The dynamics of H₂ elimination from ethylene

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Abstract

The dynamics of H₂ elimination in the photodissociation of ethylene at 193 nm were investigated through measurements of the translational energy distribution and rovibrational state distribution of H₂ products. Using 1,1-D₂C=CH₂ and 1,2-HDC=CDH, it was shown that both four-centered and three-centered elimination of H₂ could take place with an acetylene to vinylidene formation ratio of approximately two-thirds. Limited 1,2 hydrogen atom migration occurred during the fragmentation, presumably through an ethylidene-type structure. The relatively high rotational excitation of the H₂ fragment suggests that the transition is not symmetric; as the two ethylene hydrogen atoms approach each other and reach the transition state, one C–H bond should be significantly longer than the other. The vibrational energy distributions can be roughly characterized by a vibrational temperature of 4800 K and an average translational energy, which is dependent on the rovibrational state of H₂, exceeding 20 kcal mol⁻¹.

1. Introduction

Unimolecular decomposition may be characterized by either simple bond rupture reactions, in which a single bond is broken and no new bonds are formed, or by concerted decomposition reactions, in which old bonds are broken and new bonds are formed simultaneously [1, 2]. In most cases of simple bond rupture, the transition state, which does not have a potential energy barrier in the exit valley, is termed “loose”. The distribution of product translational energies reflects both the lack of interaction between recoiling products and the statistical distribution of internal energies at the transition state. There is a significant lowering at the transition state of the vibrational frequency associated with the bond being broken as compared with the same frequency in the excited molecule, allowing for an essentially adiabatic treatment of other internal degrees of freedom. In a “loose” transition state, the effective potential energy for radial separation of the products peaks at the centrifugal barrier. The distribution for translational energy release peaks at very low energies.

In the case of concerted decomposition, the transition state is termed “tight”. There is a potential energy barrier in the exit valley and a coupling between relative translation of the products and their internal degrees of freedom. In general, at a tight transition state, once the reaction proceeds past the transition state in the exit valley, the products formed near the top of the potential energy barrier are rapidly repelled from each other with enhanced translational energy. In addition, certain bending vibrations of a given transition state may correlate with free rotation of the

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products, causing the distribution of product kinetic energies to be peaked away from zero. Of course, the concerted movement of electron density from old bonds to new during the reaction necessarily involves certain symmetry considerations [3].

The structure of the transition state predetermines the initial conditions before products separate, especially the initial vibrational excitation and repulsive energy release. Thus, a study of the product translational and internal energy distributions from concerted decompositions may yield information about the transition state structure as well as the reaction dynamics in the exit valley. Correlations between translational and internal energy release may reveal the coupling between these degrees of freedom as products separate.

The concerted decomposition producing molecular hydrogen is a special case that deserves attention. Not only is it a primary process occurring in the photochemistry of many organic molecules, but it is particularly interesting for fundamental reasons. The spectroscopy of H₂ is extremely well characterized. The very large energy spacing between rovibrational quantum states implies that there will be a limited number of product states produced in a decomposition process. This allows for accurate measurement of the complete translational and internal energy distributions. Furthermore, the simplicity of H₂ elimination from a small organic molecule should allow for ab initio calculation of the relevant transition states and a detailed comparison of experiment with theory.

2. Ethylene photochemistry

Ethylene is the simplest unsaturated hydrocarbon. In spite of this, the details of its UV photochemistry remain unresolved [4]. Early investigations were performed in “bulbs” using the techniques of pulse radiolysis [5], mercury sensitization [6], flash photolysis [7] and discharge lamps [8-12]. The consensus was that there are two equiprobable primary reaction channels, one eliminating molecular hydrogen and the other atomic hydrogen. They can be depicted as follows

\[
\begin{align*}
C_2H_4 \rightarrow & \text{HC}=\text{CH}+H_2 \quad (1a) \\
C_2H_4 \rightarrow & \text{H}_2\text{C} \rightarrow \text{C}^* + H_2 \quad (1b) \\
C_2H_4 \rightarrow & \text{C}_2\text{H}_3^+ + H \quad (2a) \\
C_2H_4 \rightarrow & \text{HC}=\text{CH}+2H \quad (2b)
\end{align*}
\]

The energetics of these processes are shown in Fig. 1.

