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Photofragment Translational Spectroscopy of Three Body Dissociations and Free Radicals

S.W. North
(Ph.D. Thesis)

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Three Body Dissociations and Free Radicals**

Simon William North
Ph.D. Thesis

Department of Chemistry
University of California, Berkeley

and

Chemical Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

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MASTER

Photofragment Translational Spectroscopy of Three Body Dissociations and Free Radicals

by

Simon William North

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Committee in charge:

Professor Yuan T. Lee, Chair

Professor Daniel M. Neumark

Professor Y. Ron Shen

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Abstract

Photofragment Translational Spectroscopy of Three-body Dissociations and Free Radicals

by

Simon William North

Doctor of Philosophy in Chemistry

University of California at Berkeley

Professor Yuan T. Lee, Chair

This dissertation describes several three-body dissociations and the photodissociation of methyl radicals studied using photofragment translational spectroscopy. The first chapter provides an introduction to three body dissociation, examines current experimental methodology, and includes a discussion on the treatment of photofragment translational spectroscopy data arising from three-body fragmentation.

The ultraviolet photodissociation of azomethane into two methyl radicals and nitrogen is discussed in chapter 2. The two methyl fragments possess disparate translational energies indicating that the dissociation is non-symmetric. The angles between the asymptotic velocity vectors of the three fragments are strongly correlated implying that the CH_3N_2 intermediate dissociates in less than a rotational period, < 1 ps.

Chapter 3 describes the photodissociation of acetone at 248 nm and 193 nm. At 248 nm the translational energy release from the initial C-C bond cleavage matches the exit barrier height and a comparison with results at 266 nm suggests that $\langle E_T \rangle$ is invariant to the available energy. A fraction of the nascent CH_3CO radicals spontaneously disso-

ciate following rotational averaging. The $\langle E_7 \rangle$ for the second C-C bond cleavage also matches the exit barrier height. At 193 nm the experimental data can be successfully fit assuming that the dynamics are analogous to those at 248 nm. A simplified model of energy partitioning which adequately describes the experimental results is discussed. Experiments on acetyl halides provide additional evidence to support the proposed acetone dissociation mechanism. A value of 17.0 ± 1.0 kcal/mole for the barrier height to CH_3CO decomposition has been determined.

The photodissociation of methyl radical at 193 nm and 212.8 nm is discussed in the chapter 5. The formation of CH_2 ($^1\text{A}_1$) and H (^2S) was the only single photon dissociation pathway observed at both wavelengths. Methylene internal excitation in excess of predictions from Franck-Condon or impulsive model analysis implies the presence of significant exit channel couplings and highlights the need for detailed *ab initio* calculations on the CH_3 excited state.

To my Mother, Father, Alison

and

Diana

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Chapter 1

Photodissociation Involving Multiple Bond Ruptures

I. Introduction

Photodissociation dynamics is concerned with understanding molecular interactions on a microscopic level. The overwhelming emphasis in the literature has been two-body photodissociation¹,

The discipline of photodissociation dynamics seeks answers to the following types of questions;

What is the chemical identity of the photofragments?

What is the time scale of the dissociation? i.e. is there a correlation between the direction of the polarized light and the direction of the photofragments recoil?

Do non-adiabatic processes, such as intersystem crossing (ISC) or internal conversion (IC), precede bond cleavage?

How is the available energy partitioned among the product degrees of freedom?

To what extent are the vector properties of the photofragments correlated?

Although it is now possible to measure state-to-state differential cross sections for the photofragmentation of simple molecules, the inversion of the experimental data to obtain the multidimensional potential energy surface remains theoretically challenging. It is not surprising, therefore, that very few experiments or theoretical work have involved

cases where three photofragments emerge from the dissociation melee.

Chapters 2-4 of this dissertation describe several gas phase three-body processes whose dynamics have been elucidated using photofragment translational spectroscopy. A three-body dissociation is one in which sufficient energy is deposited into a molecule often by the absorption of a single ultraviolet photon, to produce three asymptotically separated fragments,

where A, B, and C can represent either atomic or polyatomic species. In order to produce three asymptotic fragments a minimum of two chemical bonds must be broken. Of experimental interest, and central to the discussions in this dissertation, are the temporal and energetic correlations of the bond cleavage steps that exist in such a dissociation. For example;

What is the time interval between the two bond scission steps?

Does the second bond break prior to intramolecular energy redistribution (IVR) in the intermediate? i.e. are the internal energies of the fragments correlated?

Does the second bond break prior to rotation of the intermediate?

How is the overall available energy partitioned between the degrees of freedom in the three asymptotically separated fragments?

If fragments A, B, and C are all distinguishable then the two chemical bonds that are cleaved are, by definition, non-equivalent. Even in the case of a rapid two bond scission process preferential elongation of one bond occurs initially. On the ground state

potential energy surface this bond corresponds to the weaker of the two and it is, therefore, possible to assign the photofragments as originating from either the primary or the secondary dissociation step. Since the internal and translational energy distributions of the products reflect the dynamics of the respective steps, the analysis of the overall dissociation mechanism is often straightforward.

In three-body dissociations involving the cleavage of chemically equivalent bonds,

where v, j and u_i are the associated vibrational and rotational quantum states and the center-of-mass velocity of each fragment, the nature of the dissociation is considerably more intriguing and difficult to unravel. Does the dissociation involve a symmetric cleavage of the identical bonds or does the dissociation proceed sequentially, involving the spontaneous decomposition of an intermediate species?

In the gas phase near ultraviolet (~360 nm) photodissociation of azomethane,

a definitive answer to this fundamental question eluded the scientific community for almost 60 years. In fact, in the past decade the interpretation of the dissociation

mechanism has ranged from a concerted symmetric C-N bond cleavage via a single transition state² to a two step process involving an anomalously long lived (~5 ns) CH_3N_2 intermediate.³ Experiments detailed in the Chapter 1 have demonstrated that the dissociation is *asymmetric*, the two methyl radicals possess substantially different internal and translational excitation.⁴ However, the CH_3N_2 intermediate is sufficiently short lived (< 1 ps) for the dissociation to be considered *concerted*, a result which is consistent with the recent high level *ab initio* calculations of Hu and Schaeffer.⁵

In order to discuss three-body dissociation, it is useful to adopt practical definitions for the various limiting cases. Dewar⁶ has provided widely used definitions based on the Evans-Polanyi reaction coordinate diagrams that are schematically depicted in Figure 1. According to Dewar, a stepwise dissociation is one that occurs in two distinct kinetic steps via a *stable* intermediate. The spontaneous decomposition of the intermediate, therefore, is rate limiting. In a concerted reaction the secondary dissociation of the intermediate is not rate limiting and the overall process, therefore, occurs in a single kinetic step. A synchronous dissociation is one in which the two breaking bonds have proceeded to equal extents at the transition state, *i.e.* the intermediate is the transition state.^{6,7}

Although the definitions proposed by Dewar suffice when dealing with observables for kinetic experiments they are not sufficiently precise, with the exception of synchronous processes, for interpreting the results of dynamics experiments. Recent advances in experimental methodologies have afforded an increasingly detailed examination of three-body photodissociation. The ability to measure nascent asymptotic properties of the dissociation such as translational energy distributions, quantum state distributions, and associated vector correlations requires an alternative set of definitions.

The definition of a synchronous reaction is essentially identical to Dewar's but can be recast in terms of dynamical observables. Since the bonds must break with equal phase and force, the identical fragments should possess, on average, indistinguishable internal state and translational energy distributions. An example of such a dissociation⁸ is the fragmentation of *s*-tetrazine studied by Zhao *et al.*⁹ using photofragment translational spectroscopy. Following excitation at several wavelengths *s*-tetrazine was shown to dissociate exclusively into two HCN molecules and N₂,

The time-of-flight spectra of the HCN fragments consisted of a single narrow peak suggesting that the HCN fragments had indistinguishable asymptotic velocities. Combined with the measured N₂ velocity distribution, linear momentum conservation required that the dissociation was *symmetric*. Attempts to fit the experimental data using a sequential dissociation scheme were unsuccessful. Other examples of synchronous processes are the 248 nm photodissociation of CF₂I₂ studied by Wannemacher *et al.*¹⁰ and the triple-symmetric dissociation of 1,3,5-triazine into three indistinguishable HCN molecules studied by Ondrey and Bersohn.¹¹ As Dewar has previously pointed out, synchronous bond ruptures are rare and should only occur when the retention of aromaticity or steric hinderance lower the energy of the synchronous pathway relative to a non-synchronous one. The synchronous dissociation of CF₂I₂ is, therefore, surprising in light

of phase space considerations but is consistent with recent theory on repulsive potential energy surfaces.¹²

If the dissociation is asymmetric then the identical chemical species are more likely to possess disparate energy distributions, on average, than equivalent ones. These non-synchronous dissociations can be divided into two classes, concerted and stepwise. Strauss and Houston¹² have provided a criterion for concertedness based on the lifetime of the intermediate species, specifically whether or not the lifetime of the intermediate is longer than its rotational period. If the intermediate undergoes secondary decomposition prior to rotationally averaging then the dissociation is considered to be *concerted*. In this case the asymptotic velocity vectors of the three photofragments are well correlated.¹³ Synchronous dissociations are merely a subset of concerted processes in the limit of zero time delay between the two bond dissociation steps.

If the intermediate rotates many times before dissociating the correlation between the relative velocity vectors of the primary and secondary events is lost and the dissociation is termed *stepwise*. Furthermore, if IVR successfully competes with dissociation of the intermediate then the overall process is denoted *fully stepwise*.¹¹ In this case, there is essentially no energetic correlation between the primary and secondary dissociation steps, *i.e.* the secondary dynamics are only loosely dependent on the dynamics of the initial bond cleavage. As will be demonstrated shortly, these definitions are exceptionally well suited to the technique of photofragment translational spectroscopy and are used without remorse throughout the remainder of the dissertation.

Since there are currently a variety of experimental methodologies capable of probing the dynamics of *gas phase* three-body dissociations, the next two sections will

briefly highlight the most important of these in order to provide a comparison to photofragment translational spectroscopy, via the time-of-flight technique, which is discussed in the section III.

II. Time Resolved Techniques

In a three-body dissociation perhaps the most fundamental piece of information is the time interval between the multiple bond cleavages. Undoubtedly the most direct way to measure this temporal correlation is via time resolved techniques. This is accomplished by observing the appearance times of the photoproducts relative to some initial time zero.¹⁴ Experiments on the three body photodissociation of CF_2ICF_2I by Zewail and co-workers provide a clear illustration of this technique.¹⁵ In the experiments the time delay between two picosecond laser pulses, one to initiate the photodissociation by promoting a non-bonding electron on the iodine atom to a σ^* orbital localized on the C-I bond and the second pulse to probe the resulting $I(^2P_J)$ atoms, was varied allowing the evolution of the fragmentation to be measured. Tuning the wavelength of the probe laser provided selective detection of either spin-orbit state of the I atom products. The appearance of excited state ($^2P_{1/2}$) I atoms occurred within the time resolution of the experimental apparatus (~ 1 ps). The ground state ($^2P_{3/2}$) I atoms, however, exhibited a *bi-exponential* accumulation. A fraction of the ground state I atoms showed an experimentally limited rise time similar to the excited state atoms suggesting the initial C-I bond cleavage is extremely rapid and produces *both* excited and ground state products,

The slow component ($\tau \sim 30$ ps) of the I ($^2P_{3/2}$) appearance curve was attributed to the spontaneous secondary decomposition of nascent CF_2ICF_2 radicals that contained sufficient internal energy to dissociate,

The observed time dependence of the slow channel represented a *direct* measure of the energy averaged first order rate constant of CF_2CF_2I dissociation. The experimental rate can be used to evaluate and test various microcanonical models of unimolecular decomposition.

Determination of the time delay between the two bond cleavages using time resolved techniques requires that the first bond cleavage is direct and/or provides a well defined time zero from which to clock the reaction. Alkyl halides, where the initial $n \rightarrow \sigma^*$ excitation ensures primary C-X bond cleavage within a single vibrational period, are thus ideally suited for such studies. Unfortunately many molecules are predissociative and involve non-adiabatic curve crossing prior to fragmentation. In the dissociation of azomethane (Chapter 2) and acetone (Chapter 3) the loss of photofragment anisotropy suggests an excited state lifetime in excess of the parent rotational period. As a consequence, the time interval from photon absorption to the initial bond cleavage may be as long or longer than the time interval between the first and second bond cleavages. In such cases resolution of the temporal correlation between the two steps in a three-body dissociation using time resolved experiments is either severely compromised or unattainable. As will be demonstrated shortly, photofragment translational spectroscopy is a technique

capable of determining the time delay between successive bond cleavages regardless of the relative time intervals involved.¹⁶

III. Internal State Distributions

The advent of high resolution lasers has provided a means to examine the internal states of gas phase molecules with unprecedented precision. In cases where the spectroscopy of the products is sufficiently mature it is possible to characterize the dissociation dynamics from the internal state distributions of the nascent photofragments. In the absence of accurate potential energy surfaces, comparing the observed ro-vibrational distributions to simplified statistical or impulsive models of energy partitioning can provide considerable insight into the dissociation dynamics.

If a three-body dissociation produces two chemically equivalent species, can one distinguish between synchronous, concerted, and stepwise mechanisms based on the internal state distributions of the indistinguishable fragments alone? Bimodality in the vibrational or rotational spectra of the nascent identical fragments, if observed, may provide a clear indication of the origins of each fragment. Cases can be imagined in which the energetics or dynamics of each dissociation step are so different that the nascent identical fragments should possess distinct internal energies. Unfortunately for the practitioners of spectroscopic characterization, the dream of such separable distributions has yet to be realized and the interpretation of the three-body dissociation mechanism must rely on considerable scientific acumen. One of the most studied three-body dissociations using spectroscopic techniques is the ultraviolet photodissociation of acetone,

The internal state distributions of the CH_3 photofragments have been exhaustively measured using a variety of techniques.¹⁷ There is now substantial evidence to suggest that the nascent methyl radicals have nearly indistinguishable rotational and vibrational energy distributions. The magnitude of the methyl vibrational energy content, however, has been the subject of considerable controversy. Differing experimental techniques have determined values of CH_3 vibration excitation ranging from 10% to 50% of the total available energy. Not surprisingly, these results have lead to contradictory models for the overall dissociation mechanism. Only recently has a consensus been reached concerning the nature of the dissociation and is discussed in chapter 3 of this dissertation.¹⁸

In the three-body dissociation of ABA, it may be more helpful to look at the chemically distinguishable B fragment. For example, in the case of acetone at 193 nm the rotational energy of the CO fragment has lead to the dismissal of a synchronous dissociation mechanism (of course, the synchronous dissociation of such a system should be highly improbable and so this not such a surprising result). More importantly, the magnitude of the rotational angular momentum is inconsistent with statistical partitioning of the available energy, suggesting the second step involves dynamical effects. Since the CO fragment carries information from both steps convoluted together, determining the origins of the internal excitations is demanding. As a result, the CO rotational and vibrational distributions are still the subject of intense analysis despite the fact that the general features of the dissociation are now well understood.

It is important to note that the measurement of product internal state distributions

significantly augments the results of photofragment translational spectroscopy experiments. The combination of both complementary techniques provides a richer insight into the dissociation dynamics than could be obtained from the measurement of a single photofragment degree of freedom.

IV. Photofragment Translational Spectroscopy

A. *Forward Convolution Formalism*

Photofragment translational spectroscopy is a technique that involves the determination of the asymptotic translational energies of the photodissociation products. There are presently numerous variations of this technique, *e.g.* conventional Doppler spectroscopy, VADS, and several time-of-flight (TOF) methods, and recent reviews discuss the relative merit of each methodology.²⁰ The work in this dissertation involves photofragment translational spectroscopy (PTS) via the TOF method.²¹ Analysis of the experimental TOF spectrum is achieved by the forward convolution technique in which an assumed set of energy and angular distributions is used to simulate a TOF spectrum. The simulated TOF spectrum is then compared to the experimental TOF and the set of distributions is adjusted until a satisfactory fit is obtained.

The forward-convolution formalism, specifically the simulation of *secondary* photofragment time-of-flight spectra and the associated approximations, is now briefly discussed. A more detailed treatment can be found in the dissertations of Wodtke²² and of Zhao²³. Consider the photodissociation of a jet cooled beam of ABC parent molecules into three distinguishable polyatomic fragments (A, B, and C) via the intermediate AB,

(10)

If the dissociation is sequential then it can be separated into two independent center-of-mass reference frames in which linear momentum is conserved. A hypothetical newton diagram in Figure 2 schematically illustrates the relationships between angles and velocities in the laboratory and both center-of-mass frames.

It has been demonstrated that in a two-body dissociation the center-of-mass energy and angular distributions are weakly coupled and can be factored²⁴,

$$P(E_T, \Theta) = P(E_T) P(\Theta) \quad (11)$$

The product angular distribution for single photon excitation in the parent center-of-mass frame as expressed by Zare²⁵ is given by,

$$P(\Theta) = \frac{1}{4\pi} (1 + \beta P_2(\cos \Theta)) \quad (12)$$

where $P_2(x)$ is the second Legendre polynomial, $\beta = P_2(\cos \theta)$, and θ is the angle between the recoil velocity vector and the electronic transition dipole. In the spontaneous secondary decomposition of the AB primary photofragment it is first assumed that the secondary angular distribution, $P(\Omega)$, is independent of the primary angular distribution, $P(\Theta)$. The distribution function for the secondary fragments is then given by,

$$P(E_T, \Theta, E_T', \Omega) = P(\Theta) P(\Omega) P(E_T'; E_T) P(E_T) \quad (13)$$

The total center-of-mass translational energy distribution of the secondary fragments, $P(E_T'; E_T)$, is a function of the primary translational energy release. If fragment C is an atom, the primary translational energy release corresponds to a well defined internal energy of the AB intermediate. Randomization of the internal energy throughout the vibrational degrees of freedom of the AB intermediate prior to dissociation permits the use of approximate RRK-type forms of the secondary translational energy distribution which can be trivially evaluated. For example, one such functional form adopted by Hintsa *et al.*²⁶ is the following,

$$P(E_T'; E_T) \propto (E_T' - b)^d (E_{avail} - E_T')^n \quad (14)$$

where b is the exit barrier, *i.e.* the difference between the recombination barrier height and the bond dissociation energy, d is the dimensionality of the reaction coordinate, and n is the number of active vibrational modes. In reality, the physical significance of b , d , and n is questionable and are, therefore, simply treated as parameters in the fitting procedure. E_{avail} is the total energy available for the secondary dissociation and is given by,

$$E_{avail} = E_{hv} - D_o^o(1) - D_o^o(2) - E_T \quad (15)$$

where E_{hv} is the photon energy, $D_o(1)$ is the primary bond dissociation energy, $D_o(2)$ is the secondary bond dissociation energy, and E_T is the primary translational energy. This approximation was highly successful in treating the experimental data in the

stepwise three-body dissociation of 2-bromoethanol by Hints et al.²⁶ If both of the primary fragments are polyatomics then there is no longer a simple relationship between the E_T and internal energy of the AB fragment. If it is assumed (*vide infra*) that $P(E_T)$ and $P(E_T')$ can be factored, with the constraint that the total available energy is conserved, then the total probability distribution for secondary photofragments can then be expressed as the product of four decoupled distributions,

$$P(E_T, \Theta, E_T', \Omega) = P(\Theta) P(\Omega) P(E_T) P(E_T') \quad (16)$$

In this case $P(E_T')$ represents an *averaged* secondary translational energy distribution. The validity and consequences of the assumptions that lead to this separability will be discussed in the following section. Forward convolution simulation of the time-of-flight distribution for secondary fragment A at a given laboratory angle, Φ , can be obtained by inclusion of instrumental response functions and relevant transformation Jacobians.^{22,23} The end result is given by,

$$N_A^+(t, \Phi) \propto \frac{v_A^2}{t} \left\{ \frac{m_{ABC} m_{AB}}{m_A} \right\} \left\{ \frac{m_A m_{AB}}{m_B} \right\} \int_{(t, \Phi)} du_{AB} \sin \Theta d\Theta dv_{ABC} d\Phi_{ABC} d\Phi_A$$

$$(1 + \beta P_2(\cos \Theta)) P(E_T) u_{AB} \frac{P(E_T') P(\Omega)}{u_A}$$

where m_i are the masses of the various photofragments and v_A is the laboratory velocity of fragment A. This allows all four decoupled distributions to be *adjusted independently* in order to iteratively fit the experimental time-of-flight data and significantly simplifies the forward convolution fitting procedure.

B. The Secondary Angular Distribution

As discussed previously, characterization of the dissociation mechanism rests on whether or not fragmentation of the intermediate occurs prior to its rotation. This involves determining the extent to which the relative velocity vectors arising from the first and second bond cleavage steps are correlated. The secondary angular distribution, $P(\Omega)$, carries all the information regarding this dependence. In the present section various limiting secondary angular distributions that arise from long-lived, rotationally averaged, intermediates are classically derived. A general criterion for distinguishing between stepwise and concerted dissociations using photofragment translational spectroscopy is then discussed.

In the absence of parent rotation and neglecting angular momentum associated with electronic excitation or spin, the total angular momentum of the system, J , is zero. When the parent molecule absorbs a photon and dissociates into fragments AB and C, conservation of angular momentum requires that,

$$J = L + J_{AB} + J_C = 0 \quad (18)$$

where L is the orbital angular momentum associated with the relative motion of the fragments and J_{AB} and J_C are the rotational angular momenta of the photofragments AB and C respectively. Assuming the additional simplification that fragment C possesses negligible rotational excitation, the rotational and orbital angular momentum vectors are equal in magnitude and opposite in sign,

$$J_{AB} = -L = \mu g b \quad (19)$$

where μ is the reduced mass of the AB and C fragments, g is their relative velocity, and b is the classical exit impact parameter. Both the orbital angular momentum and rotational angular momentum of the AB fragment are perpendicular to the relative velocity vector. If fragment AB subsequently dissociates, the angular distribution of the resulting A and B fragments in the AB center-of-mass frame can be derived using classical mechanics. In the simplest case, the secondary fragments are confined to a plane perpendicular to the axis of J_{AB} as shown in the upper panel of Figure 3. If rotational averaging occurs prior to dissociation then the secondary fragments have an equal probability of recoiling at any angle in the plane. In the absence of anisotropy in the initial dissociation step there is azimuthal symmetry about g and the resulting distribution of the photofragments exhibits a build-up of intensity at the poles, 0° and 180° . The normalized classical angular distribution is given by,

$$P(\Omega) = \frac{1}{2\pi^2} (\sin \Omega)^{-1} \quad (20)$$

Intermediates whose decomposition results in such a $P(\Omega)$, shown by the solid line in Figure 4, are known as *prolate complexes* and have been observed in crossed beam experiments of alkali atoms with alkali halides.²⁷ Unfortunately, due to the frequent occurrence of near prolate complexes in reaction dynamics, rotational averaging has become synonymous with strong forward-backward peaking in the angular distribution. Of course, forward-backward peaking does indicate rotational averaging but the reverse, however, is not always true.

If J_{AB} has a projection, M' , upon the relative velocity of the secondary fragments, g' , then for a given M' the fragments are distributed about a cone of half angle α' (shown in the lower panel of Figure 3),

$$\alpha' = \cos^{-1}\left(\frac{M'}{J_{AB}}\right) \quad (21)$$

Following azimuthal averaging of g' about g , the classical angular distribution is given by,

$$P(\Omega) = \frac{1}{2\pi^2} (\sin^2\Omega - \cos^2\alpha')^{-1/2} \quad (22)$$

The dotted line in Figure 4 shows the angular distribution resulting from $\alpha'=30^\circ$. For cases where $M' \approx J_{AB}$ the angular distribution peaks close to $\Omega=90^\circ$. This limiting case, arising from a predominately *prolate complex*, is shown as the dashed line in Figure 4 and is uncommon. The reaction of $F + C_2H_4$ to give hydrogen atoms scattered perpendicularly to g , the initial relative velocity vector, is a rare example.²⁸

Of course, the parent molecule can dissociate from a range of geometries and translational energies resulting in a distribution over J_{AB} . In addition there is also a distribution over M' due to distributions of α' and J_{AB} . Functional forms for the J_{AB}/M' distribution were first developed for the study of particle-induced fission by Halpern and Strutinski.²⁹ The statistical model, involving a Boltzmann distribution of rotational states in the complex results in a Gaussian distribution about a most probable M' , and was successful in fitting data from a number of crossed molecular beam experiments.²⁷ Refinements to the model, most notably the use of microcanonical transition state theory to describe the distribution of quantum states in the complex have even permitted predictions of the transition state based on the measured angular distribution.³⁰ The accuracy of such predictions has been received with justifiable skepticism since exit channel couplings can dramatically influence the observed angular distribution. A proper treatment of these effects would require a detailed knowledge of the potential energy surface. However, the qualitative nature of the intermediate, whether it is predominately prolate or oblate, can be reliably ascertained.

Since the rotational excitation of the intermediate may be broad and its dissociation may involve significant rearrangements or exit channel couplings, the measured secondary angular distribution is highly averaged. Therefore, approximate forms of $P(\Omega)$ that reflect the average correlation between g and g' are often sufficient to fit the experimental data. Two such generalized forms are considered in this dissertation although only the first is experimentally observed. In the event that the intermediate behaves as a prolate complex the following $P(\Omega)$ has been proven to provide satisfactory fits to the time-of-flight data,

$$P(\Omega) = \frac{\sin \Omega^\circ}{\sin \Omega}, \quad \text{for } \Omega^\circ < \Omega < \pi - \Omega^\circ \quad (23)$$

$$P(\Omega) = 1, \quad \text{otherwise} \quad (24)$$

where Ω° is a parameter that can be varied from 0° to 90° to modify $P(\Omega)$ from the classical limiting case to a purely isotropic distribution.³¹ Figure 5 shows two such distributions for $\Omega^\circ=15^\circ$ (solid line) and $\Omega^\circ=30^\circ$ (long dashed line). Angular distributions of this form were first utilized to fit cross molecular beam data and later in fitting secondary fragments arising from three-body dissociations.^{26,32} In three-body dissociations oblate distributions correspond to cases in which the orbital angular momenta associated with both dissociation steps dominate photofragment rotation.

If the intermediate can be described, on average, as an oblate complex then a gaussian distribution,

$$P(\Omega) = A e^{-\frac{1}{2} \left(\frac{\cos \Omega}{\cos \Omega^\circ} \right)^2} \quad (25)$$

should be sufficient to simulate the time-of-flight of the secondary photofragments. To date, however, secondary angular distributions of this general form have not been experimentally observed as the result of a three-body photodissociation.

