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HIGH-RESOLUTION PHOTOFragmentation-TRANSLATIONAL SPECTROSCOPY

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Publication Date
1986-09-01
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September 1986
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1. Background Information

The advancement of lasers in combination with the molecular beams technique has made a great impact on our understanding of primary photophysical and photochemical processes in the past twenty years. The ever increasing spectral and time resolution, in addition to the power and range of wavelengths available, have made it possible to excite molecules selectively and with high efficiency, to study their time evolution and to carry out state specific detection of dissociation products. The supersonic molecular beam source, which provides large densities of molecules with translational and rotational temperatures below a few degrees Kelvin, has provided many new possible ways to study photochemical processes under isolated conditions.

While a number of photodissociation studies measure properties in transition between excitation and dissociation,[1] the vast majority determine so-called asymptotic properties of the dissociation process, either measuring product quantum state distributions or velocity and angular distributions of the products. For state specific detection
of smaller fragments, especially diatomics, laser induced fluorescence (LIF), multiphoton ionization (MPI) and coherent raman scattering (CRS) have provided extremely detailed information on the dynamics of photodissociation.\(^2\) Unfortunately, the vast majority of photochemically interesting product molecules can either not be detected by these methods or it is impractical to derive useful information from their spectra. The reasons for this are manifold. Consider LIF for example, where in order to determine product state distributions, quite a number of requirements must be satisfied. First, one must have a good knowledge of the identities of all the products of the photolysis. Second, these molecules must have optical transitions that can be efficiently probed. Third, their line strengths and transition frequencies must be well characterized. Finally, the excited state produced by the probe laser must have a fairly large quantum yield for emission of a photon as opposed to dissociation or some other dissipation process.

For most polyatomic radicals, one or more of these conditions cannot be satisfied. Even when they are, because of the large excess energy disposed into the products, one may need to know a great deal more than what is provided by conventional room-temperature spectroscopy. In addition for highly internally excited molecules, the inverse density of states may be much smaller than the laser bandwidth, preventing resolution and identification of the state distribution of interest.
The detection of primary dissociation products using mass spectrometers with electron impact ionization has the advantage of very high sensitivity, <1 molecule/cc, and universal detection ability. In the past the dissociation inherent to the ionization process has made it difficult to experimentally distinguish between daughter ions from electron impact induced dissociative ionization and photon induced fragmentation and has limited the usefulness of mass spectrometry in the identification of primary photoproducts. An example of this can be found in the infrared multiphoton dissociation (IRMPD) of 2-nitropropane.\[3\]

In this system there are two possible dissociation pathways:

\[
\begin{align*}
\text{C}_3\text{H}_7\text{NO}_2 \xrightarrow{\text{hv}} & \left[\text{C}_3\text{H}_7\text{NO}_2\right]^+ \rightarrow \text{C}_3\text{H}_7 + \text{NO}_2 & \text{I} \\
\text{C}_3\text{H}_7\text{NO}_2 \xrightarrow{\text{hv}} & \left[\text{C}_3\text{H}_7\text{NO}_2\right]^+ \rightarrow \text{C}_3\text{H}_6 + \text{HONO} & \text{II}
\end{align*}
\]

Mass spectrometric detection of laser dependent signal at m/e=46, NO\(_2^+\), and m/e=43, C\(_3\text{H}_7^+\), would be a good indication of the presence of channel I; unfortunately, because of the presence of C\(_3\text{H}_7\) which also gives C\(_3\text{H}_6^+\) daughter ions, the detection of m/e=42 would not necessarily mean that process II were present. Additionally, because HONO appears only as NO\(^+\) at m/e=30, a strong peak in the mass spectrum of NO\(_2\), it would be indistinguishable by simple mass spectrometric methods. In order to determine whether the observation of a low m/e signal is due to a neutral fragment of that mass number or merely the ionizer induced ionic fragment of a heavier neutral component, analytical chemists tackling the problem of complex
mixture analysis, often have to use a hybrid technique combining gas chromatography with mass spectrometry (GC/MS), for example.

It is a general feature of photodissociation that products from different decomposition pathways appear with different recoil velocities, governed not only by the interaction potential and the propensity of the system to channel energy into translation, but dependent also upon the relative masses of the recoiling fragments. Therefore, if one performs high resolution measurements of the product velocity distribution, in combination with mass spectrometric detection, it is not at all essential that the photoproducts appear at their parent m/e's. This is like GC/MS on the µsec time scale using vacuum as the chromatography column!

In practical terms, we accomplish this by producing a molecular beam, in which all of the molecules of interest have approximately the same direction and velocity. By firing a pulsed laser at the beam, only dissociation products, which can recoil away from the beam direction, are observed in the mass spectrometric detector, which is facing the beam/laser intersection region but is situated away from the beam direction. By measuring the arrival time distribution of the neutral photoproducts over a calibrated flight length as a function of detector angle away from the beam direction, the translational energy distribution and angular distribution of the products can be obtained.

In the IRMPD of nitropropane mentioned earlier, because of a substantial activation barrier to molecular elimination and the particular dynamics of this molecule, HONO is produced with much more
translational energy than NO\textsubscript{2} and can be clearly resolved in the "GC/MS", monitoring NO\textsuperscript{+} at m/e=30, shown in fig. 1d. By resolving the two components, it is possible to quantitatively determine the relative probabilities of reactions I and II.

The sensitivity and resolution of the molecular beam photofragmentation translational spectroscopic method, originally introduced by Wilson and coworkers\cite{4}, has been improved immensely using second generation molecular beam machines in our laboratory over the last ten years. The determination of collision-free dissociation pathways and their relative probabilities even for quite large polyatomic molecules with complex sequential decomposition processes is a standard capability of this technique\cite{5}. This was a critical feature of recent experiments that demonstrated bond selective photochemistry\cite{6}. Secondary photodissociation of primary free radical photoproducts can also be resolved by this method and can yield interesting information on free radical photochemistry\cite{7}.

Because of total energy conservation, the translational energy distribution directly gives the product internal energy distribution. For example in the photodissociation of O\textsubscript{3}\cite{8} and CH\textsubscript{3}I\cite{9}, the vibrational population distribution of O\textsubscript{2}(\textsuperscript{1}A) and the CH\textsubscript{3} umbrella mode vibrational distribution, respectively, have been determined.