The molecular decomposition appears to have two pathways: a four-centered elimination (4CE) producing the acetylene molecule (eqn. (1a)) and a three-centered elimination (3CE) producing the vinylidene radical (eqn. (1b)). The atomic elimination reaction may also have two pathways. The first, shown in eqn. (2a), is hydrogen atom loss from ethylene producing an energized vinyl radical. The vinyl radical may also have enough energy to spontaneously decompose, as implied by eqn. (2b). The detection [7, 14] of the vinyl radical confirmed the occurrence of eqn. (2a). Early isotope substitution studies indicated that the photochemical intermediary had free rotation about the C–C bond and that all hydrogens could participate although they did not exchange. A ratio of 4CE to 3CE of 2:3 was obtained. A subsequent study [15] using UV flash photolysis, detected the presence of triplet vinylidene (\(^3\)B₂) and suggested that neither acetylene nor singlet vinylidene were primary products, in contradiction with previous work. A recent investigation [16] of ethylene photochemistry at 193 nm
Fig. 1. Heats of reaction of various species involved in ethylene photochemistry. The photon energy is 148 kcal mol$^{-1}$ (i.e. 193 nm). Many of the heats of formation are not well known. The values used here are discussed in ref. 13.

confirmed the existence of several pathways, but was unable to elucidate them. Most recently [17], a laser-induced fluorescence study of atomic elimination from the 193 nm photolysis of ethylene characterized the decomposition by C–H bond rupture as being of Ramsberger-Rice-Kassel-Marcus (RRKM) type following internal conversion to a vibrationally hot ground state.

The spectroscopy and excited states of ethylene have been reviewed in some detail [18]. The planar ground state is labeled N($^1A_1$). The first excited state of ethylene is labeled V($^1B_2$). The broad diffuse V ← N band system extends from 215.0 nm to the first Rydberg transition at 174.4 nm. The intensity rises rapidly towards shorter wavelengths. The V state of ethylene is twisted; it has a potential energy minimum for the methylene groups in a perpendicular configuration. However, it is capable of free internal rotation for 193 nm excitation. The V ← N transition may be regarded as the prototype for $\pi^* ← \sigma$-type transitions. The second lowest excited singlet state of ethylene is labeled Z($^1A_1$) and it is also twisted. It displays the interesting phenomenon of sudden polarization [19]; the dipole moment of this state drastically increases as the methylene groups rotate and pyramidalize. This geometry may be thought of as having zwitterionic character, i.e. $^+\text{H}_2\text{CCH}_2^-$. The point of interest here is that the V and Z states interact strongly in the twisted configuration, lending ion-pair character to the V state. A possible photochemical consequence [20] of this effect is the potentially increased facility of 1,2 hydrogen atom shift, analogous to the well-known 1,2 carbonium shift. A recent vacuum UV resonance Raman study [21] of the V state confirmed that the initial motions on the excited state are CH$_2$ twisting and pyramidalization.

A considerable amount of theoretical work has been carried out relating to the problem of ethylene photochemistry. A seminal study [22] of the energetics and symmetry-allowed correlations of various states of ethylene presented important conclusions which are discussed below.
The V state of ethylene correlates directly, with a small barrier, to both the singlet ground state of vinylidene (H₂C≡C:) plus H₂ and the singlet ground state of ethylidene (HCCH₃) as shown below:

\[ \text{C}_2\text{H}_4[\text{V}^1\text{B}_2] \rightarrow \text{H}_2\text{C}=\text{C}:+\text{H}_2 \]  \hspace{1cm} (3)

\[ \text{C}_2\text{H}_4[\text{V}^1\text{B}_2] \rightarrow \text{HCCH}_3 \]  \hspace{1cm} (4)

The process shown in eqn. (3), the ethylene to vinylidene transformation, is Woodward-Hoffmann forbidden for C₂v symmetry and only becomes allowed for C₁ symmetry, suggesting that the transition state for this path is of low symmetry. This path is not necessarily a statistical unimolecular decomposition.

The reaction shown in eqn. (4) would correspond to a 1,2 hydrogen atom shift and is related to the sudden polarization phenomenon. The "ethylidene radical" was found to be completely unstable [23] with respect to rearrangement to ethylene; it is merely a saddle point on the ethylene ground state surface. There is, however, an "ethylidene-type" transition state that leads directly [22, 23] to ground state acetylene plus H₂:

\[ \text{HCCH}_3^+ \rightarrow \text{HC}=\text{CH}+\text{H}_2 \]  \hspace{1cm} (5)

It should be pointed out that the available energy of 148 kcal mol⁻¹ (i.e. 193 nm) far exceeds the barriers in the ground state for H₂ elimination from vinylidene, acetylene or "ethylidene". The observation of the vinyl radical in eqn. (2) is confirmation of internal conversion to the hot ground state of the ethylene molecule since the V state does not correlate directly with the atomic elimination channel. The hydrogen atom is expected to be eliminated through unimolecular decay with a few kilocalories per mole of the exit barrier potential energy.