The previous discussion applies only to angular distributions arising from the dissociation of rotationally averaged intermediates. What if the intermediate decomposes on a time scale comparable to its rotational period? In this event the exact form of $P(\Omega)$ will be determined by a number of factors including the lifetime of the intermediate, its

rotational excitation, the transition state geometry, and the secondary dissociation dynamics. Fortunately, it is a much simpler task to determine whether or not rotational averaging has occurred. *In the event of any asymmetry about 90° in the secondary angular distribution, fragmentation of the intermediate precedes its rotation and the three-body dissociation can be characterized as concerted.*

C. Validity of Approximations

In order to facilitate forward convolution simulation, the primary and secondary angular and translational energy distributions were considered as completely separable. The validity and severity of two of the successive decoupling approximations will now be briefly discussed. Additional approximations associated with the treatment of the instrumental response functions has been presented previously.²³

The factoring of $P(E_T)P(E_T';E_T)$ into $P(E_T)P(E_T')$ is reasonable, provided that the secondary dissociation dynamics are not significantly influenced by *either* the magnitude or form of the intermediate's internal excitation. In cases where dissociation proceeds via a large exit barrier it has been experimentally demonstrated that the translational energy distribution is relatively insensitive to the available energy. At available energies near the threshold to dissociation the average translational energy release will reflect some fraction of the exit barrier. Any additional available energy results in only a modest change in the $P(E_T)$ corresponding to the statistical probability of finding excess energy in the reaction coordinate. A secondary process possessing a substantial exit barriers can, therefore, be approximated as independent of primary translational energy release. In all three-body dissociations discussed in this dissertation the spontaneous decomposition of the interme-

diate proceeds via a large exit barrier. In chapter 4 the near invariance of the translational energy release with increasing internal energy is explicitly demonstrated. The decoupling of the primary and secondary translational energy distributions can, therefore, be viewed as a reasonable approximation.

The separability of primary translational energy, $P(E_T)$, and the secondary angular distribution, $P(\Omega)$, will hold providing that the intermediate is long-lived with respect to its rotational period, *i.e.* $P(\Omega)$ exhibits symmetry about 90° . This is the case in the photodissociation of acetone and the acetyl halides discussed Chapters 3 and 4. The photodissociation of azomethane, however, involves a rapid decomposition of the intermediate species. Since $P(E_T)$ reflects *both* the lifetime of the intermediate, via the relative magnitude of internal energy, and the rotational excitation, $P(\Omega)$ should be strongly coupled to $P(E_T)$. However, the success with which the experimental TOF data can be fit using a decoupled approach suggests that either the correlation of $P(\Omega)$ and $P(E_T)$ is weak or that $P(\Omega)$ is a such highly averaged quantity that it is not a sensitive indicator of the dissociation dynamics.

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Figure Captions

- Figure 1 Schematic energy level diagram adapted from Ref. 2 illustrating the different three-body dissociation mechanisms. Upper panel shows a stepwise reaction pathway, the middle panel shows a concerted pathway, and the lower panel shows a synchronous dissociation pathway (see text for details).
- Figure 2 Newton diagram for a typical sequential three-body process illustrating the relationship between the laboratory angles and velocities and those in the primary and secondary center-of-mass frames.
- Figure 3 Geometric relationships between the velocity and the angular momenta vectors associated with a sequential dissociation process in which the parent rotation is considered negligible.
- Figure 4 Secondary center-of-mass angular distributions, $P(\Omega)$, for limiting cases in which the intermediate species is prolate (solid line) or oblate (dashed line). Also shown is angular distribution associated with $\alpha'=30^\circ$ (dotted line).
- Figure 5 Secondary center-of-mass angular distributions associated with the approximate functional forms discussed in the text. The solid and long-dashed lines correspond to long-lived prolate complexes with $\Omega^\circ=15^\circ$ and 30° respectively. The short-dashed and dotted lines correspond to oblate complexes with $\Omega^\circ=30^\circ$ and 70° respectively.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Chapter 2

Ultraviolet Photodissociation Dynamics of Azomethane: Evidence for Concerted Bond Cleavages

Abstract

The photodissociation of azomethane following absorption of a single 351 nm photon ($S_1 \leftarrow S_0$) was studied using the method of molecular beam photofragment translational spectroscopy. The dissociation was observed to proceed exclusively via the cleavage of both C-N bonds to yield a nitrogen molecule and two methyl radicals. The measured time-of-flight spectra show evidence that the two methyl radicals possess unequal velocities in the azomethane center-of-mass demonstrating that the dissociation is *not symmetric*. The angles between the asymptotic center-of-mass velocities for all three fragments are strongly correlated implying that the methyldiazenyl radical (CH_3N_2) intermediate decomposes within a fraction of its rotational period. We conclude, therefore, that the dissociation is *concerted* and not stepwise as was inferred from the recent time-resolved CARS experiments of Andrews *et al.* (*J. Chem. Phys.*, **96**, 1111 (1992)). Calculations on the CH_3N_2 barrier height and unimolecular decomposition rates are consistent with the present experimental findings. The overall translational energy distributions for all the photofragments in the azomethane center-of-mass reveal that an average of 60% of the total available energy appears as translation. A possible mechanism, consistent with both the correlation of the asymptotic velocity vectors and the disparate partitioning of the translational energy between the two methyl fragments, is proposed and discussed.

I. Introduction

Azoalkanes are an interesting class of organic compounds whose photochemistry has been extensively studied for many years.¹ The characteristic near ultraviolet diffuse absorption band at ~360 nm has been attributed to an $\pi^* \leftarrow n$ transition.² This electric dipole forbidden transition corresponds to a singlet (S_0) to singlet (S_1) excitation.

Although this results in *cis-trans* isomerization in condensed phases, the dominant fate of acyclic azoalkanes in the gas phase is dissociation into alkyl radicals and nitrogen.³ The most palatable aspect of symmetric azoalkanes as radical precursors is that N_2 is the sole by-product. The photolytic decomposition of azoalkanes has, therefore, proven to be a viable source of alkyl radicals for kinetic⁴, spectroscopic⁵, and dynamics⁶ measurements.

The simplicity of azomethane makes it a potential benchmark in both the theoretical understanding and the experimental investigation of azoalkane photodissociation dynamics. Since the spectroscopy of the photofragments, CH_3 and N_2 , is well established, the complete characterization of their nascent internal state distributions is feasible. The S_1 state is bound along both C-N coordinates and consequently dissociation must proceed on an alternative potential energy surface. *Ab initio* results predict that the first excited singlet is labile about the N-N bond and that crossing to the ground state surface may occur at a dihedral angle of 90° .⁷ In fact, concerted torsional motion and C-N-N bending provides an efficient "funnel" for internal conversion to the ground state. Whether or not internal conversion (IC) occurs efficiently in the *gas phase* will determine if photodissociation proceeds via an identical mechanism to thermolysis. If the dissociation does not occur on the ground state potential energy surface then azomethane dissociation may

occur on the energetically accessible first excited triplet state.⁸ Rates of intersystem crossing (ISC) for azoalkanes have been predicted to range from rapid⁹ to phlegmatic¹⁰. Although numerous experimental techniques^{1,11} have been used to assess the participation of the triplet state in azoalkane photochemistry, the results are often contradictory. Despite the vast quantity of research on azoalkane photochemistry, the electronic state(s) involved and the detailed mechanism of dissociation remain the subject of much speculation.

If sufficient energy is deposited in a molecule to ensure the eventual cleavage of two bonds, the sequence of events that lead to the multiple bond rupture is of fundamental mechanistic importance. In molecular beam photodissociation studies of halocarbons involving secondary processes the initial step is direct and results in a highly vibrationally excited photofragment. If intermolecular vibrational energy redistribution (IVR) competes with dissociation the rate of decomposition of the photoproduct is a known function of its internal energy. Those possessing vibrational energy in excess of the barrier to dissociation undergo secondary fragmentation while those with insufficient vibrational energy persist. In such cases the dissociation has been historically termed *stepwise*. If the cleavages of both bonds are strongly coupled, occurring in a single kinetic step¹², then the dissociation pathway is considered a concerted process. A detailed study of acetone dissociation following excitation to the $^1(n,3s)$ Rydberg state, yielded nascent product state distributions and CH_3 translational energy distributions that suggested a non-synchronous concerted mechanism.^{13,14} However, more recent experiments have provided evidence that the dissociation of acetone should be considered a stepwise process.^{15,16}

Work by Weisman *et al.*¹⁷⁻¹⁹ using time-resolved coherent anti-stokes Raman spectroscopy (CARS) yielded the first direct information on the detailed dynamics of azomethane photodissociation. The experiment endeavored to answer the salient question of whether or not the dissociation proceeds via a concerted or a stepwise mechanism. Although there is recent consensus on gas phase thermolysis proceeding by initial single bond scission^{20,21}, there had been little experimental evidence on the lifetime of the CH_3N_2 intermediate. Under *collisional* conditions, two bands of the totally symmetric stretch, one without any quanta of ν_2 umbrella mode and the other containing a single quantum of ν_2 , exhibited very different appearance kinetics. Each band was assigned to a different bond cleavage step. On the basis of these findings the authors concluded that the methyl radicals from each step of the dissociation contained disparate internal energies supporting an asymmetric dissociation. The 1st step to produce the *hot* methyl fragments was shown to be instantaneous within the ~ 1 ns experimental time resolution and the onset of the second, *colder*, methyl radicals at 5.3 ± 1.0 ns provided evidence of a finite CH_3N_2 lifetime. Thus, Weisman and co-workers concluded that the dissociation, following excitation to the S_1 state, was fully *stepwise* (1-2).¹⁸

Conventional wisdom had held that the "more unsymmetrical the azoalkane the

more unsymmetrical it cleaves".¹ Evidence of the asymmetric cleavage of the simplest symmetric azoalkane was, therefore an important result and further illustrated the rich photochemistry of azoalkanes.

The distinction between concerted and stepwise mechanisms rests in the lifetime and inherent stability of the $\text{CH}_3\text{N}_2(^2\text{A}')$ intermediate. The decomposition of methyldiazenyl radical is known to be exothermic by 23.8 kcal/mole.²² The calculated activation barrier to dissociation has ranged from as low as 1.8-2.3 kcal/mole^{22,23} to as high as 14.5-17.4 kcal/mole.^{24,25} A schematic energy level diagram for azomethane dissociation is shown in Figure 1. The existence of a barrier for methyldiazenyl decomposition implies that the lifetime of this fragment, and hence the overall dissociation mechanism, will be strongly dependent on both the height of the exit barrier and the internal energy of the nascent CH_3N_2 . Assuming that the barrier is close to the most recently reported value of ~ 2 kcal/mole, the 5.3 ± 1.0 ns CH_3N_2 lifetime determined previously¹⁸ appears anomalously long. The role of collisional deactivation, however, was considered to be important in stabilizing the nascent radicals.²⁶ Under the *collisionless* conditions of a molecular beam experiment, elucidation of the initial dissociation dynamics that are a result of intrinsic properties of azomethane is feasible, as is investigation of the dissociation of the methyldiazenyl radical without the complications of secondary collisions.

This chapter describes the investigation of azomethane photodissociation at 351 nm using photofragment translational spectroscopy (PTS). The translational energy and angular distributions for the photofragments determined in this study provide insight into both the partitioning of the available energy in the dissociation and *temporal* information,

via asymptotic velocity vector correlations, on the time delay between CH_3 eliminations.

II. Experimental

These measurements were performed on a molecular beam apparatus with a fixed source and a rotatable detector that has been described previously.²⁷ The machine has been modified to allow study of molecular photodissociation. Figure 2 shows a schematic diagram of the molecular beam apparatus. A pulsed valve²⁸ (1.0 mm nozzle) utilizing a Physik-Instrumente piezocrystal was operated at 50 Hz. Helium was bubbled through azomethane held at -55°C resulting in a $\sim 15\%$ mixture with a total pressure behind the nozzle of 350 torr. The pulsed molecular beam was expanded into a source region typically maintained at 10^{-6} to 10^{-5} torr. A time-of-flight method was used with a spinning slotted wheel to measure the velocity and velocity spread of the molecular beam. An appropriate time delay between the wheel and the pulsed valve ensured accurate sampling of the irradiated region of the pulse. Using an assumed form for the velocity distribution, $P(v) \propto v^2 \exp[-(v/\alpha S)^2]$, the beam velocity was determined to be 10.4×10^4 cm/sec with a full width at half maximum (FWHM) spread of 20%. Although narrower spreads in beam velocity could be achieved in the dense part of the beam pulse the formation of dimers necessitated using the earlier, warmer, leading edge.²⁹

The resulting pulsed beam was collimated with two skimmers to a FWHM angular divergence of less than 3° and passed into a second differential region maintained at $\sim 10^{-7}$ torr where it was crossed at 90° with the output of a Lambda Physik EMG 202 MSC excimer laser operating at the XeF (351 nm) transition. The laser was run at 50 mJ/pulse

and focused with a 30 cm focal length convex MgF lens to a 2.0x4.0 mm spot. The laser was typically delayed 30 μ sec the onset of the molecular beam pulse allowing time for the molecules to move from the nozzle to the interaction region 8.0 cm downstream. Experiments were also performed using the third harmonic, 355 nm, of a Quanta Ray DCR-1 Nd:YAG laser. The laser was typically run at 10 Hz and 50-70 mJ pulse. A spherical lens focussed the laser spot to a 0.28 cm² area in the interaction region.

The neutral photofragments recoiled 20.8 cm where they were ionized by an electron bombardment ionizer, mass selected by a quadrupole mass spectrometer, and detected by a Daly ion counter. Data was collected by a computer interfaced multi-channel scaler triggered from the laser pulse. A copper cryopanel, cooled to ~6 K by a closed cycle He KOCH compressor/expansion engine system, greatly reduced the *m/e* 15 and *m/e* 28 background in the detector.

The detected products varied linearly with laser power confirming the single photon nature of the process. The absorption cross section of azomethane at 351 nm is $\sim 1.9 \times 10^{-20}$ cm², and with a photon flux of $\sim 10^{18}$ photon/cm² per pulse, saturation of the initial photon absorption will not occur.² Polarization measurements were performed using a parallel plates polarizer which consisted of 10 quartz plates at Brewster's angle with respect to the direction of laser propagation. This resulted in >95% polarized light which could then be rotated by rotation of the polarizer.

Trans-azomethane was synthesized by the method of Renaud and Leitch³⁰ and was purified by trap-to-trap distillation prior to use.

III. Results and Discussion

Signal was collected at m/e 28 (N_2^+), m/e 15 (CH_3^+), m/e 14 (CH_2^+), and m/e 13 (CH^+). The time dependent backgrounds due to dissociative ionization of the pulsed molecular beam were obtained by blocking the laser and were subtracted from the original signal. Time-of-flight spectra for m/e 13 (CH^+) and m/e 28 (N_2^+) at laboratory angles 20° , 35° and 50° are shown in Figures 3 and 4. Time dependent background from the beam pulse at m/e 15 (CH_3^+), the dominant daughter ion of azomethane, was sufficient to cause difficulty in subtraction. At m/e 14 (CH_2^+) there was significant contamination from N_2^{++} or N^+ . Since the first and second step methyl radicals should possess similar internal energies, within several kcal/mole, they should exhibit comparable ionization cracking patterns. We therefore restrict ourselves to m/e 13, a daughter fragment of methyl radical, because of the superior signal-to-noise ratio. The data at m/e 13 fits well with a 1:1 ratio of first to second step methyls confirming the validity of this assumption. No detectable photodissociation signal was observed at the parent methyldiazenyl mass (m/e 43) nor was there any indication of the presence of CH_3N_2 at the daughter masses suggesting that the CH_3N_2 fragment is short lived on the time scale of the $\sim 1 \times 10^{-4}$ s flight time to the detector.

The two distinct peaks in Figure 3 correspond to a dissociation in which both methyl groups recoil with unequal velocities in the azomethane center-of-mass. Simultaneous *symmetric* fission of the identical C-N bonds would yield a single TOF peak reflecting the indistinguishability of the two methyl radicals. The data was initially fit by assuming that the two C-N bonds cleaved sequentially. Since there was ambiguity as to

which peak in the methyl TOF spectra to assign to the initial impulse, two schemes, differing only in this assignment were considered. In both cases the dissociation was decomposed into two center-of-mass frames in which linear momentum is conserved.

A. Sequential Analysis

In the first sequential analysis it was assumed that the methyl that possesses a higher lab velocity originated from the initial dissociative impulse. The analysis was performed by using well known forward convolution techniques for treating the primary³¹ and secondary dissociations³² from photofragment translational spectroscopy experiments. The total primary translational energy distribution, $P(E_T)$, shown in the upper panel of Figure 5 was derived from the fast component of the time-of-flight spectra of CH_3 shown in Figure 3 and assuming CH_3N_2 to be the other counter fragment. The distribution has an average value of 19.2 kcal/mole and a FWHM of ~ 11 kcal/mole. Since the CH_3N_2 fragment does not survive to the detector, it is not possible to momentum match the initial CH_3 as a means of gauging the integrity of the primary $P(E_T)$. However, by fitting the m/e 13 TOF over a wide range of laboratory angles, we have reasonable confidence in the derived primary $P(E_T)$. There was no observed correlation between the angle of laser polarization and the product intensity or TOF profile. This corresponds to an anisotropy parameter of $\beta=0$ (ref. 33) and indicates that the lifetime of the excited azomethane may be longer than its rotational period.

The slower peak in the m/e 13 time-of-flight spectra was then assigned as the second step methyl radical. If the CH_3N_2 intermediate persists for longer than its rotational period the secondary methyl radical should exhibit a bimodal velocity distri-

bution reflecting the forward-backward symmetry^{34,35}, with respect to the primary relative velocity vector, of the secondary angular distribution in the CH₃N₂ reference frame. The manifestation of only the slower component in the TOF spectra indicates that the second methyl radical is preferentially *backwards* scattered with respect to the CH₃N₂ recoil velocity vector. The secondary total center-of-mass P(E_T) derived from fitting the slow contribution to the *m/e* 13 TOF spectra is shown in the lower panel of Figure 5.

The anomalously fast and narrow *m/e* 28 (N₂⁺) time-of-flight spectra (Figure 4) are further evidence of an asymmetric angular distribution in the second step. The conservation of linear momentum requires that, for a methyl/nitrogen pair with a common CH₃N₂ parent, backward scattered CH₃ results in *forward* scattered N₂. Figure 6 shows a contour map illustrating the angular and velocity distributions of the secondary photofragments in the CH₃N₂ center-of-mass. The arrows on the contour plot represent the most probable velocities that conserve momentum in the azomethane center-of-mass. The velocity vector at 0° represents the CH₃ from the initial impulse. Although the angles appear to conflict with the peaks in the secondary angular distributions, the strong forward and backward peaks in P(Ω) may be the result of two overlapping shoulders of sideways peaked distributions along the relative velocity vector of the initial dissociation step. In order to further demonstrate the sensitivity of the technique to this anisotropy the data was fit assuming that rotational averaging precedes the secondary dissociation. A typical secondary P(Ω),

$$P(\Omega) = \frac{\sin \Omega^\circ}{\sin \Omega}, \quad \text{for } \Omega^\circ \leq \Omega \leq \Omega^\circ - \pi \quad (3)$$

$$P(\Omega) = 1, \text{ for } \Omega \leq \Omega^\circ \text{ and } \Omega \geq \pi - \Omega^\circ \quad (4)$$

where $\theta=33.5^\circ$, shown in the upper panel of Figure 7 was used in the forward convolution fitting procedure. The resultant fit to the m/e 28 spectrum at 35° is shown by the solid line in lower panel of Figure 7. The presence of exclusively forward scattered nitrogen clearly illustrates the anisotropy in the secondary angular distribution.

The data can also be analyzed, in a similar manner, by assuming that the *slow* methyl in the m/e 13 TOF spectra originates from the initial dissociation. The $P(E_T)$ derived from fitting this feature is shown in Figure 8 (upper panel). The distribution is peaked at 4 kcal/mole with a long high energy tail. A very impulsive translational energy release was required for the secondary dissociation in order to fit the fast component in the m/e 13 TOF spectra. The $P(E_T)$ for the secondary process is shown in the lower panel of Figure 8 and is peaked significantly away from zero (~ 22 kcal/mole) with a FWHM of ~ 12 kcal/mole. Not surprisingly, the strong angular correlation between the asymptotic velocities of all three photofragments, found in the preceding scheme, is also manifest in this method of analysis. Satisfactory fitting of the fast m/e 13 peak and the m/e 28 TOF spectra required that the nitrogen be scattered slightly forward and the methyl radical scattered backwards with respect to the CH_3N_2 velocity vector. Figure 9 shows the product of both the velocity and the most pronounced angular distribution for the secondary fragments in the CH_3N_2 center-of-mass.

B. CH_3N_2 Lifetime

The anisotropy in the secondary angular distributions implies a methyldiazenyl

radical lifetime less than its rotation period. A two-step dissociation in which the second bond breaks prior to the rotational averaging of the intermediate species is an accepted criterion for concertedness.³⁶ A tentative upper limit to the lifetime of the CH_3N_2 fragment can be estimated by first calculating the degree of rotational angular momentum generated from the initial impulse and then using the rotational period as a *clock* of the secondary process. Using the *cis* equilibrium geometry as a reasonable dissociative structure³⁷ and assuming that the CH_3N_2 is a rigid rotor the orbital and rotational angular momentum can be calculated by the following expression,

$$L = \mu g b = -J_{\text{CH}_3\text{N}_2} \quad (5)$$

where μ is the reduced mass of the two fragments, g is the relative velocity, and b is the classical exit impact parameter. In equation 5 it is assumed that the dissociation results in negligible CH_3 rotational excitation. The relative velocities of the initial fragments can be derived from the respective peaks in the primary translational energy distributions. From the calculated angular momentum rotational periods of ~ 0.6 and ~ 1.5 ps can be extracted suggesting that the lifetime is *less than a picosecond*. Although there is modest uncertainty in this result, there is certainly a large disparity between this lifetime and the one determined in previous experiments.³⁸ In light of this $> 10^3$ discrepancy several methods are considered to provide an independent order-of-magnitude estimate for the CH_3N_2 lifetime. If the randomization of internal energy occurs prior to dissociation, the methyldiazenyl lifetimes can be obtained from RRKM rate calculations. Given

the most recent *ab initio* value of the barrier height and the vibrational frequencies at both the equilibrium and transition state geometries given in Table 1, the rates of decomposition at various CH_3N_2 internal energies can be calculated. Although it is difficult to surmise the average internal of the nascent CH_3N_2 photofragments, the RRKM lifetime of those fragments with only 2.8 kcal/mole of vibrational energy, only 0.5 kcal/mole in excess of the barrier, is < 1 ps. Unfortunately the shallowness of the minimum, the sparseness of states, and the sub-picosecond lifetime³⁹ all suggest that such a calculation may not be meaningful. It has been pointed out that in the photodissociation studies of Weisman and co-workers that collisional deactivation was important and could be responsible for the difference in their observed CH_3N_2 lifetime compared to the present one. In those experiments the CH_3N_2 , produced by photolysis in 500 torr of He, would undergo a hard sphere collision every 70 ps. The results of the present experiment strongly suggest that CH_3N_2 photoproduct would dissociate *prior to their first collision* with the buffer gas. If the nascent CH_3N_2 radicals were completely thermalized then their lifetime can be deduced from the classical thermodynamic formulation of the first-order rate constant, k_c , is given by⁴⁰,

$$k_c = \left(\frac{kT}{h} \right) \exp \left(\frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \right) \quad (6)$$

where $\Delta S^\ddagger$ and $\Delta H^\ddagger$ are the entropy and enthalpy differences between the reactant and the transition state, respectively. Assuming thermalization to a 298 K bath temper-

ature $k_c = 1.28 \times 10^{11} \text{ s}^{-1}$ corresponding to a lifetime of 7.8 ps. In fact, even if the nascent methyldiazenyl radicals were produced with no vibrational energy in the reaction coordinate and there was a dynamical bottle-neck to IVR the CH_3N_2 could dissociate via quantum mechanical tunnelling in < 1 ns. Using a parabolic barrier, whose curvature is related to the imaginary frequency at the transition state, the one-dimensional tunnelling rate, k_t , can be calculated within the WKB approximation⁴¹ by the following equation,

$$k_t = \frac{\nu_7}{1 + \exp(2\pi(V_0 - E)/h\nu_7^\ddagger)} \quad (7)$$

where $(V_0 - E)$ is the barrier height taken to be 805 cm^{-1} , ν_7 is the equilibrium frequency, and $\nu_7^\ddagger$ is the imaginary frequency at the transition state. Using the values of ν_7 and $\nu_7^\ddagger$ given in Table 1, the tunnelling rate is $1.68 \times 10^{11} \text{ s}^{-1}$ corresponding to a first order CH_3N_2 lifetime of 5.9 ps. Thus, there appears to be overwhelming evidence, given the thermodynamic instability of CH_3N_2 and diminutive barrier to dissociation predicted by recent high level *ab initio* methods, to support a sub-picosecond gas phase lifetime under *either* collisionless *or* collisional conditions.

It is difficult to reconcile these results with the observation of turnaround products in the condensed phase photodissociation of 3-(methylazo)-3-methyl-1-butene (MAMB). In those studies end product analysis demonstrated that the following process occurred upon irradiation at 337 nm (Ref. 42),

From this result the authors concluded that the CH_3N_2 intermediate must persist for sufficient time to allow the dimethylallyl radical to rotate in the hexane solvent cage before recombination. The quantum yield of this rearrangement was not quantified but was thought to be extremely minor. The extent to which solvent cage stabilization may prolong the lifetime of the CH_3N_2 radical or mediate which electronic states are involved in generating such "turn-around" products is unclear. Adams *et al.* subsequently used the time resolved CARS technique to observe the gas phase photodissociation of MAMB.⁴³ In that study the two alkyl fragments exhibited different appearance kinetics. The dimethylallyl radical was observed to appear within the ~ 1 ns time resolution of the experimental apparatus and the appearance time of the methyl radicals suggested a 12 ± 2 ns lifetime for the CH_3N_2 intermediate. Although the larger alkyl fragment may accommodate more available energy in its internal degrees of freedom and therefore result in "colder" CH_3N_2 radicals the N-C bond energy for the larger alkyl substituent is considerably weaker and will likely offset this result. However, the conclusion of the present calculations (*vide supra*) imply that only a fraction of vibrational energy needs to reside in the CH_3N_2 fragment to result in a subpicosecond lifetime. It is our belief, therefore, that the results of Adams *et al.* (ref. 43) suffer from the same shortcomings that were present in the analogous time-resolved study of azomethane photodissociation.

Our experiments clearly indicate that after the initial $S_1 \leftarrow S_0$ excitation the excited azomethane molecule persists for many rotational periods. However, when the molecule starts to dissociate, the two C-N bonds break within a subpicosecond interval of each other. It is important to note that if the first step is not prompt and provides no well defined time zero by which to clock the reaction, conventional time-resolved experiments are not feasible for studying the temporal correlations of the bond cleavages in such systems.