In addition, the high resolution available makes the determination of very accurate thermochemical data possible\cite{10}. The small or non-existent absorption cross sections at the energy
Fig. 1. **TOF Spectra for the IRMPD of 2-nitropropane:** The lab angle is 10° from the molecular beam. The arrows indicate the beam arrival if it were to appear at this angle. The dash-dotted line is from molecular elimination while the dashed line is from simple-bond rupture. a) m/e=46, NO$_2^+$ from NO$_2$. b) m/e=43, C$_3$H$_7^+$ from C$_3$H$_7$. c) m/e=42, C$_3$H$_6^+$ from C$_3$H$_7$ and C$_3$H$_6$. d) m/e=30, NO$^+$ from HONO and from NO$_2$. 
Fig. 1
threshold for dissociation of most molecules and the substantial barriers to dissociation in many molecules make it impossible to measure dissociation energies by observing the photodissociation yield as a function of wavelength. However, by photodissociating molecules well above the dissociation threshold, where the absorption cross section is substantial and by measuring the maximum release of translational energy of the products, i.e. the translational energy corresponding to production of ground state products, the heats of formation of important free radicals can be obtained. Although the resolution of the translational energy measurement is limited to ~1 kcal/mol, it avoids the complications of using large thermochemical cycles typical of photoionization threshold approaches which can introduce large systematic uncertainties. High resolution TOF measurements can also yield thermochemical data on excited electronic states of free radicals which are commonly formed in photodissociation. Fig. 2 shows the way in which the singlet-triplet splitting of methylene was determined from the photodissociation of ketene. [11]

One very exciting additional fact is that the translational energy distribution reflects the forces present during dissociation and as such can be used to glean very clear information on the nature of the potential energy surface (PES). For instance molecular elimination from formaldehyde channels a large amount of the available energy into translation, whereas simple bond rupture to form HCO + H does not. This is due to a large barrier in the exit channel of the
Fig. 2. The Singlet-Triplet Splitting in Methylene: Two experiments at different photon energies were performed. The two values of the maximum release of translational energy were measured, marked $E_T$. $\Delta E$ is the derived singlet-triplet splitting. All energies are in kcal/mol.
PES which efficiently channels energy into translation through a strong repulsion between the newly formed products.

The unimolecular decomposition of vibrationally excited molecules is another problem ideally suited to study by photofragmentation translational spectroscopy. Early experiments on thermal decomposition were by necessity done under collisional conditions since collisions were the pumping mechanism. Today, it is possible to study pyrolysis under collision free conditions using infrared multiphoton excitation to deposit a large amount of energy into the vibrational degrees-of-freedom of a polyatomic molecule. Simple bond rupture reactions,\textsuperscript{[12]} three and four center elimination reactions,\textsuperscript{[13]} as well as concerted dissociations that proceed through five and six membered rings have been systematically studied.

In the past two years, we have constructed a new molecular beam apparatus specifically designed and optimized for the study of photodissociation processes. This apparatus is configured with a rotating source and a fixed detector and incorporates some new ideas for background reduction and resolution enhancement. The greatly increased resolution and reduced background have enhanced our ability to study many of the questions to which we have already alluded. A few of the most recent examples will be discussed in this article.

2. Experimental Apparatus

Fig. 3 shows a detailed, scaled drawing of the instrument used in all of the experiments to be described. A continuous molecular beam
Fig. 3 The Rotating Source Machine:

is produced at 1 by expanding the molecule to be studied, diluted in rare gas and typically at a pressure of 200-500 torr through a 125 μm nozzle. The nozzle can be heated with coaxial heating wire, shown at 2, to increase the beam velocity and to remove clusters that can form due to the low internal temperature of the molecules in the beam. The pressure in the molecular beam source chamber is ordinarily ~10^-4 torr when the beam is running and is pumped by two 6" diffusion pumps, one of which is shown at 10, providing a total of ~5000 L/s pumping speed. A region of differential pumping between the source region and the main chamber helps to carry away the large gas load of the molecular beam source so that the operating main chamber pressure is ~10^-7 torr. The pressure in the main chamber is maintained by a 10" Edwards Diffstack, 9, and the cryopumping action of several large liquid nitrogen cooled copper panels, 6. The source and differential pumping chambers are welded to a rotating vacuum seal and can themselves rotate about point 5, where the molecular and laser beams cross. The velocity of the parent molecular beam can be measured with the retractable slotted chopping wheel shown at 8. This entire assembly can slide downward, out of the way of the detector, without breaking vacuum when the photodissociation experiment is performed.

The laser, either a Lambda-Physics EMG103MSC excimer or a GENTEC TEA CO₂, is focussed by the lens at 4 and propagates along the beam source rotation axis.

The pulse of photons intersects the molecular beam at 5 and induces dissociation. A small angular fraction of the photoproducts
travels through the acceptance apertures of the detector, traversing an average of 36.75 cm through two ultrahigh vacuum differential pumping chambers before arriving at the ionizer. The ionization chamber is equipped with an electron impact Brink's ionizer, with an ionization length of 5 mm.\[14\] This gives a velocity resolution of 1.4 percent \((\Delta L/L = 0.5/36.75 = 0.014)\). The walls of the ionization chamber are cooled with liquid nitrogen to reduce background. The ions formed at \(11\) are mass analyzed by an electric quadrupole MS at \(12\), and counted by a Daly-type ion counter, \(15, 16, 18\). The differential pumping regions of the detector and the ionization chamber are pumped by 360 L/s grease-sealed turbomolecular pumps, \(17\), and a magnetically suspended 500 L/s turbomolecular pump, \(13\), respectively. The absence of any lubricating fluid in the magnetically suspended pump provides a very clean vacuum.

A liquid helium cooled collimation slit at \(3\) reduces background originating in the main chamber by about a factor of 10. For many experiments the limit to the background reduction possible with differential pumping is due to those molecules which pass directly through the defining slits from the main chamber to the ionizer after scattering from other background molecules or after desorbing from a surface within the viewing window of the detector. The "background gobbler" at \(3\) ensures that all surfaces within the detector viewing window are at \(-30^\circ K\). Under our experimental conditions where the main chamber is held at \(10^{-7}\) torr, the mean free path exceeds 100 meters. Almost all of the molecules which pass directly through the
defining slits have to bounce off the surface in front of the
detector. Cooling this surface to 300K essentially eliminates this
source of background.

The detector can be sealed off with the gate valve assembly, 7,
when the main chamber needs to be vented. The entire detector with
all of the pumping equipment is mounted with ball bearing rollers on
two stainless steel rails and can be rolled away from the main chamber
under vacuum for intense baking out. This detector design is
especially effective for reducing hydrocarbon background. A partial
pressure for CH₄ of 10⁻¹³ torr is easily obtained in our apparatus
and with careful handling, much lower partial pressures are possible.

The TOF spectrum is recorded by triggering a multichannel scaler
with the laser pulse and recording the ion counts at each m/e which
shows detectable signal as a function of arrival time. The typical
time resolution of the experiment is 1-2 μs although we have the
ability to go down to 150 ns when necessary.

3. Laser Selective Photochemistry in CH₂BrI[6]

One of the most exciting topics in modern photochemical research
is the possibility of carrying out bond selective or mode specific
dissociation of polyatomic molecules with a laser. To succeed, two
requirements must be satisfied. First, it must be possible to put the
photon energy specifically into the bond that is to be broken.
Second, processes that destroy the specificity of the excitation must
be slow compared to the rate of dissociation. Many attempts in the
past have focussed on the photochemical behaviour of predissociative excited electronic states and the excitation of molecules through a specific vibrational degree of freedom by multiphoton processes. Predissociation gives rise to simple structured spectra where the first requirement above can be easily satisfied. However, it has been found essentially uniformly, that energy redistribution occurs very rapidly compared to dissociation both in predissociation of excited electronic states[15] and in IRMPD.[16] This is not at all surprising since for predissociating states by definition energy redistribution, IVR, IC or ISC must precede dissociation.

