidvarthi et al., 1976). Most calculations on azomethane have been concerned the isomerization or thermolysis pathways, so there is little known about the mechanism for photodissociation. Ab initio SCF calculations on the stability and dissociation pathway of the methyldiazenyl radical have been performed by Yamashita et al. (1981). They determined that although the dissociation of the radical is exothermic by
18.3 kcal/mol, it has a 14.5 kcal/mol barrier to dissociation along the C-N stretching reaction coordinate. From the CARS experiments, it seems that the diazenyl radical could not be stabilized even with the collisional conditions used here: 75 hard sphere collisions with He or 75 collisions with He and 3 with SF$_6$ within its lifetime. Without more information about the structure and energetics of the methyl diazenyl intermediate, it would be difficult to explain the lifetime of the radical.

Ab initio calculations for the transition state of the methyl diazenyl radical were performed by Kim Andrews (Burton et al., to be published). Using the UHF method with a 6-31G* basis set and full geometry optimization, he calculated the N-N bond distance to be 1.132 Å, the CNN bond angle to be 115.3 °, and the NCH bond to be 107.6 °. Since the N-N bond distance is 1.10 Å in free nitrogen and 1.247 Å in azomethane, it seems very reasonable that there would be little vibrational excitation in the nascent nitrogen photoproduct. Andrews used the calculated structure to determine the Franck-Condon factors between the methyl diazenyl v=0 and the free nitrogen v=0, v=1 levels. He concluded that approximately 85% of the nitrogen photofragment would be in the v=0 and 15% in the v=1, in very good agreement with the experimental results.

From a consideration of the force exerted on the nitrogen as the C-N bond is broken, there would have to be rotational excitation in the nitrogen photofragment. This is consistent with the 2500 K rotational temperature determined from the experimental results. On the other hand from the transition state geometry for the methyl diazenyl, the methyl radical would seem to be pushed almost along its C$_3$ axis giving little or no rotational excitation. This is inconsistent with the experimental determination of a 1300 K rotational temperature. Since the photofragments are known to have a large amount of translational energy, is might be possible that the methyls are formed rotationally cold but become excited through collisions. Varying the probe delay from 3
to 10 ns yielded the same rotational temperature for the methyl radicals, but if the methyl radicals were translationally hot, these delays might not be precollisional. For a methyl radical to collide with sample molecule in 3 ns, it would have to be moving at a rate 5 times that of a thermal methyl molecule. This would require that the methyl radicals have about 7000 cm\(^{-1}\) of translational energy. A total of 16,800 cm\(^{-1}\) of energy is available to the photofragments. Some of the energy is distributed in the photofragments in the following internal modes: \(N_2\) vibrations, 400 cm\(^{-1}\); \(N_2\) rotations, 1700 cm\(^{-1}\); methyl vibrations, 900 cm\(^{-1}\); methyl rotations, 1300 cm\(^{-1}\). This would leave 12,500 cm\(^{-1}\) of energy available for translational excitation. It is therefore possible that the methyl rotational spectrum is not nascent, and that the high rotational temperature actually comes from T-R transfer. It would be fairly easy to prove whether or not the measured methyl rotational distribution is nascent by repeating the high resolution scan with a lower azomethane pressure at a delay of 3 ns.

The quantum calculation also suggests that the second methyl would be formed with some vibrational excitation, since the NCH bond angle is 107.6 \(^\circ\), considerably closer to that of a tetrahedral than a planar species (NCH of 90 \(^\circ\)). This prediction seems inconsistent with the observation that less than 20\% of the second methyl radicals are formed with excitation in the \(v_2\) mode. The calculations carried out by Andrews include no correlation effects, and it is possible that more extensive calculations will lead to better agreement with the experimental results.
Chapter 4
3-(methylazo)-3-methyl-butene (MAMB)

Introduction

MAMB is a highly unsymmetrical azoalkane whose photolysis has been studied using transient CARS (Adams et al., 1986). MAMB was chosen for study in hopes that it would dissociate on the nanosecond time scale yielding photoproducts that could be detected using CARS. In solution phase photolysis studies, MAMB partially dissociated and formed "turnabout" products (Engel and Gerth, 1983). The explanation of Engel and Gerth was that the trans azoalkane converted to the unstable cis isomer following irradiation and then thermally dissociated to form the 3-methyl-1-buten-3-yl or dimethylallyl radical and the methyl diazenyl radical. They estimated that the lifetime of the diazenyl intermediate was 7.7 ns. That MAMB would undergo a sequential dissociation is not surprising; the C-N bond to the dimethylallyl group is weaker than that to the methyl radical, and it is expected to break first to form a relatively stable dimethylallyl radical.

\[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{N} \equiv \text{N} \\
\text{C} \equiv \text{CH}_2 \\
\text{H}_3\text{C} \\
\text{CH}_3
\end{array}
\]

MAMB

The gas phase photodissociation of MAMB was studied using transient CARS. The details of these experiments have been reported elsewhere (Adams, 1989; Adams et al., 1986), so the results will be discussed only briefly here. MAMB was found to dissociate through a stepwise mechanism into a dimethylallyl fragment and a
methyldiazenyl radical. The methyldiazenyl lived for approximately 12 ns and broke
apart into N$_2$ and CH$_3$.

\[ \text{H}_3\text{C} \quad \text{N} = \text{N} \quad \text{C} = \text{C} \quad \text{C} = \text{CH}_2 \quad \text{hv} < 2 \text{ ns} \quad \text{C} = \text{C} \quad \text{CH}_2 \quad \text{H}_3\text{C} \quad \text{N} = \text{N}. \]

\[ \text{H}_3\text{C} \quad \text{N} = \text{N} \quad \text{ca.} \ 12 \text{ ns} \quad \cdot \text{CH}_3 \quad + \quad \text{N}_2 \]

The dimethylallyl fragment was observed to have vibrational features in the C-H
stretching region centered about 2993 cm$^{-1}$. The methyl photoproduct was identified
through the Q Branch of its $\nu_1$ symmetric stretch, and N$_2$ was distinguished by its well
known 2330 cm$^{-1}$ vibration. No Raman spectrum had been reported for the dimethylallyl
radical, and it was identified partially through comparison with matrix IR studies. Since
the transient assigned to dimethylallyl persisted after 110 hard sphere collisions with SF$_6$,
it seemed unlikely that it could be a methyl hot band. Only the kinetics of the three
photofragments were studied; no product state distributions were determined.