C. Three Body Analysis

Since both sequential fitting schemes yield asymptotic velocity correlations consistent with a subpicosecond CH_3N_2 lifetime, the preceding method of analysis may not afford the best description of the dissociation. The exact time interval between bond cleavages is relevant to this discussion. Using an averaged value of g , the relative velocity vector from the primary dissociation, the distance of the primary methyl radical from the CH_3N_2 is $\sim 20 \text{ \AA}$ at $\sim 1 \text{ ps}$. In this case, a sequential method of analysis is justified since the interaction of departing CH_3 on the methyldiazenyl decomposition is minimal. If however, the nascent CH_3N_2 dissociates in only 100 fs then the primary CH_3 has moved only 2 $\text{\AA}$ away from the intermediate and should significantly influence the secondary dissociation dynamics. Based on the uncertainty regarding this time interval, it is prudent to also analyze the data in terms of a three-body dissociation. The individual translational energy distributions for all three fragments in the azomethane center-of-mass shown in Figure 10 were obtained by independent iterative fitting of each peak in the TOF spectra. Substantial translational energy was observed for the nitrogen and one methyl radical. The

other CH_3 fragment has a $P(E_T)$ that is peaked close to zero with an average energy of 3.8 ± 0.5 kcal/mole. Since the two features in the methyl TOF spectra are not completely resolved, some uncertainty arises regarding the low energy tail of the fast methyl and the high energy portion of the slower methyl. However, since the ratio of 1:1 between the two methyls is strictly enforced in the forward convolution fitting procedure this uncertainty is minor, having the largest affect on the average translational energy calculated for the slowest methyl fragment.

If the dissociation is concerted then of interest is the fraction of the *total* available energy partitioned into translation of all three fragments. The pertinent energetics for the photodissociation of azomethane are shown in Figure 1. Absorption of a single 351 nm photon deposits 81.5 kcal/mole into azomethane. From the heats of formation for azomethane⁴⁴ (15.0 kcal/mole) and methyl radical⁴⁵ (35.0 kcal/mole) there should be 55.0 kcal/mole of available energy for the asymptotic separation of all three fragments. The combined rotational and vibrational energy of azomethane at room temperature is estimated to be ~ 1.7 kcal/mole and should be significantly reduced following the supersonic expansion. An average overall translational energy release can be obtained by adding the mean center-of-mass translational energy of all three fragments. The average value of 28.2 ± 1.0 kcal/mole corresponds to $\sim 60\%$ of the total available energy appearing as recoil of the photofragments.

The center-of-mass velocity distribution for each fragment was obtained directly from the calculated $P(E_T)$ and used in the generation of the vector diagram shown in Figure 11. The nitrogen has an average center-of-mass velocity of 1780 m/s and methyl

radicals recoil with mean velocities of 3300 m/s and 1350 m/s. Conservation of linear momentum uniquely determines the angles between all three fragments given the center-of-mass velocity of each fragment. The asymptotic angle between N_2 and the faster CH_3 is approximately 160° as would be expected, intuitively, if these two fragments experienced the majority of the repulsive energy released during the dissociation. This is agreement with the assertion of Weisman and co-workers that available energy is partitioned differently between the two methyl radicals. Based on the translational energy distributions, two methyl fragments with disparate internal excitation, particularly in the v_2 umbrella mode, is not unreasonable. In an impulsive dissociation the v_2 distribution is determined by the Franck-Condon excitation associated with the rapid change in the methyl geometry from pyramidal to planar. The v_2 excited methyl fragment observed by Weisman and co-workers^{18,19}, therefore, most likely corresponds to the "faster" methyl in the present experiment. As discussed in chapter 1, the use of internal state distributions to describe the sequence of events in a three body dissociation must be viewed with caution. In light of the observed internal energy content of the methyl radicals, suggestive of both impulsive and statistical bond cleavages, it is tempting to equate the statistical methyl fragment with IVR in the CH_3N_2 intermediate. This requires that the methyldiazenyl radical not only persist for sufficient time to allow IVR to occur but also that the ~ 20 kcal/mole exothermicity is not preferentially partitioned into product translation. The temporal correlation of the two bond cleavages would have been difficult to predict from the internal state distribution alone.

The derived vector relations of the three fragments (Figure 11) are in close

agreement with those derived from the sequential analysis.

D. Dissociation Mechanism

Any proposed mechanism of azomethane dissociation must be consistent with both the correlation of the asymptotic velocity vectors and the unequal partitioning of translational energy between the two departing methyl radicals. A mechanism in which concerted asymmetric scission of the C-N bonds is driven by the pairing of electrons to form the N-N triple bond fulfills both requirements. This is feasible because the CH_3N_2 intermediate is unstable with respect to C-N bond cleavage and possesses only a modest ~ 2 kcal/mole barrier to dissociation.²² The extension of one C-N bond, therefore, may need only to reach a critical length in azomethane where electronic rearrangement and concerted C-N bond cleavage can occur. The CH_3 group that is farthest removed from the CH_3N_2 as the closed shell N_2 is formed behaves much like a spectator during the dissociation and receives only a modest degree of recoil. However, the other CH_3 , due to its proximity to the closed shell N_2 , experiences the majority of the repulsive potential energy release. This mechanism is the three body analogue to the elimination of molecular hydrogen from ethylene⁴⁶ and formaldehyde.^{47,48} In both cases one C-H bond elongates considerably more than the other, and as the H_2 molecule forms, the impulses along the C-H bonds are unequal resulting in considerable rotational excitation of the H_2 . If this is indeed the mechanism of dissociation, it may be important in understanding similar systems that undergo molecular elimination concurrent with the formation of further unsaturation. For example, following the loss of one iodine atom from $\text{CH}_2\text{ICH}_2\text{I}$, the loss of the second iodine and formation of ethylene is exothermic.⁴⁹ The dissociation of the

two C-I bonds may also occur, therefore, simultaneously when one C-I bond reaches a critical distance.

The absence of observable fluorescence from the S_1 state indicates that azomethane must undergo rapid internal conversion or intersystem crossing. This is consistent with the lack of correlation between the angle of laser polarization and the measured product angular distributions. Although the first triplet state, T_1 , lies below S_1 in energy there has been conflicting evidence for its relevance. No phosphorescence has ever been observed from any azoalkane necessitating the use of indirect means to study the potential participation of T_1 .^{1,11} Triplet sensitized reactions have been effective in achieving azomethane decomposition but exhibit much lower quantum yields for dissociation than photolysis.¹ It has been debated whether or not this is due to an alternate mechanism that does not proceed via the triplet state, the involvement of a *second* triplet surface, or the efficiency of energy transfer from the sensitizer to the azoalkane. The last argument would support the existence of a barrier on the triplet surface. If sufficient energy is not deposited into the triplet state to overcome the barrier to dissociation de-excitation competes effectively with decomposition. Certainly our results are consistent with this mechanism. Intersystem crossing followed by dissociation over a barrier on the triplet potential energy surface would account for both the finite excited state lifetime and impulsive energy release observed. The transition state on the excited triplet potential energy surface is predicted, by *ab initio* calculation^{22,23}, to be asymmetric with one C-N bond 34% longer than the other which remains close to its equilibrium bond length.

If internal conversion occurs readily in the *gas phase* then the dissociation could

proceed on the ground state potential energy surface. In fact, the ground state is considered to be the most likely destination of azomethane following $n \rightarrow \pi^*$ excitation.⁵⁰ Internal conversion in azomethane has been predicted to be facilitated by the proximity of the S_1 and S_0 states in both the twist and semilinear geometries.⁷ This allows IC to occur without the participation of the excited triplet state. Significant rotation about the N-N bond on the S_1 state prior to IC will insure that both ground state *cis* and *trans* isomers would be equally populated. The thermal barrier to isomerization is thought to be ~50 kcal/mole^{7,51} so that further isomerization may take place on the ground state surface depending on the relative rate of isomerization compared to dissociation. Although the relative energies of *cis* and *trans* azomethane have not been experimentally observed, the *cis* isomer has been estimated to be 9.3 kcal/mole higher in energy.^{7,21} The large amplitude motion that is expected based on the quantity of internal energy would certainly allow reaching a highly asymmetric configuration on the ground state potential energy surface. RRKM calculations⁵² predict that the azomethane lifetime on the ground state is ~5 ns. Since Weisman and co-workers¹⁸ observed the onset of methyl fragments within 1 ns, a ground state dissociation was considered to be highly unlikely. The results of this experiment, however, show no evidence to suggest that the dissociation could not occur from the S_0 state.

IV. Concluding Remarks

Azomethane has been shown by photofragment translational spectroscopy to undergo dissociation to two methyl radicals and nitrogen following excitation to its first excited singlet state. We find that there is a strong correlation of the asymptotic velocity

vectors of all three fragments indicating that the dissociation is *concerted* rather than stepwise as had been previously reported. The overall translational energy distributions for all three fragments in the azomethane center-of-mass clearly illustrate the disparate partitioning of energy between the two recoiling methyl fragments. If the dissociation occurs via a transition state that is asymmetric with regards to the C-N bond lengths, then a simultaneous pairing of the electrons to form the N-N triple bond would result in the departing CH₃ groups having vastly different recoil velocities. The electronic state on which the dissociation proceeds, however, remains unclear.

The utility of this technique to clearly differentiate between concerted and stepwise mechanisms is impressive. It is also important to note that since non-adiabatic transitions occur prior to dissociation, the excited azomethane possesses a first order lifetime in excess of its rotational period as demonstrated by a lack of photofragment anisotropy. However, once dissociation commences, both C-N bonds cleave in rapid succession. Since the time before the initial C-N bond breaks is much longer than the time delay between the two bond cleavages, conventional pump and probe time-resolved experiments are not feasible for studying the relation between the first and second bond ruptures in such a system. Further experiments using infrared multiphoton dissociation (IRMPD) in a molecular beam should provide valuable insight into the ground state decomposition of azomethane and increase our understanding of its ultraviolet photochemistry.

Table 1: *Ab Initio*^a Vibrational Frequencies of the Methyldiazenyl Radical (²A')

Vibrational Mode	Minimum	Transition State
ω_1	3252 ^b	3320
ω_2	3153	3174
ω_3	1935	2010
ω_4	1548	1512
ω_5	1459	1234
ω_6	1148	884
ω_7	854	424
ω_8	472	1041 i
ω_9	3254	3324
ω_{10}	1547	1513
ω_{11}	1104	847
ω_{12}	162	96

a. Performed at the TZ2P CISD level of theory (ref. 22)

b. All frequencies given in cm⁻¹

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Figure Captions

Figure 1 Energy level diagram for the 351 nm photodissociation of azomethane. Thermodynamic quantities are referenced in the text.

Figure 2 The schematic diagram of the fixed source rotatable detector apparatus. (1) pulsed valve (2) cryopanel cooled to ~ 7 K (3) interaction region of the laser and the molecular beam (4) electron bombardment ionizer (5) quadrupole mass filter.

Figure 3 Time-of-flight spectra for m/e 13 (CH^+) at laboratory angles 20° , 35° and 50° . The open circles represent data points. The contributions from the first (dotted line) and second (dashed line) step methyl radicals as well as the total fit to the data (solid line) are the forward convolutions of both the primary and secondary center-of-mass translational energy distributions shown in Figure 5 and $P(\Omega)$ shown in Figure 6.

Figure 4 Time-of-flight spectra for m/e 28 (N_2^+) at laboratory angles 20° , 35° , and 50° . The slow signal in the spectrum at 20° is due to time dependent background from the pulsed valve. The fit is the forward convolution of the two translational energy distributions shown in Figure 5 and $P(\Omega)$ shown in Figure 6.

Figure 5 The primary (solid line) and secondary (dashed line) total translational energy distributions derived from the first sequential analysis of the data (see text).

Figure 6 Contour plots of the secondary velocity distributions for CH_3 (solid line) and

N_2 (dashed line). Each plot corresponds to the first sequential analysis described in the text. Arrows show the methyl radical from the primary impulse (0°) and the most probable secondary velocities that conserve momentum.

Figure 7 Upper panel shows a typical forward-backward symmetric secondary angular distribution, $P(\Omega)$. The lower panel shows the resulting fit to the m/e 28 TOF spectrum at 35° using the $P(\Omega)$ shown above (solid line). The dashed line using the anisotropic angular distribution shown in Figure 6 is the dotted line fit.

Figure 8 The primary (solid line) and secondary (dashed line) total translational energy distributions derived from the second sequential analysis of the data (see text).

Figure 9 Contour plots of the secondary velocity distributions for CH_3 (solid line) and N_2 (dashed line). Each plot corresponds to the first sequential analysis described in the text. Arrows show the methyl radical from primary impulse (0°) and the most probable secondary velocities that conserve momentum.

Figure 10 The translational energy distributions for each fragment in the azomethane center-of-mass.

Figure 11 Newton diagram in the azomethane center-of-mass showing the most probable velocities of all three fragments in solid lines.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Chapter 3

Photodissociation of Acetone at 248 nm and 193 nm: Evidence for Stepwise Dissociation Dynamics

Abstract

The technique of molecular beam photofragment translational spectroscopy has been used to study the dissociation of acetone following $S_1 \leftarrow S_0$ (248 nm) and $S_2 \leftarrow S_0$ (193 nm) excitation. Excitation at 248 nm resulted in the production of CH_3 and CH_3CO with 14.2 ± 1.0 kcal/mole on average of the available energy appearing as translation of the photofragments. Comparison of the measured $\langle E_T \rangle$ with values reported at 266 nm suggest that the energy partitioning is dominated by the exit barrier caused by an avoided crossing on the potential energy surface. A substantial fraction ($30 \pm 4\%$) of the nascent acetyl radicals from the primary dissociation contain sufficient energy to undergo spontaneous secondary decomposition. From the onset of the truncation of the CH_3CO $P(E_T)$ a threshold of 17.8 ± 3.0 kcal/mole for the dissociation of the acetyl radical has been determined in agreement with recent results on the photodissociation of acetyl chloride. The translational energy release in the dissociation of CH_3CO closely matches the experimentally determined exit barrier. At 193 nm the only observed dissociation pathway was the formation of two methyl radicals and carbon monoxide. On average $\sim 38\%$ of the available energy is found in product translation suggesting that significant internal energy resides in the nascent CH_3 fragments consistent with the results of Hall *et al.* (*J. Chem. Phys.*, **94**, 4182 (1991)). We conclude that the dynamics and energy partitioning for dissociation at 193 nm is similar to that at 248 nm.

I. Introduction

Acetone, the simplest ketone, has been used as a model system for understanding the rich photochemistry of this entire class of carbonyl compounds. Photolysis proceeding via α -bond cleavage (Norrish type I) is the most studied of the photochemical processes. At sufficiently high excitation energies acetone represents a prototypical three body dissociation process involving the cleavage of two identical chemical bonds. Of dynamical interest is the extent to which the two bond breaking steps are energetically and temporally coupled. The existence of spectroscopic methodology for probing the photofragments has resulted in the extraction of considerable information concerning the nascent energy distributions of the products. However, despite numerous recent studies on the photodissociation dynamics of acetone, the sequence of events leading to the three asymptotically separated fragments is still largely unresolved. The present experiments were pursued in order to further clarify the gas phase UV photodissociation dynamics of acetone.

The first absorption band in acetone centered at ~ 260 nm corresponds to an $\pi^* \leftarrow n$ ($S_1 \leftarrow S_0$) transition.¹ This involves promotion of a non-bonding electron on the oxygen to an anti-bonding orbital localized on the carbonyl moiety. Within this wavelength region acetone dissociates to yield methyl and acetyl radicals²,

The initial excitation is to the A'' adiabatic potential energy surface which is bound along the C-C coordinate. Bond cleavage can occur by either internal conversion or inter-

system crossing to the C_s $^3\sigma\sigma^*$ configuration via out-of-plane motion.^{3,4} Excited state dissociation then proceeds over a small barrier caused by an avoided crossing on the T_1 surface. This barrier has been measured by Zuckermann *et al.* who observed a pronounced decrease in the fluorescence emission at 305.8 nm corresponding to a barrier for dissociation of 93.4 kcal/mole above the ground state.⁵ Hancock and Wilson used photofragment translational spectroscopy (PTS) to examine the photodissociation dynamics at 266 nm and found that 13.9 kcal/mole on average of the available energy appeared as product translation.⁶ Waits *et al.* measured the translational energy of the vibrationless CH_3 radicals by 2+1 resonance enhanced multiphoton ionization (REMPI) ionization/time-of-flight mass spectrometry and obtained a similar $\langle E_T \rangle$ value.⁷ The large fraction of energy partitioned into translation of the photofragments was attributed by both groups to a barrier in the exit channel. The similarity between the observed translational energy release and the barrier height of 13.2 kcal/mole determined by Zuckermann *et al.* suggested that the dissociation proceeds on the T_1 surface. The spatial distribution of the photofragments in both studies^{6,7} was found to be isotropic, contrary to the work of Solomon *et al.* who observed anisotropy in the dissociation.⁸

The spontaneous decomposition of the acetyl radical is possible if its internal energy exceeds the barrier to dissociation,

Kinetics studies of CH_3 addition to CO yielded a CH_3CO barrier to dissociation of 17.2 ± 0.5 kcal/mole.⁹ A number of other kinetic studies have obtained values ranging from

11.1 to 21.7 kcal/mole.^{10,11} Recent PTS studies in our laboratory on acetyl chloride photodissociation at 248 nm showed that ~35% of the acetyl radical fragments underwent secondary decomposition.¹² The barrier height to CH_3CO dissociation was determined to be 17.0 ± 1.0 kcal which is consistent with the result of Watkins and Word.

The second absorption band ($S_2 \leftarrow S_0$) in acetone results from an $3s \leftarrow n$ Rydberg excitation. The S_2 state is predissociative, coupling to the $\{S_1, T_1\}$ state via skeletal bends and CH_3 torsion.^{13,14} Figure 1 shows a schematic energy level diagram for the photodissociation of acetone. Pilling and co-workers have shown by end product analysis that dissociation into two methyl radicals and carbon monoxide,

accounts for >95% of the photolysis products.¹⁵ This observation, in addition to the large absorption cross section at 193 nm demonstrated the potential of acetone as a clean source of methyl radicals for higher temperature kinetics studies. The first determination of the internal state distribution of a nascent photofragment was obtained from time resolved infrared emission of CO by Donaldson and Leone.¹⁶ The significant rotational excitation observed was attributed to a stepwise dissociation mechanism. Excitation in the $\text{CH}_3 \nu_3$ vibration was also monitored and showed evidence for at least one methyl possessing substantial vibrational energy. Woodbridge *et al.* subsequently measured the CO distributions with higher resolution and concluded that the rotational temperature was slightly greater than observed by Donaldson (~3360 K).¹⁷ Vibrational excitation in the CO fragment has been found to range from 1200-2700 K in several independent studies.¹⁶⁻¹⁸

In a comprehensive study, Trentelman *et al.* measured the ro-vibrational and translational energy of all the photofragments.¹⁸ The CO distributions were obtained using rotationally resolved VUV laser-induced fluorescence ($A^1\Pi \leftarrow X^1\Sigma^+$) excitation spectroscopy and significant rotational excitation was observed (3000 K Boltzmann). The translational energy of the CO fragment was also determined from the Doppler widths of several of the ro-vibronic transitions. Line widths of $0.5\text{--}0.6\text{ cm}^{-1}$ were attributed to a center-of-mass velocity of 1600 m/s and a kinetic energy of 8.6 ± 1.0 kcal/mole. The methyl fragments were probed via 2+1 REMPI through the $3p^2A_2'' \leftarrow 2p^2A_2''$ transition and observed to be vibrationally cold (76% in $v=0$) with most of the vibrational energy in the v_2 mode. Using the pulsed field extraction time-of-flight technique, Trentelman *et al.* measured the translational energy of the $CH_3\ 0_0$ band to be 10.5 ± 2 kcal/mole. The translational energy distributions for both methyl radicals were found to be indistinguishable. The low internal energy content of the methyl fragments was interpreted by Trentelman as evidence for a dissociation which occurred prior to randomization of the available energy.¹⁸ Recent diode laser absorption/gain experiments on the 193 nm photolysis of acetone- d_6 by Hall *et al.* suggest, however, that the vibrational energy excitation of the nascent methyl radicals is significantly higher.¹⁹ A *stepwise dissociation* involving almost complete randomization is consistent with the observed 6% population of CD_3 photofragments formed in the vibrationless state.

By measuring the translational energy of all the photofragments averaged over all product quantum states we hope to obtain a more complete picture of the dissociation dynamics. Photodissociation at 248 nm represents an important extension of earlier work performed at 266 nm. The variation in the partitioning of available energy into product

translation as a function of excitation wavelength within the same absorption band can reveal much about the topology of the potential energy surface. In addition, photodissociation at 248 nm presents the opportunity to extract additional evidence concerning the barrier height to CH_3CO decomposition as well as its unimolecular dissociation dynamics. In light of the recent disparate dissociation mechanisms proposed by Hall and Trentelman, the photodissociation of acetone at 193 nm clearly warrants further investigation. The translational energy distribution of the CH_3 photofragments following 193 nm ($\text{S}_2 \leftarrow \text{S}_0$) excitation have previously been determined for only the vibrationless methyl products. It is our belief that a re-measurement of this particular degree of freedom is crucial to elucidating the true partitioning of the available energy.

II. Experimental

These measurements were carried out on a molecular beam apparatus with a fixed source and a rotatable detector that has been adapted to perform photofragment translational spectroscopy experiments.^{20,21} For the majority of the experimental data acetone seeded in helium was expanded using a pulsed valve²² (1.0 mm nozzle) with a Physik-Instrumente piezocrystal. The conditions of the molecular beam varied from 5%-20% acetone at stagnation pressures ranging between 150-680 torr. An extension on the pulsed valve nozzle heated to 200°C significantly reduced formation of clusters in the beam. A time-of-flight method was used with a spinning slotted wheel to measure the velocity and velocity spread of the molecular beam. An appropriate time delay between the wheel and the pulsed valve ensured accurate sampling of the region of the pulse that was irradiated.

The resulting collimated pulsed beam was crossed at 90° with the output of a

Lambda Physik EMG 202 MSC excimer laser operating at the ArF (193.3 nm) and KrF (248.5 nm) transitions. The laser fluence at both wavelengths was typically 40-160 mJ/cm². The neutral photofragments recoiled 20.8 cm where they were ionized by electron bombardment, mass selected using a quadrupole mass spectrometer, and counted with a Daly ion detector. A computer interfaced multi-channel scaler, triggered from the laser pulse, was used to collect and store the data. Polarization of the laser was achieved with 10 quartz plates at Brewster's angle with respect to the direction of laser propagation. The resulting >95% polarized light could then be rotated by adjusting the orientation of the polarizer.

The data was fit using an iterative forward convolution technique that has been previously described.^{23,24} Briefly, a center-of-mass translational energy distribution is chosen, convoluted with the instrument response functions and transformed into laboratory time-of-flight spectra. The calculated TOF is then compared to the experimental TOF and the translational energy distribution is iteratively adjusted until a satisfactory fit is obtained.

III. Results and Analysis

A. *Excitation at 248 nm*

Product time-of-flight data were collected for m/e 15 (CH₃⁺), m/e 28 (CO⁺), and m/e 43 (CH₃CO⁺) at detector angles ranging from 15° to 55° from the molecular beam. Subtraction of the laser-off spectra from the laser-on spectra was performed on all time-of-flight spectra. The m/e 15 TOF spectra shown in Figure 2 consists of three components; methyl radicals and acetyl radicals from reaction 1 and secondary methyl radicals from

reaction 2.

The fast peak at $\sim 60 \mu\text{sec}$ in Figure 2 corresponds to methyl radicals from reaction 1. The energy available to be partitioned between the degrees of freedom of the primary photofragments is given by the following expression,

$$E_{\text{avail}} = E_{h\nu} - D_o(\text{CH}_3\text{CO} - \text{CH}_3) + E_{\text{int}}^P \quad (4)$$

where $E_{h\nu}$ is the photon energy (115 kcal/mole), $D_o(\text{CH}_3\text{CO}-\text{CH}_3)$ is the bond dissociation energy of 83.7 kcal/mole (Ref. 25) and E_{int}^P is the internal energy of the parent molecule. The vibrational energy content of acetone at room temperature is estimated to be ~ 1.5 kcal/mole based on the known vibrational frequencies.^{26,27} Most of this excitation should involve the low frequency modes, skeletal bends and methyl torsions, which are expected to undergo partial or complete relaxation in the supersonic expansion. Assuming that the internal energy of the parent is negligible, the available energy is 31.3 kcal/mole following C-C bond cleavage. The total center-of-mass translational energy distribution for reaction 1 is shown by the solid line in Figure 3. The $P(E_T)$ has an average value of 14.2 ± 1.0 kcal/mole and a FWHM of ~ 12 kcal/mole corresponding to an average of 45% of the available energy appearing as product translational energy.

At longer times ($\sim 130 \mu\text{sec}$) in Figure 2 is a peak resulting from dissociatively ionized CH_3CO . Since the acetyl radical is the momentum matched fragment of the primary methyl it should share the same $P(E_T)$. However, the slow component is noticeably absent from the TOF profile. This is more evident in the m/e 43 (CH_3CO^+) TOF spectra shown in Figure 4. By conservation of energy, the smaller the translational

energy of the photofragments the greater their internal excitation. When the internal energy exceeds the barrier to dissociation of CH_3CO these radicals fail to persist long enough to reach the detector. This resulting truncation of the low energy CH_3CO radicals is illustrated in the center of mass velocity distributions of Figure 5. A dotted line that starts to deviate from the $\text{CH}_3 \text{P}(\text{E}_\text{T})$ in Figure 3 at ~ 12 kcal/mole marks the truncation of the low energy side of the $\text{CH}_3\text{CO} \text{P}(\text{E}_\text{T})$. The m/e 43 spectrum at 25° shown in Figure 4 was used to fit the slow portion of the $\text{CH}_3\text{CO} \text{P}(\text{E}_\text{T})$ and yields a reasonable fit to the slow component in the m/e 15 TOF spectra. For comparison, the forward convolution fit to the data without the truncation in the primary $\text{P}(\text{E}_\text{T})$ is shown by the dashed line in Figure 4. Based on the relative integrated area of the truncated region to the entire primary $\text{P}(\text{E}_\text{T})$ an estimate of the fraction of acetyl radicals that undergo secondary dissociation can be obtained. This gives a value of $30 \pm 4\%$ which is in good agreement with the CO quantum yield of 0.35 determined at 250 nm by Gandini and Hackett.¹¹ The uncertainty reflects our measure of confidence in fitting the slow side of the m/e 43 peak in the TOF spectra.

The m/e 43 TOF spectra for vertical and horizontal linear polarization of the photolysis laser with respect to the molecular beam axis showed no difference in intensity. The acetyl radical fragment was monitored because the TOF flight spectra have only a single component and superior signal-to-noise compared to m/e 15. The absence of any correlation between the fragments recoil and the angle of laser polarization is consistent with the findings of references 6 and 7 but contrary to the anisotropy reported in ref. 8. Based on our measured polarization dependence an anisotropy parameter²⁸ of $\beta=0$ was used to fit the entire set of experimental data.