In contrast to the spectra of predissociating molecules, haloalkanes have very broad UV spectra because the upper electronic PES's are repulsive and do not support bound states. The electronic spectra of CH₂BrI has two broad but well separated bands. One, peaking at 255 nm, is excitation of a non-bonding electron on the I atom to an anti-bonding orbital of the C-I bond, while the other, peaking at 215 nm, is a Br non-bonding electron going to a C-Br anti-bonding orbital. Consequently, despite the lack of discrete structure in these spectra, specific excitation is still possible. Furthermore, since dissociation from the excited state will occur within one vibrational period, \(<10^{-13} \text{ s}\), CH₂BrI is a good candidate for bond selective photochemistry since dissociation might be much faster than intramolecular energy transfer.
Fig. 4 shows the TOF data for the photodissociation of CH₂BrI at 210 nm, exciting an electron on the C-Br bond. The solid curve that fits the data in the CH₂I⁺ TOF spectrum and the dashed curve that fits the fast peak in the Br⁺ TOF spectrum are calculated TOF spectra based on the following reaction:

\[ \text{CH}_2\text{BrI} \xrightarrow{210 \text{ nm}} \text{CH}_2\text{I} + \text{Br} \quad \text{III} \]

This means that the arrival time of the CH₂I, ~380 μs, and the arrival time of the Br atom, ~280 μs, correspond to velocities in the center of mass frame of reference that conserve linear momentum between the products of the above reaction. The fact that linear momentum must be balanced, provides a powerful way to sort out which peaks in the spectra come from the same dissociation process and is used over and over in the analysis of TOF data. For instance, it is clear that the fast peak in the I⁺ TOF spectrum is merely an electron impact induced fragment of the CH₂I radical since it arrives at exactly the same time as the fast peak in the CH₂I⁺ TOF spectrum, ~380 μs. The very slow portions of the I⁺ and Br⁺ TOF spectra are due to three body dissociation of CH₂BrI to CH₂ + Br + I, which accounts for 1/3 of the dissociation events. This appears with much less translational energy release since more energy is required to break two bonds. The most exciting result is that no signal appears in the CH₂Br⁺ TOF spectrum meaning that C-I bond rupture does not occur. Since the C-Br bond strength is 68 kcal/mol and the C-I bond strength is 55 kcal/mol, this experiment is the first clear example where the laser is used to selectively break the stronger of two bonds in a molecule.
Fig. 4

TOF Data from the Photodissociation of CH₂BrI: The circles are the data and the curves are the fit to the data based on two center-of-mass translational energy distributions. Refer to text for further explanation.
Fig. 4
It is important to realize that the measurement of the translational energy in this experiment was critical to the successful demonstration of the presence of primary C-Br bond rupture and the absence of C-I bond rupture when CH$_2$BrI is excited at 210 nm. Without this knowledge there would have been no way to distinguish between C-I bond rupture, which was not occurring and the three body dissociation channel. Laser methods could have detected the presence of Br or I or both but they could not have made this subtle distinction.

In a similar attempt to observe bond selective photochemistry in CF$_2$BrCF$_2$I, in which the C-Br and C-I bonds are parallel, C-Br excitation at 193 nm resulted in slightly more C-I than C-Br bond rupture.[17] Apparently, intramolecular electronic energy transfer from the C-Br to the C-I bond occurs very rapidly in this molecule.

4. The Dynamics of the UV Photodissociation of Simple Polyatomic Molecules

By preparing molecules with a narrowband laser, the precise starting point of a photodissociation event can be created and by quantum state specific detection of the products, the distribution of endpoints can be determined. What happens in between is a very interesting question since photodissociation typically involves more than one PES. For small molecules, the increasing accuracy of ab-initio quantum mechanical calculations on excited state PES's, promises to give the most detailed information. However, for moderate and large sized molecules such information is not readily available.
Since the product angular and translational energy distributions reflect the nature of the forces operating between the fragments at the critical moment of dissociation, it is possible to make inferences about the electronic states of the parent involved in dissociation. Fig. 5 compares the translational energy distributions of the products for photodissociation of CH$_2$O$^{[18]}$ and C$_2$H$_2$$^{[7]}$, reactions IV and V, both dissociating after excitation to their lowest electronically excited singlet states.

\[
\text{H}_2\text{CO} \xrightarrow{283.9 \text{ nm}} \text{HCO} + \text{H} + 14 \text{ kcal/mol} \quad \text{IV}
\]
\[
\text{C}_2\text{H}_2 \xrightarrow{193.3 \text{ nm}} \text{HC}_2 + \text{H} + 16 \text{ kcal/mol} \quad \text{V}
\]

The translational energy distribution for reaction IV is qualitatively similar to many simple bond rupture reactions studied by IRMPD. The fact that it peaks near zero, indicates that the dissociation is from an attractive PES without an exit barrier. It was also observed that molecular elimination becomes less important at higher photon energy.$^{[18]}$ RRKM theory predicts reactions with small A-factors, for example molecular eliminations, become less important at higher total energy in comparison to simple bond rupture reactions which have large A-factors and the experimental observation is precisely what would be expected if electronically excited formaldehyde were to undergo internal conversion (IC) to $S_0$ before dissociation. This conclusion is also consistent with a great deal of other experimental and theoretical work.$^{[2(d), 2(e)]}$
Fig. 5  Comparison of the Translational Energy Distributions for the Photodissociation of CH₂O and C₂H₂: The solid curve is for C₂H₂→C₂H + H while the dashed curve is for CH₂O→HCO + H. The labels on the peaks of the solid curve refer to the text.
In contrast, the translational energy distribution for reaction V is qualitatively different. It peaks at ~6 kcal/mol, suggesting that IC to the ground state is unimportant, and rather that the excited electronic state is predissociated by either a repulsive PES or one with an exit barrier.[7] In fact, ab-initio calculations on isoelectronic HCN predict a repulsive PES that is due to the interaction between the departing H atom and the forming closed-shell π orbital all in the plane of the molecule.