After reexamination of azomethane photolysis revealed large amounts of
vibrationally hot methyl radicals, the assignment of the 2993 cm$^{-1}$ transient from MAMB
was questioned. A high resolution scan over this band could differentiate between a hot
methyldiazenyl radical and a large radical that would show no rotational structure under these
experimental conditions. Since both azomethane and MAMB are thought to dissociate
through a diazenyl intermediate, the product state distribution of the MAMB's fragments
could confirm the proposed mechanism and shed more light on the nature of the
intermediate. For these reasons, MAMB was briefly reinvestigated.
Results

The MAMB sample had previously been prepared by Steve Adams. A ground state spectrum was taken to confirm its identity and purity. The etalon was then placed in the probe oscillator cavity, and a high resolution scan was taken at early time under rotationally relaxed conditions of the dimethylallyl and methyl radicals (Figure 23). Comparison with Figure 9 shows that the cold methyl radical is present in both spectra, but that the two features at lower frequency are different. A close analysis of the data in Figure 23 reveals however that the feature near 2993 cm⁻¹ exhibits some reproducible modulation very similar to that of the hot methyl formed in dissociation of azomethane. From a comparison with data in Figure 9 as well as simulated spectra of the hot band's rotational contour, approximately 20% of the methyl radicals seem to be formed with 1 quantum of excitation in the ν₂ mode. No further hot bands were detected. Due to the paucity of MAMB sample, no attempt was made to determine the nascent rotational temperature of the methyl radical, but instead the rotational and vibrational distributions of the nitrogen fragment were measured.

There was a large nonresonant transient pedestal observed from MAMB in both the C-H and N₂ regions. This was probably due to a MAMB transient photoprocess. The large nonresonant background made it necessary to limit the MAMB sample pressure to 1.5 torr, consequently limiting the quality of the data. To determine the vibrational distribution of the nitrogen, low resolution scans were taken over the ν=0→1, ν=1→2 and ν=2→3 transitions under rotationally relaxed conditions. No signal was observed at the ν=2→3 band, but the reduced data for the lower two transitions are shown in Figure 24. From these data, we find 84 ± 4% of the nascent nitrogen in the ν=0 level, 16 ± 4% in the ν=1 level and 0 ± 5% in the ν=2 level.
Figure 23. High resolution spectrum of the two photofragments from MAMB. The feature on the right is the totally symmetric stretch of the methyl radical. The feature on the left is a superposition of a small signal that arises from methyl radicals with one quanta of excitation in the \(\nu_2\) mode on top of a larger signal from the dimethyl allyl radical. The scan was taken at a delay of 25 ns. The sample contained 5 torr of MAMB and 250 torr of helium.
Figure 24. Low resolution spectra showing the vibrational distribution of the nitrogen photoproduct from MAMB. The vibrational distribution is discussed in the text. The scan was taken at a delay of 15 ns. The sample contained 2 torr of MAMB and 275 torr of helium.
To determine the nitrogen rotational distribution, high resolution scans were taken at 10 and 15 ns delays. There is no discernable difference between the scans at these two times, and the averaged spectrum is shown in Figure 25. As was mentioned earlier, lower sample pressures combined with a large nonresonant background led to much poorer quality data. The negative-going component at low J values originates from ground state nitrogen that had built up during the scan being collisionally removed from the probe volume. This is coupled with a dispersive band shape due to the nonresonant background. This nonresonant background was not seen with azomethane, and so this recoil effect is more pronounced than in Figure 19, making the deduced population distribution less reliable. To account for the nonresonant pedestal, rotational intensities were measured from line drawn along the Y-axis of the spectrum. This line corresponded to a baseline where the even to odd J ratio was equal to 2:1. From these intensities a Boltzmann plot was constructed for the nitrogen's rotational states (Figure 26). The line through the data points is a least squares fit to the data with a correlation coefficient of .88. Although the data is noisier, the plot is still linear implying that a Boltzmann temperature can used to describe the rotational distribution. The temperature determined from the slope of the plot is approximately 2000 K.

Discussion

The high resolution spectrum of the transient feature assigned to the dimethylallyl radical indicates that only a small portion of the signal originates from methyl radicals excited in their \( \nu_2 \) mode. This basically confirms the original interpretation and rules out the possibility that the prompt rise of the 2993 cm\(^{-1} \) feature is due to multiphoton production of hot methyl while the delayed rise is due to a single photon dissociation. This assignment is also consistent with the observation that the 2993 cm\(^{-1} \) band persists under vibrationally relaxing conditions.
Figure 25. High resolution spectra of the nascent rotational distribution of the nitrogen photoprodct from MAMB. The scan was taken at a delay of 10 ns. The sample contained 2 torr of MAMB.
Figure 26. Boltzmann plot of the nascent nitrogen rotational data from MAMB. The straight line through the data points is the least squares fit to the data. The rotational data can be described by a Boltzmann temperature of 2100 K.
The vibrational and rotational distributions for the nitrogen photofragment from MAMB were found to be very similar to those found from azomethane. Low vibrational excitation of the nitrogen photoproduction is consistent with the ab initio calculation that predicts that N-N bond distance in the methyldiazenyl transition state to be very close to the distance in free nitrogen. The rotational distribution is also consistent with the calculated structure of the diazenyl radical transition state. In the C-N bond breaking, a force would be exerted on the emerging nitrogen molecule that would cause rotational excitation. The rotational temperature for the nitrogen from the MAMB dissociation appears to be lower than that for the azomethane dissociation. This is possibly due to the lower quality MAMB data. The similarities between the rotational and vibrational distributions from the MAMB and azomethane photolyses would indicate that both proceed through the same intermediate: the methyldiazenyl radical.
Chapter 5
Azoisopropene

Introduction

In an attempt to further elucidate the gas phase photolysis mechanism for symmetric azoalkanes, studies of a sample with a longer dissociative lifetime would be desired. An azoalkane with a dissociative lifetime on the $10^{-8}$ second scale could provide more information about the dissociative state as well as the diazenyl intermediate. High pressure studies of the photolysis of azoisopropene (AIP) led Chervinsky and Oref (1977) to calculate a dissociative lifetime for AIP of $4 \times 10^8 \text{s}^{-1}$ (2.5 ns). Adachi and Bosco (1981) found that the lifetime was $1.6 \times 10^8 \text{s}^{-1}$ (6 ns). Both groups assumed that the dissociation occurred from an excited triplet state and that the C-N bonds broke in a concerted fashion. Transient CARS studies of gas phase photolysis of AIP could shed more light on the nature of the C-N bond cleavage as well as the nature of the excited state precursor.

