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The photodissociation of the vinyl radical (C_2H_3) at 243 nm studied by velocity map imaging

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Abstract

The technique of velocity map imaging (VELMI) has been applied to study the photodissociation of the vinyl radical (C_2H_3) at 243.2 nm in a molecular beam. Using momentum conservation, we show that the primary product is singlet vinylidene (H_2CC ($\tilde{X}\ ^2A'$)), or singlet acetylene at energies where interconversion between the H_2CC and HCCH geometries is facile. In addition, a minor contribution is seen which is assigned to triplet acetylene (C_2H_2 ($\tilde{a}\ ^3B_2$)). We argue that out-of-plane motion of the third H atom is necessary to bring the excited states, of A″ symmetry, to an A′ symmetry leading to products, and the observed tranlsational energy distribution may show evidence of the barrier to this process. The heat of formation of vinylidene is derived to be 100.3±4.0 kcal/mol in agreement with literature values. From the translational energy release, we derive the T_0 for triplet acetylene C_2H_2 ($\tilde{a}\ ^3B_2$) to be 28900 cm^{-1}, which does not agree well with recent ab-initio calculations. Possible reasons for the disagreement are discussed.

Introduction:

To date there has been no direct experimental study on the photodissociation dynamics of the vinyl radical. This is surprising given the importance that vinyl and related radicals play in hydrocarbon fuel combustion chemistry[1]. Experimental studies have been limited to inference based upon the secondary photodissociation of vinyl radicals formed in the near UV photodissociation of ethylene[2] and chloro-ethylenes[3]. However, there have been a number of theoretical studies on the photodissociation processes for the vinyl radical. Sevin et al[4] carried out ab-initio calculations of the potential energy surfaces for bond rupture and hydrogen migration pathways for the ground and excited states of the vinyl radical. They considered only C_{2v} dissociation, and found a direct adiabatic pathway taking the excited vinyl radical to the ground state of acetylene + H, over a high barrier. They did not consider the C_s dissociation pathway to vinylidene + H. Paddon-Row and Pople[5] studied both the ground state and the first excited surfaces of vinyl in an effort to understand experimentally observed scrambling of the H atoms joined to a common carbon site. They found this interconversion occurs through an inversion mechanism on the ground state with a barrier of 4.4 kcal/mol, while in the first excited state the analogous process occurs through out-of-plane motion of the third H atom with a barrier of 7.3 kcal/mol.

Recently Wang et al[6] calculated the bond dissociation energy for the vinylidene (84.46 kcal/mol) and acetylene (40.70 kcal/mol) channels of the vinyl radical, and extended these studies to identify the excited electronic states of the vinyl radical and calculate a vibronic spectrum[7]. Peterson and Dunning[8], using correlated molecular wave

functions, have also calculated the bond dissociation energy (85.8 and 40.2 kcal/mol) for the vinyl radical.

Glukhovtsev and Bach[9] have carried out an ab initio study on the thermochemistry of the vinyl radical and derived the heat of formation ΔH_f^0 to be 73.09 kcal/mol. Ervin et al.[10] using negative ion photoelectron spectroscopy and gas-phase proton transfer kinetics experiments reported an experimental value for ΔH_f^0 as 72.68±0.79 kcal/mol. The National Institute of Standards (NIST) webbook database[11] recommends a value of 71.53±1.20 kcal/mol, while an earlier compilation[12] of thermochemical data cites 63.40±0.96 kcal/mol.

A visible absorption spectrum due to the $\tilde{A} \leftarrow \tilde{X}$ electronic transition of the vinyl radical has been detected using photochemical modulation spectroscopy in Hg-photosensitised reactions[13]. The threshold of absorption is at 495.5 nm and reaches maximum intensity around 400 nm. Two Rydberg states (164.71 and 168.33 nm) of the vinyl radical have been detected via absorption in the vacuum ultraviolet using flash photolysis[14]. Very recently, a UV spectrum for vinyl has been reported for the region 225-238 nm[15]. The absorption cross section increases from 2×10^{-18} at 238 nm to nearly 1×10^{-17} at 225nm. There have been no other recent spectroscopic investigations on the excited states of the vinyl radical; theorists, however, have been actively pursuing the study of these excited electronic states[6,7]. There is also considerable controversy surrounding the ionization potential, with experimental values ranging from 8.25 to 8.95 eV[9].