In a repulsive dissociation of a rotationally cold molecule, the rotational angular momentum of the products is balanced by the orbital angular momentum of the dissociation so that total angular momentum is conserved. Due to the small mass of the departing H atom and the limited available energy, only a small amount of rotational energy can be acquired by the C_2H fragment. Consequently, the vibronic structure of C_2H is partially resolved in the translational energy distribution and it is possible to make some very detailed conclusions about the product energy distribution. Table I shows the structure of acetylene in its ground state, its electronically excited state, reached after photon absorption and in its "product state", C_2H + H, based on the most recent spectroscopic data. While the C-C bond length and the CCH bending angle change substantially throughout the dissociation process, the C-H bond length changes only slightly. In fact, the changes in C-H bond length are quite a bit smaller than zero point fluctuations. We therefore expect the vibrational energy to appear as C-C stretch and C-C-H bending vibration and assign peak 1 to
Table I
Acetylene's Molecular Geometry
During its Photodissociation

<table>
<thead>
<tr>
<th></th>
<th>C-C Bond Length (Å)</th>
<th>C-C-H Bond Angle (°)</th>
<th>C-H Bond Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_2H_2(X)$ (a)</td>
<td>1.2047</td>
<td>180</td>
<td>1.0585</td>
</tr>
<tr>
<td>$C_2H_2(\tilde{A})$ (b)</td>
<td>1.383</td>
<td>120.2</td>
<td>1.08</td>
</tr>
<tr>
<td>$C_2H(X)$ (c)</td>
<td>1.2165</td>
<td>180</td>
<td>1.0464</td>
</tr>
</tbody>
</table>

a. Ref. 19
b. Ref. 20
c. Ref. 21
the vibrationless state of \( \text{C}_2\text{H} \) and peak 2 to excitation of 1 quantum of C-C stretch. The rising edge of peak 1 at 16.25 kcal/mol and that of peak 2 at 11 kcal/mol is within 100 cm\(^{-1}\) of the recently measured \( \nu_3 \) fundamental in \( \text{C}_2\text{H} \).\(^{[22]}\) Unfortunately, the bending fundamental is too low, 250 cm\(^{-1}\), to resolve.\(^{[22]}\) While it is clear that the C-C stretch and the CCH bend are highly excited in the photolysis; an unambiguous interpretation of peaks 3, 4, and 5 will require further theoretical and experimental effort. There appear to be two quite reasonable possibilities. One proposes that both electronic states of \( \text{C}_2\text{H} \) can be formed in roughly equal amounts by the photolysis. Peaks 3, 4, and 5 of fig. 5 are then assigned to \( \nu=0, 1 \) and 2 of the excited \( \pi \) state bending vibration. This assignment implies that the adiabatic excitation energy is \(~3000 \pm 200\) cm\(^{-1}\) while the \( \pi \) electronic state bending fundamental, \( \bar{\nu} \), is in the neighborhood of 550 cm\(^{-1}\).

This would appear to be the most commonplace interpretation; however, it should be stated in no uncertain terms that this is not the only possible explanation of the observed translational energy distribution. A very interesting alternative supposes that the barrier to formation of \( ^2\pi \text{C}_2\text{H} \) in excited state acetylene is high enough to essentially prevent formation of the excited state. Because it is expected that to a very good approximation, the fragmentation of excited state acetylene occurs in a plane, dynamically it is very improbable to produce \( \text{C}_2\text{H} \) with angular momentum about the C-C internuclear axis. This is especially true for the slower part of the
translational energy distribution. Because of the cylindrical symmetry of the bending vibrational motion, only the even quanta of bending vibration can occur with vibrational angular momentum about the C-C axis equal to zero. Therefore, it is plausible that only even quanta of $v_2$ could be excited in the photodissociation process. Since the harmonic frequency has been found to be $250 \text{ cm}^{-1}$ and a negative anharmonicity is expected,[23] an energy separation of $550 \text{ cm}^{-1}$ is entirely consistent with this explanation. The disappearance of the progression at larger translational energy could be explained by the increase of product rotation at higher H atom recoil velocities or by the inherently poorer experimental resolution at larger observed lab velocities.

In contrast to acetylene, the photodissociation of vinylbromide, $\text{C}_2\text{H}_3\text{Br}$, involves substantial product rotational excitation. The translational energy distribution for formation of ground state vinyl radical at 193 nm is shown in fig. 6. Because the excited state dissociates promptly, $\sim10^{-14} \text{ s}$, it is constrained to dissociate from geometries close to the equilibrium structure of the ground electronic state, implying a non-zero departing impact parameter. This fact, the large mass of the Br atom, the large release of translational energy and the stiffness of the $\text{C}_2\text{H}_3$ radical, imply the validity of a pseudotriatomic rigid product model for a basic understanding of the dissociation dynamics. In this model energy is only allowed to appear in rotation and translation. The partitioning of energy between the two is determined by the C-C-Br angle at dissociation. We can directly
Fig. 6  The Translation Energy Distribution for the Formation of Vinyl Radical from the Photodissociation of Vinyl Bromide at 193 nm. The data that this is derived from will be presented in section 5, fig. 8.
invert the measured translational energy distribution to get the half collision opacity function, shown in fig. 7. One can see that the opacity function is dominated by dissociation near a C-C-Br bond angle of $120^\circ$, as expected. However, due to the much smaller bending force constant of the excited PES it is possible for dissociation to occur with quite a deviation from the most favoured angle. This gives rise to the very long high energy tail on the translational energy distribution which gradually goes to zero as the probability for near collinear dissociation is vanishingly small.

5. The Determination of Free Radical Heats of Formation

Because of their role as reaction intermediates, free radicals are one of the most interesting subjects of chemical research and it is very important to have accurate thermochemical data about them. This is particularly true for the prediction of chemical reactivity of a radical in near thermoneutral reactions where a change in the heat of reaction of only a few kcal/mol can have a drastic effect on the rate. Because of the ease of detecting ions, much of present-day data is derived from threshold photoionization measurements. For example, by measuring the difference in the thresholds of reactions VI and VII and by knowing the ionization potential for Br, 11.847 eV, one can obtain the ionization potential for the $\text{C}_2\text{H}$ radical.$^{[24]}$

\[
\begin{align*}
\text{C}_2\text{HBr} & \quad 15.56 \text{ eV} \quad \rightarrow \quad \text{C}_2\text{H}^+ + \text{Br} + \text{e}^- & \text{VI} \\
\text{C}_2\text{HBr} & \quad 15.90 \text{ eV} \quad \rightarrow \quad \text{C}_2\text{H} + \text{Br}^+ + \text{e}^- & \text{VII}
\end{align*}
\]
Fig. 7  The Opacity Function for C-Br Bond Rupture in the Photodissociation of Vinyl Bromide at 193 nm: $\Theta$ is the C-C-Br bond angle.
Combining this with the measurement of the threshold of reaction VIII[25]

\[ \text{C}_2\text{H}_2 \xrightarrow{17.37 \text{ eV}} \text{C}_2\text{H}^+ + \text{H} + \text{e}^- \quad \text{VIII} \]

yields the C-H bond energy in acetylene and the heat of formation of the C\(_2\)H radical. By using high resolution VUV monochromators, precisions of one kcal/mol are obtainable.

Despite the high precision, there are a number of possible systematic difficulties with threshold measurements that give rise to large deviations between experiments, far outside of the stated error bars. First of all, since it is difficult to anticipate the nature of excited states of the molecule of interest at energies as high as 15 eV, it is often an implicit assumption that ion formation is possible at the thermodynamic threshold. Problems may result from barriers to dissociation on the excited PES's or wave function symmetry restrictions which prevent the formation of ground state products.

Secondly, ordinarily only positive ions are detected. Since most atoms and molecules have finite electron affinities, for any dissociative photoionization there will be the possibility of an ion pair production process that may form the positive ion of interest slightly below the true threshold.