![AIP molecule](image)

AIP

The gas phase photolysis of AIP was first studied by Durham and Steacie (1953) who reported that the basic mechanism for photolysis at 366 nm could be described as:

\[
\text{AIP} + \text{hv} \rightarrow \text{AIP}^* \\
\text{AIP}^* + \text{M} \rightarrow \text{AIP} \\
\text{AIP}^* \rightarrow 2 \text{IP} + \text{N}_2.
\]
The quantum yield for photodissociation at 355 nm (n→π*) is unity at low pressures, but as the pressure is increased, photoisomerization becomes the major channel. At a CO₂ pressure of 42 torr, the quantum yield for photodissociation drops to 0.69 (Fogel and Steel, 1976). Studies by Chervinsky and Oref (1977) have shown that helium is a much less efficient collisional partner than CO₂, and pressures of less than 1 atm of He should have little effect on the quantum yield for photodissociation. In solution phase, the quantum yield is 0.025 (Pritchard et al., 1979). The quantum yield for photodissociation at 200 nm (n→π*) is one for CO₂ pressures up to 400 torr (Arin and Steel, 1972). At this higher photon energy, the dissociation of AIP appears more complicated, and a number of different dissociative pathways have been suggested.

Although alkyl radicals are important species in combustion and atmospheric photochemistry, their spectra have only recently been studied in detail. Ultraviolet transient absorption spectra of the isopropyl radical show strong absorptions below 260 nm (Wendt and Hunziker, 1984). Ab initio SCF calculations by Lengsfield et al. (1984) confirmed Wendt and Hunziker's findings and assigned the UV absorptions to Rydberg transitions. The infrared spectrum of the isopropyl radical was measured by observing the photolysis products produced by irradiating diisobutyryl peroxide in an argon matrix at wavelengths greater than 280 nm (Pacansky and Coufal, 1980). In the C-H stretching region, these workers assigned a band at 3058 cm⁻¹ with a shoulder at 3069 cm⁻¹ to the stretching of the radical center's C-H bond. They also assigned three CH₃ stretches at 2920, 2850 and 2830 cm⁻¹.

Chettur and Snelson (1987) irradiated AIP in an argon matrix and found photoproduct features similar to those of Pacansky and Coufal (1980). Chettur and Snelson assigned a feature at 3052 cm⁻¹ to a C-H stretch on the radical center, but no other features in the C-H stretching region were observed. This may have been due to
overlap with ground state peaks from the parent AIP. Chettur and Snelson also found that if the isopropyl radical was irradiated with a Hg arc lamp, the feature at 3052 cm\(^{-1}\) disappeared and a band at 3028 cm\(^{-1}\) grew in. They postulated that this feature might be the n-propyl radical since the enthalpy difference between i-propyl and n-propyl is only 3 kcal/mol. Theoretical calculations of the isopropyl structure have also been performed (Pacansky and Dupuis, 1980; Pacansky and Yoshimine, 1987). A Raman spectrum of the isopropyl radical has never been reported.

In the present project, transient CARS was used to probe for the photofragments of the gas phase photolysis of AIP after 355 nm excitation. The maximum absorption for the n\(\to\)\(\pi^*\) transition in t-AIP sample occurs at 355 nm with a molar extinction coefficient of about 10 M\(^{-1}\)cm\(^{-1}\) (Yamashita et al., 1973).

**Experimental details**

AIP was synthesized by Kim Andrews and Anne Culotta. AIP tautomerizes to the hydrazone relatively quickly at room temperature, so the sample was replaced every 3 or 4 days. A ground state spectrum was taken of pure AIP to determine the frequencies of its ground state transitions (Figure 27). Many of the vibrations of a low symmetry species such as the isopropyl radical may be both IR and Raman active. As a number of these modes have been assigned from IR spectroscopy, a knowledge of the ground state spectrum of the parent compound will help to determine if the transient can be distinguished from the parent species. All measurements were taken at 295 ± 2K.

**Results**

Obtaining the transient CARS spectra in the C-H region was hampered by the presence of a large amount of methylene chloride impurity remaining from the synthesis. Methylene chloride has a strong Raman active transition at about 2997 cm\(^{-1}\). Numerous scans were performed over the entire C-H stretching region under rotationally relaxed
Figure 27. Ground state spectrum of 2 torr of AIP.
and unrelaxed conditions before a weak transient feature was observed at about 3045 cm\(^{-1}\). A typical scan taken with 8 torr of AIP under rotationally relaxed conditions is shown in Figure 28. The shape of the transient feature varies little as the amount of rotational relaxation is changed. Searches over the remainder of the C-H stretching region showed no other transient features.

Attempts were made to study the 3045 cm\(^{-1}\) band under vibrationally relaxed conditions. When low pressures of SF\(_6\) were added to the 8-10 torr of AIP sample, the transient decreased in magnitude and the amount of nonresonant interference increased dramatically. As more SF\(_6\) was added, it became progressively more difficult to observe the transient.

Kinetics of the transient were measured at 3045 cm\(^{-1}\) under a variety of collisional conditions. With lower pressures of He buffer gas (below about 300 torr), the data could not be adequately modeled. Kinetics of the transient with higher He pressures were measured (Figure 29) and fit with the following model:

\[
\begin{align*}
&C_3H_7N_2C_3H_7^* \rightarrow C_3H_7 + N_2C_3H_7 \quad k_1 \\
&N_2C_3H_7 \rightarrow C_3H_7 + N_2 \quad k_2 \\
&C_3H_7 + C_3H_7 \rightarrow \text{Products} \quad k_3
\end{align*}
\]

where \(k_3\) describes either the reaction of C\(_3\)H\(_7\) to form products. From fits of transient rises with higher pressure buffer gas pressures, \(k_1\) was determined to be about 1 x 10\(^{10}\) s\(^{-1}\) unresolvably prompt on our time scale, and \(k_2\) was found to be 1.7 ± 1 x 10\(^8\) s\(^{-1}\).