The last component of the m/e 15 TOF in Figure 2 is a broad underlying feature

due to methyls from the secondary decomposition of acetyl radicals (reaction 2). Since this feature arises from acetyl radicals that are absent from the total $P(E_T)$ for reaction 1, the primary distribution of CH_3CO translational energies was obtained by subtracting the CH_3CO $P(E_T)$ from the *true* primary $P(E_T)$ used to fit the CH_3 radicals from the initial bond cleavage step. In order to fit the apparent bimodal shape in the TOF, a forward-backward symmetric secondary angular distribution, $P(\Omega)$, was used, consistent with the fated acetyl radicals persisting for longer than their rotational period.²⁹ The secondary angular distribution is shown in Figure 6.

$$P(\Omega) = \frac{\sin\Omega^\circ}{\sin\Omega}, \quad \text{for } \Omega^\circ \leq \Omega \leq \Omega^\circ - \pi \quad (5)$$

The fits to the secondary components of the TOF spectra were reasonably sensitive to both the secondary $P(E_T)$ and $P(\Omega)$. Provided that the forward-backward symmetry of $P(\Omega)$ was maintained and the secondary $P(E_T)$ was peaked ~5-7 kcal/mole away from zero, reasonable fits to the data could be achieved. We, therefore, adopted a simple model in which the primary and secondary translational energy distributions were decoupled but constrained to conserve the available energy. This resulted in appropriate truncation of the secondary $P(E_T)$ when required. The best fit was obtained with a broad gaussian secondary $P(E_T)$ shown in Figure 7 with a most probable value that closely matched the experimental exit barrier height (~6 kcal/mole).^{9,12} Figure 8 shows the m/e 28 (CO^+) TOF spectrum at a laboratory angle of 35° . The spectrum contains contributions from primary acetyl fragments and CO from reaction 2.

The intensity of all detected fragments from acetone photodissociation varied linearly with laser power indicating that the observed processes involve a single photon.

B. Excitation at 193 nm

Time-of-flight spectra for m/e 15 and m/e 28 were collected at detector angles ranging from 15° to 55° . Signal was not observed at m/e 43, the parent mass of the acetyl radical. Although CH_3CO could dissociatively ionize to lower masses, there was no evidence for acetyl at its daughter masses. TOF spectra were also measured at several other masses that would correspond to the products from the following proposed minor channels in the 193 nm photolysis of acetone,¹⁵

No photodissociation signal was detected at m/e 16 (CH_4^+) or m/e 42 (CH_2CO^+) that would arise from reaction 5. In order to ascertain the importance of reaction 6 the experimental apparatus was modified to facilitate the detection of hydrogen atoms.³¹ The only single photon laser dependent signal observed at m/e 1 was due to methyl radicals from reaction 3 that had dissociatively ionized.³² Although reactions 5 and 6 may still be occurring at levels below the limit of our detection they are minor channels at most.

Time-of-flight data for m/e 15 at laboratory angles of 20° , 35° and 50° are shown in Figure 9. The observation of only a single peak in the TOF spectra is consistent with the

indistinguishability of the velocity distributions reported by Trentelman.¹⁸ If the single peak is the result of methyls originating from a synchronous three-body dissociation then, since the methyl radicals are identical, the treatment of the data is straightforward. A method for the analysis of a synchronous dissociation was recently developed for the study of *s*-tetrazine and a thorough description of the method is presented therein.³³ Briefly, the experimental data is analyzed by the same forward convolution technique used to fit two-body dissociations but with several important differences. First, an energy independent set of most probable angles between the asymptotic velocity vectors is chosen. Gaussian functions describe the spread about these angles and a total translational energy distribution is assumed. All three are then iteratively adjusted until a satisfactory fit to the data is obtained. The present data could not be fit in this manner by constraining the dissociation to be symmetric about the two C-C-O angles.³⁴ This suggests that a *non-synchronous dissociation* with overlapping CH₃ distributions is more probable than a synchronous one. This is consistent with the high degree of CO rotation observed previously.¹⁶⁻¹⁸ Since the dissociation is non-synchronous, involving two impulses separated by a finite time interval, the inability to resolve the two methyl radicals makes a unique determination of the translational energy distributions from each step impossible.

The least biased approach to fitting the methyl TOF spectra involves obtaining the independent fragment $P(E_T)$ for the methyl radical in the *acetone* center-of-mass. This is accomplished by using the forward convolution procedure with assumption that in fitting the TOF spectrum of each fragment there is a corresponding momentum matched fragment of infinite mass. Figure 10 shows the derived distribution which has an average value of 7.7 ± 1.0 kcal/mole and a FWHM of ~ 15 kcal/mole. The CO fragment (m/e 28)

TOF spectra at laboratory angles 35° and 50° are shown in Figure 11. In a similar fashion the CO center-of-mass translational energy distribution can be derived and is shown in Figure 12. The $P(E_T)$ has an average value of 4.8 ± 0.5 kcal/mole.

Polarization measurements were performed at both m/e 15 and m/e 28. The m/e 15 spectra exhibited no variation in either intensity or shape with the change of laser polarization. Since the single peak in the TOF spectra is a composite of methyl fragments from both the first and second bond cleavages, the ability to measure a small degree of anisotropy in the initial dissociation step is dubious. However, the lack of any apparent polarization dependence suggests that if the dissociation is not completely isotropic the anisotropy parameter is negligibly small.

IV. Discussion

A. Excitation at 248 nm

Primary Dissociation: The large fraction of available energy that is found in product translation for reaction 1 is not indicative of typical simple bond rupture via a loose transition state.³⁵ The prior treatment³⁶, which represents the maximum entropy description of the energy partitioning, is a useful method of generating statistical energy distributions. Using the rigid rotor-harmonic oscillator approximations and treating the photofragments as spherical tops, the fraction of available energy appearing as center-of-mass product translation, f_T , is given by the following normalized distribution³⁷,

$$p^o(f_T) = \frac{\Gamma\left(s_1 + s_2 + \frac{9}{2}\right)}{\Gamma\left(\frac{3}{2}\right)\Gamma(s_1 + s_2 + 3)} [1 + f_T]^{s_1 + s_2 + 2} [f_T]^{\frac{1}{2}} \quad (8)$$

where s_1 and s_2 are the number of atoms in fragments 1 and 2 respectively. The prior distribution and experimental primary $P(E_T)$ are shown together in Figure 13. A more quantitative measure of the "entropy deficiency" of the experimental $P(E_T)$ can be obtained by a linear deviation from the information theoretic distribution³⁶,

$$P(f_T) = P^o(f_T) \exp(-\lambda_0 - \lambda f_T) \quad (9)$$

A plot of $-\ln[p(f_T)/p^o(f_T)]$ vs. f_T gives a slope of λ , the surprisal parameter, and provides a measure of deviation from a purely statistical distribution. The surprisal plot shown in the inset of Figure 13 is characterized by a surprisal parameter of ~ 70 . The average fraction of energy in translation predicted by the prior treatment is given by,

$$\langle f_T \rangle = \frac{3}{2(s_1 + s_2) + 9} \quad (10)$$

in agreement with the equipartition theorem. For acetone dissociation, excitation at 248 nm should result in $\langle E_T \rangle = 3.2$ kcal/mole. This is substantially lower than the 14.2 kcal/mole observed.

The preponderance of energy that appears as fragment recoil could have several origins. Incomplete randomization of the available energy could result in a greater than statistical fraction in the reaction coordinate. This, however, seems difficult to reconcile given the available energy and an excited state lifetime at 260 nm of ~ 1 ns measured by Breuer and Lee.³⁸ A limiting, impulsive model for predicting the disposal of available energy between the translation and internal motion of the photofragments has been

presented for triatomics by Busch and Wilson.³⁹ A generalization of the model to treat polyatomics has been developed by Tuck.⁴⁰ The soft fragment impulsive approximation assumes that all of the available energy appears in the dissociative coordinate as repulsion between the two atoms linked by the dissociating bond (see Appendix). The remaining atoms are then considered as spectators and the redistribution of the initially localized energy proceeds in accordance with classical kinematics. The soft fragment impulsive model predicts that 54% of the available energy should appear as fragment translation. Interestingly, the $\langle E_T \rangle$ reported here, 14.2 ± 1.0 kcal/mole, is very similar to the ~ 14 kcal/mole value determined at 266 nm despite a difference of *ca.* 8 kcal/mole in the available energy. Since the energy partitioning in the impulsive model is based solely on mass factors, the fraction of the available energy in translation should be invariant with respect to the excitation energy. The agreement between the impulsive model and the experimental translational energy release at 266 nm is therefore fortuitous. The insensitivity of the photofragment translation to the excitation energy suggests that the dissociation dynamics are mediated by the substantial exit barrier on the potential energy surface. The origin of this barrier is an avoided crossing on the T_1 surface which is reached via inter-system crossing (ISC) from the excited S_1 state. If intermolecular vibrational redistribution (IVR) occurs prior to dissociation, as implied by the excited state lifetime of ~ 1 ns, then the translational energy release will be dominated by the repulsive forces acting beyond the transition state rather than the magnitude of the available energy. Dissociation will occur when sufficient energy, which is statistically redistributed among the vibrational modes of the parent, flows into the reaction coordinate to overcome the barrier on the potential energy surface. Photofragment translation, therefore, should increase with

available energy in proportion to the probability of finding excess energy in the reaction coordinate. This dependence is small, affecting mostly the width of the energy distribution, in comparison to the large translational energy release originating from the exit barrier.

There are many reasons why the photodissociation of a polyatomic molecule would lead to an isotropic spatial distribution of the fragments. Several of these have been discussed in regards to $^1(n,\pi^*)$ excited acetone.⁶ If the dissociation is less than prompt, the correlation between the direction of the electric dipole moment (μ) and the relative velocity vector (g) of the photofragments will be eroded by parent rotation. Once the lifetime of the excited acetone exceeds several rotational periods then the angular distribution will approach isotropic. Given the ~ 1 nsec lifetime of the S_1 state, rotation prior to dissociation appears to be a plausible explanation for the lack of observed spatial anisotropy.

Secondary Dissociation: Photofragment translational spectroscopy has been successful in determining the energetics of radical decomposition by comparing the time-of-flight spectra for a radical photofragment and its momentum matched partner. This has been demonstrated by Minton *et al.* in determining the exothermicity of C_2H_4Cl dissociation⁴¹ and more recently has been applied to the case of the acetyl radical.¹² Although the acetyl radical can undergo secondary dissociation, the primary methyl radical can not. The truncation of the CH_3CO $P(E_T)$ represents the maximum product internal energy at which the CH_3CO is stable. If $E_{T(min)}$ denotes the value corresponding to the onset of truncation then the barrier to CH_3CO dissociation can be calculated from the following expression:

$$E_{barr}(CH_3-CO) = E_{hv} - D_o(CH_3CO-CH_3) - E_{T(min)} = E_{avail} - E_{T(min)} \quad (11)$$

$$= 31.3 - 13.5 \text{ kcal/mole}$$

$$E_{barr}(CH_3-CO) = 17.8 \pm 3.0 \text{ kcal/mole}$$

It is assumed that acetone, following supersonic expansion, possesses negligible internal energy. Rice-Ramsperger-Kassel-Marcus (RRKM) calculations indicate that acetyl radicals with 0.1 kcal/mole in excess of the barrier to dissociation have a lifetime of $\sim 5 \times 10^{-10}$ s, far shorter than the $\sim 1 \times 10^{-4}$ s flight time to the detector. Consequently the uncertainty introduced by the detection of acetyl radicals at energies just above the CH_3CO threshold to dissociation is minor. There are several factors that contribute to the less-than-abrupt truncation of the CH_3CO $P(E_T)$. The first is that a fraction of the product internal excitation can be partitioned into the methyl radical fragment. A detailed determination of the nascent ro-vibrational distributions of the methyl radical products has not been done at 248 nm although experiments at 266 nm have shown minor CH_3 excitation in the out-of-plane mode.⁷ As a consequence, some internal energy above the threshold for CH_3CO stability can be accommodated by the CH_3 partner fragment. As some of the available energy is partitioned into the internal degrees of freedom in the methyl fragment, the truncation will become more gradual. However, as long as a non-negligible quantity of internally cold CH_3 is produced, the onset of the truncation will still reflect the barrier height to CH_3CO dissociation. Another effect that may result in an overestimation of $E_{barr}(CH_3-CO)$ is rotational metastability of the CH_3CO fragment. From consideration of

the non-planar acetone transition state geometry, the acetyl fragment should contain ~ 1 kcal/mole of rotational energy. The angular momentum will be projected predominantly along the C-C bond and therefore most of this energy will be unavailable to couple into the reaction coordinate. A severe example of this effect was observed in the dissociation of bromoethanol by Hints *et al.* which, following initial C-Br bond cleavage, produces a highly rotationally excited C_2H_4OH radical that could be detected despite containing substantial internal energy in excess of its barrier to dissociation.^{29d} The barrier height of 17.8 ± 3.0 kcal/mole should, therefore, be viewed as an upper limit. Since none of these factors are present in the photodissociation of acetyl chloride, the 17.0 ± 1.0 kcal/mole value obtained in that experiment and discussed in detail in chapter 4 is more reliable.

The secondary $P(\Omega)$ and $P(E_T)$ derived from fitting the m/e 15 and m/e 28 TOF spectra provide a detailed measure of the dissociation dynamics of the acetyl radical. In order for the forward-backward (non-symmetric about 90°) secondary angular distribution of a long-lived complex to be justified the lifetime of the acetyl radicals that dissociate would need to be longer than their respective rotational periods. Treating the CH_3CO as a rigid rotor, its rotational excitation can be calculated based on the exit impact parameter derived from the dissociative geometry and the most probable recoil velocity of the primary fragments. It is assumed that the primary bond cleavage results in negligible CH_3 rotational excitation, tantamount to requiring the dissociative impulse to lie along the methyl C_{3v} axis and that there be no exit channel effects that couple rotation and translation. A non-planar dissociation, consistent with the geometry of the transition state³, predicts a rotational period of < 1 ps. RRKM calculations were performed using the vibrational frequencies of the radical and activated complex given by Watkins and Word.⁹

Given an average internal energy of 24 kcal/mole for those CH_3CO radicals that decompose and our experimentally determined barrier height of 17.8 kcal/mole, a lifetime of ~ 10 ps is predicted which is longer than the rotational period. The present observations are also consistent with long-lived CH_3CO seen in the photodissociation of acetyl iodide^{29b} where the rotational excitation of the acetyl radical should be considerably less since the dissociation geometry is planar. In addition, the nascent CH_3CO radicals from acetyl iodide photodissociation contain ~ 45 kcal/mole of internal energy and should, therefore, possess much shorter lifetimes.

The remarkable similarity between the average translational energy of the secondary step and the exit barrier to CH_3CO decomposition suggests that the dissociation dynamics of the acetyl radical are analogous to the initial C-C bond cleavage in acetone, *i.e.* the energy partitioned into translation is determined by the repulsive forces acting in the exit channel. Further evidence to support this claim rests in the nearly identical secondary $P(E_T)$ required to fit the CH_3 and CO fragments from CH_3CO decomposition in the photodissociation of acetyl chloride and acetyl bromide despite the significantly different vibrational energy content of the nascent acetyl radical photofragments as discussed in the following chapter.

B. Excitation at 193 nm

Energy Partitioning: Complementary product state distributions of the photofragments arising from acetone photodissociation at 193 nm have provided valuable insight into the dynamics of the bond breaking process. Donaldson¹⁶, and later Woodbridge¹⁷, both concluded that a non-synchronous dissociation was necessary to account for the

angular momentum reflected in the highly excited CO rotational distributions.

Measurement of the ν_3 emission from the nascent CH_3 fragments by Donaldson suggested that at least one of the methyl radicals possessed significant vibrational energy. Based on these two observations Donaldson proposed that the dissociation was a two-step process although the time scale between C-C bond cleavages could not be unambiguously determined. A step-wise dissociation mechanism was supported by the work of Baba *et al.* who saw evidence for long lived CH_3CO in the intensity dependent signal of CH_3CO^+ .⁴² Trentelman, however, found that the CH_3 fragments probed using 2+1 REMPI contained little internal excitation and substantial translation energy.¹⁸ Both statistical and impulsive model predictions were compared to the experimental results in an effort to discern the dissociation dynamics. Statistical models were found to overestimate gravely the partitioning of the available energy into CH_3 vibration while underestimating the translational energy of all the fragments. A two-step prior calculation predicts that the average center-of-mass translational energy for the methyl radicals would be ~ 4.0 kcal/mole. The severe failure of the statistical models suggested that no randomization of the available energy occurs prior to *either* the first or second C-C bond cleavage. A modified impulsive model^{39,40} was utilized in which the energy available to all three asymptotic fragments was partitioned equivalently between the two C-C bonds and the dissociation then treated as two independent impulses in two center-of-mass reference frames that conserved momentum. It was assumed that following the first bond cleavage all the vibrational energy of the acetyl fragment was coupled into the second C-C bond cleavage. Favorable agreement between the model and the experimental results supported the conclusion that the dissociation involved almost no randomization of the available energy between either

bond breaking step. The measured average energies in the various degrees of freedom of the fragments as well as the predictions of the impulsive model are shown in Table 1.

Although the impulsive model was successful in matching the experimental data, the energy partitioning observed by Trentelman, specifically the vibrational energy of the methyl fragments, was subsequently contradicted by the results of Hall *et al.*¹⁹ Following the 193 nm photolysis of acetone-*d*₆ in a gas flow cell, the time dependent increase in the vibrationless state population was measured by absorption of the ν_2 fundamental. A significant increase, consistent with the time scale of vibrational relaxation, was observed and suggested that only 6% of CD₃ radicals were formed in the $v=0$ state. It was concluded that the nascent methyl radicals are "produced in a large number of vibrational states with no strong preference for any particular vibrational mode".¹⁹ The shortcomings of REMPI for extracting accurate vibrational state populations for the methyl radical, owing to the lack of information regarding the effects of predissociation and Franck-Condon factors, was cited as a possible source of the discrepancy in regard to the Trentelman data. Of course this observation necessitated a reassessment of the dissociation mechanism of acetone which was characterized by the authors as being fully stepwise, involving randomization sufficient to generate methyl radical fragments with near *prior* distributions in vibrational energy.

Despite the overlap of the two methyl radical translational energy distributions, their cumulative $P(E_T)$ still provides insight into the partitioning of the available energy in the dissociation process. The measured $\langle E_T \rangle$ of 7.7 ± 0.5 kcal/mole for each methyl (Figure 10) differs markedly from the $\langle E_T \rangle$ of 10.5 ± 1.9 kcal/mole reported by Trentelman *et al.*¹⁷ The CH₃ O₀ band origin, probed in that experiment, reflects the kinetic

energy of *only the vibrationless methyl radicals*. If a large fraction of the available energy resides in the CH_3 fragments as Hall has suggested, then the translational energy of the vibrationless methyl radicals is not representative of the overall dissociation dynamics. It is not surprising, therefore, that our measured $\langle E_T \rangle$ is substantially lower than the result of Trentelman. The average translational energy of the CO fragment, 4.8 ± 0.5 kcal/mole, is also considerably less than previously reported.¹⁸ Figure 12 shows a comparison between the derived $P(E_T)$ from this experiment and a Boltzmann distribution at 3000 K as suggested by the results of Trentelman. Although the peaks of the two distributions are similar the 3000 K Boltzmann possesses a larger high energy contribution which results in a greater $\langle E_T \rangle$. Assuming that the combined average rotational and vibrational energy of the nascent CO fragments is ~ 9.0 kcal/mole¹⁶⁻¹⁸, the total CH_3 internal energy content can be obtained using our derived average translational energies,

$$E_{\text{int}}(\text{CH}_3) = E_{\text{avail}} - \{2(E_T(\text{CH}_3)) + E_T(\text{CO}) + E_{\text{int}}(\text{CO})\} \quad (12)$$

$$E_{\text{int}}(\text{CH}_3) = 52.8 - \{15.4 + 4.8 + 9.0\} = 23.6 \text{ kcal/mole}$$

As expected, our translational energies imply that the methyl fragments must contain appreciable internal excitation.

Stepwise vs. Concerted: If the absorbed photon provides enough energy to produce three asymptotically separated fragments, the sequence of the bond cleavages is of mechanistic importance. It is particularly intriguing in the case of chemically equivalent

bonds. A salient question in these systems is whether the bonds break in a *concerted* (synchronous or non-synchronous) or a *stepwise* manner. Although Dewar⁴³ has provided a commonly used description of each type of case, we adopt distinguishing definitions more suited to our technique.⁴⁴ This involves rotation of the intermediate as gauge for the time delay, and hence the correlation between the first and second bond ruptures. Secondary bond cleavage that occurs before the intermediate, formed by the initial bond breaking, undergoes rotational averaging results in a strong correlation between the asymptotic velocity vectors of all three photofragments and is considered a *concerted* process.^{21,44}

An information theoretic approach to examine the correlation in molecular photodissociation predicted, using the experimental data of Houston and co-workers, that acetone dissociation was intermediate between concerted and stepwise mechanisms.⁴⁴ More recent calculations¹⁹ have removed an overly severe approximation in the original calculations. The revised analysis was found to be consistent with a loss of angular correlation between the asymptotic velocity vectors of the CH₃ fragments, corresponding to complete rotational averaging in the second dissociation step. There is also experimental support for a stepwise dissociation at 193 nm. As discussed earlier, PTS studies of acetyl halides have demonstrated forward/backward symmetry in the secondary angular distribution at various average internal energies of the primary acetyl radical photoproduct. Acetyl chloride and acetyl bromide dissociated at 248 nm result in an average internal energy in the primary acetyl radical of 24 and 33 kcal/mol respectively, and in both cases rotational averaging of the acetyl radical precedes secondary decomposition (Chapter 4). In light of the results of the previous section, specifically equation 11, the primary dissoci-

ation of acetone at 193 nm will likely release an average of ~ 8 kcal/mol in translation and ~ 12 kcal/mol to internal excitation of the primary methyl. As a consequence the acetyl radical fragment will contain $\langle E_{int} \rangle \sim 45$ kcal/mol. Thus, the most relevant acetyl halide comparison is the dissociation of acetyl iodide at 266 nm studied by Kroger and Riley where following primary dissociation the acetyl radicals have $\langle E_{int} \rangle \sim 44$ kcal/mol.^{29b} Kroger and Riley observed forward/backward symmetry in the secondary decomposition products demonstrating the lifetime of the acetyl radical to be comparable to or longer than its rotational period. Acetyl radicals produced from the 266 nm photodissociation of acetyl iodide should possess comparable internal energy, and less rotational excitation, to acetyl radicals from acetone dissociation at 193 nm. This suggests that the acetone data should be fit with as a sequential dissociation.

In order to fit the data at 193 nm with a stepwise mechanism it is first necessary to assume a primary $P(E_T)$ given the following considerations. Although the CH_3 fragments possess a high degree of internal excitation consistent with substantial redistribution of the available energy, the overall translational energy release is clearly greater than predicted by a statistical, *prior*, distribution. In fact the overall translational energy is not significantly different from the dissociation, involving the secondary decomposition of activated acetyl radicals, at 248 nm. If the energy disposal at 193 nm follows the trend seen at 266 nm and 248 nm then one would expect statistical partitioning of the available energy superimposed onto the partitioning controlled by the two exit barriers on the potential energy surface. Since the initial bond cleavage in acetone at 193 nm, following internal conversion, eventually proceeds on the same potential energy surface as at 248 nm there is no reason *a priori* to expect a dramatic difference in the dissociation dynamics. The

assertion of Trentelman that acetone containing ~ 50 kcal/mole of excess energy in the excited state should be insensitive to ~ 11 kcal/mole exit barrier is questionable since the dissociation involves intersystem crossing, via out-of-plane motion, in conjunction with sufficient energy in the C-C stretching coordinate to surmount the barrier. We therefore assume a primary $P(E_T)$ at 193 nm based on the primary translational energy distributions measured for acetone at 266 nm and 248 nm suitably adjusted to the available energy. The resultant stepwise fits to the m/e 15 and m/e 28 TOF spectra are shown in Figure 14. The primary $P(E_T)$ is peaked at 16 kcal/mol and is shown as the solid line in Figure 15. The TOF data was then successfully fit with a forward/backward secondary distribution (shown in the insert in Figure 15) and a secondary $P(E_T)$ peaked at 6 kcal/mol and shown as the dashed line in Figure 15. The fit to the data was found to be sensitive to both the shape of the secondary $P(E_T)$ and the secondary angular distribution. The successful fitting of the data in this way, specifically the use of the near identical secondary $P(E_T)$ and the forward/backward $P(\Omega)$ used to fit the data at 248 nm, provides strong evidence of a stepwise dissociation for acetone at 193 nm.

Model of the Dissociation Dynamics: In order to test further the validity of a step-wise mechanism and obtain information concerning the disposal of the internal energy we have applied a dynamical model to the dissociation of acetone at 193 nm. The nature of the dissociation requires a model that reflects both the impulsive nature of reactions with large barriers to recombination as well as the statistical distribution of energy in excess of the barrier height. The present treatment represents a simple extension of the impulsive and statistical models that are currently employed.

The barrier impulsive model (BIM) is conceptually very simple. The total

available energy is divided into two "energy reservoirs", one which is denoted *statistical* and the other *impulsive*,

$$E_{avail}(tot) = E^{stat}(tot) + E^{imp}(tot) \quad (13)$$

The energy content of the first reservoir, $E^{imp}(tot)$, is chosen to be the height of the exit barrier and it is assumed that once the molecule is beyond the transition state the *localized* release of the potential energy from the exit barrier can be adequately described by the impulsive model. The remaining energy, $E^{stat}(tot)$, is then partitioned among the product rotational, vibrational, and translational degrees of freedom according to a simple statistical method. A schematic diagram illustrating the division of the available energy is shown in Figure 16. By partitioning the energy in this way the model reduces to the impulsive model at the dissociation threshold and to a simplified statistical model in the absence of a barrier. Furthermore, since the translational energy of the products from the impulsive reservoir is fixed by the barrier height, the total translational energy increases with available energy statistically which is consistent with experimental observation. The impulsive reservoir can be partitioned among the fragment degrees of freedom according to either the soft or the rigid fragment models. The statistical reservoir is partitioned assuming that the energy is freely distributed among the *parent* modes up to the transition state. These vibrational modes are divided into three overlapping ensembles from which the statistical contributions to product R, V, and T are calculated. The average energies from each reservoir, which independently conserve linear and angular momentum, are combined to obtain the final average R, V, and T energies of the products. A more detailed

description of the model is provided in the appendix.

For the impulsive reservoir of the BIM, a barrier height of 13.2 kcal/mole was used based on the measurements of Zuckermann *et al.*⁵ A non-planar dissociative geometry consistent with the geometry of the transition state was utilized in treating the impulsive reservoir.³ The impulse was assumed to be through the C_{3v} symmetry axis of the CH_3 group and therefore, resulted in no CH_3 rotational excitation. The statistical reservoir was partitioned using ground state acetone vibrational frequencies as an approximation to those of the $^{1,3}(n,\pi^*)$ excited state and are given in Table 1.²⁷ Of the 24 modes of acetone, 6 disappear upon dissociation, evolving into product translation and rotation. Two of these modes, the symmetric and antisymmetric C-C stretch, were assigned to the translation ensemble. Two methyl rocking modes, a methyl torsion and the C-C-C skeletal bend were assigned to the rotational ensemble. The Beyer-Swinehart algorithm was used to calculate the vibrational density of states for all ensembles. The moments of inertia for the CH_3CO fragment were determined from the *ab initio* equilibrium geometry calculated by Baird and Kathpal.⁴⁵ Vibrational frequencies of the parent were those used in the RRKM calculations of Watkins and Word.⁹ The secondary bond cleavage assumed a total available energy equal to the average internal energy of the acetyl fragment from the initial step minus the endothermicity of the reaction. An exit barrier height of 5.5 kcal/mole, derived from the dissociation barrier determined in reference 12 and the reaction endothermicity, was used for acetyl dissociation.