Thirdly as with any thermodynamic determination, in photoionization threshold measurements it is often necessary to rely on other thermodynamic determinations in order to build a thermochemical cycle, the missing leg of which is the process of interest. These
cycles can be very complex. For example in the above photoionization experiment, the cycle begins at $\text{C}_2\text{HBr} + \text{H}$. The energy required to go to $\text{C}_2\text{H}^+ + \text{H} + \text{Br} + \text{e}^-$ is measured, process VI, and the energy released in going to $\text{C}_2\text{H}_2 + \text{Br}$ is obtained from another experiment, process VIII. The well known IP of Br provides the energy required to make $\text{C}_2\text{H}_2 + \text{Br}^+ + \text{e}^-$ and the missing leg of the cycle takes us to $\text{C}_2\text{H} + \text{H} + \text{Br}^+ + \text{e}^-$. Finally the second measured step, process VII takes us back to the beginning. Since the energy change around the cycle is zero the energy of the missing leg can be gotten.

While this strategy provides the experimentalist with an endless number of possible approaches to the heat of formation of a given molecule, each additional leg of a thermochemical cycle is an opportunity for the accumulation of uncertainty in the data. For the case of $\text{C}_2\text{H}$, the problem is one of combinatorial possibilities. All of the possible combinations of the three IP determinations of $\text{C}_2\text{H}$, the two determinations of the threshold of process VIII and the implied acetylene C-H bond energy are tabulated in table II.

In photoelectron spectroscopy, this sort of difficulty has been overcome by photoionizing the parent well above threshold where the absorption is strong and measuring the maximum release of translational energy in the photoelectron. In this way, the ionization potential can be obtained and in addition, the ionization potentials for excited states of the ion can be determined in high resolution measurements.\[29\] However, photoelectron spectroscopy is not as useful in the determination of dissociative ionization energies since the translational energy of the molecular fragments is not measured.
Table II
Combinatorial Possibilities of the C-H Bond Energy in Acetylene

<table>
<thead>
<tr>
<th>Combination</th>
<th>C-H Bond Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>DWM a WS</td>
<td>133 kcal/mole ± 12 kcal/mole</td>
</tr>
<tr>
<td>DWM a MB</td>
<td>135 kcal/mole ± 1.4 kcal/mole</td>
</tr>
<tr>
<td>DWM a OD</td>
<td>125 kcal/mole ± 1.4 kcal/mole</td>
</tr>
<tr>
<td>ON a WS</td>
<td>116 kcal/mole ± 1.2 kcal/mole</td>
</tr>
<tr>
<td>ON a MB</td>
<td>118 kcal/mole ± 1.8 kcal/mole</td>
</tr>
<tr>
<td>ON a OD</td>
<td>107 kcal/mole ± 1.8 kcal/mole</td>
</tr>
</tbody>
</table>

where:

DWM[25] and ON[26] are for the dissociative photoionization threshold of acetylene.
WS[27], MB[24] and OD[28] are for the determination of ionization potential of C2H.

This work: D_0(C_2H-H) = 132 ± 2 kcal/mol
We have been exploring the reliability of an analogous technique for the determination of bond energies. For instance, the heat of formation of C₂H can be determined by measuring the maximum release of translational energy in the photodissociation of acetylene, reaction V. By studying the nozzle temperature dependence of the TOF spectra, the fastest C₂H, marked H in fig. 5, was determined to be due to vibrationally excited acetylene that was not fully relaxed in the expansion. Therefore the maximum release of translational energy is 16 ± 2 kcal/mol. By taking the difference between this and the photon energy, 148 kcal/mol, it is easily found that the C-H bond energy in acetylene is 132 ± 2 kcal/mol.

While our result is a rigorous upper limit to the bond energy, the experiment of Abramson et. al. provides a lower limit.[30] They performed anti-crossing experiments by monitoring the time resolved fluorescence quantum beats of S₁ acetylene at a total energy of 129.5 kcal/mol and tuning triplet levels into resonance with the monitored level using a magnetic field. The large density of triplet states that was observed implied strong mixing of the triplet with S₀. In order for quantum beats to exist between S₁ and S₀, the bond energy must be greater than 129.5 kcal/mol.

Very recently using a synchrotron radiation source, the threshold for proton formation from acetylene, C₂H₂ → C₂H + H⁺, has been measured.[31] Since, the IP of H is well known, this experiment gives the most direct measurement of the C-H bond energy in acetylene by photoionization methods. The synchrotron experiments conclude that
the C-H bond energy is 132 ± 2 kcal/mol, in excellent agreement with the photofragmentation work.

As has already been discussed, the assignment of the translational energy distribution in fig. 5 is not completely unambiguous. However, it seems likely that the peaks labelled 3, 4, and 5 are due to the excited $^2\pi$ electronic state of C$_2$H. If this is true the data implies that the adiabatic excitation energy to the excited electronic state is 3000 cm$^{-1}$, the energy difference between the rising edge of peak 1 and peak 3. This value has been particularly difficult to obtain because of extensive vibronic coupling between the two electronic states which greatly complicates the spectrum.[32]

Another very important free radical is the vinyl radical, the heat of formation of which determines the C-H bond energy in ethylene. Over the years, many attempts to determine the vinyl radical's heat of formation have been made, the results of which vary over about 13 kcal/mol.[33] By photodissociating C$_2$H$_3$Br and measuring the maximum release of translational energy, it was hoped that a more accurate determination could be made.

The C$_2$H$_3$ radical TOF spectrum is shown in fig. 8. First of all, it is clear that there are two components. These are due to the lowest two electronic states of C$_2$H$_3$.

$$C_2H_3Br \xrightarrow{193.3 \text{ nm}} C_2H_3(\tilde{X},\tilde{A}) + Br$$

The long high energy tail on the ground state translational energy distribution used to fit the fast component of the TOF spectrum is
Fig. 8  The TOF Distribution for the Vinyl Radical from the Photodissociation of Vinylbromide at 193 nm: The circles are the data points. The dashed line shows the contribution from ground electronic state vinyl (Translational energy distribution in fig. 6), while the dotted line shows the contribution from electronically excited state.
shown in fig. 6. The maximum release of translation energy, 71 kcal/mol, yields an upper limit to the heat of formation of $71 \pm 3$ kcal/mol.

One of the assumptions implicit in this method is that all of the available energy can appear as translation in some of the products. While this assumption was found empirically to be a good one in acetylene, vinylbromide is not an ideal case and as such is a much tougher test of this assumption for several reasons. First, the excess energy is about four times larger here than in acetylene. In addition, for a large release of translational energy, which is what we are specifically interested in, it is very improbable for an appreciable fraction of the energy not to appear as rotation. This is due to the large mass of the Br atom, and the non-zero exit impact parameter implied by the structure of the excited state. See section 4.