3. Experimental details

Two experimental techniques used in the study of ethylene photochemistry at 193 nm are discussed in the following sections. The first, molecular beam photofragment translational energy spectroscopy (PTS) [24], provides the detailed kinetic energy distributions of mass-selected photolysis products and branching ratios between competing channels. The second, a vacuum UV laser-based pump-and-probe technique [25] provides rotational and vibrational energy distributions for the H₂ product as well as the dependence of the average product translational energy on the rovibrational quantum state of H₂.

3.1. Photofragment translational energy spectroscopy

The experimental apparatus used in these high resolution photofragmentation studies has been described previously [13]. Briefly, an unskimmed pulsed supersonic molecular beam is expanded into a differentially pumped vacuum chamber where it is crossed at right angles with the 193 nm output (500–1500 mJ cm⁻²) of an ArF excimer laser. Recoiling photofragments pass into a separate chamber where they are detected, after traveling a distance of 39 cm, by a multiple differentially pumped rotating mass spectrometer detector. In this particular case, because the products have an isotropic angular distribution in the center-of-mass coordinate system, and the velocities of the atomic and molecular hydrogen fragments so exceed the velocity of the parent molecule, the entire product translational energy distribution may be
collected at a single angle, perpendicular to the plane containing the photolysis laser and the molecular beam. Transient signals at a given charge-to-mass ratio are captured and signal averaged by a computer-controlled multichannel scaler system. The product translational energy distributions are extracted from the raw data using the forward convolution technique [26].

3.2. Vacuum UV laser pump-and-probe technique

The ultrahigh resolution vacuum UV–XUV (XUV, extreme UV) laser system and molecular beam apparatus used in these experiments has been described previously [27, 28]. The relative populations of H₂ rovibrational states are probed via (1+1) resonance-enhanced multiphoton ionization (REMPI) through either the B(^3Σ_u) or C(^3Π_u) states [29]. In addition, the inherent high resolution of the laser allows the Doppler profiles of the H₂ transitions to be scanned, permitting an analysis of the correlations between product translation and internal energy.

A skimmed, differentially pumped, pulsed molecular beam is expanded into a vacuum chamber where it passes through the extraction region of a Wiley–McLaren-type time-of-flight (TOF) mass spectrometer. There it is crossed by the 193 nm output (10–80 mJ cm⁻²) of an unstable resonator ArF excimer laser. Collinear and counterpropagating with this are the vacuum UV plus UV probe laser beams which interrogate the nascent H₂ photoproducts at a time delay of 20 ns.

The probe laser system, described in detail elsewhere [25, 27], is based on pulsed amplification of a ring dye laser. Typically, over 100 mJ pulse⁻¹ of visible light is produced with a bandwidth of 95 MHz. This is doubled and then converted to vacuum UV–XUV by either tripling or sum-frequency mixing in a pulsed free jet expansion of argon or xenon. Laser powers are monitored on a shot-to-shot basis in order to normalize accurately the collected signals. Doppler spectra are recorded by scanning the ring laser under computer control. The same laser system also allows for the detection of hydrogen and deuterium atom photoproducts via (1 + 1) REMPI (using the Lyman–α transition) by tripling in a pulsed free jet of krypton gas.

Normalized H₂⁺ signals are fitted to a line shape function and converted to relative populations using the well-known H₂ line strength factors.

4. Results and discussion

4.1. Photofragment translational energy spectroscopy

4.1.1. Molecular hydrogen elimination

The H₂ product TOF spectrum for ethylene photolysis is shown in Fig. 2. The product translational energy distribution P(E_i) which fits this spectrum is shown in Fig. 3. The maximum in P(E_i) is peaked away from zero, consistent with a concerted elimination process.

If 4CE of H₂ to form nascent acetylene, as in eqn. (1a), was the only process, the maximum translational energy would be about 108 kcal mol⁻¹. On the other hand, if 3CE of H₂ to form nascent vinylidene, as in eqn. (1b), was the only process, the maximum translational energy would be about 64 kcal mol⁻¹. The observed maximum translational energy was 88 kcal mol⁻¹, confirming the occurrence of 4CE. However, it does not indicate the absence of 3CE. In fact, the abrupt change in slope (near 60 kcal mol⁻¹ in Fig. 3), usually indicating the presence of another channel, is suggestive of 3CE.

In order to confirm the presence of both 3CE and 4CE, it was necessary to study the elimination of HD and D₂ form two isotopically substituted ethylenes, namely
Fig. 2. H$_2$ TOF spectrum from photolysis of C$_2$H$_4$ at a 193 nm laser power of 130 mJ pulse$^{-1}$. The full line is the best fit calculated using the $P(E)$ shown in Fig. 3.