The results of the model and, for comparison, the average translational energies of the photofragments derived from the stepwise fitting procedure are shown in Table 2. The predictions from the model are in good agreement with the present experimental results.

This is not too surprising since the translational energy release in each step closely matches the corresponding exit barrier height. More interesting are the calculated average internal energies which show that, assuming the complete randomization of available energy in excess of the barriers, the initial methyl possesses substantially more internal excitation than the second. The total internal energy of both methyl fragments according to the model is 26.6 kcal/mole, which is consistent with the results of Hall *et al.* but much higher than the 6.2 kcal/mole predicted by the Trentelman model.

Since all of the fragment vibrational energy is determined by partitioning in the statistical reservoir, non-statistical excitation of specific degrees of freedom due to dynamical exit channel effects will not be reproduced by the model. For example, in repulsive dissociation that result in CH_3 fragments, excitation of the methyl ν_2 umbrella mode is commonly observed due to the large, C_{3v} to D_{3h} , geometrical change. The barrier impulsive model is, therefore, only useful in predicting total average internal energies rather than particular vibrational excitations. Not surprisingly, the model underestimates the CO vibrational energy from the secondary decomposition of CH_3CO . Recent FTIR emission experiments on the 193 nm photodissociation of diethyl ketone reveal a greater deviation from statistical behavior in this degree of freedom than is observed in acetone suggesting dynamical effects operating the dissociation.⁴⁶ These findings will be discussed thoroughly in the next chapter.

V. Concluding Remarks

At 248 nm ($S_1 \leftarrow S_0$) acetone dissociates to produce a methyl and acetyl radical. On average 14.2 ± 1.0 kcal/mole is observed in photofragment translation. The similarity of

this value to the height of the exit barrier and its invariance when compared to excitation at longer wavelengths in the same absorption band strongly suggests that the energy partitioning, specifically the translational energy release, is mediated by the exit barrier on the potential energy surface. Of the nascent acetyl radicals $30 \pm 4\%$ have sufficient internal energy to undergo secondary decomposition. An upper limit to the CH_3CO barrier to dissociation has been determined to be 17.8 ± 3.0 kcal/mole, in agreement with the 17.0 ± 1.0 kcal/mole value derived from the photodissociation of acetyl chloride. The translational energy of the CH_3 and CO fragments arising from the decomposition of the nascent acetyl radicals is consistent with the magnitude of the exit barrier.

Following excitation at 193 nm acetone was observed to dissociate exclusively into two methyl radicals and carbon monoxide. The average translational energies for the photofragments were found to be considerably less than determined previously, suggesting that a significant fraction of the available energy is partitioned into methyl internal excitation in agreement with the work of Hall *et al.* A stepwise method of analysis, using only slightly modified energy and angular distributions analogous to those derived at 248 nm, was successful in fitting the experimental data. We, therefore, conclude that the mechanism of dissociation at 193 nm can be characterized as fully stepwise, involving substantial randomization of the available energy and complete rotational averaging in the second step. Consequently, the dissociation dynamics of acetone at 193 nm can be viewed as a simple extension of the mechanisms that occur at both 266 nm and 248 nm giving credence to the notion that even modest exit barriers can greatly influence the partitioning of the available energy in photodissociation processes.

VI. Appendix

A. *The Statistical Reservoir*

The partitioning of the statistical reservoir between the two fragments relies upon ideas developed for the Separate Statistical Ensembles method (SSE)⁴⁷, Phase Space Theory (PST)⁴⁸, and the prior distribution.⁴⁹ The prior distribution and PST, which assume a loose transition state, include only information regarding the product states, without treating explicitly the vibrational modes of the parent molecule that develop asymptotically into product rotation and translation. The SSE method assumes that vibrations become adiabatic prior to rotations and uses different ensembles to calculate the vibrational and rotational distributions. The basic assumption of our method of partitioning the statistical reservoir is that the energy is distributed statistically in the *parent* molecule up to the transition state. The breaking of the bond is viewed as an instantaneous event, which prevents any further rearrangement of energy. Following this reasoning, it makes sense to partition the statistical energy into translation, rotation, and vibration at the transition state using information only from the parent, and not information from the products as in PST and the prior distribution. The method used to divide the statistical reservoir into T, R, and V is very similar to the SSE procedure. Product vibrations can develop out of all parent vibrational modes, while product rotations and translations develop only out of those modes of the parent molecule that disappear during the course of the reaction.

Three ensembles are utilized. The vibrational ensemble includes *all* vibrational modes of the parent and overlaps with the other two ensembles. The rotational ensemble includes those disappearing modes that lead to rotational excitation of the products. These

modes can include methyl torsions, skeletal bends, etc. The third ensemble is a translational ensemble that includes modes that disappear into product translations. Identification of which modes belong in which ensemble can be a subtle matter for large parent molecules, but three basic rules can be easily applied:

- 1) Parent torsions and skeletal bends go into the "rotational" ensemble,
- 2) Parent skeletal stretches go into the "translational" ensemble, and
- 3) *all* parent vibrational modes go into the "vibrational" ensemble.

Here we have made the rather severe assumption that beyond the transition state bends and torsions evolve *adiabatically* into product rotations. For torsions this approximation is not unreasonable but for skeletal bends the impulsive nature of the potential energy surface should effectively couple rotation and translation. Consequently, this results in an overestimation of photofragment rotation at the expense of translational energy. Although attempts can be made to correct this deficiency, we do not anticipate that this will significantly alter the average energy quantities.

The statistical energy reservoir is partitioned into rotations in the following manner:

$$\langle E_R^{stat} \rangle = \frac{\int_0^{E^{stat}} dE_V \int_0^{E^{stat}-E_V} dE_T \int_0^{E^{stat}-E_V-E_T} dE_R \rho_P(E_V) \rho_R(E_R) \rho_T(E_T) \delta(E^{stat}-E_V-E_T-E_R) E_R}{\int_0^{E^{stat}} dE_V \int_0^{E^{stat}-E_V} dE_T \int_0^{E^{stat}-E_V-E_T} dE_R \rho_P(E_V) \rho_R(E_R) \rho_T(E_T) \delta(E^{stat}-E_V-E_T-E_R)} \quad (i)$$

where ρ_P , ρ_R , and ρ_T are the densities of states for the P (parent), R, and T ensembles of parent vibrational modes. The parent ensemble is made up of all vibrational

modes of the parent molecule. In the harmonic approximation, the densities of states can be computed easily using the Beyer-Swinehart algorithm. The expressions for $\langle E_V^{stat} \rangle$ and $\langle E_T^{stat} \rangle$ are similar to the one for the rotational energy that is given above.

Essentially, it is assumed that the energy above the barrier is going to be distributed statistically between the three ensembles, where the ensemble for vibrations can sample from the other two ensembles. The statistics, and hence the energy distribution, are governed by the vibrational frequencies of the parent as well as a judicious choice of modes for membership in each ensemble.

Dividing $\langle E_T^{stat} \rangle$ between the two fragments is easily accomplished by conserving linear momentum,

$$E_T^{stat}(A) = \frac{\langle E_T^{stat} \rangle}{\left(1 + \frac{m_A}{m_B}\right)} \quad (ii)$$

$$E_T^{stat}(B) = \frac{\langle E_T^{stat} \rangle}{\left(1 + \frac{m_B}{m_A}\right)} \quad (iii)$$

and $\langle E_R^{stat} \rangle$ is similarly partitioned by requiring conservation of angular momentum.

$$E_R^{stat}(A) = \frac{\langle E_R^{stat} \rangle}{\left(1 + \frac{I_A}{I_B}\right)} \quad (iv)$$

$$E_R^{stat}(B) = \frac{\langle E_R^{stat} \rangle}{\left(1 + \frac{I_B}{I_A}\right)}$$

The only remaining difficulty is to divide the vibrational energy from the statistical reservoir between the two fragments. It seems reasonable to view the impulse as an instantaneous event, so that the energy is frozen in the parent modes. The energy in the modes that develop into fragment vibrations should then be assigned to the appropriate fragment. Identifying these modes and obtaining their frequencies seems to be impossible for all but the simplest of molecules. By approximating the frequencies of these modes at the transition state by the frequencies of the fragment modes themselves, one obtains the following expression for the vibrational energy partitioned into fragment A from the statistical reservoir:

$$\langle E_V^{stat}(A) \rangle = \frac{\int_0^{E_V^{stat}} dE_A \int_0^{E_V^{stat}-E_A} dE_B \rho_A(E_A) \rho_B(E_B) \delta(E_V^{stat} - E_A - E_B) E_A}{\int_0^{E_V^{stat}} dE_A \int_0^{E_V^{stat}-E_A} dE_B \rho_A(E_A) \rho_B(E_B) \delta(E_V^{stat} - E_A - E_B)} \quad (vi)$$

where ρ_A and ρ_B are the vibrational densities of states of fragments A and B respectively. It should be noted that in partitioning the statistical reservoir reasonable results can be obtained using the equipartition theory on the separated fragments.

B. The Impulsive Reservoir

The basic premise of the standard impulsive model is that all of the available

energy is released as a repulsion localized in the reaction coordinate. For the present model, the available energy is replaced with the height of the exit barrier. In the rigid fragment limit the dissociation results in no vibrational excitation of the fragments.

$$E_V^{imp}(A) = E_V^{imp}(B) = 0 \quad (vii)$$

The impulsive reservoir is therefore partitioned only between fragment rotation and translation,

$$E^{imp}(tot) = E_T^{imp}(tot) + E_R^{imp}(A) + E_R^{imp}(B) \quad (viii)$$

$$E^{imp}(tot) = \frac{1}{2}\mu_{AB}g^2 + \frac{(J_A)^2}{2I_A} + \frac{(J_B)^2}{2I_B} \quad (ix)$$

where g is the relative velocity of A and B. Since the dissociation must conserve angular momentum, initially assumed to be zero, the translational energy is constrained as follows:

$$E_T^{imp}(tot) = \frac{E^{imp}(tot)}{1 + \frac{(b_A)^2\mu_{AB}}{I_A} + \frac{(b_B)^2\mu_{AB}}{I_B}} \quad (x)$$

where b_A and b_B are the classical exit impact parameters and μ_{AB} is the reduced mass of the fragments. Hence, the translational energy of the products predicted by the rigid fragment model is intimately dependent on the choice of the dissociative geometry.

Once the translational energy has been determined, the rotational energy of the fragments can be expressed in terms of $E_T^{imp}(tot)$,

$$E_R^{imp}(A) = E_T^{imp}(tot) \frac{(b_A)^2 \mu_{AB}}{I_A} \quad (xi)$$

$$E_R^{imp}(B) = E_T^{imp}(tot) \frac{(b_B)^2 \mu_{AB}}{I_B} \quad (xii)$$

The two reservoirs are then combined to give average translational energies for the two fragments as follows:

$$E_T(A) = E_T^{stat}(A) + E_T^{imp}(A) \quad (xiii)$$

$$E_T(B) = E_T^{stat}(B) + E_T^{imp}(B) \quad (xiv)$$

Similar equations are used for rotational and vibrational energies.

Although the rigid fragment treatment of the impulsive reservoir was highly successful in predicting the average translational energies in the photodissociation of acetone, the soft fragment impulsive model can be used when only a fraction of the exit barrier height is observed in translation. In the soft fragment impulsive model the two previously bonded atoms, α (on fragment A) and β (on fragment B), are considered to be loosely coupled to their respective fragments which behave as spectators during the dissociation. The atoms recoil with relative translational energy according to the conservation of linear momentum,

$$E_T^{imp}(\alpha) = \frac{m_\beta}{M} E^{imp}(tot) = E^{imp}(A) \quad (xv)$$

$$E_T^{imp}(\beta) = \frac{m_\alpha}{M} E^{imp}(tot) = E^{imp}(B) \quad (xvi)$$

where m_α , m_β , and M are the masses of atom α , the mass of atom β , and the total mass ($m_\alpha + m_\beta$) respectively. This kinetic energy also determines the total energy, $E^{imp}(A)$ and $E^{imp}(B)$, each atom transfers to its respective polyatomic fragment A and B . The translational energy of each fragment is obtained from the conservation of momentum,

$$E_T^{imp}(A) = \frac{m_\alpha}{m_A} E^{imp}(A) \quad (xvii)$$

$$E_T^{imp}(B) = \frac{m_\beta}{m_B} E^{imp}(B) \quad (xviii)$$

Rearranging the above equations the total translational energy released in the dissociation can be obtained,

$$E_T^{imp}(tot) = \frac{\mu_{\alpha-\beta}}{\mu_{A-B}} E^{imp}(tot) \quad (xix)$$

where $\mu_{\alpha-\beta}$ is the reduced mass of atoms α and β . The fact that in a two-body dissociation the total translational energy is determined only by a mass factor ($\mu_{\alpha-\beta}/\mu_{A-B}$) and the available energy is the most important result of the soft fragment impulsive model.

A general method for determining the partitioning of the internal energy involves first obtaining the rotational energy from the conservation of angular momentum. The

fragment vibrational energy is then determined from the conservation of energy. The angular momentum associated with each atom as it recoils about its respective fragment's center-of-mass is given by,

$$J_{\alpha} = b_{\alpha} \sqrt{2m_{\alpha} E_T^{imp}(\alpha)} \quad (xx)$$

$$J_{\beta} = b_{\beta} \sqrt{2m_{\beta} E_T^{imp}(\beta)} \quad (xxi)$$

The angular momenta of the atoms are conserved, evolving into fragment rotation.

The resulting rotational energy of each fragment is then,

$$E_R^{imp}(A) = \frac{(J_{\alpha})^2}{2I_A} \quad (xxii)$$

$$E_R^{imp}(B) = \frac{(J_{\beta})^2}{2I_B} \quad (xxiii)$$

The remaining energy in each fragment is vibrational,

$$E_V^{imp}(A) = E^{imp}(A) - E_T^{imp}(A) - E_R^{imp}(A) \quad (xxiv)$$

$$E_V^{imp}(B) = E^{imp}(B) - E_T^{imp}(B) - E_R^{imp}(B) \quad (xxv)$$

C. Test Case: Acetic Acid

The present model was also used to compare predicted energy partitioning with experimental results in the photodissociation of acetic acid at 218 nm and 200 nm.^{50,51} Both wavelengths involve $^1(n,\pi^*)$ excitation but differ by ~ 12 kcal/mole in the energy available for dissociation. The barrier height was assumed to be 13.0 kcal/mole and the dissociative geometry was non-planar. Vibrational frequencies were taken from Herman and Hofstadter⁵² with the mode assignments of Haurie and Novak.⁵³ The C-O(H) stretch and the COO bend were assumed to evolve into product translation while the OH torsion and rocks were partitioned into rotation. The OH and CH₃CO vibrational density of states were calculated using the method of Beyer-Swinehart. Table 3 shows the BIM results and includes predictions of the soft fragment impulsive model (SFIM). The favorable agreement of the model to the experimental results of Hunnicutt *et al.* suggest that the barrier impulsive model has general applicability for those cases that involve impulsive-type potential energy surfaces. We expect that this model will work for systems like the two shown above that satisfy several criteria: 1) IVR should occur prior to dissociation, 2) the molecules should be large enough to contain many modes that are not directly involved in the dissociation, and 3) the dynamics beyond the transition state should permit facile treatment of the impulsive reservoir. The photodissociation of carbonyl compounds, excited to their $^1(n,\pi^*)$ state, appears to be well suited for the above treatment. In general these molecules dissociate over a barrier that results from an avoided crossing between the $^3(n,\pi^*)$ and $^3(\sigma,\sigma^*)$ configurations in non-planar geometries. Since the dissociation ultimately involves the cleavage of only a single bond, the impulsive model can be used in a straightforward manner. In addition, the lack of measured anisotropy in the photodisso-

ciation of these compounds suggests that the excited state should exist for sufficient time to allow almost full randomization of the initial excitation energy.

D. Test Case: Azomethane

The experimental results presented in the previous chapter and the associated controversy concerning the overall dissociation mechanism of azomethane make it an interesting test case for the barrier impulsive model. Since information on the internal⁵⁴ and translational energy content of all the photofragments has now been catalogued, a reasonable comparison can be made between the experimental data and various simplified models of energy partitioning. Recent theoretical investigations suggest that following initial excitation IC could occur rapidly via a convenient funnel between the excited and ground state. If the dissociation proceeds on the ground state potential energy surface then the first C-N bond cleavage is barrierless and the available energy is 31.5 kcal/mole.⁵⁵ The disposal of the available energy can be accomplished using a prior treatment. The second step is exothermic by 23.4 kcal/mole and there is a ~2.0 kcal/mole barrier to CH₃N₂ dissociation.⁵⁶ The total energy associated with the exit barrier is, therefore, 25.4 kcal/mole and is treated by the rigid fragment impulsive model. The remaining available energy, mostly CH₃N₂ internal energy from the initial step is partitioned in accordance with prior calculation. Azomethane and CH₃N₂ frequencies and assignments were obtained from the *ab initio* results of Hu and Schaeffer.^{55,56} Table 4 outlines the BIM results and includes the predictions from purely impulsive and statistical (prior) models. The agreement between the experimental data and the BIM not only suggests that a ground state dissociation could lead to the observed fragment distributions but that the fast CH₃ most likely originates

from the second bond cleavage.

Table 1: Vibrational Frequencies (cm⁻¹) for Acetone

mode	frequency ^a	mode description
ω_1	3020	C-H stretch
ω_2	2926	
ω_3	1738	
ω_4	1438	
ω_5	1360	
ω_6	1067	
ω_7	779 ^T	symmetric C-C stretch
ω_8	483 ^R	skeletal C-C-C bend
ω_9	2973	
ω_{10}	1432	
ω_{11}	495 ^R	CH ₃ torsion
ω_{12}	105	
ω_{13}	2973	
ω_{14}	1438	
ω_{15}	1093 ^R	CH ₃ out-of-plane rock
ω_{16}	384	
ω_{17}	105	
ω_{18}	3020	
ω_{19}	2926	
ω_{20}	1426	
ω_{21}	1363	
ω_{22}	1218 ^T	asymmetric C-C stretch
ω_{23}	896 ^R	CH ₃ in-plane rock
ω_{24}	528	

a. R and T superscripts indicate whether the mode was considered part of the rotational or translational ensemble.

Table 2: Average Fragment Energies (kcal/mole) for Acetone Photodissociation at 193 nm

	Ref. 18	Impulsive Model ^a	This Work	BIM ^b
$E_T(\text{CH}_3)$	10.5 ± 1.9	10.5	10.5 ± 0.5	10.7
$E_{\text{int}}(\text{CH}_3)$	2.6 ± 1.2	2.6	---	17.2
$E_T(\text{CO})^c$	6.6 ± 1.2	6.7	2.3 ± 0.5	2.1
$E_{\text{int}}(\text{CO})$	9.1 ± 1.1	10.3	---	5.7
$E_T(\text{CH}_3)^c$	12.1 ± 1.9	14.3	4.3 ± 0.5	4.0
$E_{\text{int}}(\text{CH}_3)$	2.6 ± 1.2	3.6	---	9.4

a. The method is outlined in reference 18

b. The details of the calculation are presented in the appendix

c. Translational energies for these fragments are given in the secondary center-of-mass reference frame

**Table 3: Product Energy Partitioning for Acetic Acid
Photodissociation at 200 nm and 218 nm**

	$E_R(OH)$	$E_V(OH)$	$E_T(OH)$	$E_{int}(CH_3CO)$	$E_T(CH_3CO)$
Experiment ^a					
218 nm	1.21 ^b	<0.2	9.81	12.9	3.89
200 nm	1.36	<0.4	10.4	23.73 ^c	4.11
BIM					
218 nm	1.39	0.23	9.79	12.73	3.87
200 nm	2.05	0.80	10.15	22.99	4.01
SFIM					
218 nm	0.08	0.63	11.30	11.53	4.46
200 nm	0.12	0.90	16.14	16.47	6.38

a. Reference 50 and Reference 51.

b. All energies are expressed in kcal mol⁻¹.

c. Inferred from E_{avail} and all other measured quantities.

Table 4: Average Energies (kcal/mole) for Azomethane Photodissociation

	Experiment	BIM	Impulsive	Statistical
$E_T(\text{CH}_3)$	3.3 ± 0.8^a	1.9	12.5	1.5
$E_R(\text{CH}_3)$	3.9 ± 0.5^b	3.4	0.0	2.5
$E_V(\text{CH}_3)$	unmeasured	8.2	1.8	8.1
$E_T(\text{N}_2)$	9.0 ± 1.0^a	8.0	8.8	2.2
$E_R(\text{N}_2)$	5.0 ± 0.6^b	5.9	4.5	4.3
$E_V(\text{N}_2)$	1.0 ± 0.4^b	1.8	1.2	4.3
$E_T(\text{CH}_3)$	14.8 ± 1.0^a	14.4	13.4	3.6
$E_R(\text{CH}_3)$	unmeasured	1.4	0.0	6.5
$E_V(\text{CH}_3)$	$4.1 (\nu_2)^c$	9.9	5.2	19.5

a. Reference 21.

b. Reference 54.

c. Only the ν_2 mode experimentally observed

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Figure Captions

Figure 1: Energy level diagram for acetone dissociation adapted from reference 18.

Thermodynamic quantities are referred to in the text.

Figure 2: TOF spectra at 248 nm of m/e 15 (CH_3^+) at laboratory angles 25° and 35° . Circles represent data points. Contributions are shown for CH_3 (solid line) and CH_3CO (dashed line) from reaction 1 and CH_3 originating from reaction 2 (dotted line).

Figure 3 Center-of-mass translational energy distribution, $P(E_T)$ for reaction 1 used to fit the data in Figures 1 and 3. The solid line is the derived from fitting the methyl radical from reaction 1 and the dotted line is derived from fitting the m/e 43 spectra.

Figure 4 TOF spectrum at 248 nm of m/e 43 (CH_3CO^+) at a laboratory angle of 25° . Circles represent data points and the solid line is the forward convolution fit using the $P(E_T)$ in Figure 3 truncated as shown by the dotted line. The dashed line shows the fit without the truncation in the primary $P(E_T)$.

Figure 5 Center-of-mass velocity distributions for CH_3 (left) and CH_3CO (right) from reaction 1. The shaded region indicates CH_3CO radicals that are unstable with respect to secondary dissociation.

Figure 6 Center-of-mass angular distribution, $P(\Omega)$ used to fit the secondary fragments from reaction 2. 0° corresponds to the direction of the acetyl radical velocity

vector.

Figure 7 Secondary center-of-mass translational energy distribution, $P(E_T)$ for reaction 2 used to fit the data in Figures 1 and 8.

Figure 8 TOF spectrum of m/e 28 (CO^+) at 248 nm. The open circles are the data. The lines are the contributions from primary acetyl fragments (dashed line) and CO fragments from secondary dissociation.

Figure 9 TOF spectra at 193 nm of m/e 15 (CH_3^+) at laboratory angles 20° , 35° , and 50° . Circles represent the data and the line is the forward convolution fit using the $P(E_T)$ in Figure 10.

Figure 10 Center-of-mass translational energy distribution derived from fitting the m/e 15 TOF spectra at 193 nm.

Figure 11 TOF spectra at 193 nm of m/e 28 (CO^+) at laboratory angles 35° and 50° . Circles represent data points and the line is the best forward convolution fit to the data.

Figure 12 Center-of-mass translational energy distribution derived from fitting the m/e 28 TOF spectra (solid line). The dashed line shows a Boltzmann distribution at 3000 K suggested by the results of reference 18.

Figure 13 The solid line is the experimental primary $P(E_T)$ from Figure 3 and the dashed is the $P(E_T)$ predicted by an information theoretic treatment. The inset shows

the surprisal plot comparing the two distributions.

Figure 14 TOF spectra at 193 nm of (a) m/e 15 (CH_3^+) and (b) m/e 28 (CO^+) at 35° . The open circles are the data. The contributions in (a) are CH_3 from reaction 1 (dotted line) and CH_3 from reaction 2 (dashed line). In (b) the solid line is CO originating from reaction 2. The $P(E_T)$ and $P(\Omega)$ used in the forward convolution fits are shown in Figure 15.

Figure 15 Center-of-mass primary and secondary translational energy distributions derived from fitting the m/e 15 and m/e 28 TOF spectra shown in Figure 14. The inset shows the secondary center-of-mass angular distribution.

Figure 16 Schematic diagram illustrating the relations between various energetic quantities in the barrier impulsive model.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14

Figure 15

Figure 16

Chapter 4

Ultraviolet Photodissociation of Acetyl Halides: Investigation of CH_3CO Energetics and Dissociation Dynamics

Abstract

The ultraviolet photodissociation of acetyl chloride and acetyl bromide has been investigated by the technique of photofragment translational spectroscopy. In the dissociation of acetyl chloride a comparison of the translational energy distributions required to fit the chlorine atom and the acetyl radical time-of-flight spectra indicates that a significant fraction (~35%) of the CH_3CO fragments undergo secondary decomposition to CH_3 and CO. From an analysis of the center-of-mass translational energy distributions a value of 17.0 ± 1.0 kcal/mole for the barrier height to acetyl radical dissociation has been determined. The secondary translational energy distribution of those acetyl radicals that dissociate is consistent with the result obtained in the photodissociation of acetone at 248 nm and 193 nm, *i.e.* that $\langle E_T \rangle$ closely resembles the exit barrier height. The secondary decomposition of acetyl radicals from the photodissociation of acetyl bromide at 248 nm and acetyl chloride at 193 nm provides further evidence that the partitioning of the available energy is non-statistical. In both cases the spontaneous secondary decomposition of CH_3CO radical occurs following rotational averaging and results in a translational energy release of 6-7 kcal/mole. The dissociation dynamics of the acetyl radical are reexamined in light of recent experimental results and *ab initio* calculations.

I. Introduction

The acetyl radical, CH_3CO , is a prevalent chemical intermediate. It is known to be involved in combustion processes, specifically hydrocarbon oxidation reactions¹, and is a common product in the photodissociation of ketones and other carbonyl compounds². Despite its importance there is little consensus regarding even fundamental thermodynamic quantities such as the C-C bond dissociation energy or the barrier height to dissociation.