In order to evaluate the possible error associated with the ground state fragment assumption, we compared this result to a very accurate calibration experiment based on the crossed-beam reaction $F + C_2D_4 \rightarrow C_2D_3 + DF(v' = 4)$.[34] In this experiment, the maximum release of the translational energy yields the heat of formation of the $C_2D_3$ radical, which can easily be converted to the heat of formation of $C_2H_3$. Fig. 9 shows the angular distribution for the above reaction and the fit to the data assuming a maximum release of translational energy of $1.3 \pm 0.5$ kcal/mol. This particular experiment is very sensitive to the true value and yields a heat of formation for the vinyl radical of $66.7 \pm 0.5$ kcal/mol, slightly lower than the
Angular Distribution of the DF Product from the Reaction of $F + C_2D_4 \rightarrow C_2D_3 + DF(v' = 4)$: The circles are the data points. The solid line shows the best fit $P(E_T)$ assuming 1.3 kcal/mol maximum translational energy. The long-dashed line assumes 0.8 kcal/mol and the short-dashed line assumes 1.8 kcal/mol.
photodissociation experiment as expected. The fact that it is only 4.3 kcal/mol lower than the photodissociation result gives us very valuable information on the validity of the ground state fragment assumption. As we would expect, it is important for the departing atom to be light, the excess energy must not be too large, and we should be suspicious of our ability to derive the maximum translational energy when the translational energy distributions tails away very gradually.

Turning to the translational energy distribution for the excited state radical, a careful inspection of the inset of fig. 8. shows a pronounced, discontinuous change in the slope of the data at a translational energy release of 29 kcal/mol. Since there is about half as much excess energy, even if the same proportion of rotational excitation prevents the formation of ground state fragments, the error should be substantially smaller than the 4.3 kcal/mol found for the ground state. This data yields a heat of formation for the electronically excited vinyl radical of 113 ± 1.5 kcal/mol.

Recently, the X→A absorption spectrum was measured by Hunzicker and a C-C stretching progression was observed.[35] However, an absolute assignment of the lines was impossible since small Franck-Condon factors prevented the observation of the electronic origin. By using the derived $T_{oo}(X→A)$, 46 ± 1.5 kcal/mol, we were able to make the assignment of their spectrum shown in table III. If this assignment were correct, the extrapolated $T_{oo}(X→A)$ from ref. 35 would be 46.9 kcal/mol.
Table III
Assignment of the Vibronic Transitions of the Vinyl Radical

<table>
<thead>
<tr>
<th>Observed Transition</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(16,414) cm</td>
<td>0→0</td>
</tr>
<tr>
<td>(17,616)</td>
<td>0→1</td>
</tr>
<tr>
<td>(18,818)</td>
<td>0→2</td>
</tr>
<tr>
<td>20,020</td>
<td>0→3</td>
</tr>
<tr>
<td>21,222</td>
<td>0→4</td>
</tr>
<tr>
<td>22,427</td>
<td>0→5</td>
</tr>
<tr>
<td>23,629</td>
<td>0→6</td>
</tr>
<tr>
<td>24,815</td>
<td>0→7</td>
</tr>
<tr>
<td>25,981</td>
<td>0→8</td>
</tr>
<tr>
<td>27,137</td>
<td>0→9</td>
</tr>
</tbody>
</table>

a. Ref. 35. Values in parentheses are extrapolated.

b. Excitation from v=0 of the ground electronic state to v=m of the C–C stretch in the excited electronic state.
Since the photodissociation determination was fairly accurate, even in a very unfavourable case, it appears that the method of photofragment spectroscopy has a bright future in regard to the determination of thermochemical quantities. The success of this method hinges on its simplicity, since the thermochemical cycles employed in these experiments could not be smaller. Moreover, this is one of the very few ways of deriving accurate thermodynamic data for excited electronic states of free radicals.

In addition to the method of measuring the maximum release of translational energy, the C-X bond energies in quite a number of halogen containing free radicals have been obtained by a somewhat different approach, using the photofragmentation technique. By photodissociating dihalogenated alkanes, for example CH₂ClCH₂I at 248 nm the C-I bond is broken and vibrationally excited CH₂ClCH₂ radicals are formed with a distribution of internal energies.[36] Radicals observed at short arrival times corresponding to a large release of translational energy, are the internally coldest and can be easily detected. By determining the minimum translational energy release, i.e. the maximum internal energy, at which the free radical can be detected, the energy required to remove both halogens from the dihalogenated alkane is obtained. Since C-I bond energies are fairly similar from one molecule to another, the C-Cl bond energy in the free radical is obtained. The results for a number of such molecules are given in table IV.[37]
Table IV

Carbon, Halogen Bond Energies in a Number of Halogen Containing Free Radicals

<table>
<thead>
<tr>
<th>Free Radical</th>
<th>C-X Bond Energy(^{(a)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_2)CH(_2)-Cl</td>
<td>19.5 ± 1 kcal/mol</td>
</tr>
<tr>
<td>CF(_2)CH(_2)-Br</td>
<td>11.7 ± 2</td>
</tr>
<tr>
<td>CF(_2)CF(_2)-Br</td>
<td>21.3 ± 1</td>
</tr>
<tr>
<td>CF(_2)CF(_2)-I</td>
<td>8.1 ± 1.5</td>
</tr>
</tbody>
</table>

\(^{(a)}\) Refer to ref. 37 for details.
6. Collision Free Pyroysis Experiments

The discovery of collision-free IRMPD was first thought to signal the dawning of a new age of photochemistry, where chemists would be able to tailor reactions based on the ability to specifically and directly deposit vibrational energy into a chosen vibrational degree of freedom. This hope rested upon the assumption that IVR would be slower than the IR pumping rate and the dissociation rate. It later became fully understood that this assumption was wrong by several orders of magnitude for molecules excited to near their dissociation limits. That is, under favourable circumstances one could deposit IR photons at a rate of $10^9$/s, but for polyatomic molecules near their dissociation limit, IVR proceeds on a picosecond time scale.

Still, the death knell of mode specific chemistry was the harbinger of a greatly increased understanding of unimolecular decomposition. The application of statistical theories of dissociation rates, especially RRKM theory, provided a quantitative connection between thermodynamics and kinetics and could also predict the product energy distributions for many reactions. For example, by knowing the total internal energy, RRKM theory can accurately calculate the translational energy distribution of simple bond rupture reactions with no exit barrier in the PES. The dynamics of concerted molecular elimination reactions cannot, however be understood with RRKM theory. Because of the substantial exit barrier in the PES, a great deal of the available energy gets channelled into translation at the expense of vibration.

Because of picosecond IVR, the internal distribution of vibrational energy created by IRMPD is not substantially different than that produced in
collisional pyrolysis experiments. So by using a CO\textsubscript{2} laser in a molecular beam, it is possible to "heat" a molecule in a collision free environment. This allows the unambiguous determination of primary dissociation mechanisms.