To verify that step 2 describes the formation of the isopropyl radical from the dissociation of isopropylidiazonyl intermediate, the appearance kinetics of the nitrogen photoproduct were investigated. The appearance of the nitrogen was measured in the same manner as described in Chapter 3. Transient CARS measurements of AIP photolysis in the nitrogen region were plagued with the same large ground state
Figure 28. Low resolution spectrum of the isopropyl radical from AIP. The scan was taken at a delay of 30 ns. The sample contained 8 torr of AIP and 250 torr He.
Figure 29. Appearance kinetics of the isopropyl radical from AIP. The kinetics were taken at a frequency of 3047 cm\(^{-1}\). The solid line through the data points is the computed fit. The parameters for the fit are discussed in the text. The sample contained 10 torr AIP and 500 torr He.
Probe delay (ns) vs. Induced (CARS Signal)
nonresonant background observed for azomethane and MAMB, and as a consequence, lower pressures of AIP also had to be used (about 2 torr). Appearance kinetics for nitrogen taken with less than 300 torr of added He buffer gas could not be fit with our kinetics program. However, data taken with higher buffer pressures (and correspondingly prompter rotational relaxation) could be fit with the same model described above, assuming of course that N₂, rather than the C₃H₇, is the species being probed. A representative data file and kinetic fit are displayed in Figure 30. From the fits to the nitrogen data, k₁ was found to be prompt on our time scale and k₂ was 2.5 ± 0.5 x 10⁸ s⁻¹, independent of helium pressure between 300 and 700 torr.

To compare the nitrogen formation process with those from azomethane and MAMB, the nascent rotational and vibrational distributions of the nitrogen were determined. The results of scans taken over the v=0→1 and v=1→2 transitions under rotationally relaxed conditions are displayed in Figure 31. No transient signal was observed in the v=2→3 region. The population distributions were calculated to be 85 ± 3% in v=0, 15 ± 3% in v=1 and 0 + 5% in v=2.

The nascent rotational distribution was measured from the v=0→1 band under two sets of conditions. In the first, a static 2 torr sample of AIP was used, and a high resolution rotational contour was obtained (Figure 32). A high resolution spectrum was also measured under pseudo flowing-sample conditions. To achieve such conditions, the cell was evacuated and refilled with fresh sample six times during the scan to avoid the buildup of nitrogen. Both of these scans were taken at early times (5-8 ns delays). The rotational contour seen under these "flowing-sample" conditions was the same as in Figure 32 at high J levels, but there was no negative-going feature at low J values. This similarity at high J values would indicate that the rotationally excited N₂ was not formed by collisional excitation of pre-existing nitrogen molecules.
Figure 30. Appearance kinetics of the nitrogen photopproduct from AIP. The solid line through the data is the computed fit. The parameters for the fit are discussed in the text. The sample contained 2 torr AIP and 300 torr He.
Figure 31. Low resolution scan of the vibrational distribution of the nitrogen from AIP. The scans were taken at a delay of 15 ns. The vibrational distribution is discussed in the text. The sample contained 2 of AIP and 700 torr of helium.
Figure 32. High resolution spectrum of the nascent rotational distribution of the nitrogen photoproduct from AIP. The spectrum was obtained at a delay of 5 ns. The sample contained 2 torr of AIP.
To determine if the rotational distribution can be described by a Boltzmann temperature, the natural log of the intensity at each J value divided by 2J + 1 was plotted against the state energy (Figure 33). The straight line through the data points is a least squares fit to the data. The correlation coefficient for the least squares fit is 0.95. The deviation from linearity is more likely due to noisy data rather than a non-Boltzmann distribution. The rotational temperature was determined to be approximately 2100 K.

Discussion

It is necessary to confirm that the transient seen at 3045 cm\(^{-1}\) is the isopropyl radical. Pacansky and Coufal (1980) reported that the C-H stretching vibration on the radical center has a frequency of 3058 cm\(^{-1}\). Chettur and Snelson (1987) reported that the same species under virtually identical conditions (matrix isolation with infrared spectroscopy) has a frequency of 3052 cm\(^{-1}\). A difference of 7 to 13 cm\(^{-1}\) between an IR matrix study and a gas phase Raman spectrum is reasonable, and the 3045 cm\(^{-1}\) transient is most likely the isopropyl radical. However, other possibilities should be considered.

Since the feature has a component with a rapid appearance (1 \(\times\) 10\(^{-10}\) s\(^{-1}\)), it is possible that it has a multiphoton origin. Sufficiently energetic isopropyl and n-propyl radicals are known to dissociate into CH\(_3\) and ethylene (Schultz \textit{et al.}, 1984). No ethylene was observed either as a permanent photoproduc or as a transient species, nor was any methyl radical transient observed. Studies of the photolysis of azo-n-propane described in the next chapter show a transient at 3028 cm\(^{-1}\), the same frequency reported for the n-propyl radical by Chettur and Snelson (1987). The IR spectrum of the ethyl radical reported by Pacansky and Dupuis (1982) shows a number of vibrations including a C-H stretch at 3033 cm\(^{-1}\).

It seems unlikely that the transient feature at 3045 cm\(^{-1}\) could be either the n-propyl or ethyl radical. It also seems unlikely that it could originate from the
Figure 33. Boltzmann plot of the nascent nitrogen rotational data from AIP. The straight line through the data points is the least squares fit to the data. The rotational data can be described by a Boltzmann temperature of 2100 K.
multiphoton dissociation of AIP, since neither methyl radicals nor ethylene were observed. For this species to be an excited state precursor of the i-propyl radical and isopropyldiazenyl, it would have to disappear prior to the appearance of the nitrogen photoprodut. Kinetics analyses show that the rise of the 3045 cm\(^{-1}\) transient has a prompt component while the appearance of the nitrogen is delayed.

Comparisons were made between ground state spectrum of the heavily photolyzed sample and spectra obtained on our apparatus for authentic samples of some possible permanent photoproducts. Only diisopropyl, propane and propene (the combination and disproportionation products for the isopropyl radical) were detected in our sample. Ground state spectra of a photolyzed sample that contained SF\(_6\) as a buffer showed that little dissociation had taken place. This is consistent with the transient spectral scans where the intensity of the 3045 cm\(^{-1}\) feature decreased with increasing pressures of SF\(_6\). This behavior could reflect increasing collision-induced photoisomerization, conversion of the trans-AIP to the cis isomer, at the expense of photodissociation.