The dissociation of CH_3CO into methyl radical and carbon monoxide,

has been the subject of an exhaustive number of experimental investigations. The reported barrier to acetyl radical dissociation obtained from kinetics studies has ranged from 11.1 to 21.7 kcal/mole.³ For small cited values of the barrier height, anomalously low pre-exponential factors were required to explain the observed rates. These A-factors were rationalized by proposing that acetyl radical decomposed via a non-adiabatic process. Watkins and Word later determined the barrier to be 17.2 ± 0.5 kcal/mole from extensive kinetics measurements on the addition of methyl radical to carbon monoxide over a wide temperature range.⁴ In addition, a pre-exponential factor of $13.2 \pm 0.2 \text{ s}^{-1}$ which was more consistent with this type of reaction was concluded. Using a more direct experimental approach Gandini and Hackett measured a barrier height of 20.3 kcal/mole from observing the $\text{CO} (A^1\Pi \rightarrow X^1\Sigma^+)$ resonance fluorescence arising from acetone dissociation between 330 and 250 nm.⁵ *Ab initio* calculations on the CH_3CO reaction

coordinate by Fukui and co-workers suggested a much lower barrier height, 14.9 kcal/mole.⁶ However, the study also severely underestimated the C-C bond dissociation energy. More recent *ab initio* calculations at the MP2/cc-pVTZ level of theory predict a barrier height of 19.1 kcal/mole and expect a reduction in this value when a multiconfiguration wavefunction is used to correct for correlational effects.⁷ As discussed in the previous chapter of this dissertation, a recent experiment on the photodissociation of acetone at 248 nm has yielded a barrier height to acetyl radical dissociation of 17.8 ± 3.0 kcal/mole.⁸

The focus of the present series of experiments is two-fold. The first is the accurate determination of the barrier height to CH_3CO decomposition by the method of photofragment translational spectroscopy (PTS). PTS is a proven technique, capable of extracting accurate thermodynamic quantities such as bond dissociation energies and barrier heights.⁹ The spontaneous decomposition of acetyl radicals in this experiment can be monitored in two ways: 1) since a large portion of the nascent CH_3CO fragments dissociate prior to detection, these *missing* radicals provide an indication of the energy at which the radicals become thermodynamically unstable, 2) observation of the secondary dissociation products, CH_3 or CO , allows independent confirmation and quantification of the secondary decomposition of CH_3CO radicals. Although the PTS technique allowed an initial barrier height determination from the photodissociation of acetone at 248 nm, the measurement had several shortcomings. The photodissociation of acetyl chloride presents and opportunity to correct these deficiencies and obtain a more reliable determination.

The second goal of this chapter is to elucidate the dissociation dynamics of the CH_3CO radical. By observing the CH_3 and CO photofragments that originate from spontaneous dissociation of the CH_3CO product, it is possible to study the dissociation

dynamics of this *transient species* under *collisionless* conditions. In a primary dissociation, much can be gleaned concerning the relevant potential energy surfaces by observing how the energy partitioning varies as a function of available energy. This is most often achieved by changing the photon wavelength as demonstrated in the dissociation of acetone. In the photodissociation of the acetyl halides the photon energy can be fixed but the difference in the C-X (X=Cl, Br) bond energies results in the preparation of acetyl radicals with varying amounts of internal energy. Insight into the dissociation dynamics of the acetyl radical can be obtained by observing the translational energy and angular distributions of the CH₃ and CO fragments as a function of the internal energy CH₃CO.¹⁰

II. Experimental

The fixed-source/rotatable-detector apparatus used in this experiment is described in detail elsewhere.¹¹ In brief, 50 torr of 12% acetyl chloride seeded in helium was expanded through a continuous 0.37 mm nozzle into a source region maintained at 1×10^{-4} torr. The nozzle was heated to 80°C in order to reduce the formation of dimers in the supersonic expansion. The average beam velocity was 9.8×10^4 cm/s with a full-width-at-half-maximum (FWHM) of 15% as measured *in situ* by a spinning chopper wheel. For the acetyl bromide experiments ~5% of acetyl bromide in He was expanded at a total stagnation pressure of 45 torr. The continuous nozzle was heated to 64°C, producing a beam with a peak velocity of 12.2×10^4 cm/s. Acetyl bromide and acetyl chloride were obtained from Aldrich (99%) and purified prior to use by several freeze-pump-thaw cycles.

Following expansion the molecular beam was collimated with two stainless steel

skimmers (0.6 mm and 1.5 mm diameters) and subsequently intersected at a right angle with the unpolarized output of a Lambda Physik EMG 101 excimer laser operating at the KrF transition (248 nm). Laser power was maintained between 50-70 mJ/cm² and focused with a spherical MgF lens to a 2.0x5.0 mm spot in the interaction region. All observed signals exhibited a linear dependence on the laser power confirming that the observed photodissociation processes involved a single photon. Neutral photofragments recoiled 20.8 cm where they were ionized by electron impact with ~200 eV electrons, mass selected with a quadrupole mass filter, and detected with a Daly ion counter. Product time-of-flight (TOF) spectra were collected using a computer interfaced multichannel scaler triggered from the laser with a bin width of 2 μ s. Typically 50 000-100 000 laser shots were recorded for each product TOF spectrum.

Total center-of-mass primary translational energy distributions of the photofragments were determined from the TOF spectra using the forward convolution technique.¹² The secondary center-of-mass energy and angular distributions were derived assuming the decoupled representation discussed in chapters 1-3.¹³

III. Results and Discussion

A. Acetyl Chloride at 248 nm

Primary Dissociation: The photodissociation of acetyl chloride at 248 nm has been the subject of numerous recent studies.^{7,14-17} Although the initial transition is a localized ¹(n, π^*) excitation on the CO moiety, the dissociation involves exclusive α -cleavage of the stronger C-Cl over the C-C bond.

This preference can be understood by a simple consideration of the adiabatic potential energy surfaces for both processes.¹⁸ In this picture the C-Cl bond cleavage occurs adiabatically on the $^1A''$ surface which has $^1\pi^*(C=O)$ character in the Franck-Condon region, and as a result of an avoided crossing the dissociation proceeds over a barrier into an area which resembles the repulsive $np(Cl) \sigma^*(C-Cl)$ surface. In contrast, C-C bond fission does not adiabatically correlate to ground state products. It can occur via either a combination of the $^3\sigma\sigma^*(C-C)$ and $^3\pi\pi^*(C=O)$ surfaces or on the ground state surface. Cleavage of the C-C bond must, therefore, be preceded by intersystem crossing or internal conversion. Nimlos *et al.* have estimated that the first electronic excited state of the acetyl radical, $^2A''$, lies ~30 kcal/mole above the ground state.¹⁹ The following discussion is, therefore, limited to consideration of the acetyl ground state potential energy surface.

Product TOF spectra were collected at m/e 35 (Cl^+), m/e 42 (CH_2CO^+), and m/e 15 (CH_3^+) at a variety of detector angles with respect to the molecular beam axis. The TOF spectra for m/e 35 (Cl^+) at detector angles of 15° and 30° are shown in Figure 1. The spectra show only a single feature corresponding to the Cl atomic fragment originating from primary C-Cl bond cleavage. There was no evidence of a COCl fragment which, if it were a primary dissociation product resulting from C-C bond cleavage, would also be observed at m/e 35 following dissociative ionization. No other signal consistent with primary C-C bond scission was observed, confirming the conclusion of recent studies that C-Cl bond cleavage is the exclusive primary dissociation process.^{15,16} Deshmukh *et al.*

using an ion imaging technique following 2+1 REMPI of the Cl (2P_J) atoms observed a slow component constituting $\sim 10\%$ of the total Cl atom yield.⁷ These slow Cl atoms exhibited an isotropic angular distribution in contrast to the $\beta = 1.0 \pm 0.2$ of the fast Cl channel. The lack of photofragment anisotropy and the diminutive translational energy release of the slow C-Cl bond cleavage channel was interpreted as the result of unsuccessful dissociative trajectories that consequently sample a wider region of the potential energy surface. No such component, however, was observed in the present study even at small laboratory angles where the sensitivity to low translational energy fragments is significantly enhanced. The origin of the slow component in the experiments of Deshmukh *et al.* may, therefore, be the result of artifacts in the detection method in which the pulsed molecular beam strikes the center of the MCP imaging detector.⁷ Figure 2 shows the TOF spectra at 15° and 30° for the momentum matched acetyl fragment which was monitored at m/e 42 (CH_2CO^+) due to the enhanced signal-to-noise as compared with its parent mass.²⁰

The translational energy distribution, $P(E_T)$, for the primary dissociation was derived from the forward convolution fit to the Cl atom (m/e 35) TOF spectra and is shown as the solid line in Figure 3. An anisotropy parameter of $\beta = 1.0$, consistent with the measurement of Person *et al.* (ref. 14), was used in fitting the TOF spectra of the primary dissociation products. The distribution is peaked at 14.5 kcal/mole with a FWHM of ~ 15 kcal/mole which is quantitatively equivalent to the $P(E_T)$ reported previously.^{15,16} The soft fragment impulsive model has been found to adequately describe the energy partitioning in photodissociation involving *direct* C-X ($X = \text{Cl}, \text{Br}, \text{I}$) bond cleavage. The total center-of-mass translational energy release presented by Busch and Wilson²¹ is given by,

$$E_T(tot) = \left(\frac{\mu_{\alpha-\beta}}{\mu_{A-B}} \right) E_{avail} \quad (3)$$

where $\mu_{\alpha-\beta}$ and μ_{A-B} are the reduced masses of the previously bonded atoms, the carbon and halogen atoms in this case, and their respective fragments. The model predicts that 46% of the available energy should appear as translation, or 14.7 kcal/mole which is in close agreement with the measured $\langle E_T \rangle$. More importantly, $E_T(tot)$ scales correctly with the available energy as demonstrated by the $\langle E_T \rangle$ observed by Deshmukh *et al.* using 237 nm confirming that the impulsive model is a reasonable description of the primary dissociation dynamics.

In order to fit the momentum matched CH_3CO (m/e 42) TOF spectra, however, it was necessary to sharply truncate the $P(E_T)$ at 15.0 kcal/mol as shown by the dotted line in Figure 3, leaving only the high energy portion of the translational energy distribution. The fits to the acetyl TOF spectrum at a laboratory angle of 30° with truncation of the $P(E_T)$ occurring at 13.2 kcal/mol and 16.8 kcal/mol are shown in Figure 4 demonstrating the sensitivity of the fit to the position of truncation. Truncation of the $P(E_T)$ is the result of primary acetyl photofragments which undergo secondary dissociation. This effect has also been observed and discussed in the previous chapter with respect to acetone photodissociation at 248 nm and has been used to determine the C-Cl bond dissociation energy in $\text{C}_2\text{H}_4\text{Cl}$ radicals produced by the photolysis of 1-2-chloroiodoethane at 248 nm and 266 nm by Minton *et al.*²²

Since one of the photoproducts is an atomic species, all the energy that is not

released into translation must reside as internal energy in the CH_3CO fragment. This is actually not entirely true since the chlorine atom can be formed in its ($^2\text{P}_{1/2}$) spin-orbit excited state. Fortunately, the onset point of truncation and hence the determination of the barrier height should be unaffected. The agreement of the determined barrier height reported here (*vide infra*) to the one measured in the dissociation of acetone suggests that a significant fraction of acetyl chloride dissociation at 248 nm leads to Cl in its ground spin-orbit state, ($^2\text{P}_{3/2}$). In fact, Deshmukh and Hess have measured $\text{Cl}(^2\text{P}_{3/2})$ to $\text{Cl}(^2\text{P}_{1/2})$ ratio of 3:2 at 237 nm.¹⁷ Most likely the fit to the slow side of the CH_3CO TOF spectra could be slightly improved by including a small contribution from the coincident formation of $\text{Cl}(^2\text{P}_{1/2})$.

Acetyl fragments that possess internal energies exceeding their barrier to dissociation will not persist for sufficient time to reach the detector. These fated radicals with high internal energies, and therefore low translational energies, do not contribute to the parent TOF spectra. In the present case this is manifest as a deviation of the CH_3CO $\text{P}(E_T)$ from the Cl, or *true* primary $\text{P}(E_T)$. The truncation in the CH_3CO $\text{P}(E_T)$ represents the *maximum* internal energy at which the acetyl radical is stable with respect to decomposition. Following the method outlined in the preceding chapter, if $E_T(\text{min})$ denotes the value corresponding to the onset of truncation then the barrier to acetyl radical dissociation, $E_{\text{barr}}(\text{CH}_3\text{CO})$, is given by,

$$E_{\text{barr}}(\text{CH}_3\text{CO}) = E_{\text{hv}} - D_0(\text{CH}_3\text{CO}-\text{Cl}) - E_T(\text{min}) = E_{\text{avail}} - E_T(\text{min}) \quad (4)$$

where E_{hv} is the photon energy and $D_0(\text{CH}_3\text{CO}-\text{Cl})$ is the C-Cl bond energy in

acetyl chloride. From the known heats of formation of CH_3CO and Cl atoms, a C-Cl bond dissociation energy of 83.0 kcal/mole can be obtained.²³ Given that the $E_{hv}(248\text{nm})$ is 115.0 kcal/mole, the available energy, E_{avail} , in the acetyl chloride center-of-mass is 32.0 kcal/mole. The best fit to the CH_3CO TOF spectra was obtained with $E_T(\text{min})=15.0$ kcal/mole corresponding to 17.0 ± 1.0 kcal/mole for the barrier height to acetyl decomposition. Comparison of the region of the truncation to the entire normalized $P(E_T)$ corresponds to 35% of the nascent radicals undergoing spontaneous secondary dissociation. Despite this estimate the signal-to-noise ratio in the study by Person *et al.* was insufficient to observe either truncation in the CH_3CO TOF spectra or CH_3 or CO fragments originating from secondary dissociation.^{15,16} At 237 nm the quantum yield of CH_3 detected by 2+1 REMPI was estimated at ~28%. This value, however, should be considered a lower limit since the intensity of only the v_2 lines were used in the calculations.

The location of the truncation near the peak in the primary translational energy distribution is significant. Since this region of the $P(E_T)$ constitutes a relatively large fraction of the distribution, the fit to the CH_3CO data is extremely sensitive to the point of truncation. Changing the value of $E_T(\text{min})$ by ± 1.8 kcal/mole significantly reduced the quality of the fit to the experimental data as shown in Figure 4. This measurement is superior to the analogous one derived from acetone dissociation at 248 nm for two important reasons. First, in acetone photodissociation the primary methyl radical, which reflects the *true* primary $P(E_T)$, is overlapped in the m/e 15 TOF spectrum by contributions from both secondary methyl radicals and CH_3CO daughter ions. This hinders an accurate determination of the primary $P(E_T)$ for the dissociation. Second, the internal energy in the acetone dissociation can be distributed between *both* the CH_3 and CH_3CO fragments.

Therefore, even at internal energies exceeding the CH_3CO barrier to dissociation some of the energy can be accommodated by ro-vibrations of the CH_3 counter fragment. Consequently the truncation in the $P(E_T)$ is less abrupt and thus the assignment of $E_T(\text{min})$ is considerably more difficult.

There are several implicit assumptions when using equation 4 to estimate the barrier height. Some of these have already been discussed in chapter 3. Although the average vibrational energy of the parent molecules at 80°C is ~ 1.4 kcal/mole, this should be significantly reduced following the supersonic expansion and has been neglected in calculating the available energy. For example, even at $T_{\text{vib}}=200$ K the parent should only contain ~ 0.3 kcal/mole of vibrational excitation. In the event that the parent vibrations are not fully relaxed in the expansion then there will be more available energy resulting in a corresponding underestimation of the barrier height. It has also been assumed that *unstable* acetyl radicals, those that possess internal energy in excess of their barrier to dissociation, do not contribute to the CH_3CO TOF spectra. This is reasonable since Rice-Ramsperger-Kassel-Marcus (RRKM) calculations using the CH_3CO frequencies shown in Table 1 indicate that acetyl radicals with internal energy exceeding their barrier by 0.1 kcal/mole dissociate in $\sim 5 \times 10^{-10}$ seconds, which is much shorter than the neutral flight time to the detector ($\sim 10^{-4}$ seconds). The effect of rotational metastability of the nascent CH_3CO radicals has also not been considered. This was observed to be pronounced in the case of $\text{CH}_2\text{CH}_2\text{OH}$ originating from the photodissociation of 2-bromoethanol due to the large exit impact parameter and reduced mass.²⁴ However, based on the measured anisotropy of Butler and co-workers^{15,16} and the acetyl chloride equilibrium geometry²⁵, the exit impact parameter should be very small. A rigid fragment impulsive model (RIFM)

calculation indicates that < 0.2 kcal/mole on average should appear in CH_3CO rotational excitation and the majority of the rotation can effectively couple to the reaction coordinate. Of course, implementation of an impulsive model description neglects any significant out-of-plane forces or other exit channel torques in determining the magnitude of CH_3CO rotation.

Further evidence for the secondary dissociation of acetyl fragments is seen in the TOF spectrum at m/e 15 (CH_3^+) at a laboratory angle of 20° as shown in Figure 5. The TOF spectrum in Figure 5 has been fit with two components. The narrow component, indicated by the dashed line, arises from primary acetyl fragments from the initial C-Cl bond cleavage that dissociatively ionize to form the daughter ion CH_3^+ . The broad bimodal component shown by the dotted line corresponds to methyl radicals from secondary dissociation of the primary acetyl radicals. Comparison of the 248 nm photodissociation acetyl chloride with acetone photodissociation at 248 nm, where the acetyl cracking pattern can be absolutely determined, suggests that the relative contributions of the acetyl radical to methyl radical in the m/e 15 TOF spectra is consistent with $\sim 35\%$ secondary dissociation.²⁶

Secondary Dissociation: In order to fit the bimodal component in the m/e 15 TOF spectrum shown in Figure 5 the primary translational energy distribution of those CH_3CO fragments that undergo secondary decomposition must be determined. This distribution is obtained by subtracting the $P(E_T)$ derived from fitting the CH_3CO TOF spectra from the $P(E_T)$ derived from fitting the $\text{Cl}(^2\text{P}_j)$ TOF spectra. Using this, corrected, primary $P(E_T)$ the secondary total center-of-mass $P(E_T)$ and angular distribution, $P(\Omega)$, can be extracted. As discussed previously, the forward convolution fitting procedure

involving secondary dissociation assumes that all energy and angular distributions can be decoupled within the constraint that the available energy be conserved. The validity of this approximation and associated caveats are addressed in chapter 1. A forward-backward symmetric angular distribution, synonymous with rotational averaging of the intermediate prior to dissociation, was required to fit the bimodality in the TOF spectrum. The fit to the data was not overly sensitive to the exact form of the angular distribution as long as the forward-backward symmetry was maintained. In light of the previous experimental evidence a form for the secondary angular distribution given by,

$$P(\Omega) = \frac{\sin \Omega^\circ}{\sin \Omega}, \quad \text{for } \Omega^\circ \leq \Omega \leq \Omega^\circ - \pi \quad (5)$$

$$P(\Omega) = 1, \quad \text{for } \Omega \leq \Omega^\circ \quad \text{and} \quad \Omega \geq \pi - \Omega^\circ \quad (6)$$

and consistent with the decomposition of a long-lived prolate top, was adopted (see Chapter 1). A secure fit to the data could be obtained with an almost gaussian secondary $P(E_T)$ peaked at 5.5 kcal/mole and a FWHM of ~5 kcal/mole. The position of the peak in the translational energy distribution is accurate to ± 1.0 kcal/mole although there is some uncertainty regarding the actual width. The secondary $P(E_T)$ derived is quantitatively identical to the $P(E_T)$ observed in the 248 nm photodissociation of acetone. Figure 6 shows the resultant derived secondary translational energy distribution and $P(\Omega)$ (shown in the inset).

The bimodality in the m/e 15 TOF spectrum, indicating forward-backward symmetry in the secondary angular distribution, is in sharp contrast to the results of

Deshmukh *et al.*¹⁷ In the ion imaging experiments, however, there are several clearly erroneous observations. Since the primary process is anisotropic ($\beta=1.0$), unless the secondary dissociation results in a translational energy release substantially larger than the translation arising from the initial dissociation step, which is certainly not the case in the CH_3COCl system, the CH_3 and CO fragment angular distributions should reflect the primary step anisotropy. Remarkably, the images appear isotropic and are rationalized by invoking rotational averaging of the CH_3CO intermediate as the cause for the loss of anisotropy. Of course, the form of the secondary angular distribution is irrelevant to such a discussion. More importantly, from the CH_3 and CO ion images and center-of-mass energy distributions linear momentum is not conserved. *Both* fragments exhibit preferential "backwards" scattering as indicated by the absence of CH_3 or CO observed with a comparable velocity to the Cl fragment which, due to the similarity in mass, should reflect the velocity of the CH_3CO fragments. For this reason, we restrict ourselves to the CH_3 and CO internal state distributions measured by Deshmukh *et al.* but will refrain from further discussion concerning their translational energy or angular distributions.

B. Acetyl Bromide at 248 nm

Although the photochemistry of acetyl chloride and acetyl iodide is well documented, there is a lack of information regarding the intermediate acetyl halide, CH_3COBr . To our knowledge, this study represents the first measurements on the photodissociation dynamics of this compound at any wavelength. More importantly, the primary C-Br bond cleavage in acetyl bromide represents a means of preparing nascent CH_3CO radicals with 40% more internal energy than in the 248 nm dissociation of

CH_3COCl . Of interest is the qualitative effect of this additional internal energy on the dissociation dynamics of CH_3CO .

Product TOF data were collected for m/e 15 (CH_3^+) and m/e 79 (Br^+) at detector angles ranging from 15° to 50° from the molecular beam. No signal was observed at m/e 43 (CH_3CO^+) or m/e 42 (CH_2CO^+), suggesting that the vast majority of the nascent acetyl radicals undergo secondary dissociation. There was also no signal observed at masses corresponding to products from initial C-C bond cleavage. Time-of-flight data for m/e 79 at laboratory angles of 15° and 30° are shown in Figure 7. The single peak corresponds to bromine atoms arising from primary C-Br bond cleavage,

The forward convolution fit to the data, indicated by the solid line, was achieved using the $P(E_T)$ shown in Figure 8. The distribution peaks at 21 kcal/mole with a FWHM of 12 kcal/mole. The C-Br bond dissociation in acetyl bromide is not well established but from the known heats of formation or group additivity has been estimated as 74 ± 5 kcal/mole.²³ For photodissociation at 248 nm this corresponds to an available energy of 41 kcal/mole. However, based on the 17.0 ± 1.0 kcal/mole barrier height for CH_3CO dissociation (*vide supra*) and the measured translational energy release, at least ~40% of the nascent acetyl radicals should be thermodynamically stable. Since no acetyl radicals are detected, the C-Br bond dissociation energy must be significantly lower than 74 ± 5 kcal/mole. A bond dissociation energy of ~65 kcal/mole would result in only a vanishingly small amount of detectable CH_3CO . The soft fragment impulsive model predicts that 34%

of the available energy should appear as translation. Given the measured $\langle E_T \rangle$, this would correspond to 61 kcal/mole of available energy or an unreasonably small bond dissociation energy of 54 kcal/mole. Numerous PTS experiments have observed that in direct C-Br bond cleavage ~42% is found in product translation.^{24,27} A $D_0(\text{CH}_3\text{CO}-\text{Br})$ of 65 kcal/mole is consistent with this result and is, therefore, adopted as the true value for the subsequent discussion. No evidence was seen in the m/e 79 TOF spectra for Br atoms in different spin-orbit states. Since the spin-orbit splitting in bromine is 10.5 kcal/mole if the identical translational energy distribution applied to both ($^2\text{P}_J$) states one would expect to detect significantly more acetyl radicals. This result suggests that the ground ($^2\text{P}_{3/2}$) state of bromine is preferentially formed in the dissociation.

Figure 9 shows the m/e 15 (CH_3^+)TOF spectrum at a laboratory angle of 15° . The spectrum is dominated by a bimodal feature assigned to secondary methyl radicals from the dissociation of the primary CH_3CO fragments. Although a small contribution at 70 μsec , indicated by the dashed line, representing those acetyl radicals that are thermodynamically stable is shown, within the signal-to-noise the assignment of such a feature is extremely speculative. However, it does illustrate the forward-backward symmetry of the secondary dissociation and is left in solely for that purpose. The m/e 15 TOF spectrum was fit using the same procedure outlined previously and the best fit to the data was obtained using an almost identical $P(\Omega)$ to the one derived in CH_3COCl dissociation. The total secondary center-of-mass $P(E_T)$ was also peaked at 5.5 kcal/mole but more asymmetric and possess a higher energy tail resulting in an $\langle E_T \rangle = 6.3$ kcal/mole. The best fit $P(E_T)$ and $P(\Omega)$ are shown in Figure 10.

C. Acetyl Chloride at 193 nm

In order to provide additional qualitative information regarding the spontaneous decomposition of the acetyl radical, acetyl chloride was also photodissociated at 193 nm. This wavelength corresponds to the S_2 state of CH_3COCl which was thought to contain contributions from both $n \rightarrow \sigma^*$ and $n \rightarrow 3s$ transitions. Recent *ab initio* calculations, however, indicate that the transition most likely involves a $n \rightarrow 3s$ excitation.

Product TOF spectra were collected at m/e 35 and m/e 15 at laboratory angles from 15° to 40° . The m/e 35 (Cl^+) TOF spectrum at 40° is shown in Figure 11. Only fragments corresponding to initial C-Cl bond fission and the subsequent dissociation of CH_3CO were observed in agreement with the near unit quantum yields of CH_3 and CO measured by Maricq and Szenté.²⁸ The single feature can be fit with the $P(E_T)$ shown in the inset of Figure 11. Photofragment center-of-mass angular distribution is isotropic and is consistent with an indirect dissociation. The distribution peaks at ~ 25 kcal/mole and has a FWHM of ~ 15 kcal/mole. From the derived $P(E_T)$ the nascent CH_3CO fragments should contain 40 kcal/mole of internal energy on average. The absence of m/e 43 or m/e 42 TOF signal, implying the *complete* spontaneous dissociation of the acetyl radicals, is consistent with this degree of internal excitation. Figure 12 shows the m/e 15 TOF spectrum at a laboratory angle of 30° . Although the forward convolution fit to TOF spectrum is not as sensitive to the secondary $P(E_T)$ and $P(\Omega)$ as the fits in the previous two sections, a best fit was achieved with a similar forward-backward symmetric secondary angular distribution and an average translational energy release of 6.5 kcal/mole.

D. CH_3CO Dissociation Dynamics

In the preceding sections the energy and angular distributions arising from the

dissociation of CH_3CO were determined. Each primary C-X bond cleavage discussed above resulted in acetyl fragments containing an average of 20, 30 and 40 kcal/mole of internal energy.²⁹ In all cases the secondary distributions were observed to be invariant to the internal excitation of the acetyl radical. The following section discusses these results in light of recent measurements of the CH_3 and CO internal state distributions and *ab initio* calculations.