Fig. 3. $P(E)$ for H$_2$ formation used to fit the TOF spectrum shown in Fig. 2. The arrows indicate the maximum H$_2$ translational energies expected for acetylene, vinylidene, excited state acetylene and excited state vinylidene formation.

(1,1)-D$_2$C=CH$_2$ and cis-(1,2)-HDC=CDH. The experimentally observed product ratios can be self-consistently related to the branching ratio for 3CE over 4CE.

The measured relative yields of HD and D$_2$ form the (1,1) and cis-(1,2) isotopomers are given in Table 1. The first important point is that the four hydrogen atoms are not equivalent — they do not become completely scrambled. If they did then equal amounts of HD and D$_2$ would be formed for each isotopomer, which is not the case. The second important point is that 4CE cannot be the only channel. If this were true, it would be impossible to form D$_2$ from the (1,1) isotopomer. A simple model [13] for molecular elimination allowed for an estimation of the expected HD to D$_2$ ratios for the case of pure 3CE and pure 4CE from each isotopomer. Deviation from these limiting cases was used to obtain the branching ratio. It was found that the 3CE (forming vinylidene) to 4CE (forming acetylene) ratio for H$_2$ from the 193 nm photolysis
TABLE 1
Relative amounts of HD and D₂ products formed in the photolysis of (1,1)-D₂C=CH₂ and cis-(1,2)-HDC=CDH. The yields are normalized to the yield of HD product from the (1,1) isotopomer.

<table>
<thead>
<tr>
<th>Isotopomer</th>
<th>D₂ (m/e = 4)</th>
<th>HD (m/e = 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1,1)-D₂C=CH₂</td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>cis-(1,2)-HDC=CDH</td>
<td>0.2</td>
<td>2.0</td>
</tr>
</tbody>
</table>

of ethylene was 2:3

\[ 4\text{CE (HC}=\text{CH)}:3\text{CE (H}_2\text{C}==\text{C:)}=2:3 \]  

(6)

The relationship expressed in eqn. (6) can be used to extract separate translational energy distributions for 3CE and 4CE in each isotopomer. In the analysis [13] of HD elimination from the (1,1) isotopomer (forming acetylene) and D₂ from the same isotopomer (forming vinylidene), it was discovered that, while the acetylene 4CE channel creates more energetic product as expected, the vinylidene 3CE channel seems to produce product with up to 78 kcal mol⁻¹ in translation. This exceeds the available energy for vinylidene formation of 64 kcal mol⁻¹. This may provide some preliminary evidence for the contribution of an ethylidene-type mechanism. As the D₂ molecule is forming in the energized (1,1) isotopomer, a hydrogen atom from the adjacent carbon starts to transfer over, enhancing the repulsive force on the departing D₂.

4.1.2. Atomic hydrogen elimination

An estimation of the branching ratio between atomic and molecular elimination may be procured from a consideration of the integrated TOF spectra for atomic and molecular hydrogen generated in the photolysis of C₃H₄. The branching ratio was 1.0 ± 0.15 over the range of laser intensities from 800 to 1500 mJ cm⁻². However, the shape of the hydrogen atom TOF spectrum depended strongly on laser intensity. The leading edges of all spectra corresponded to a translational energy exceeding that expected from a consideration of accepted C—H bond strengths in ethylene [30]. This suggests that multiphoton effects contribute to the hydrogen atom elimination channel. A likely scenario is secondary absorption by the nascent vinyl radical (which has an absorption cross-section much larger than that of ethylene at 193 nm). This will be discussed in greater detail later.

The primary and secondary channels may be deconvoluted [31] and P(Eₜ) for the primary channel extracted. This, shown elsewhere [13], peaks near zero kinetic energy and is consistent with simple bond rupture in a hot ground state ethylene molecule, producing the vinyl radical. The secondary dissociation channels can be divided into two groups [13]. The first is spontaneous decomposition of the over-energized vinyl radical into acetylene plus a hydrogen atom with 0–5 kcal mol⁻¹ in translation. The second hydrogen atom elimination channel is considered to be photodissociation of the nascent vinyl radicals (including a large fraction of over-energized species), producing very fast hydrogen atoms. The analysis of this secondary P(Eₜ) suggests that electronically excited molecular products are formed. In particular, the P(Eₜ) has a threshold (approximately 100 kcal mol⁻¹) close to that expected for forming triplet vinylidene, H₂C=C:(³B₂). This point is supported by a previous study [15] of ethylene photochemistry in which the direct observation of ³B₂ vinylidene was reported.
4.2. Vacuum UV pump-and-probe

4.2.1. Product state distributions

The vibrational state distribution of the H$_2$ product from the 193 nm photodissociation of C$_2$H$_4$ is shown in Fig. 4. The detailed rotational distributions for vibrational levels $v=0$–3 are given in Fig. 5. The populations were determined from the normalized Doppler scans by fitting to a line shape function, extracting the line intensity and converting this to a population using the well-known H$_2$ line strength factors. Each population was measured 4–6 times, using P, Q and R transitions whenever possible.