The appearance of the nitrogen photoprodut was delayed and had a rate coefficient of \(2.5 \pm 0.5 \times 10^8\) s\(^{-1}\), independent of He pressure between 300 and 700 torr. This pressure independence shows that rotational relaxation was not the rate-limiting step. Also, since the nitrogen was formed only slightly vibrationally excited its delayed appearance in the v=0 state cannot be due to collisional vibrational relaxation. The 4 \(\pm\) 1 ns lifetime for the precursor to the nitrogen agrees within error with the 6 \(\pm\) 2 ns lifetime found for the second step of the 3045 cm\(^{-1}\) rise. The only satisfactory explanation for this observation is that the 3045 cm\(^{-1}\) feature is a band of the isopropyl radical.
The mechanism for the gas phase photolysis of AIP at 355 nm can be described by:

\[
\begin{align*}
\text{H}_2\text{C} & \text{N=N} \text{C} \text{CH}_3 \quad \text{h v} \quad \text{N=N} \text{C} \text{CH}_3 & + & \text{CH}_3 \text{C-H} \\
\text{H}_2\text{C} & \text{N=N} \text{C} \text{CH}_3 & \text{N=N} \text{C} \text{CH}_3 & + & \text{N}_2
\end{align*}
\]

> $10^9 \text{ s}^{-1}$

$-2 \times 10^8 \text{ s}^{-1}$

Since the nitrogen photoprodct is produced through a diazynyl intermediate, it may have nascent rotational and vibrational distributions similar to the nitrogen from azomethane and MAMB.

The vibrational distribution of the nitrogen photoprodct was 85% in $v=0$ and 15% in $v=1$, the same within experimental uncertainty as for the nitrogen formed through a methylidiazynyl intermediate. The rotational data can be described by a Boltzmann temperature of 2100 K. This is very similar to that from MAMB and slightly lower than that from azomethane. The rotational data from AIP are of lower quality than the azomethane data, and there is therefore greater uncertainty in the temperature determination. The product state distribution for the nitrogen from AIP would indicate that the N-N bond length in the isopropylidiazynyl dissociative transition state is only slightly greater than in free nitrogen, and the CNN bond angle is similar to that of the dissociating methylidiazynyl radical. No quantum chemical calculations have been performed on the structure of the isopropylidiazynyl radical. The kinetics for the
isopropyl radical and the nitrogen photoproduct demonstrate that this symmetric
azoalkane dissociates in a stepwise fashion through an isopropyldiazenyl intermediate.
The product state distributions of the nitrogen are similar to those seen in the dissociation
of azomethane and MAMB and are consistent with a stepwise mechanism.
Chapter 6

Azo-n-propane

Introduction

One of the least studied but potentially most interesting azoalkanes is azo-n-propane (ANP).

\[
\begin{aligned}
\text{HN} & \quad \text{H} \\
\text{HN} & \quad \text{H} \\
\text{C} & \quad \text{C} \\
\text{N} & \quad \text{N} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{aligned}
\]

ANP

ANP is known to dissociate in the gas phase to produce two n-propyl radicals and N₂ (Kerr and Calvert, 1961).

\[
\begin{aligned}
\text{ANP} + \text{hv} & \rightarrow \text{ANP}^* \\
\text{ANP}^* + \text{M} & \rightarrow \text{ANP} + \text{M} \\
\text{ANP}^* & \rightarrow 2\text{C}_3\text{H}_7 + \text{N}_2
\end{aligned}
\]

The quantum yield for photodissociation at low pressures is one (Terry and Futrell, 1967). As the pressure is increased, the quantum yield for photodissociation decreases and the Stern-Volmer plot is curved (Chervinsky and Oref, 1977; Pritchard et al., 1979). From the analysis of such plots, Chervinsky and Oref determined the rate coefficient the dissociative state for ANP to be \(4 \times 10^7\) s\(^{-1}\). Adachi and Bosco (1981) found the rate coefficient to be \(6.6 \times 10^7\) s\(^{-1}\). They both used a model in which the ANP dissociated in one kinetic step from the excited triplet surface.
The absorption maximum for the broad \( n \rightarrow \pi^* \) transition in ANP is at 360 nm and has an extinction coefficient of approximately 2 M\(^{-1}\) cm\(^{-1}\) (Yamashita et al., 1973). A mass spectrometric study was done on the photodecomposition of ANP (Yamashita and Hayakawa, 1973). These workers found a minor peak that they assigned to the n-propylidazeny1 radical suggested that the species had a 50 \( \mu \)s lifetime. However, the conclusions presented in this paper were not substantiated, and this report has been generally ignored by the azoalkane community.

The structure and spectroscopy of the n-propyl radical has been studied in some detail. The structure of the n-propyl radical was first determined in 1973 by ESR spectroscopy (Adrian et al., 1973). Pacansky et al. (1977) obtained an infrared spectrum of the radical in a rare gas matrix that revealed three bands in the C-H stretching region. The bands at 3112.5 and 3032 cm\(^{-1}\) were assigned to vibrations associated with the radical center CH\(_2\) group. An anomalous feature was seen at 2840 cm\(^{-1}\). Chettur and Snelson observed a species that grew in when the isopropyl radical was irradiated with \( \lambda < 280 \) nm. They assigned these features at 3028 and 3118 cm\(^{-1}\) to the n-propyl radical. UV transient absorption experiments have been performed on the photodissociation of ANP, and the experimenters found that the n-propyl radical had a strong absorbance at 245 nm (Adachi and Bosco, 1981). Calculations have also been performed to determine the structure of the n-propyl radical (Pacansky and Dupuis, 1979).

In the present work, transient CARS spectroscopy has been used as a probe to study the photolysis of ANP with 355 nm excitation. Since previous experiments have suggested that the dissociative state of ANP is moderately long lived (15-25 ns), information about this state as well as the nature of the photolysis mechanism might be determined.
Experimental Details

ANP was synthesized by Steve Adams. All experiments were performed at 295 ± 2K. Static sample pressures of 5 torr ANP were usually used in conjunction with helium and SF₆ as buffer gases. The original ANP sample used had a large amount of hexane impurity as shown by GC analysis. Since the Raman spectra of hexane is almost identical with that of ANP, it was nearly impossible to detect the hexane impurity over the ground state ANP CARS spectrum. This hexane impurity was probably formed when the sample was inadvertently stored at room temperature; all azoalkanes need to be stored in a refrigerator or a freezer. When a new, pure ANP sample was acquired, a ground state CARS spectrum was taken (Figure 34). No features were observed in the area where n-propyl IR transitions had been reported.