For instance, reaction X has always been assumed to be the only primary dissociation channel in the thermal decomposition of nitromethane.

\[ \text{CH}_3\text{NO}_2 \xrightarrow{\Delta} \text{CH}_3 + \text{NO}_2 \quad \text{X} \]

The TOF spectra for the collision free thermal decomposition of nitromethane, studied by molecular beam IRMPD, is shown in fig. 10. Signal is observed at m/e = 46, 30 and 15, as expected from reaction X. In addition however, substantial signal at m/e=29 indicates the formation of methoxy radical, reaction XI.

\[ \text{CH}_3\text{NO}_2 \xrightarrow{\text{hv}} [\text{CH}_3\text{NO}_2]^\dagger \rightarrow [\text{CH}_3\text{ONO}]^\dagger \rightarrow \text{CH}_3\text{O} + \text{NO} \quad \text{XI} \]

Because of the lower endothermicity of reaction XI, the signal at m/e=29 appears with slightly more translational energy. By careful inspection of the m/e=30 TOF spectrum, it is clear that the reaction partner NO is also appearing. The branching ratio between X and XI can be calculated from the ionization cross sections, fragmentation patterns and Jacobian transformation factors between the lab frame and the center of mass frame. The result of such analysis shows that .38 of the dissociation events follow channel XI under our experimental conditions. This was the first observation of the unimolecular isomerization of CH\textsubscript{3}NO\textsubscript{2} into CH\textsubscript{3}O + NO.\cite{38}
Fig. 10  TOF Data from the IRMPD of

$\text{CH}_3\text{NO}_2$: The lab angle is $10^\circ$
from the molecular beam. The arrows
indicate the beam arrival if it were
to appear at this angle. The
dash-dotted line is from
isomerization while the dashed line
is from simple-bond rupture. The
circles are the data and the curves
are the fit to the data based on two
$P(E_T)$'s. a) m/e=46, NO$_2^+$ from
NO$_2$. b) m/e=15, CH$_3^+$ from
CH$_3$. c) m/e=30, NO$^+$ from NO$_2$
and NO. d) m/e=29, HCO$^+$ from
CH$_3$O.
Fig. 10
These results point out how useful qualitative information about the thermal decomposition of polyatomic molecules can be gotten from experiments done under collision free conditions. Information that would be very difficult to obtain by other methods due to fast secondary reactions of the primary reaction products. In addition, because of the ability to determine accurate product branching ratio's and translational energy distributions, it is possible to derive quantitative kinetic parameters. This is the subject of the next subsection.

The Derivation of Activation Energies from IRMPD experiments.— By knowing the A-factors for decomposition of the energized CH₃NO₂ molecule into both of its possible product channels, one can use RRKM theory to predict the product branching ratio as a function of the relative heights of the barrier to isomerization and the C–N bond energy at a given total excitation energy. Because RRKM theory can be used to calculate the translational energy distribution of simple bond rupture reactions without exit barriers given the total energy, one can work backwards to obtain information on the excitation energy distribution of the dissociating ensemble of molecules by finding the excitation energy distribution that gives a good RRKM predicted fit to the observed simple bond rupture translational energy distribution. In our experimental arrangement, the excitation energy distribution will be dependent upon the characteristics of the laser radiation. That is, if the laser intensity is low, the molecules will dissociate with only
a small amount of excess energy. On the other hand if the laser intensity is high, the molecules will on the average be pumped up quite high above the dissociation limit before the RRKM dissociation rates becomes as fast as the up-pumping rate.

Fig. 11 shows a schematic representation of a calculation designed to determine the barrier height to isomerization in reaction XI. The dynamic analysis consists of using a master rate equation simulation program to determine the magnitude of the absorption cross sections in the quasicontinuum that give rise to a simple bond rupture yield curve that will reproduce the experimental translational energy distribution for process X. This puts constraints on and gives a rough estimate of the excitation distribution in the decomposing parent molecule. Then by varying the barrier height to isomerization, it is possible to fit the experimental branching ratio. The rate constants as a function of excitation energy are determined using RRKM theory and the theoretical A-factor of Dewar et. al. for isomerization. This branching ratio matching method yields a nitromethane isomerization barrier height of 55.5 kcal/mol. The barrier height determination can be converted to an activation energy using RRKM theory and this is usually about a 1 kcal/mol correction.

We have also tested the branching ratio matching method on two known decomposition systems, reactions XII and XIII.

\[
\begin{align*}
\text{C}_2\text{H}_5\text{NO}_2 & \xrightleftharpoons[\text{C}_2\text{H}_5\text{NO}_2^+] {\text{n}_\text{hv}} \rightarrow \text{C}_2\text{H}_4 + \text{HONO} \\
\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5 & \xrightleftharpoons[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5^+] {\text{n}_\text{hv}} \rightarrow \text{CH}_3\text{CO}_2\text{H} + \text{C}_2\text{H}_4
\end{align*}
\]
Fig. 11  
Schematic Representation of the  
Barrier Height Determination for the  
Isomerization of CH$_3$NO$_2$: The  
levels shown are separated by the  
photon energy of the laser. By  
adjusting the absorption  
cross-section of the molecule in the  
quasicontinuum and knowing the rate  
of decomposition as a function of  
internal excitation from RRKM  
theory, the bond rupture yield curve  
is adjusted to fit the observed  
translational energy distribution  
and the isomerization barrier height  
is adjusted to fit the observed  
branching ratio between the two  
reaction channels. See ref. 3 for  
details.
Fig. 11
In both cases we have obtained excellent agreement, within the ±1.5 kcal/mol error of our determination, with known activation energies. Some of the derived barrier heights and activation energies are listed in table V.

The Position of the Transition State Along the Reaction Coordinate. As mentioned earlier, RRKM theory cannot predict the translational energy distribution for concerted molecular elimination reactions with high exit potential barriers. In order to understand the dynamics of this kind of unimolecular decomposition it is necessary to perform accurate calculations of the multidimensional PES and carry out classical trajectory dynamics calculations. Alternatively, we perform experiments. There have now been quite a number of experimental measurements of translational energy distributions for molecular elimination reactions. It is possible to compare these results and obtain a qualitative understanding of some of the aspects of these types of reactions.

In the past, several four center HCl elimination reactions have been studied.[13] The results of these experiments are presented in table VI. Typically, these reactions release 15-25 percent of the exit barrier into translation indicating that the products are left with a lot of vibrational energy. This is indicative of the strained nature of the four membered cyclic transition state. It is very interesting to ask the following question: if one studies molecular elimination reactions proceeding through five and six center cyclic transition states, does the percentage of the barrier height going
Table V
Activation Energies and Barrier Height
Derived from IRMPD Experiments

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Barrier Height</th>
<th>Activation Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$NO$_2$ $\rightarrow$ CH$_3$ONO$^{(a)}$</td>
<td>55.5 kcal/mol</td>
<td>54.0 kcal/mol</td>
</tr>
<tr>
<td>C$_2$H$_5$NO$_2$ $\rightarrow$ C$_2$H$_4$ + HONO$^{(a)}$</td>
<td>46.0</td>
<td>45.0</td>
</tr>
<tr>
<td>2-C$_3$H$_7$NO$_2$ $\rightarrow$ C$_3$H$_6$ + HONO$^{(a)}$</td>
<td>41.0</td>
<td>40.0</td>
</tr>
<tr>
<td>CH$_3$CO$_2$C$_2$H$_5$ $\rightarrow$ C$_2$H$_4$ + CH$_3$CO$_2$H$^{(b)}$</td>
<td>49.0</td>
<td>48.0</td>
</tr>
<tr>
<td>CH$_3$CO$_2$CH$_3$ $\rightarrow$ CH$_2$CO + CH$_3$OH$^{(b)}$</td>
<td>72.0</td>
<td>71.0</td>
</tr>
</tbody>
</table>

a. Ref. 3
b. Ref. 40
Table VI
Translational Energy Release for the Four Center Molecular Elimination of HCl

<table>
<thead>
<tr>
<th>REACTION</th>
<th>Exit Barrier Height</th>
<th>Fraction of Barrier in Translation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CF₂Cl → CH₂F₂⁺ HCl</td>
<td>55 kcal/mol</td>
<td>.22</td>
</tr>
<tr>
<td>CH₃CCl₃ → CH₂Cl₂⁺ HCl</td>
<td>42 kcal/mol</td>
<td>.19</td>
</tr>
</tbody>
</table>

a. The exit barrier is defined as the energy difference between the transition state and the products.

b. This is defined as the most probable translational energy release divided by the exit barrier height.
into translation increase, due to the smaller amount of strain present in the ring.