The rotational distributions for H$_2$ elimination from the (1,1) dideuterated isotopomer were measured for $v=0$ and $v=1$. These have been interpreted as arising

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Fig. 4. Distribution of vibrational energy in H$_2$ from the photodissociation of C$_2$H$_4$ (filled bars). A statistical fit to the data (with $T=4979\pm120$ K) is also shown (hatched bars).

Fig. 5. Detailed H$_2$ rotational distributions for $v=0$–3. Errors bars indicate one standard deviation.
from a pure 3CE mechanism. The distributions were fitted to rotational “temperatures”
of $2500 \pm 200$ K for $v = 0$ and $2000 \pm 160$ K for $v = 1$. The important point here is that
these distributions are significantly rotationally cooler than for those for H$_2$ from C$_2$H$_4$.

The cooler rotational temperature for 3CE allows us to speculate on the bimodal
character of the rotational distributions, in order to deconvolute the rovibrational
distributions for 3CE and 4CE channels, two major assumptions were required. The
first was that the overall branching ratio between 4CE and 3CE is 2:3, as obtained
from the above-mentioned molecular beam TOF studies. The second was that the
vibrational “temperature” for 3CE was one-half of that for 4CE. This was based on
the observation that the exothermicity for 3CE is approximately one-half of that for
4CE and is in accordance with the rotational temperature for 3CE obtained from the
(1,1) dideruterated isotopomer study mentioned above. From these assumptions, we
speculate that the bimodal vibrational distribution is as shown in the first column of
Table 2.

For the vibrational levels $v = 0$ and $v = 1$, it was possible to deconvolute directly
the 4CE rotational distribution since the 3CE rotational distribution was known from
the (1,1) isopomer photolysis discussed above. For the $v = 2$ and $v = 3$ levels, the
two rotational temperatures were varied to best fit the observed data with the constraint
that the ratio of 3CE to 4CE matched the vibrationally resolved branching ratio from
the first column of Table 2. The rotational temperatures speculated for the two
elimination channels are shown, as a function of $v$ level, in Table 2.

Several points are worth noting. The bimodal fit to the vibrational distribution
shows the fraction of 3CE decreasing from nearly 70% in $v = 0$ to less than 20% in
$v = 3$. The rotational temperatures for 3CE are consistently much cooler than those
for 4CE. These differences can be understood primarily in terms of the energy available
to each channel (4CE has twice as much). The highly rotationally excited products
from 4CE are suggestive of a quite asymmetric transition state, wherein the two
recoiling hydrogen atoms, on their way to forming an H$_2$ molecule, experience unequal
repulsive forces. In the case of 3CE, the rotational temperatures, although cooler, are
still much hotter than those observed for the recoil of H$_2$ from a highly symmetric
transition state such as that found in the photolysis of 1,4-cyclohexadiene [32]. This
suggests that the pure 3CE case also has an asymmetric transition state, perhaps
analogous to the well-known case of H$_2$ elimination from formaldehyde [33]. It may
also be suggestive of some contribution from an ethylidene-type component in the
3CE transition state, where the hydrogen atom from the adjacent carbon starts
transferring as the H$_2$ departs.

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**Table 2**

Speculated bimodal fit to 3CE and 4CE for the H$_2$ rotational distributions in the photolysis of
C$_2$H$_4$. The rotational temperatures for 3CE and 4CE are shown as a function of vibrational
state. Also shown is the percentage of 3CE contributing to the total signal at each $v$ level

<table>
<thead>
<tr>
<th>Vibrational state</th>
<th>3CE (%)</th>
<th>$T_{rot}(3CE)$ (K)</th>
<th>$T_{rot}(4CE)$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>67</td>
<td>$2500 \pm 200$</td>
<td>$3500 \pm 940$</td>
</tr>
<tr>
<td>1</td>
<td>49</td>
<td>$2000 \pm 160$</td>
<td>$4200 \pm 800$</td>
</tr>
<tr>
<td>2</td>
<td>32</td>
<td>$1200$</td>
<td>$4000 \pm 1200$</td>
</tr>
<tr>
<td>3</td>
<td>19</td>
<td>$600$</td>
<td>$2700 \pm 350$</td>
</tr>
</tbody>
</table>
4.2.2. Correlations with translational energy