In 1965, R. G. W. Norrish asserted that combustion research followed two principal lines of investigation, one of which is "to find the nature of the chain centers,

and intermediate products, and to examine quantitatively their reactions, and also involves analytical photochemical and spectroscopic studies" [16]. Following in that vein we have started a new project to study the photodissociation of free radicals in molecular beams using velocity map imaging (VELMI)[17]. The study of the dynamics of photodissociation can give detailed information on the nature of the potential energy surfaces and the coupling between them, the structure of the transition state, and the identity and thermodynamics of the dissociation pathways[18]. It is with an eye to the thermodynamics of dissociation processes that we report in this letter the first experimental investigation of the photodissociation of the vinyl radical.

Experimental:

The molecular beams apparatus has been described in detail in a recent publication[19]. A modification in the present experiment was to install a closed cycle He cryo-pump to minimize hydrocarbon background in the detection chamber. The vinyl radical (C_2H_3) beam was generated by photolysing a 5% mixture of vinyl chloride (C_2H_3Cl) in He, using the focussed 193 nm output of a ArF excimer laser (Lambda-Physik), at the nozzle of a Prock-Trickl[20] piezoelectric pulsed valve. After the radical beam was collimated by a skimmer, it was crossed by a second photolysis and probe (one color) laser beam on the axis of a velocity focusing time-of-flight mass spectrometer. A schematic of the experimental apparatus is shown in Fig. 1. The product H atoms formed from the vinyl radical photodissociation were ionized using a one color (2+1) resonant enhanced multiphoton ionization (REMPI) scheme[21]. The probe light around 243 nm was generated by doubling the output of a seeded Nd-YAG (Spectra-Physics GCR 290-30)

pumped dye laser (Laser Analytical Systems LDL) operating at 729 nm in β- barium borate (BBO), then mixing the resultant UV light with the dye fundamental in a second BBO crystal.

The H^+ ion was accelerated toward a 80-mm diameter dual microchannel plate (MCP) (Galileo 3075FM) coupled to a phosphor screen and imaged on a fast scan charge-coupled device camera with integrating video recorder (Data Design AC-101M). Camera threshold and gain were adjusted in conjunction with a binary video look-up table to perform integration of single ion hits on the MCP free of video noise. Images were accumulated while scanning across the Doppler profile of the H atom, since the line width of the laser light was narrower than the Doppler spread.

Results:

The judicious combination of radical precursor in conjunction with the appropiate photolysis wavelengths allows us to prepare an intense vinyl radical beam for photodissociation studies. Vinyl chloride has a maximum absorption at 193 nm[22] (precursor photolysis wavelength), and it has no detectable absorption at 243 nm (radical photolysis wavelength). There is no published absorption spectrum for the vinyl radical at near UV wavelengths. In the experiments reported here, the H atom signal was over 100 times more intense with the excimer laser on compared to off, essentially providing us with a background free environment.

A potential problem in our experiments is the generation of H atoms in the photolysis of the radical precursor vinyl chloride. Blank et al.[2] have recently shown that in addition to the Cl elimination channel in the photodissociation of vinyl chloride at 193

nm there is also a H atom elimination channel. These H atoms will be entrained in the beam and will be detected in addition to any H atoms that are formed in the photodissociation of the vinyl radical itself. The VELMI technique allows us to circumvent this problem, since all entrained H atoms with the same initial velocity vector in the plane parallel to the detector are focussed to the same point, regardless of their distance from the ion lens axis. A raw image of H atoms formed in the photodissociation of the vinyl radical is shown in Fig. 2(a). The direction of the molecular beam is from the upper right to the bottom left of the image, and the laser propagation direction is through the center of the image from right to left. The extremely bright spot near the center are the H atoms formed in the photolysis of vinyl chloride. The rest of the image is composed of H atoms formed via vinyl radical photodissociation. There is also structure in the outer edges of the image: two rings which can be seen in Fig. 2(a) are marked. In addition, there is another very slow feature. This was studied in greater detail, by reducing the acceleration fields to expand the image, and scanning the Doppler profile across this feature only. Fig. 2(b) shows this magnified image of the inner area of the H atom distribution. Offset from the bright spot of H atoms formed via vinyl chloride dissociation at the nozzle, we see an added ring corresponding to extremely slow H atoms. The offset between the H atom spot and the center of this ring indicates that there is velocity slippage between the entrained H atoms and the vinyl radicals formed in the beam.