Table VII shows the results of several experiments performed recently for five and six center cyclic transition states. For all of these systems, at least .65 of the exit barrier appears as translation, confirming that ring size is indeed a very important factor to consider in these types of reactions.

However, in principle the dynamics should also depend on the electronic structure of the transition state. That is, if the transition state at the top of the mechanical barrier has a delocalized, hybrid electronic structure between products and reactants, we would expect more energy to go into internal degrees of freedom, since the barrier is substantially made up of potential energy due to bond extension. On the other hand if the electronic structure of the barrier looks like the products, alot of energy will appear as translation, since the barrier is mainly made up of energy due to the repulsion of two closed-shell molecules being held at bonding distances from one another. This question is equivalent to asking if the barrier to molecular elimination is a late one or an early one.

Light is shed on this issue of reaction coordinate position of the transition state by considering the results of three, four-center elimination reactions.

\[
\begin{align*}
\text{CH}_3\text{CO}_2\text{CH}_3 & \xrightarrow{\text{nhv}} [\text{CH}_3\text{CO}_2\text{CH}_3]^+ \rightarrow \text{CH}_2\text{CO} + \text{CH}_3\text{OH} & \text{XIV} \\
\text{CH}_3\text{CO}_2\text{H} & \xrightarrow{\text{nhv}} [\text{CH}_3\text{CO}_2\text{H}]^+ \rightarrow \text{CH}_2\text{CO} + \text{H}_2\text{O} & \text{XV} \\
\text{C}_2\text{H}_5\text{OC}_2\text{H}_5 & \xrightarrow{\text{nhv}} [\text{C}_2\text{H}_5\text{OC}_2\text{H}_5]^+ \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{C}_2\text{H}_4 & \text{XVI}
\end{align*}
\]
Table VII
Translational Energy Release
for Five and Six Center
Molecular Elimination
Reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(a) Exit Barrier Height</th>
<th>(b) Fraction of Barrier in Translation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_2\text{H}_5\text{NO}_2 \rightarrow \text{C}_2\text{H}_4 + \text{HONO} ) (^{(c,d)} )</td>
<td>28 kcal/mol</td>
<td>.71</td>
</tr>
<tr>
<td>( 2\text{C}_3\text{H}_7\text{NO}_2 \rightarrow \text{C}_3\text{H}_6 + \text{HONO} ) (^{(c,d)} )</td>
<td>23</td>
<td>.65</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CO}_2\text{C}_2\text{H}_5 \rightarrow \text{CH}_3\text{CO}_2\text{H} + \text{C}_2\text{H}_4 ) (^{(e,f)} )</td>
<td>38</td>
<td>.61</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_3\text{OC}_2\text{H}_5 \rightarrow \text{CH}_3\text{CHO} + \text{C}_2\text{H}_4 ) (^{(e,g)} )</td>
<td>38</td>
<td>.63</td>
</tr>
</tbody>
</table>

a. Same as table VI.
b. Same as table VI.
c. five center elimination
d. Ref. 3
e. six center elimination
f. Ref. 40
g. Ref. 41
We have performed photofragmentation IRMPD experiments on the above four center elimination reactions and table VIII shows the results. Reactions XIV-XVI release substantially more of the exit barrier energy into translation, >0.5 of the barrier compared to 0.2 for HCl elimination. It appears that for the case of four center elimination of alcohols and water, the transition state at the top of the barrier has an electronic structure much closer to products than does the transition state for HCl elimination. These experiments, perhaps more than any of the others described, show how the translational energy distribution can give very detailed information on the interfragment potential energy surface.

6. Conclusions

The purpose of this article has been to show the various kinds of information that can be obtained by the application of high-resolution photofragmentation-translational spectroscopy by presenting a few examples of the most recently accomplished experiments. In summary: a novel approach to bond selective photochemistry has been described; some aspects of UV photodissociation dynamics have been investigated; the derivation of accurate thermochemical data for free radicals has been presented and the study of collision free pyrolysis has been examined. The role of this method in the overall field of photochemistry is a unique one due to the general nature of the detection method which allows the study of an essentially unlimited range of polyatomic molecules. We can certainly look forward to
Table VIII
Translational Energy Release
for the Four Center Molecular
Elimination of ROH

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Exit Barrier Height</th>
<th>Fraction of Barrier in Translation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CO₂CH₃ → CH₂CO + CH₃OH&lt;sup&gt;(c)&lt;/sup&gt;</td>
<td>34 kcal/mol</td>
<td>.62</td>
</tr>
<tr>
<td>CH₃CO₂H → CH₂CO + H₂O&lt;sup&gt;(c)&lt;/sup&gt;</td>
<td>36</td>
<td>.64</td>
</tr>
<tr>
<td>C₂H₅OC₂H₅ → C₂H₅OH + C₂H₄&lt;sup&gt;(d)&lt;/sup&gt;</td>
<td>49</td>
<td>.53</td>
</tr>
</tbody>
</table>

---

a. The exit barrier is defined as the energy difference between the transition state and the products.
b. This is defined as the most probable translational energy divided by the exit barrier height.
c. Ref. 40
d. Ref. 42
substantial advancement of this technique in the future. In particular, there is nothing in principle that limits the improvement of the resolution of this method by up to a factor of five or more. This would allow a new generation of extremely high resolution experiments to be performed. It is also anticipated, that with the increasing availability and reliability of short wavelength lasers, e.g. the F$_2$ laser at 157 nm, the understanding of hydrocarbon photochemistry will be greatly improved. The usefulness of the molecular beam technique to prepare reactive species, such as free radicals, in a collision free environment has yet to be fully exploited and it is expected that the study of radical photochemistry will blossom soon. In addition the role of collision-free isomerization in UV photochemistry can be studied using isotopic labeling techniques. The investigation of these as well as many other topics offers a bright future for researchers using this technique.

ACKNOWLEDGMENT

We would like to acknowledge the efforts of Dr. Douglas J. Krajnovich and Dr. Laurie J. Butler, who both participated in the construction of the apparatus used in these experiments. In addition, the support of the Office of Naval Research (contract No. N00014-83-K-0069) and the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy (Contract No. DE-AC03-76SF00098) over the years has been invaluable.
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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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