From the measured barrier to dissociation of 17.0 ± 1.0 kcal/mole and the well known 11.5 kcal/mole endothermicity of the C-C bond cleavage in CH_3CO (Ref. 30) there should be a 5.5 ± 1.0 kcal/mole barrier to the recombination of CH_3 and CO. This exit barrier is consistent with the kinetically derived value of 6.0 kcal/mole obtained by Watkins and Word.⁴

A recent *ab initio* calculation of the reaction path by Xantheas and co-workers has provided valuable insight into the fundamental topology of the $^2\text{A}'$ ground state potential energy surface.¹⁷ The slope of the exit channel may be gradual enough to allow adiabatic transformation to the vibrational ground state of the products. For example, the CO bond length change of only 0.01 Å from the transition state to the free carbon monoxide. In addition, the methyl moiety is nearly planar, possessing an H-C-H angle of 117.4° at the transition state. Dissociations of CH_3CO near threshold should, therefore, result in little vibrational excitation of the products. Of course, since the energy associated with one quantum of CO vibration is 6.12 kcal/mole, there is insufficient available energy at threshold for CO vibrational excitation.

The internal state distributions of the CH_3 and CO fragments arising from acetyl chloride photodissociation at 237 nm have been measured recently by Deshmukh *et al.*^{7,17}

The methyl radicals were probed using two different 2+1 REMPI schemes, through the $4p_z$ and $3p_z$ Rydberg states. Only a small fraction of the methyl radicals were found to be vibrationally excited, with at most a single quantum in the ν_2 umbrella mode. The rotational energy distribution did not extend beyond $N''=5$. From these measurements the average CH_3 internal energy was considered to be less than 0.5 kcal/mole. It is important to note that the underestimation of Φ_{CH_3} suggests that not all the populated vibrational states of the nascent methyl radicals were detected. The CO photoproducts were also probed using 2+1 REMPI through the $\text{B}^1\Sigma$ state and found to contain significant rotational excitation, up to $J''=30$. Unfortunately, the actual rotational distribution was not reported and consequently prohibits a quantitative measure of the CO rotational energy. No CO vibrational excitation was observed in the 2+1 REMPI spectrum.

In this study, the average translational energy of the CH_3 and CO fragments arising from acetyl chloride photodissociation at 248 nm has been determined to be 5-6 kcal/mole in the CH_3CO center-of-mass. Although the wavelengths used in the two experiments differ, 248 nm vs. 237 nm, the slight increase in the primary translational energy release at 237 nm results in only a modest 3 kcal/mole difference in the internal energy of the nascent acetyl radicals. Given the energy available for the asymptotically separated fragments and the measured product translational energy, there is ~3-5 kcal/mole to be partitioned among the remaining degrees of freedom. Since there is negligible vibrational excitation, 0.5 kcal/mole, and the methyl rotational content is insignificant the excess energy must be accommodated by CO rotation.

In order to more fully understand the origin of this non-statistical partitioning a hybrid model was used to predict the energy disposal in acetyl radical decomposition. The

results of the *Barrier Impulsive Model*, BIM, for acetyl chloride dissociation at 248 nm are shown in Table 2. A detailed description of the model is presented in the previous chapter and will only be highlighted. The energy available to the asymptotic CH_3 and CO fragments in all cases was derived from the average internal energy of those acetyl radicals that spontaneously dissociated minus the C-C bond dissociation energy. The energy associated with the exit barrier, assumed to be 5.5 kcal/mole, is treated in accordance with the rigid fragment impulsive model. The CH_3CO transition state geometry was used to assign the classical exit impact parameters. The remaining available energy is partitioned using a statistical procedure. This relies on the assumption that the excited CH_3CO persists for sufficient time for IVR to occur and is consistent with the experimental observation of rotational averaging. The results of both energy *reservoirs* are then combined to obtain the average rotational, translational, and vibrational energy of each fragment. Despite the naive simplicity of the model it serves to illustrate some of the important features of the dissociation dynamics. The model correctly predicts that following acetyl chloride dissociation at 248 nm, the majority of the CH_3CO available energy should reside in translation, ~ 5.2 kcal/mole, consistent with experimental observation. Upon increase of the CH_3CO internal energy, corresponding to acetyl bromide dissociation at 248 nm and acetyl chloride dissociation at 193 nm, the translational energy of the fragments changes only slightly, from 5.8 kcal/mole to 6.3 kcal/mole despite twice the available energy. The translational energy release is, therefore, determined by repulsive exit channel interactions. Perhaps more interesting, is the variation of the rotational and vibrational excitation with available energy, *i.e.* the internal excitation of the acetyl radical. The model predicts a CO vibrational content, 1.6 kcal/mole, following

acetyl chloride dissociation at 193 nm in close agreement with the laser diode experiments of Maricq and Szenté.²⁸ The statistical increase in CO vibrational energy supports the assumption that there may be at least some redistribution of energy prior to dissociation. Although there is insufficient experimental information regarding the CO rotational distributions as a function of CH_3CO internal energy, the model severely underestimated the energy in this particular degree of freedom in the 193 nm photodissociation of acetone.²⁶ In the model rotational excitation originates from two independent effects; the impulsive treatment of the repulsion associated with C-C bond cleavage and adiabatic evolution of statistically populated skeletal bends into free rotations of the fragments. The influence of anisotropy in the potential energy surface has been implicitly ignored. However, there is theoretical evidence to suggest that the C-C-O bend serves to promote CH_3CO dissociation. The C-C-O angle contracts from 128.1° at the equilibrium geometry to 115.9° at the transition state implying that the stretching and bending modes are strongly mixed in the dissociation. As the CH_3 and CO fragments separate this angle further contracts to 109.3° . Since an impulse along the C-C bond will tend to cause the CO to rotate in the same direction the two effects will augment each other resulting in more CO rotational energy than predicted by an impulsive treatment.

The lack of accurate measurements of the CH_3 rotational and vibrational arising from acetyl bromide dissociation at 248 nm and acetyl chloride at 193 nm precludes a more quantitative interpretation of the energy partitioning. Experiments to provide internal state distributions of the nascent CH_3 fragments should afford a considerable increase in the present understanding of the dissociation dynamics.

IV. Concluding Remarks

The photodissociation of acetyl chloride and acetyl bromide using photofragment translational spectroscopy has provided considerable insight into the energetics and dissociation dynamics of the acetyl radical. From the dissociation of acetyl chloride at 248 nm, a barrier height to CH_3CO decomposition of 17 ± 1.0 kcal/mole has been determined. This value is in quantitative agreement with the results of Watkins and Word⁴ and an independent measurement from this laboratory.⁸ A comparison of the variation in the secondary translational energy release with internal energy of CH_3CO has elucidated the origins of the energy disposal in the dissociation of the acetyl radical. The invariance of the $\langle E_T \rangle$ suggests that the translational energy of the CH_3 and CO fragments is controlled by the repulsive interaction beyond the transition state.

Table 1: *Ab Initio*^a Vibrational Frequencies of the Acetyl Radical (²A')

Vibrational Mode	Minimum	Transition State
ω_1	3193 ^b	3325
ω_2	3188	3321
ω_3	3080	3144
ω_4	1928	2027
ω_5	1478	1452
ω_6	1477	1445
ω_7	1361	901
ω_8	1062	568
ω_9	960	566
ω_{10}	884	496 i
ω_{11}	468	276
ω_{12}	101	43

a. Performed at the MP2/cc-pVTZ level of theory (ref. 7)

b. All frequencies given in cm^{-1}

Table 2: Photofragment Energy Partitioning for Acetyl Chloride Photodissociation at 248 nm

	Experiment	BIM	Statistical
$E_T(\text{CH}_3)^a$	3.5 ± 0.5	3.3	0.7
$E_R(\text{CH}_3)$	0.1	0.3	1.5
$E_V(\text{CH}_3)^b$	0.5	1.3	4.1
$E_T(\text{CO})^a$	1.9 ± 0.3	1.8	0.4
$E_R(\text{CO})$	-	1.6	1.9
$E_V(\text{CO})$	0.0	0.2	0.7

a. Translational energies are given in the secondary center-of-mass frame.

b. This represents a lower bound (Ref. 17) since only the v_2 mode used in this estimate.

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Figure Captions

- Figure 1 TOF spectra of m/e 35 (Cl^+) from acetyl chloride dissociation at 248 nm at laboratory angles of 15° and 30° . The open circles represent data and the solid lines are the forward convolution fits to the data using the center-of-mass $P(E_T)$ shown in Figure 3 (solid line).
- Figure 2 TOF spectra of m/e 42 (CH_2CO^+) at laboratory angles of 15° and 30° . The open circles represent data and the solid lines are the forward convolution fits using the $P(E_T)$ shown in Figure 3 truncated at 15 kcal/mol as shown by the dotted line.
- Figure 3 Center-of-mass translational energy distributions used to fit the data in Figures 1 and 2. Dotted line represents point of truncation used to fit Figure 2.
- Figure 4 TOF spectrum of m/e 42 (CH_2CO^+) at a laboratory angle of 30° . The dotted and dashed lines represent the forward convolution fits using the $P(E_T)$ in Figure 3 truncated at 13.2 kcal/mol and 16.8 kcal/mol respectively (± 1.8 kcal/mole as compared to the truncation used to fit the TOF spectra in Figure 2).
- Figure 5 Time-of-flight spectrum of m/e 15 (CH_3^+) at 20° . The open circles are the data. The lines are contributions from primary acetyl radicals (dashed line) and methyl radicals from secondary dissociation (dotted line). The solid line is the total fit to the data.
- Figure 6 Secondary center-of-mass translational energy distribution derived from fitting

the m/e 15 TOF spectrum shown in Figure 5. The inset shows the secondary angular distribution, $P(\Omega)$.

Figure 7 TOF spectra of m/e 79 (Br^+) from acetyl bromide dissociation at 248 nm at laboratory angles of 15° and 30° . The open circles represent data and the solid lines are the forward convolution fits to the data using the center-of-mass $P(E_T)$ shown in Figure 8.

Figure 8 Total center-of-mass translational energy distribution derived from fitting the TOF spectra shown in Figure 7.

Figure 9 Time-of-flight spectrum of m/e 15 (CH_3^+) at 15° from acetyl bromide dissociation. The open circles are the data. The lines are contributions from primary acetyl radicals (dashed line) and methyl radicals from secondary dissociation (dotted line). The solid line is the total fit to the data.

Figure 10 Secondary center-of-mass translational energy distribution derived from fitting the m/e 15 TOF spectrum shown in Figure 9. The inset shows the secondary angular distribution, $P(\Omega)$.

Figure 11 TOF spectra of m/e 35 (Cl^+) from acetyl chloride photodissociation at 193 nm at a laboratory angle of 40° . The open circles represent data and the solid line is the forward convolution fit to the data using the center-of-mass $P(E_T)$ shown in the inset.

Figure 12 Time-of-flight spectrum of m/e 15 (CH_3^+) at 30° from acetyl chloride dissociation at 193 nm. The open circles are the data. The solid line is the forward convolution fit to the data (see text for details).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Chapter 5

Photodissociation of the Methyl Radical at 193 nm and 212.8 nm

Abstract

The photodissociation dynamics of the methyl radical have been investigated at 193 nm and 212.8 nm using high resolution photofragment translational spectroscopy. A flash pyrolytic source, adapted from Chen and co-workers (*Rev. Sci. Instrum.*, **63**, 4003 (1992)), has permitted the generation of a high intensity pulsed supersonic beam of methyl radicals. The formation of CH_2 and H was the only dissociation pathway observed at both wavelengths. Although it is not possible to assign the spin state of the methylene unambiguously, the experimental evidence suggests that methylene is produced predominantly in the $\tilde{a}^1\text{A}_1$ excited state. At 193 nm the translational energy distribution of the products is peaked at ~ 13 kcal/mole which is consistent with the magnitude of the exit barrier on the excited state potential energy surface. The breadth of the distribution indicates that the methyl radicals dissociate from a wide range of geometries or that there exist substantial exit channel couplings. From the photofragment angular distribution at 193 nm an anisotropy parameter of $\beta = -0.9 \pm 0.1$ has been determined. Excitation at 212.8 nm, via the 2^1_1 hot band transition, results in a significantly broader translational energy distribution than observed from band origin dissociation at 216 nm. Although the initial umbrella motion of the parent should couple into CH_2 rotation, methylene internal excitation in excess of predictions using Franck-Condon analysis suggests the influence of significant exit channel effects and highlights the need for detailed *ab initio* calculations.

I. Introduction

Although the ground state reactivity and decomposition of methyl radical have been the subject of numerous studies¹, there is a paucity of information regarding the photochemistry of even the lowest electronically excited state. In fact, there are only two reports which have *directly* detected a dissociation product arising from B-state photochemistry.^{2,3} This is surprising in light of the considerable attention given to the analogous $\tilde{A}$ -states of NH_3 and H_2O (ref. 4) and is presumably due to the difficulty associated with developing high intensity radical beam sources.

The ultraviolet spectroscopy of the methyl radical was first examined by Herzberg and Shoosmith⁵ and the transition originating at 216 nm was assigned to an excitation of the unpaired $2p_z$ electron to a 3s Rydberg orbital. The broadening of the CH_3 transition was attributed to a rapid predissociation of the excited state due to H-atom tunnelling.⁶ Callear and Metcalfe subsequently resolved vibrational features between 216-204 nm beyond which the spectrum evolves into a broad continuum.⁷ The transition at 193 nm, therefore, is an excitation not to a discrete band but an absorption to the dissociative continuum. Methyl radical photodissociation has been observed at this wavelength as both a primary process⁸ and as a secondary process in the dissociation of acetone⁹ and azomethane.¹⁰

At 193 nm there are three energetically allowed dissociation pathways, two involving the loss of an H-atom and one involving the elimination of H_2 . Orbital correlations in the dissociation of the methyl radical were first examined theoretically by Yu *et al.*⁴ In agreement with the earlier postulation of Herzberg, the B-state was found to correlate with the formation of singlet methylene, $\text{CH}_2(\tilde{a}^1\text{A}_1)$,

and the ground state methyl radicals correlate to two asymptotic dissociation channels,

which are predicted to occur in comparable yields at vibrational energies corresponding to ~216 nm excitation followed by internal conversion.² Although the elimination of molecular hydrogen does not correlate with the $CH_3(^2A_1')$ state along either C_{2v} or C_s -pyramidal pathways, C_s -planar or C_I pathways are allowed. At 216 nm reaction 3 was inferred from OH fluorescence produced via the reaction of $CH(^2\Pi)$ with O_2 .¹¹ However, Ye *et al.* found that $CH(A,B \rightarrow X)$ fluorescence resulting from methyl radical photodissociation at 193 nm was quadratically dependent on the laser power.⁸ The authors concluded that CH originated from the secondary dissociation of methylene implying that at 193 nm H_2 elimination does not compete efficiently with simple C-H bond cleavage. *Ab initio* calculations by Yu *et al.* predicted a barrier to dissociation of 11.5 kcal/mole at $R_{C-H}=1.55$ Å for reaction 1. It was noted, however, that the calculated barrier may be reduced to 4.6-9.2 kcal/mole with a more substantial basis set and increased configuration inter-

action. Resonance Raman experiments carried out by Kelly and co-workers have addressed the ro-vibronic dependence of the predissociation lifetimes of the B-state.^{12,13} J-dependent tunneling rates of the B-state origin band were modelled with a 1-dimensional cubic potential and a best fit to the experimental data yielded a barrier of 6.29 kcal/mole at $R_{C-H}=1.38 \text{ \AA}$ (Ref. 13). Recent high level *ab initio* calculations performed by Botschwina *et al.* were in accord with the results of Kelly and co-workers.¹⁴ Figure 1 shows the energy level diagram for the photodissociation of methyl radical including correlations for a HCH angle of 120° .

Despite the theoretical work and spectroscopic measurements there have been few experimental investigations involving the photodissociation of the methyl radical. Chen *et al.* investigated the photochemistry of methyl radical at $\sim 216 \text{ nm}$ and detected the CH_2 (m/e 14) photofragment by photoionization at 10.5 eV although the spin state of the methylene could not be assigned.² No m/e 13 (CH^+) product was observed but since the 10.5 eV photon lies below the CH ($^2\Pi$, $v=0$) adiabatic ionization potential, determination of the branching ratio between H-atom and H_2 elimination was not possible. Recently, Dixon and co-workers measured high resolution Rydberg H-atom time-of-flight spectra arising from methyl radical photodissociation at 216.3 nm. The methyl radicals were prepared from the photolysis of methyl mercaptan, CH_3SH , which dissociates via two accessible channels,¹⁵

In the 216 nm photodissociation of the resulting methyl radicals, and contrary to all theoretical predictions, ground state methylene (3B_1) was determined to be the counter fragment. This conclusion was based on energetic considerations, *i.e.* there was insufficient energy available concomitant with the formation of $CH_2(\tilde{a}^1A_1)$ to account for the short arrival times of the observed H-atoms. It was postulated that the formation of triplet methylene resulted from a coupling between the ground and excited state potential energy surfaces in the exit channel at small CH_2 angles ($\sim 104^\circ$). The structure in the time-of-flight, originally thought to be $CH_2(^3B_1)$ bending excitation, was later found to be inconsistent with the dissociation of CH_3 .³ These features have since been attributed to H-atoms arising from the photolysis of CH_3S ,¹⁶

A re-investigation of methyl radical dissociation at 216.3 nm suggests that only $CH_2(\tilde{a}^1A_1)$ is produced in agreement with theoretical predictions.³ The H-atom TOF spectrum consisted of a single narrow peak indicating that the nascent methylene is produced with little vibrational and rotational excitation. The measured translational energy release however, is energetically consistent with either singlet or triplet methylene.¹⁷

In this chapter, results on the photodissociation of methyl radical excited at 193 nm and 212.8 nm using high resolution photofragment translational spectroscopy are presented. These are the only experiments which have directly measured the H-atom to H_2 elimination branching ratio at any wavelength. The only observed products at both

wavelengths were CH_2 and H . This result is extremely relevant to those interested in the 193 nm photolysis of acetone and azomethane as a sources of methyl radicals for kinetics studies. Although our methodology cannot unambiguously discriminate between the different spin states of the methylene, based on the translational energy and photofragment anisotropy at 193 nm the CH_2 photoproducts are likely formed in the $\tilde{a}^1\text{A}_1$ excited state. Since out-of-plane motion serves to couple the ground and excited states, methyl radical photodissociation via the 2^1_1 hot band transition should allow the significance of non-adiabaticity in this system to be examined. Furthermore, a comparison of the CH_2 internal excitation arising from origin band and 2^1_1 band transitions may provide valuable insight into the exit channel dynamics.

II. Experimental

Three experimental configurations were used in this work. All of the photofragments, with the exception of H and H_2 , were measured using a fixed-source rotatable-detector apparatus as described previously.^{18,19} The pulsed beam of radicals was generated from the pyrolysis of a suitable precursor. Although both azomethane and di-*tert*-butyl peroxide (DTBP) were employed with similar success, all of the data presented in this paper was obtained with DTBP as the precursor. The thermal decomposition of DTBP results in two methyl radicals and two acetone molecules and has been shown to be an efficient source of CH_3 .²²

A pulsed valve²⁰ fitted with a SiC pyrolysis nozzle (1.0 mm I.D.) was operated at 80 Hz. The source employed is an adaptation of the one designed and characterized by Chen *et al.* and a more complete description can be found elsewhere.²¹ Figure 2 shows a

schematic diagram of the pyrolytic source used in the experiment. Briefly, a SiC tube was resistively heated by a DC current limited power supply to an external temperature of ~1400 K, as determined from optical pyrometry. Calculations have demonstrated that at SiC wall temperatures of ~1400 K the gas temperature is ~800 K.²³ The time it takes for the decomposition of 99% of the DTBP precursor is given by the following first order rate expression,

$$\tau = \frac{1}{k_{uni}(T)} \ln \left(\frac{1}{0.01} \right) \quad (7)$$

From the known first order rate constant, $k_{uni}(800)$, $\tau \sim 18 \mu\text{sec}$. The gas transit time through the heated region of the nozzle is $\sim 20 \mu\text{sec}$ ensuring almost complete conversion of DTBP to methyl radicals and acetone. DTBP, <1%, was expanded in helium at a total stagnation pressure of ~ 800 torr. Shown in Figure 3 are mass spectra of the molecular beam with the nozzle unheated (upper trace) and heated (lower trace). The lower spectra shows the quantitative loss of the parent (m/e 146, m/e 73, and m/e 57), the appearance of the known cracking pattern for acetone, and a large contribution from the methyl radical parent at m/e 15. The CH_3 number density in the laser interaction region can be estimated from the following,

$$\rho_z = \rho_0 \left(1 + \frac{M_z^2}{3} \right)^{-\frac{3}{2}} \quad (8)$$

where ρ_0 is the density at the nozzle opening and M_z is the Mach number. Using

approximate equations to describe the supersonic expansion of a monatomic gas²⁴ the Mach number can be evaluated and assuming a near complete conversion of DTBP to methyl radicals, $\rho_z \sim 6.37 \times 10^{12}$ CH₃ molecules cm⁻³.

The beam was measured *in situ* and had a velocity of ~3600 m/s with a FWHM of ~15%. The pulsed beam was twice collimated to an angular divergence of 2° and crossed at a right angle with the output of a Lambda-Physik EMG 202 MSC excimer laser which was operated at the ArF transition (193 nm). The 5-30mJ/pulse output was focussed to a 2x4 mm spot in the interaction region using a spherical MgF lens (focal length 30 cm). Polarization of the laser beam was achieved by 10 quartz plates at Brewster's angle (>95% polarization). The neutral photoproducts travelled 20.8 cm where they were ionized by electron bombardment and mass selected using a quadrupole mass filter. The ions were then counted as a function of time using a Daly ion counter and a multichannel scaler interfaced to a computer that was triggered with the laser pulse.

In order to detect H and H₂ photofragments two alternative arrangements were utilized. The first involved the universal detector apparatus previously described and modification for H and H₂ detection. This adaptation has been thoroughly discussed elsewhere and will only be briefly summarized.^{25,26} As shown in Figure 4, the pulsed valve with pyrolytic nozzle attachment was mounted mutually perpendicular to both the detector and the laser axes. The radicals were photolyzed ~4.0 mm above the nozzle opening and the H-atom photoproducts passed through two 3.0 mm skimmers 28.5 cm to the detector. The neutral flight length and calibration other detector functions was achieved by monitoring the H-atom signal arising from the photolysis of a 50:50 mixture of HI/DI at 193 nm. Shown in Figure 5 is a representative H-atom time-of-flight spectrum.

Both (2P_J) spin orbit states of the I atom fragments are indicated. The TOF spectrum the D-atom is not shown. Since the photodissociation of a diatomic molecules results in a well known delta function in translational energy, the width and position of the TOF peaks provides information on instrumental broadening and the ion flight constant. The observed spread is due to two factors. The first is the $\sim 250\text{ cm}^{-1}$ bandwidth of the excimer laser and the second is from averaging over center-of-mass angles since the molecular beam is uncollimated. Although the beam velocity distribution could not be determined in this configuration, the H-atom velocity is large compared to the beam velocity and as a result the H-atom TOF spectra were found to be relatively insensitive to the beam conditions. The data was fit with the forward convolution technique. Details of the fitting procedure and the data analysis program can be found elsewhere.²⁷

Ultra high resolution time-of-flight spectra of hydrogen atoms produced by the photodissociation of CH_3 radicals at 212.8 nm were measured using the experimental technique developed by Welge and co-workers.²⁸ In this technique hydrogen atoms are excited to high principle quantum number Rydberg states ($n=50-70$) at the site of the photolysis region. The velocity of the hydrogen atoms is measured by determining the time it takes the Rydberg atoms to traverse a field free region which terminates in a region of high DC field where the Rydberg atoms are instantaneously field ionized and detected. Figure 6 shows a schematic diagram of the high resolution Rydberg H-atom time-of-flight apparatus.

For the preparation of the high- n Rydberg states a two-step excitation scheme was used consisting of Lyman- α radiation at 121.57 nm, followed by excitation at 365.13 nm. In order to generate VUV radiation at the Lyman- α transition frequency a Coherent 699-

29 ring laser, operated at 607.84 nm, was pulse-amplified in three stages obtaining pulses with an energy of up to 100 mJ with near-transform limited bandwidth of 52 MHz. A detailed description of this laser system has been given elsewhere.²⁹ The visible pulses were frequency-doubled in KDP, yielding up to 25 mJ of 303.92 nm light, and, using a 25 cm focal length achromatic lens, the co-propagating 607.84 nm and 303.92 nm laser pulses were focussed into a 40 cm long mixing cell containing 60 mbar of krypton gas. Lyman- α radiation was generated in this cell by combining two photons of the UV laser and one photon of the visible laser. The diverging Lyman- α radiation was focussed onto the molecular beam using a 12 cm focal length LiF lens. The spotsizes of the co-propagating 607.84 nm and 303.92 nm beams were ~ 5 mm at the molecular beam.

In order to obtain the 365.13 nm radiation used to excite the hydrogen atoms from the 2p level to high Rydberg states, a second Coherent 699-29 ring laser, operated near 555.71 nm was pulse-amplified in three stages yielding pulses with an energy of up to 85 mJ. These pulses were mixed with the residual 1.064 μm fundamental of the Nd:YAG laser pumping the amplifier chain in a third harmonic crystal, yielding up to 7 mJ of 365.13 nm light. The 365.13 nm radiation was focussed onto the molecular beam using a 50 cm focal length lens and was aligned counter-propagating to the Lyman- α radiation. In the presence of both the Lyman- α and the 365.13 nm laser, H^+ ions could be formed through Lyman- α excitation followed by absorption of one or more photons from either the 303.92 nm laser involved in the generation of the Lyman- α radiation or the 365.13 nm laser. The optimum conditions for preparation of the Rydberg states were determined using 1 kV/cm delayed pulsed field extraction of the H^+ in the presence of a DC field of ~ 10 V/cm. Under these conditions the H^+ ion time-of-flight contained two resolved peaks

corresponding to H^+ ions which were formed promptly by the lasers and H^+ ions formed from delayed pulsed field ionization of high Rydberg states by the high voltage pulse. Under typical conditions the H^+ ion production involving the 365.13 nm laser was about one order of magnitude larger than the H^+ ion production from the 303.92 nm laser, and the ratio of high Rydberg states to prompt H^+ ions from the 365.13 nm laser was about 2:1.

In the Rydberg atom time-of-flight measurements, the laser excitation occurred between a 5.0 cm diameter stainless steel repeller and a 90% transmitting stainless steel mesh (90 lines/inch), through which the Rydberg atoms entered the 40 cm long field free flight tube. The repeller and the mesh were separated by 2.0 cm. A -15 V DC bias was applied to the repeller to inhibit the detection of prompt H^+ ions. At the end of the field free flight tube, a double mesh assembly was mounted, through which the Rydberg atoms entered a chamber in which a Daly-type scintillation detector was setup. The -30 kV doorknob voltage in this chamber created the DC field which field ionized the Rydberg atoms. In 193 nm photolysis of both HI and DI using an EMG 101 Lambda Physik excimer laser running at 10 Hz, the time-of-flight resolution was determined to be excimer laser bandwidth limited. In order to optimize the experimental apparatus and further demonstrate both resolution and signal/noise ratio, H_2S was photodissociated at 193 nm. Figure 7 shows a representative H-atom TOF spectrum acquired for 10 000 laser shots. The nascent SH ($X^2\Pi$) vibrational distribution ($v=0-6$) is clearly visible as are the individual $^2\Pi$ spin-orbit components.