Fig. 3(a) shows the translational energy distribution ($P(E_T)$) for the H atom obtained from the inverse Abel transformed image of Fig. 2(a). The translational energy distributions were calibrated by measuring the speed of H atoms formed from the photodissociation of H_2S[23]. The most noticeable feature is that the translational energy is

peaked away from zero (maximum at 9.5 kcal/mol) and that the two rings mentioned above at the outer edges show up as little humps at 28.4 and 36.7 kcal/mol . Fig. 3(b) is the translational energy distribution for the inner ring obtained from the inverse Abel tranformed image shown in Fig. 2(b), peaking at 0.23 kcal/mol.

One revealing way to look at photodissociation dynamics and the nature of the excitation process is to observe the angular distribution of the fragments. The image shown in Fig. 2(a) does suggest that there is some anisotropy in the angular distributions resembling a perpendicular (β = -1) dissociation, particularly for the outer rings. Interestingly, this is consistent with the nature of the electronic transition expected ($A'' \leftarrow A'$) for both $\tilde{A}$ and $\tilde{B}$ state excitation of the vinyl radical. This suggests that these outer rings showing anisotropy may well be associated with a prompt dissociation process. However, we have a complication with the detection of very fast H atoms using our existing experimental setup. Due to the finite duration of the probe pulse (10 ns), and the small spot size required for the 2+1 REMPI detection scheme for H atoms, very fast H atoms moving perpendicular to the laser propagation direction will be less efficiently detected. In effect, this "flyout" will give rise to anisotropy similar to that seen in our experiments. In future studies we will use loosely focussed Lyman-α radiation (1+1 REMPI) with a second UV laser for the photodissociation of the radical, in conjunction with Monte Carlo modeling of the experiment to address this problem.

Discussion

Fig. 4 shows an energy diagram for the excited states of vinyl radical accessible with the absorption of a 243 nm (117.61 kcal/mol) photon, and the various vinylidene +

H and acetylene + H dissociation channels. For a bond scission process as shown below:

$$C_2H_3 \xrightarrow{243nm} HCCH + H + E_T$$

the bond dissociation energy can be obtained using energy and momentum conservation by the following formula

$$D_0(C_2H_2\text{-}H) = E_{photon} - E_T^{MAX}$$

where E_T^{MAX} is maximum release of translational energy if it is assumed that both the fastest products and the initial reactant are internally cold. In fact, this represents an upper bound for the dissociation energy, D_0, if the former assumption holds, and a lower bound if the latter. The bond dissociation energy for $C_2H_3 \rightarrow HCCH + H$ and $C_2H_3 \rightarrow H_2CC + H$ channels are 33.6±0.8 and 81.0±3.5 kcal/mol respectively[10]. Hence if ground state acetylene and vinylidene are formed in the photodissociation of the vinyl radical, their corresponding H atoms should reflect a maximum total translational energy release of 84.0 and 36.6 kcal/mol respectively. Examination of our $P(E_T)$) from Fig. 3(a) shows that we have a small peak at 36.7 kcal/mol which corresponds to the $C_2H_3 \rightarrow H_2CC(^1A_1) + H$ channel. Only than 1.1% of the products appear at a higher E_T (below the threshold for vinylidene formation) and these in fact may arise from 'hot band' contribution as discussed below.

Using negative-ion photoelectron spectroscopy, Ervin et al[24], reported the C-H symmetric stretch for ground state vinylidene to be 3025±30 cm^{-1}. On examination of our image (Fig. 2(a)) and the corresponding $P(E_T)$, we find the difference between the two outer rings, marked with the arrows in Fig. 3(a), corresponds roughly to an energy difference of 2900 cm^{-1}. Comparing these results with that of Ervin et al[24], we believe

that the structure that we see at the outer edges of our image corresponds to internally cold ground state vinylidene (marked '0') and that with one quanta of C-H symmetric stretch (marked '1'). Using the published heats of formation for C_2H_3 (71.48 kcal/mol)[11], and $H(^2S)$ (52.11 kcal/mol)[11] we derive the heat of formation for vinylidene ΔH_f^0 (H_2CC) to be 100.3±4.0 kcal/mol which is in excellent agreement with the results of Ervin et al[10]