The line shape for each $\text{H}_2(v, J)$ transition was fitted to a functional form [34] by assuming that a gaussian distribution of velocities contributes to the Doppler profile [25, 35]. From these fits, average and maximal translational energy releases may be correlated with $\text{H}_2$ product internal energies. A plot of the $\text{H}_2$ average translational energy as a function of $\text{H}_2$ internal energy is shown in Fig. 6. As expected, the translational energy decreases with increasing internal energy — consistent with fixed available energy. However, there is not a simple antagonistic relationship between translational and internal energy: the translational energy falls off much less quickly. This is consistent with the picture of a tight transition state where the partitioning to translation is governed by product repulsion in the exit valley.

Ethylene contains so many degrees of freedom (i.e. 12) and the excitation energy (i.e. 148 kcal mol$^{-1}$) so exceeds the exit barrier energy that dissociation could take place from a range of structures near the transition state. This is because the excess energy must become distributed in modes other than the reaction coordinate, leading to vibrationally excited transition states which have a range of geometries about the true structure at the minimum energy barrier (saddle point). Furthermore, these excess energy structures may "see" slightly different exit barriers than the minimum energy transition state. Therefore, the $\text{H}_2$ translational, rotational and vibrational distributions and their mutual correlations reveal information not only about the structure of the transition state but also the range of structures from which the $\text{C}_2\text{H}_4$ molecule dissociates.

The $\text{H}_2$ average translational energy may also be correlated with rotational energy for each vibrational state. In these plots, shown elsewhere [35], the translational energy release shows a weak negative correlation with $\text{H}_2$ rotational energy. This observation allows us to speculate further on the dynamic origins of these highly rotationally excited products. The extensive rotational excitation could be dominated by either the increased magnitude (i.e. the height of the exit barriers for various critical structures near the transition state) or increased anisotropy (i.e. asymmetry at the transition state) of the repulsive forces. If the increased magnitude dominated, we would expect a strong negative correlation between product translation and product rotation as one is traded off for the other. On the other hand, if increased anisotropy dominated, we would

![Fig. 6. Plot of translational energy vs. internal energy for the $\text{H}_2$ product from the photodissociation of $\text{C}_2\text{H}_4$. The vibrational quantum states of the $\text{H}_2$ product are indicated.](image-url)
expect a weak negative correlation. This is so because the translational energy, governed by the magnitude of the potential energy released beyond the transition state, should be relatively independent of the rotational energy, having arisen from asymmetry at the transition state. Therefore, if anisotropic forces govern the extent of rotational excitation, the correlation between translation and rotation should be weak. This is consistent with our observations. The correlation appears to be slightly weaker for higher \( v \) levels rather than low. If this is true, it may suggest that the dominance of the repulsive anisotropy is more important for the case of 4CE.

It is interesting to compare the Doppler profiles for \( \text{H}_2(v=0,1) \) elimination from the (1,1) isotopomer with those from regular ethylene. The negative correlation between product translation and product rotation is considerably stronger for the (1,1) isotopomer. This can most probably be explained by the contribution of the rotationally hotter 4CE in \( \text{C}_2\text{H}_4 \) (absent in the (1,1) isotopomer), weakening the correlation. However, 4CE contributes only about 30% to the \( v=0 \) rotational distribution in \( \text{C}_2\text{H}_4 \) (see Table 2). It could also be that in 3CE from the (1,1) isotopomer, there is a stronger translational-rotational correlation than in 3CE from \( \text{C}_2\text{H}_4 \). If this is true, it may have some bearing on the structure of the transition state for 3CE. If the anisotropy of the repulsion in the 3CE transition state is due to the transfer of an hydrogen atom during recoil, we might expect that the transfer of a deuterium atom is much less likely, reducing the anisotropy and therefore strengthening the negative correlation. This would be consistent with the observation of the faster than expected 3CE product.

![Fig. 7. H\(_2\) Doppler profiles measured by VADS for the \( v=1 \) level. Top: \( \text{H}_2 \) B-X(2,1) R(5) transition, \( \nu_o=87\,710.0 \text{ cm}^{-1} \). Middle: \( \text{H}_2 \) B-X(2,1) P(3) transition, \( \nu_o=88\,077.1 \text{ cm}^{-1} \). Bottom: \( \text{H}_2 \) B-X(2,1) R(1) transition, \( \nu_o=87\,358.2 \text{ cm}^{-1} \). The VADS profiles are shown by a thick line while the normal Doppler profiles are shown by a thin line, scaled down to match the VADS intensity.](image-url)
obtained in the comparison of HD with D₂ in the (1,1) isotopomer, as discussed in the molecular beam technique section above.