Results

Searches were made over the entire C-H stretching region and four transient features were observed. A scan taken under rotationally relaxed conditions at a delay of 50 ns is displayed in Figure 35. To determine the identity of each of these transient bands, kinetics were obtained under a variety of conditions. The features at 3002, 3014 and 3019 cm⁻¹ appeared promptly while the feature at 3026 cm⁻¹ was delayed. It was thought that one of the prompt features might represent a precursor to the delayed species, but none of the prompt species kinetics matched the rise of the delayed transient. An investigation of the ground state spectrum of the photolyzed ANP showed that the 3019 cm⁻¹ transient feature was also a permanent photoproduct.

Initial studies indicated that this 3019 cm⁻¹ species was propene, but further investigation showed that it was actually ethylene. Studies of the photolysis of azoisopropane at 200 nm have shown that the isopropyl radical can subsequently dissociate to form CH₃ and C₂H₄ (Arin and Steel, 1972). The methyl radical was seen in
Figure 34. Ground state spectrum of 2 torr of ANP.
Figure 35. Low resolution spectrum of the rotationally relaxed transient photoproducts from ANP. The scan was taken at a delay of 50 ns. The sample contained 5 torr of ANP and 200 torr of helium.
the decomposition of the n-propyl radical in the ESR studies of Adrian et al. (1973), and they postulated that the photolysis at 253.7 nm provides enough excess energy to break the n-propyl into CH₃ and ethylene. However, this process is too endothermic to occur for single photon dissociation at 355 nm.

A high resolution spectrum taken of the band at 3002 cm⁻¹ confirmed that it was the methyl radical. Low resolution spectra of this band taken at early time without buffers show that the band is narrow, indicating that the methyl radical is formed with little rotational excitation. No methyl vibrational hot bands were observed. Kinetic studies of the methyl band indicated that its appearance was prompt (subnanosecond) under partially rotationally relaxed conditions (Figure 36). The fit to the data was obtained using the following model:

$$\text{ANP}^{**} \rightarrow \text{CH}_3^* + \text{CH}_3 + Y$$  \hspace{1cm} k_1

$$\text{CH}_3^* + M \rightarrow \text{CH}_3 + M$$  \hspace{1cm} k_2

$$\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$$  \hspace{1cm} k_3

$$\text{CH}_3 \rightarrow \text{Products}$$  \hspace{1cm} k_4

where ANP^{**} is the multiply excited ANP, Y represents the N₂ and ethylene photoproducts and CH₃^* is either rotationally or vibrationally excited methyl. The relative yields of CH₃^* and CH₃ were assumed to be 1:1, but this was never verified. k₃, the second order decay rate, was determined to be unimportant compared with k₄, representing the transport of methyl out of the probe volume.

Studies of the effect of helium buffer gas on the four transients showed that all four species survived for moderately long times (greater than 200 ns) under rotationally relaxed conditions. Studies with SF₆, however, revealed that only the methyl, ethylene and the 3026 cm⁻¹ band persisted under vibrationally relaxed conditions. A spectrum of these three species with 150 torr of SF₆ is displayed in Figure 37.
Figure 36. Appearance kinetics of the methyl radical from the multiphoton dissociation of ANP. The kinetics were taken at 3003 cm$^{-1}$. The samples contained 5 torr of ANP and 50 torr of helium.
Figure 37. Low resolution spectrum of the vibrationally relaxed transient photoproducts from ANP. The scan was taken at a delay of 200 ns. The sample contained 5 torr of ANP and 150 torr of SF₆.
Since the transient at 3026 cm\(^{-1}\) was long-lived under rotationally and vibrationally relaxed conditions, it could not be an excited species. It was also not a permanent photoproduct. To verify that the species was not an excited state of the ANP parent, O\(_2\) was added to the cell to see if it could be quenched. Unfortunately, the oxygen somehow reacted with the excited ANP and formed droplets along the path of the excitation laser, preventing meaningful measurements. To determine if the transient was a free radical, azomethane was added to the sample cell. Since azomethane would also absorb at 355 nm, the methyl radicals that were produced could react with the species thought to be the n-propyl radical, and this reaction could be seen as an increased second order decay rate. However, no change was observed in the second order decay rate of the 3026 cm\(^{-1}\) with the addition of azomethane.

A ground state CARS spectrum was taken of the photolyzed sample to see what permanent photoproducts were formed. Only ethylene and hexane were conclusively identified, but neither propane or propene were seen. Since only multiphoton products and the n-propyl combination product were seen, this would indicate that ANP is dissociating into CH\(_3\), ethylene and the n-propyl radical.

It was noted earlier that in the IR matrix investigations of Pacansky et al. (1977) a vibration at 3017.5 cm\(^{-1}\) was assigned to the radical center CH\(_2\) group of the n-propyl radical. Chettur and Snelson (1987) reported this same transition at 3028 cm\(^{-1}\). These data support the assignment of the 3026 cm\(^{-1}\) transient as the n-propyl radical.

To confirm the identity and determine the behavior of the 3026 cm\(^{-1}\) transient, kinetics were taken with He and SF\(_6\) as collisional partners. The appearance of this transient was delayed under all circumstances. The kinetics obtained for the transient rise with SF\(_6\) as a collisional partner could not be fit with any model. The appearance of the transient could not be fit with any of the previous azoalkane models in which the excited
azo dissociates into the first alkyl fragment and the diazenyl, followed by the dissociation of the diazenyl. However, the appearance of the species with He as a collisional partner could be fit with a model that includes the decay of an excited state into a dissociative state before fragmentation occurs. The model can be symbolized as:

\[ \text{ANP}^* \rightarrow \text{ANP}_d \]
\[ \text{ANP}_d \rightarrow \text{C}_3\text{H}_7 + \text{N}_2\text{C}_3\text{H}_7 \]
\[ \text{N}_2\text{C}_3\text{H}_7 \rightarrow \text{N}_2 + \text{C}_3\text{H}_7 \]
\[ \text{C}_3\text{H}_7 + \text{C}_3\text{H}_7 \rightarrow \text{products} \]