The 212.8 nm radiation which was used to photolyze the methyl radicals was obtained as the 5th harmonic of a Quanta Ray DCR-1 Nd:YAG laser by mixing the fundamental and the 4th harmonic (60 mJ/pulse) of this laser in a 51° BBO crystal to produce

212.8 nm pulses with energies up to 9 mJ. The 212.8 nm light followed the same beam path as the 365.13 nm light and was focussed at the molecular beam, counter-propagating to the Lyman- α radiation, using a 50 cm focal length lens.

The DTBP 98% was obtained from Aldrich and used without further purification. Azomethane was synthesized by the method of Renaud and Leitch³⁰ and was purified by trap-to-trap distillation prior to use.

III. Results and Analysis

A. *Excitation at 193 nm*

Time-of-flight spectra (TOF) were taken at m/e 12-15, m/e 2, and m/e 1 with unpolarized light. TOF spectra of m/e 28 (CO^+) were also collected in order to confirm the photodissociation of acetone, a pyrolysis bi-product. Acetone is known to have an appreciable absorption cross section ($\sigma_{193} \sim 2.7 \times 10^{-18} \text{ cm}^2$) at 193 nm due to a 3s Rydberg transition.³¹ The dynamics of acetone photodissociation, particularly the resulting translational energy distributions of the CH_3 and CO photofragments, have been well characterized.^{28,29} All of the observed signals exhibited a linear dependence upon the laser power demonstrating that the photofragments resulted exclusively from single photon processes at the laser fluences employed. Time dependent background from the pulsed valve was collected with the laser off and subsequently subtracted from the TOF spectra. Figure 8 shows TOF spectra taken at $\Theta_{\text{lab}} = 7.5^\circ$ at m/e 15-12. The m/e 15 (CH_3^+) (Figure 8a) cannot arise from methyl radical photodissociation and was successfully fit, as shown by the solid line, with the previously determined translational energy distribution, $P(E_T)$, for the photodissociation of acetone at 193 nm.³² TOF spectra at m/e 28 were also fit using

the $P(E_T)$ for acetone photodissociation. In the m/e 14 (CH_2^+) TOF spectrum, in addition to the CH_3 daughter ion from acetone, is a second feature which appears at longer times. This is attributed to methylene originating from the photodissociation of methyl radical. An identical feature is observed at m/e 12-14 when using azomethane as the radical precursor and, therefore, the assignment of this peak can be made with some confidence.³⁰ The dashed line is the fit to the methylene contribution using the $P(E_T)$ shown in Figure 4. Any $\text{CH}(^2\Pi)$ produced from the elimination of H_2 would appear at m/e 13 (CH^+) and m/e 12 (C^+). Both of these spectra can be fit without including the $\text{CH} + \text{H}_2$ channel and therefore it appears that formation of CH_2 and H is the only active dissociation channel. Additional TOF spectra for m/e 12 at laboratory angles of 10° and 14° are shown in Figure 5.

A representative H-atom (m/e 1) TOF spectrum is shown in Figure 6 with the time dependent background subtracted. The solid line fit to the data is using the $P(E_T)$ obtained from fitting the CH_2 (m/e 14-12) TOF spectra demonstrating that this is the momentum matched fragment. Since H-atom elimination from both acetone⁹ and azomethane¹⁰ is thought to occur in minor yields at 193 nm the importance of measuring the momentum matching partner cannot be overemphasized in unambiguous determination of the dissociation channels. Similar m/e 1 TOF spectra were obtained in the pyrolysis of azomethane. Furthermore, lowering the temperature of the SiC nozzle $>100^\circ\text{C}$ eliminated the H-atom peak entirely. Shown in Figure 12 are laser on and laser off spectra at m/e 2, each accumulated for 2 000 000 shots. Within the signal-to-noise ratio of the data we conclude that there is no H_2 produced from the photodissociation of CH_3 at 193 nm. This is in agreement with the analysis above of the heavy fragments. Based on the heavy fragment

(*m/e* 15-12) and *m/e* 2 data we estimate that if the CH + H₂ channel exists it certainly represents < 5% of the dissociation products.

The center-of-mass P(*E_T*) shown in Figure 4 is peaked away from zero, <*E_T*>~15 kcal/mole, with a FWHM of 12 kcal/mole. The available energy for the formation of ground state methylene is given by,

$$E_{avail} = h\nu_{193nm} - D_o^o(H_2C-H) + E_{int}^P \quad (9)$$

where $h\nu_{193nm}$ is the photon energy (147.8 kcal/mole) and $D_o(C-H)$ is the bond dissociation energy. From the known heats of formation for CH₂ (³B₁) (92.6 kcal/mole)³⁵, H (²S) (52.1 kcal/mole)³⁶, and CH₃ (²A₂"') (34.0 kcal/mole)³⁶ the C-H bond dissociation energy in CH₃ is 110.7 kcal/mole. Therefore, the available energy for production of CH₂ (³B₁) + H is 37.1 kcal/mole. The singlet-triplet splitting in CH₂ has been the subject of a voluminous literature.³⁷ Adopting the accepted best value of 9.08 kcal/mole the available energy for the formation of CH₂(¹A₁) + H is then, 147.8-110.7-9.08=28.0 kcal/mole.

Equation 4 has neglected any internal excitation of the parent. Although we have no way of ascertaining the internal excitation in the CH₃ at 1400 K we estimate that the methyl radicals should contain ~6 kcal/mole of vibrational energy prior to supersonic expansion, with most of this residing in the low frequency ν_2 umbrella mode. Ellison and co-workers have shown that NO radicals arising from the pyrolysis of di-tert butyl nitrate at 800 K possess rotational temperatures from 20-50 K (Ref. 23) and Chen *et al.* (Ref. 34) have reported the complete vibrational relaxation of allyl radical produced under similar conditions. Even partial relaxation would leave the nascent methyl radicals with only 1-2

kcal/mole of vibrational energy on average. The maximum of the translational energy distribution, 28 kcal/mole, extends to the allowed thermodynamic limit for the formation of $\text{CH}_2(^1\text{A}_1) + \text{H}(^2\text{S})$. Although the fastest CH_2 fragments overlap with the slowest CH_3 fragments from acetone in the m/e 12-14 spectra, the H-atom TOF spectrum and the angular distribution (Figure 13) allow sensitivity to the $P(E_T)$ maximum. We are confident, therefore, that the $P(E_T)$ does not have a significant contribution beyond 28 kcal/mole. Owing to large time dependent background signal at small laboratory angles, $\Theta_{\text{lab}}=6^\circ$ was the minimum angle at which TOF data was recorded. Based on the kinematics of the dissociation, CH_2 photofragments with less than ~ 7 kcal/mole of translational energy could not be detected. Fortunately, the H-atom TOF spectra provides reliable information about the $P(E_T)$ down to 1.5 kcal/mole.

The laboratory angular distribution for the CH_2 fragments, monitored at m/e 12, is shown in Figure 13. Each point represents several individual measurements corrected for the laser power and the error bars are a single standard deviation of the data. The low time dependent background from the pulsed valve at m/e 12 (C^+) made it the preferable mass to detect. The laser was polarized in the plane of the detector and along the molecular beam axis. For each measurement the total TOF profile was integrated with a scaler and the laser off signal was subtracted from the laser on signal at alternate shots. Since the TOF spectrum at m/e 12 involves contributions from both methyl radical and acetone photodissociation, the acetone signal needed to be carefully taken into account. In order to do this counts were taken at angles $\Theta_{\text{lab}} > 20^\circ$ where only the acetone contribution was present. Using the $P(E_T)$ for CH_3 from acetone and an isotropic dissociation as has been observed previously, the angular distribution for these fragments^{28,29} was simulated using the

forward convolution program. The simulation was then normalized to the measured signal at large laboratory angles and then the acetone contribution subtracted from the m/e 12 signal. TOF spectra taken at m/e 15 provided confirmation of the acetone angular distribution. It should be noted that given the large isotropic recoil of the CH_3 fragments from acetone photodissociation, the angular distribution is almost invariant over the range of interest. The center-of-mass product angular distribution is given by,

$$P(\Theta) = \frac{1}{4\pi} \{ 1 + \beta P_2(\cos\Theta) \} \quad (10)$$

where β is the anisotropy parameter and is equal to 2 if the transition moment and the dissociating bond are parallel and -1 if they are perpendicular in the limit of prompt recoil.³⁵ Shown in Figure 13 are three simulated laboratory angular distributions using the determined $P(E_T)$ and anisotropy parameters of $\beta=0.0$, -0.5, and -1.0 corresponding to isotropic and increasingly perpendicular dissociations. From a best fit to the experimental angular distributions an anisotropy parameter of $\beta=-0.9\pm0.1$ has been determined. A negative β parameter was confirmed independently by rotating the polarization of the laser and observing the m/e 1 signal although the low signal-to-noise ratio precluded an accurate quantitative measurement.

B. Excitation at 212.8 nm

A representative high resolution Rydberg H-atom TOF spectrum resulting from methyl radical photolysis at 212.8 nm is shown in Figure 14. The signal exhibited a linear dependence on the 212.8 nm laser power, indicating that the fragments arise from a signal

photon process. At sufficiently high laser powers a fast shoulder at flight times $\sim 20 \mu\text{s}$ could be observed that displayed a quadratic power dependence. There was no detectable signal when the SiC nozzle was not heated above an exterior temperature of 1300 K. The intensity of the Rydberg H-atom signal was observed to have a polarization dependence, resulting in the greatest intensity when the laser was polarized along the molecular beam axis and perpendicular to the detector axis. This corresponds to a negative anisotropy parameter and is consistent with the symmetries of the excited and ground state. The polarization dependence also provides additional evidence that the observed TOF signal arises from the 212.8 nm dissociation of the methyl radical.

The determination of the center-of-mass translational energy distribution has been conventionally obtained by the direct inversion of the Rydberg H-atom TOF spectrum. Neglect of the initial parent velocity is a reasonable approximation when employing room temperature beams where the H-atom velocity from the dissociation event is significantly larger than that of the molecular beam. In the present experiment, however, since the radical precursor is seeded $<1\%$ in He and the gas temperature is typically 800-1000 K, the velocity and velocity spread of the molecular beam cannot be ignored. The contribution of the parent velocity distribution to the measured H-atom TOF spectrum can be accounted for using a forward convolution fitting procedure. The forward convolution technique is well established and is described in detail elsewhere. Modification of the CMLAB2 program was necessary since the Rydberg H-atom technique is intrinsically a number density measurement and not a flux measurement as in universal electron impact ionization. The best forward convolution fit to the TOF data is shown in Figure 15. The translational energy distribution, $P(E_T)$, is peaked at ~ 15 kcal/mole with a FWHM of ~ 5.5

kcal/mole. Indicated above the $P(E_T)$ in Figure 15 are marks corresponding to the translational energy coincident with forming singlet methylene with various quanta in the ν_2 bending mode. The $P(E_T)$ exceeds the maximum available energy for several reasons. It was necessary to photolyze the radicals in the early, warmer, part of the beam pulse since absorption at 212.8 nm requires the parent methyl radicals possess one quantum of umbrella excitation. In fact, the H-atom TOF signal was extremely sensitive to the region of the pulse that was irradiated. As a consequence, the rotational and vibrational modes of the methyl radicals should not be completely relaxed. The H-atom TOF spectrum, therefore, probably contains contributions from the photodissociation of rotationally and vibrationally (other one quantum in ν_2) excited CH_3 . Although this qualitatively accounts for translational energies in excess of the available energy, it is difficult to ascertain the extent to which the initial distribution of CH_3 internal states affects the structure of the derived $P(E_T)$.

Product TOF spectra at m/e 15, m/e 14, and m/e 13 were collected at laboratory angles ranging from 7° to 12° . The TOF signals at m/e 14 and m/e 13 were indistinguishable within the signal-to-noise ratio suggesting that H_2 elimination does not compete with H-atom loss at this wavelength. Shown in Figure 16 are m/e 13 (CH^+) TOF spectra at laboratory angles of 8° and 10° . At 212.8 nm acetone possesses a negligible absorption cross section ($\sigma_{212.8\text{nm}} < 1 \times 10^{-21} \text{ cm}^2$) and, therefore, does not contribute to the m/e TOF spectra. No photodissociation signal was observed at m/e 15 (CH_3^+). The solid line is the forward convolution fit to the data using the $P(E_T)$ shown in Figure 15 derived from fitting the Rydberg H-atom TOF spectrum. The m/e 13 signal exhibited a polarization dependence consistent with a perpendicular transition although insufficient signal-to-noise

prevented a quantitative determination.

IV. Discussion

A. Excitation at 193 nm

Laser Polarization Dependence: At 193 nm methyl radical is excited to the dissociative continuum above the barrier along the C-H bond dissociation coordinate. Even at excitation energies below this barrier the CH_3 lifetime is subpicosecond. Kelly and co-workers have determined predissociation lifetimes of the CH_3 origin band to be < 82 fs (Ref. 12) and the [1000] state was found to have a lifetime of ~ 13 fs which is comparable to the C-H stretching frequency.¹³ By nature of the continuum excitation at 193 nm the dissociation should occur with extreme rapidity. It is therefore unlikely that internal conversion could compete effectively with dissociation from the B-state and the observed anisotropy indicates that the *dissociation is direct*. The measured $\beta = -0.9 \pm 0.1$ indicates that the transition dipole moment lies perpendicular to the C-H bond which is consistent with the initial excitation of the out-of-plane p_z orbital on the carbon to a 3s Rydberg orbital. This represents the first measurement of the photofragment anisotropy for methyl radical dissociation from the B-state. Although the dissociation is much faster than rotation of the parent molecule any motion that contributes a velocity component perpendicular to the C-H bond will diminish the observed anisotropy. This effect would be particularly salient if the methyl radical dissociates from a range of non-planar geometries. Using the expression, $\beta = 2P_2(\phi)$, where ϕ represents the angle between the C-H bond and the dipole moment operator this range can be calculated. On average the methyl would have to dissociate from geometries 10° from planarity with $75^\circ < \phi < 90^\circ$ coinciding to the spread in the

measured anisotropy (-0.8 to -1.0). Any umbrella motion originating from either the transition at 193 nm or a hot band absorption of radicals already possessing ν_2 excitation would result in a range of dissociations from non-planar geometries.

Product Translational Energy Distribution: The barrier on the B-state arises from a "de-Rydbergization" of the 3s orbital initially localized on the carbon as it evolves into a σ^* orbital on the C-H bond, and eventually to a 1s orbital on the departing hydrogen atom. The disposal of available energy into translation of the photofragments should be dominated by the repulsive interaction as the excited state develops σ^* character in the C-H bond. Given the 6.29 kcal/mole barrier height¹³ and the 12.7 kcal/mole exoergicity of the reaction to form $\text{CH}_2(^1\text{A}_1) + \text{H}$, the total exit barrier is ~19 kcal/mole. If ground state methylene is produced then the exit barrier is increased by the magnitude of the singlet triplet splitting and is therefore ~28 kcal/mole. For a dissociation involving the cleavage of a single bond the fraction of the exit barrier appearing in translation can be estimated by using a soft fragment impulsive model.³⁶ The soft fragment impulsive model predicts that ~98% of the exit barrier should appear as product translation.³⁷ In fact, this partitioning was predicted earlier by Yu *et al.*² and is intuitively reasonable since the light H-atom should not effectively couple its impulse into the CH_2 vibrational degrees of freedom. Furthermore, the near planarity of the B-state should not facilitate any rotational excitation of the methylene fragment and even if the methyl radical dissociated from non-planar geometries the very small exit impact parameters when an H-atom recoils from the C atom in CH_2 would still result in negligible CH_2 rotation. However, only ~15 kcal/mole on average is observed in translation. This corresponds to only 80% and 54% of the exit barrier for singlet and triplet methylene respec-

tively indicating substantial internal excitation. If the dissociation is prompt, as supported by the exhibited photofragment anisotropy, and there is little interaction in the exit channel, then the internal energy distribution may be determined by the change in R_{C-H} and θ_{HCH} between the CH_3 and the free CH_2 . Although there is little change in the C-H bond length, there is a substantial change in the HCH bond angle. The methyl radical is of D_{3h} symmetry and $\theta_{HCH}=120^\circ$, while for $CH_2(^1A_1)$ $\theta_{HCH}=102.4^\circ$ and for $CH_2(^3B_1)$ $\theta_{HCH}=134^\circ$. Although Dixon and co-workers have now concluded³ that vibrationless singlet methylene is produced from methyl radical photodissociation at 216 nm (rather than ground state $CH_2(^3B_1)$ with 0-3 quanta in ν_2 excitation¹⁵), the present results indicate that singlet or triplet methylene are formed with significant internal energy. According to the measured translational energy distribution there would be no $CH_2(^3B_1)$ containing less than 8 kcal/mole of internal energy, with most $CH_2(^3B_1)$ fragments possessing 23.1 kcal/mole of internal energy on average. If, however, singlet methylene were the dissociation product it would contain ~ 13 kcal/mole of internal energy on average. Since the $P(E_T)$ extends to the thermodynamic limit there is a finite probability of forming vibrationless $CH_2(^1A_1)$. Although the slope of the $CH_2(^1A_1)$ bending coordinate in the exit channel is not as steep as for $CH_2(^3B_1)$ the breadth of the $P(E_T)$ suggests that the methyl radical samples a wide range of dissociative geometries. The absorption to the dissociative continuum is sufficiently far above the barrier to be relatively insensitive to the least motion pathway. Therefore, the observed $P(E_T)$ is certainly consistent with excitation in the other vibrational modes of the methylene. We conclude that the most likely dissociation product is $CH_2(^1A_1)$ which is consistent with theoretical prediction.⁴ In addition, wavepacket calculations on empirical potential energy surfaces find that formation of

triplet methylene requires an anomalously large coupling between the ground and excited state surfaces.⁴¹

In light of the vibrationless $\text{CH}_2(a^1A_1)$ observed by Dixon and co-workers, one must ask why the resulting energy distribution at 193 nm is so different. The apparent discrepancy can be explained by considering the fundamental differences between the dynamics imposed by a continuum compared to a tunneling dissociation. Since methyl radical at 216 nm is excited to the band origin only zero point motion will contribute to the range of dissociative geometries. In addition, the dissociation barrier depends on the HCH angle and to an extent, so should the tunneling rate. Therefore, the methyl radical excited at 216 nm dissociates from an extremely narrow range of geometries which are biased toward HCH angles $<120^\circ$. These outgoing trajectories run close to the minimum on the $\text{CH}_2(a^1A_1)$ bending potential ($\theta_{\text{HCH}}=102^\circ$) and therefore result in predominately vibrationless nascent products. At 193 nm there is no *a priori* reason to believe that the dissociation should be constrained to a small dispersion about the CH_3 equilibrium geometry. The range of dissociation geometries should be determined, in part, by the initial motion of the nuclei upon excitation to the continuum. Therefore, there is no preference for outgoing trajectories to sample that part of the potential energy surface that corresponds to a least motion pathway. If the dissociation proceeds through a broad range of coordinate space a high degree of internal excitation in the CH_2 products should result.

B. Excitation at 212.8 nm

The derived $P(E_T)$ shown in Figure 15 is significantly wider than the $P(E_T)$ observed in the 216.3 nm, origin band, photodissociation of the methyl radical. The width

of the $P(E_T)$ implies that the nascent CH_2 fragments contain significant internal excitation. Although the excited $^2A_2''$ state is predissociative, the vibrational structure in the absorption spectrum indicates that in the Franck-Condon region the excitation in the 2^1_1 band prepares electronically excited methyl radicals with one quanta of umbrella motion. The methyl radical dissociates by hydrogen tunnelling through the barrier on the potential surface. Beyond the barrier, the reaction coordinate is ~ 18 kcal/mole exothermic with respect to the asymptotically separated singlet CH_2 and H. The observed energy partitioning is, therefore, a consequence of several factors; the motions associated with the bound excited state, the dynamics of the H-atom tunneling, and the forces and torques in the exit channel. Since there is no resolved structure in the TOF spectra, the relative contributions of CH_2 rotational and vibrational excitations to the width of the $P(E_T)$ is unclear.

Assuming that all the CH_2 internal energy resides in rotation, there are several simple methods to estimate the magnitude of fragment rotational excitation. Treating the methyl radical as a *pseudo* triatomic, by collapsing the two hydrogens into a single point mass, the impulsive model can provide an estimate of the magnitude of the rotational excitation using the following expression,

$$E_R = E_{\text{avail}} \frac{m_C m_A \sin^2 \alpha_0}{(m_C + m_B)(m_A + m_B) - m_C m_A \cos^2 \alpha_0} \quad (11)$$

where m_A , m_B , and m_C are the masses of the departing hydrogen, the carbon atom, and the unified remaining hydrogens respectively. A distribution of the bending angle, α_0 , then yields a corresponding distribution of rotational energy. The distribution of α_0 was

derived from the vibrational wavefunction associated with $v=1$ in the ν_2 mode. This, of course, assumes that the geometry in the Franck-Condon region is conserved following tunnelling. Since the departing fragment is so light the rotational excitation of the CH_2 fragment is negligible, resulting in a distribution with a FWHM of < 0.3 kcal/mole. The impulsive model severely underestimates the width of the $P(E_T)$. However, the model does not include the angular momentum associated with the parent umbrella motion which, in the case of methyl radical dissociation, should be more significant.

A method of treating the evolution of parent bending motion into photofragment rotation involves calculating *rotational Franck-Condon factors*. These factors are simply projections of the angular momentum states of the parent bending wavefunctions, Y_{j0} , onto the free fragment rotor states, $\phi_Y^{(j)}$. A detailed discussion can be found elsewhere. The rotational state distribution is given by,

$$\left| \langle Y_{j0} | \phi_Y^{(j)} \rangle \right|^2 \approx \frac{1}{2} \sin^2 \left[j\gamma_e + \frac{\pi}{4} (-1)^j \right] H_1^2 \left[j (h/m\omega)^{1/2} \right] e^{-j^2 h/m\omega} \quad (12)$$

where H_1 is the Hermite polynomial of first order, ω is the CH_3 bending frequency in the B-state, and m is a mass factor.⁴³ This treatment yields a much broader distribution than the impulsive model, FWHM ~ 2.5 kcal/mole, although still inconsistent with the width of measured translational energy distribution. Both estimates of the rotational distribution correspond to the limit of elastic rotational excitation, *i.e.* the potential energy surface is assumed to be isotropic. Unfortunately, there is no *ab initio* potential energy surface for the B-state that includes the out-of-plane coordinate. Therefore, it is difficult to determine the importance of angular torques beyond the barrier and whether these effects

will serve to promote or inhibit CH_2 rotation.

Although no CH_2 vibrational excitation was observed in CH_3 photodissociation at 216 nm, the H-C-H scissor motion associated with the umbrella mode may result in some CH_2 bending excitation. Even if a fraction of the nascent methylene fragments contained one quantum in ν_2 it would provide reasonable qualitative explanation of the measured $P(E_T)$.

V. Concluding Remarks

In conclusion, the photodissociation of methyl radical at 193 nm and 212.8 nm has been studied using high resolution photofragment translational spectroscopy. At both wavelengths the only single photon products observed were CH_2 and H. This is the first time that the branching ratio between H-atom and H_2 elimination from CH_3 photochemistry has been directly determined. Although the spin-state of the methylene product cannot be unambiguously assigned, in light of the translational energy distributions and overwhelming theoretical work, $\text{CH}_2(a^1A_1)$ is most likely the predominate dissociation product at 193 nm and 212.8 nm. Since a definitive determination of the methylene spin-state resulting from CH_3 photodissociation has yet to be made at any wavelength, any measurement to this end would represent an important contribution to the further elucidation of methyl radical photochemistry. The breadth of internal energy measured in this experiment is consistent with the dissociation occurring from a wide range of dissociative geometries and exit channel couplings.

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Figure Captions

- Figure 1 Energy level diagram for methyl radical showing the energetically accessible dissociation channels and correlations following $p_z \rightarrow 3s$ excitation.
- Figure 2 Schematic diagram of the pulsed pyrolytic nozzle assembly based on the design of Chen and co-workers.
- Figure 3 Mass spectra of the molecular beam of < 1% di-tertbutyl peroxide in He taken with the pyrolytic nozzle at (a) room temperature (*heat off*) and (b) 1400 K wall temperature (*heat on*).
- Figure 4 Diagram for the detection of H and H₂ fragments on the universal detector apparatus.
- Figure 5 H atom (m/e 1) time-of-flight spectrum for HI photodissociation at 193 nm. The solid and dashed lines correspond to forward convolution fits to the $^2P_{3/2}$ and $^2P_{1/2}$ spin orbit components respectively.
- Figure 6 Schematic diagram of the ultra high resolution Rydberg H-atom time-of-flight set-up (see text for details).
- Figure 7 Rydberg H atom time-of-flight spectrum for the photodissociation of H₂S at 193 nm.
- Figure 8 Product time-of-flight spectra at a laboratory angle of 7.5° for (a) m/e 15 (CH₃⁺) (b) m/e 14 (CH₂⁺) (c) m/e 13 (CH⁺) and (d) m/e 12 (C⁺). The open cir-

cles represent data. The dotted line is the contribution from acetone dissociation, the dashed line is the contribution from CH_3 dissociation using the $P(E_T)$ in Figure 9, and the solid line is the total fit to the data.

Figure 9 Center-of-mass translational energy distribution derived from the forward convolution fit the data in Figures 8, 10, and 12. Arrows indicate the thermodynamic maximum available energies for formation of singlet and triplet methylene.

Figure 10 Product time-of-flight spectra of m/e 12 (CH^+) at laboratory angles of (a) 10° and (b) 14° . The open circles represent data. The dotted line is the contribution from acetone dissociation, the dashed line is the contribution from CH_3 dissociation using the $P(E_T)$ in Figure 9, and the solid line is the total fit to the data.

Figure 11 TOF spectrum of m/e 1 (H^+) at a laboratory angle of 90° . The open circles represent data with the time-dependent background subtracted. The solid line represents the forward convolution fit using the $P(E_T)$ in Figure 4.

Figure 12 TOF spectrum of m/e 2 (H_2^+) at 90° . The open circles are the data with the laser on and the solid line is the data taken with the laser off.

Figure 13 Laboratory angular distribution of the CH_2 photofragments detected at m/e 12 (C^+) with the laser polarized at 0° . The lines are simulated angular distributions assuming three different values of the anisotropy parameter (see text).

Figure 14 Rydberg H atom time-of-flight spectrum for methyl radical dissociation at

212.8 nm.

Figure 15 Center-of-mass translational energy distribution derived from the forward convolution fit to the data in Figure 14.

Figure 16 TOF spectra of m/e 13 (CH^+) at laboratory angles of 8° and 10° . The open circles represent the data. The solid line is the forward convolution fit using the $P(E_T)$ shown in Figure 15.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

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Figure 11

Figure 12

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Figure 15

Figure 16