An investigation into the distribution of H₂ velocities for a single rovibrational state was carried out using the technique of velocity aligned Doppler spectroscopy (VADS) [36]. This technique allows for enhanced resolution at long time delays in the determination of different velocity components contributing to a Doppler line shape. Doppler scans for three different H₂(v,J) states are shown in Fig. 7. The line shapes are split symmetrically about line center and peak at finite Doppler shifts. This indicates that the average translational energy release is peaked away from zero, in good agreement with the molecular beam TOF data, and consistent with the picture of a tight transition state. The significant width of the peaks indicates that each H₂(v,J) correlates with a large distribution of internal energies in the hydrocarbon fragment. This is not unanticipated as a consideration of the energy partitioned to the H₂ fragment reveals that this must be the case. We had hoped that the Doppler profiles would show a bimodal velocity distribution, indicating two competing elimination channels. Preliminary evidence for this appeared in a long time delay scan of the line shape for an H₂(v=2, J=1) transition, shown in Fig. 8. There is a narrower, slower velocity distribution superimposed on a broader one. The maximum Doppler shift in the broad component corresponds to a translational energy of 46 kcal mol⁻¹. Considering the internal energy of this H₂ state (23 kcal mol⁻¹), the broad peak must correspond to 4CE forming acetylene since 3CE is no longer thermodynamically possible at this high energy. Therefore, we associate the narrower, slower peak with 3CE and the broader peak with 4CE. The ratio of the areas of the broad and narrow peaks is roughly 2:1, in agreement with the bimodal vibrational distribution for a v=2 state, as shown in Table 2.

4.2.3. Atomic hydrogen elimination and multiphoton processes
A study of the atomic elimination channel in the 193 nm photodissociation of ethylene was carried out by measuring the Doppler profiles of deuterium atoms produced from C₂D₄. A typical Doppler line shape for deuterium atom elimination
is shown in Fig. 9. It is peaked at zero Doppler shift for all time delays and is considerably narrower than the Doppler profiles for molecular hydrogen elimination. This indicates that the distribution of translational energies is peaked near zero, supporting the molecular beam TOF data and consistent with a simple bond rupture process. The average translational energy release from a long time delay Doppler scan [13] was measured to be around 7.8 kcal mol$^{-1}$, in general agreement with a prior study [17].

An analysis of the maximum Doppler shift, however, reveals that multiphoton processes must be occurring. The maximum shift from Fig. 9 corresponds to a translational energy greater than 70 kcal mol$^{-1}$. There is probably faster product, as seen in the TOF data, but the ion collection becomes less efficient as the energy increases, reducing our sensitivity for the very fast products. Even so, if interpreted as simple bond rupture in C$_2$D$_4$, it would suggest a C–D bond energy of 78 kcal mol$^{-1}$, far below accepted values [30]. The recoiling deuterium atom has far too much energy for a single-photon process. This is consistent with the nascent vinyl radical absorbing a second photon, producing a very fast deuterium atom and triplet vinylidene.

Multiphoton processes are not unexpected if we consider the relative photoabsorption cross-sections of the ethylene molecule and the vinyl radical. The UV cross-section of ethylene [18] is very small, around $2 \times 10^{-20}$ cm$^2$. The UV cross-section of the vinyl radical, on the other hand, is much greater [37]. Thus, as the laser intensity is increased to produce a measurable signal from the photolysis of ethylene, it becomes very difficult to avoid secondary dissociation of the vinyl radical product.

We performed laser power studies on the deuterium atom product. With the vacuum UV probe laser set to zero Doppler shift (the Lyman–α line center), we obtained a straight line fit to the data, passing through the origin, over the range of laser intensities from 50 to 100 mJ cm$^{-2}$. However, this cannot be taken as evidence that multiphoton processes do not occur since the leading edge of the Doppler profile confirms that they do. In a second study, we set the vacuum UV probe laser far off

![Fig. 9. Doppler profile for deuterium atoms from C$_2$D$_4$ photodissociation. The broken line shows the maximum Doppler shift expected for single-photon excitation of C$_2$D$_4$ forming a deuterium atom plus a vinyl radical. The signal to the left of the broken line must originate from a multiphoton process.](image_url)
Fig. 10. Photolysis (193 nm) study with the vacuum UV probe laser set at an H₂ Doppler shift shown by the broken line in Fig. 9. The behavior at low intensity appears to be non-linear (indicating multiphoton absorption), saturating at higher intensities where it is well approximated by a straight line.