where \( \text{ANP}^* \) is some excited state of the parent ANP, \( \text{ANP}_d \) is the dissociating state of ANP, and \( \text{C}_3\text{H}_7 \) is the n-propyl radical. Representative appearance kinetics of the n-propyl radical with 700 torr He is shown in Figure 38. Only the appearance kinetics of the n-propyl in the presence of large amounts of He buffer gas ( >400 torr) could be adequately fit. From an average these fits, the following rate constants were calculated: \( k_1 = 4.7 \pm 1 \times 10^7 \text{ s}^{-1} \); \( k_2 = 7.7 \pm 3 \times 10^7 \text{ s}^{-1} \); \( k_3 = 1.8 \pm 0.7 \times 10^8 \text{ s}^{-1} \). The decay of the n-propyl was better described by the second order process in \( k_4 \) than by simple transport out of the beam.

**Discussion**

Since the multiphoton process that produces prompt \( \text{CH}_3 \) and ethylene would also produce a prompt nitrogen fragment, the nitrogen region was not studied. It would be virtually impossible to separate a prompt from a delayed nitrogen photofragment because of low sensitivity as well as accumulation of background \( \text{N}_2 \). Without the \( \text{N}_2 \) appearance kinetics from the single photon dissociation, it is difficult to prove the mechanism described for the n-propyl kinetics.

From a comparison to published IR spectra and the transient CARS spectra, the transient feature at 3026 cm\(^{-1}\) is deduced to be the n-propyl radical. Radical-radical
Figure 38. Appearance kinetics of the n-propyl radical from ANP. The solid line through the data points is the computed fit. The parameters for the fit are discussed in the text. The sample contained 5 torr of ANP and 700 torr of He.
reaction of the n-propyl with the methyl from azomethane could confirm this. The appearance kinetics for the n-propyl radical were obtained for a sample mixture of ANP and azomethane. That the addition of azomethane to the ANP sample had no apparent effect on the second order decay rate. It is possible that the n-propyl n-propyl reaction is more favorable than n-propyl with methyl. Fits to the n-propyl appearance showed that a two-step rise for the radical is always observed, indicating that a diazenyl intermediate is present. Since no prompt n-propyl is observed, it seems unlikely that this two-step rise is due to multiphoton and single photon productions of the n-propyl species. The lifetime for this n-propyl diazenyl intermediate was found to be 5.4 ± 2 ns. The presence of the diazenyl intermediate in the dissociation of ANP is consistent with the stepwise mechanism observed for azomethane and AIP. An interesting difference between ANP and other symmetricazoalkanes is the kinetic evidence for the two excited states involved in the dissociation.

It is important to consider the nature of the excited states involved. The ANP is initially excited to the S₁ state by the 355 nm pulse. Because no fluorescence has ever been observed from any acyclicazoalkane (Collier et al., 1968), the prepared S₁ state cannot live long enough to be the precursor the dissociative state. The first excited state involved in the dissociation is calculated to have a lifetime of approximately 21 ns. Perhaps the first excited state in the mechanism is a twisted S₁ as compared with the trans S₁ that would be formed upon absorption of 355 nm. This twisted S₁ could then intersystem cross to the triplet which might survive for about 15 ns before dissociating. Recent ab initio calculations suggest that the preferred state for dissociation is the T₁ (Burton et al., to be published).

It is also possible that the initially excited S₁ state intersystem crosses to T₂ which then relaxes to the dissociating T₁. Calculations by Camp et al. (1977) on azomethane
show that the surface of the $T_2$ has no minimum for twisting. This could imply that it would take some time for the $T_2$ to twist and internally convert to the dissociative $T_1$.

Any description of the nature of the excited states involved in the dissociation remains speculative, and more work will have to be done to elucidate the mechanism.

A complete search was conducted in the C-H stretching region for precursors to the n-propyl radical. None were located. UV absorption spectra are known for the cis and trans-ANP as well as the n-propyl radical (Adachi et al., 1981). Transient UV absorption spectroscopy could be used to confirm the identity of the species thought to be the n-propyl radical as well as possibly determine the excited states involved. Since the excitation intensities necessary for the transient absorption are much less than needed for transient CARS, it might also be possible to eliminate the interfering multiphoton effects (Selco et al., 1983).
Chapter 7

Conclusions

Transient CARS spectroscopy has allowed us to probe all of the photoproducts from the dissociation of azoalkanes. Kinetic analysis of the appearance of the alkyl radicals and the nitrogen has shown that both symmetrical (azomethane and AIP) and unsymmetrical azoalkanes (MAMB) dissociate in a stepwise manner. From these studies, it can be concluded that all acyclic azoalkanes dissociate in a stepwise fashion.

The internal energy distributions for the nitrogen photoproduct were obtained for azomethane, MAMB and AIP. Since the nitrogen must originate from the diazenyl intermediate, it is important to compare the experimental results with theoretical predictions. The nitrogen from all three azoalkanes is produced with little vibrational excitation: about 85% of the nitrogen is in v=0 and about 15% is in v=1. This is in good agreement with theoretical predictions for the methyldiazenyl radical. Theoretical calculations on the transition state structure of the methyldiazenyl show that a torque will be placed on the nitrogen photoproduct as the C-N bond is broken. This is consistent with the high rotational temperature (2100 - 2500 K) observed for the nitrogen photoproducts.

Since these azoalkanes are dissociating through a diazenyl intermediate, the stability of this intermediate must be considered. The methyldiazenyl radical from azomethane and the isopropyldiazenyl radical from AIP have similar lifetimes, about 5 ns, while the methyldiazenyl from MAMB has a lifetime of closer to 12 ns. The methyldiazenyl from MAMB could be longer lived because it is formed with less internal energy than the other diazenyl intermediates. This is because the dimethylallyl fragment has more internal modes and subsequently can carry away more energy than either the methyl or isopropyl radicals. If this is the case, the methyldiazenyl radical from
azomethane should be stabilized in the presence of large amounts of SF₆, a vibrational relaxer. In the presence of 50 torr of SF₆ and 650 torr of He, no stabilization was seen. The methylidiazene radical would undergo approximately three hard sphere collisions prior to dissociating using this pressure of SF₆. This may be insufficient to vibrationally de-excite and therefore stabilize the methylidiazene. Addition of SF₆ to AIP only seems to induce photoisomerization. Studies using higher pressures of SF₆ buffer gas with azomethane could determine if the methylidiazene is stabilized.

It is difficult to compare the results for the ANP dissociation with those for the other azoalkanes because of the presence of multiphoton products. No information on the nitrogen could be obtained. Because of the complexity of the appearance kinetics for the n-propyl radical, the apparent 6 ns lifetime for the n-propylidiazene radical is suspect. The obvious difference between the photodissociation of ANP and the other azoalkanes is the more delayed appearance of the alkyl radical and involvement of two excited states in the dissociation. The first step of the dissociation for the other azo compounds took place on the subnanosecond time scale. The lifetime of the dissociative state for an azoalkane depends on two quantities: the stability of the incipient radicals and the number of internal modes over which the excitation energy can distributed. Primary radicals such as methyl and n-propyl are inherently less stable than secondary radicals such as the isopropyl. ANP has many more modes over which the energy can be distributed, thereby increasing the unimolecular lifetime for the excited ANP. The combination of these two effects would increase the lifetime of ANP over that of AIP or azomethane. The very high stability of the dimethylallyl would cause the excited MAMB to have a very short lifetime. The fact that the excited states for azomethane, MAMB and AIP do not survive on our time scale does not necessarily exclude then from the photolysis mechanism. Ab initio calculations (Burton et al., to be published) predict
that azomethane dissociates from its lowest triplet surface. The lowest triplet surface could be the dissociative state for ANP. Any assignment of the possible excited states involved in the dissociation would be purely speculative.

High pressure studies of the photodissociation of various azoalkanes have shown curvatures in their Stern-Volmer plots. This would indicate that more than one excited state is involved in the photolysis. A small amount of dissociation is observed in the thermolysis of azoalkanes. Thermolysis must occur off of the $S_0^*$ surface. At very high pressures, only a small amount of residual photolysis is seen, and it is possible that this residual photolysis also occurs off of the $S_0^*$ surface. Since the Stern-Volmer studies indicate that more than one excited state is involved, it is probable that the low pressure photolysis occurs off of a surface other than the $S_0^*$. This would indicate that our findings of a stepwise dissociation mechanism for azoalkanes would not apply to thermolysis or to the residual photolysis in the high pressure regime or in solution.

Many questions remain to be answered in the photochemistry of azoalkanes. The nature of the excited states involved in the vapor phase photolysis has not been determined. The kinetics measured for the ANP indicated that both an initial and a dissociative excited state are involved in the photolysis. These states appear to survive on the nanosecond time scale. It would be very interesting to determine the nature of excited states involved. Transient UV absorption spectroscopy could be used to study the excited states, the alkyl radicals, as well as the possible isomerization.

A more complete product state distribution would be invaluable. If the translational energy of the photoproducts could be determined, the question of whether the high rotational temperatures seen for nitrogen and methyl are nascent or collisionally induced could be answered. A more sensitive spectroscopy (for example: MPI of the
methyl radical) might allow studies at lower pressures which could be used to more accurately determine the nascent rotational temperature.

In conclusion, transient CARS kinetics studies have shown that vapor phase acyclic azoalkanes dissociate in a stepwise fashion involving a diazenyl intermediate. Much information has been obtained about the dynamics of the dissociation, and the experimental product state distributions for the nitrogen from the diazenyl intermediate are in good agreement with theoretical predictions for the transition state structure for the radical.
References


Appendix

Inserting the etalon in the probe YAG cavity

The bandwidth of the probe system is normally limited by the bandwidth of the probe YAG laser which without an intracavity etalon is about 1 cm\(^{-1}\). The bandwidth of the dye laser is about 0.18 cm\(^{-1}\). To obtain high resolution spectra, the YAG laser bandwidth must be narrowed. To do this an etalon is placed in the probe oscillator cavity. The etalon that is used with our system is 50 % reflecting at 1064 nm with a 1 cm\(^{-1}\) free spectral range.

Inserting the intracavity etalon decreases the energy and the stability of the 1064 nm beam. To insure that this decrease is not severe, the YAG oscillator must be in the best possible condition. Replacing the thin film polarizer with a calcite polarizing cube seems to have removed virtually all instabilities. Since the bandwidth of the CARS system with the intracavity etalon in place will be limited by the dye laser, it is also of the utmost importance for the dye laser to be running well. The dye laser should be aligned for minimum linewidth. This can be accomplished by aligning the dye laser oscillator for maximum clarity of the rings that are observed when the light that is scattered off the grating is passed through an etalon. Align the laser for stability and clarity of rings, sacrificing energy if necessary. The lasers are running well when the standard deviations are 3% or less. With both the dye and YAG laser lasers running stably, the intracavity etalon can be inserted.

The etalon is mounted in a MM2 mirror mount that is controlled by 80 pitch screws. First adjust the etalon, before it is put in the YAG cavity, so that it will be parallel to the back mirror of the YAG. Insert the etalon in the cavity between the quarter-wave plate and the back mirror. Display the energy of both the \(\omega_1\) and the \(\omega_2\)
beams on the meters. With the intracavity etalon in place, the reading of the \( \omega_1 \) energy will go up and another scatter plate might have to be added. Adjust the horizontal axis for maximum \( \omega_1 \) energy and then adjust the vertical until both the \( \omega_1 \) and \( \omega_2 \) are maximized. This could easily require walking the two axes. The position where both the \( \omega_1 \) and \( \omega_2 \) are at a maximum should be a plateau, and the laser will behave stably.

To check if the etalon is properly inserted, put a styrofoam beam block in the green beam and look at the scattered light through an etalon with a 3 cm\(^{-1}\) FSR. If the rings are clear then the etalon is properly inserted. If the interference pattern is fuzzy, the etalon should be adjusted until the rings become clear. If the energies are then no longer at their maximum, walk the axes again. Check the ring pattern. Continue this process until the rings are clear and the energies are high.

With the etalon properly inserted, it should be stable for over an hour and will only need minor adjustments during the course of the day. The standard deviations of the \( \omega_1 \) and \( \omega_2 \) should always be less than 10\%. The standard deviations of the CARS signal will go up to 40\%. A scan with reject limits of 25,25\% or 25,30\% will give virtually no rejected shots.