Line center, near the red edge of the Doppler scan, corresponding to a translational energy release that must involve multiphoton processes. This is presented in Fig. 10. At low laser intensities, from 30 to 60 mJ cm⁻², we can see a non-linear response. Above 100 mJ cm⁻², the data are well represented by a straight line. This suggests that multiphoton processes can occur in ethylene photochemistry and saturate at relatively low intensities due to the very large absorption cross-section of the vinyl radical compared with the parent molecule.

5. Conclusions

The photochemistry of ethylene (C₂H₄) at 193 nm was studied by two complementary techniques: molecular beam photofragment translational energy spectroscopy and the vacuum UV–extreme UV pump-and-probe technique. The former was used to determine product translational energy distributions and branching ratios while the latter was employed to obtain H₂ product rotational and vibrational energy distributions. Prior experimental and theoretical work suggested that there might be two pathways to molecular H₂ elimination. The first, called three-centered elimination (3CE), brings together two hydrogen atoms from the same carbon to form H₂, leaving behind the vinylidene radical (H₂C=CH⁻). The second, called four-centered elimination (4CE), brings together hydrogen atoms from different carbons, leaving behind the acetylene molecule (HC≡CH). The 4CE channel is nearly twice as exothermic as the 3CE channel.

The elimination of atomic and molecular hydrogen, shown in eqns. (1) and (2), was found to occur in a ratio of 1:1 in agreement with previous investigations. Isotopic substitution studies of molecular hydrogen elimination using (1,1)-dideuteroethylene and cis-(1,2)-dideuteroethylene revealed that the ratio of 4CE to 3CE in C₂H₄ was 2:3, also in agreement with previous investigations. The translational energy distributions for H₂ elimination were peaked away from zero, indicating a concerted decomposition
process from a tight transition state. Translational energy distributions for hydrogen atom elimination, leaving the vinyl radical, were found to peak near zero. This suggests that excited ethylene internally converts to form a hot ground state, which then undergoes a simple bond rupture, forming the vinyl radical and a hydrogen atom. The vinyl radical appears to have enough internal energy to spontaneously decompose, forming acetylene plus a slow hydrogen atom. On the basis of the observation of very fast hydrogen atoms, secondary photolysis of the vinyl radical was postulated, forming, perhaps, a triplet vinylidene radical.

The vibrational distribution for H₂ elimination from C₂H₄ corresponded to a high temperature, near 5000 K. The speculated contribution of 3CE was estimated to be nearly 70% for ν = 0, decreasing to less than 20% for ν = 3. The H₂ rotational distributions for each ν level extended to high J levels. Speculated rotational distributions were extracted for 3CE and 4CE; the former was significantly cooler at each ν level than the latter. The high degree of rotational excitation is suggestive of asymmetry in the transition states. Correlations between translational and rotational energy were obtained by measuring the Doppler profiles of the H₂ transitions. There was a weak negative correlation between translation and rotation, suggesting that perhaps asymmetry in the transition states dominates over repulsive energy release in the determination of the degree of rotational excitation. When two hydrogen atoms are pushed together, as the energized molecule approaches the transition state, one C-H bond is significantly longer than the other. The negative correlation between translational and internal energy further suggests that the range of transition state structures (determining the energies available to the departing H₂) is mainly due to variation in the longer C–H bond distance near the transition state.

An analysis of the Doppler line shapes supported the picture of a concerted dissociation process producing H₂. Preliminary evidence for the presence of two velocity distributions in a given line shape was presented, consistent with the competition between 3CE and 4CE. The atomic elimination channel was studied by observing deuterium atom elimination from C₂D₄. The translational energy distribution peaked at zero, corroborating the molecular beam data and the notion of simple bond rupture in a hot ground state molecule. Evidence for the occurrence of multiphoton processes, based on laser power studies at a large deuterium atom Doppler shift, was presented and interpreted in terms of the secondary dissociation of vinyl radicals.

The transition state for 3CE should be asymmetric, with two unequal C–H bond distances for the departing hydrogen atoms, perhaps analogous to the formaldehyde case. There may also be some concerted interaction with a hydrogen atom from the adjacent carbon. The transition state for 4CE could be asymmetric, perhaps passing near an ethylidene-type structure. However, incomplete scrambling of the hydrogens implies that this contribution is also limited. It seems that a range of structures about the transition state saddle point should participate in the dissociation, the most probable geometrical variation involving changes in the longer of the two C–H bond distances concerned. We hope that these results will stimulate new theoretical investigations into the dynamics of concerted decomposition in ethylene.

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