An examination of the $P(E_T)$ shows that the H atoms formed concurrently with vinylidene are not peaked at zero but at 9.5 kcal/mol. This observation suggests either a barrier to the formation of vinylidene from the dissociation of the vinyl radical or an direct, impulsive dissociation. At our excitation wavelength, the $\tilde{A}$ ($1^2A''$) and $\tilde{B}$ ($2^2A''$) excited states of the vinyl radical can be accessed[7]. However, these excited states do not correlate to any ground state (A′) products, and internal conversion from these species to the ground state is not possible. Calculations by Paddon-Row and Pople[5] for the $\tilde{A}$ ($^2A''$) and Mebel et al[7] for both the $\tilde{A}$ ($^2A''$) and $\tilde{B}$ ($^2A''$) states, show that twisted A′ geometries exist for these excited states, which possess the correct symmetry to interact with the ground state surface. This twisting is thus a necessary step on the pathway from the excited species to ground state singlet products. The question then becomes the timescale for dissociation following this twisting motion, and the location of the regions of the excited and ground state surfaces where the coupling occurs. If the dissociation is fairly direct once the twisted geometries are attained, then our observed 9.5 kcal/mol barrier likely is a manifestation of the transition state between these planar and twisted geometries, which is a necessary step on the path to the ground state vinylidene (A′ in C_s) product. The earlier calculations of Paddon-Row and Pople[5] found a barrier of 7.4 kcal/mol for this out-of-plane rotation in the $\tilde{A}$ state; this would be entirely consistent

with our observations. Mebel et al. do not give values for the barrier to interconversion between these species, so it is not clear whether our results arise from initial excitation to the $\tilde{A}$ or $\tilde{B}$ states or both. The absence of ground state acetylene is not surprising given the geometric constraints of moving from the bent vinyl radical configuration to a linear one of acetylene. It is important to note, however, that for energies a few kcal/mol above the vinylidene asymptote, isomerization to acetylene is rapid, and a distinction between these species is of limited significance.

Fig. 4 shows that based on most recent calculations, apart from forming ground state vinylidene and acetylene, there are no other channels available for H atom formation with the available photon energy of 117.6 kcal/mol. However, we do observe an additional channel giving rise to very slow H atoms. The results, summarized in Fig. 3(b), show a total translational energy release peaking at only 0.23 kcal/mol. Examination of Fig. 4 shows that the nearest state available to give rise to such slow H atoms must be the lowest triplet state of acetylene C_2H_2 ($\tilde{a}\ ^3B_2$). This state correlates directly to the excited states, and involves little geometry change from the excited radical to the product. The associated dynamics are thus likely to be direct. The excitation energy for this triplet state relative to ground state acetylene has never been measured experimentally.

There has been considerable controversy surrounding the nature of triplet states of acetylene. Burton and Hunziker[25] first identified the lowest triplet state of acetylene through Hg photosensitized excitation of acetylene. On the basis of ab-initio calculations, Kammer[26] predicted the first triplet state to be more stable in its cis-bent form ($^3B_2$) than in the trans form (^3B_u) by 2258 cm^{-1}, while for the second triplet it is opposite, cis ($^3A_2$) being above trans (^3A_u) by 1290 cm^{-1}. An electronic dipole transition is allowed for the

cis geometry ($^3A_2 \leftrightarrow {}^3B_2$) but parity forbidden for the trans case ($^3A_u \leftrightarrow {}^3B_u$). When this transition was not found in the C_2H_2 Hg-photosensitization work of Burton and Hunziker[25], it was speculated that the lowest triplet might have the trans structure. Subsequent ab-initio calculations by Demoulin[27] and by Wetmore and Schaefer[28] have confirmed Kammer's results that the lowest excited state of acetylene is the cis bent $^3B_2$ state. Wetmore and Schaefer[28] earlier placed the electronic excitation energy (relative to the X $^1\Sigma_g^+$ ground state), T_0, at 28200 cm^{-1}. Wendt et al[29] reinvestigated the Hg excitation of acetylene using photochemical modulation spectroscopy and recorded the $^3A_2 \leftrightarrow {}^3B_2$ electronic absorption spectrum in the near infrared, confirming the theoretical prediction of the lowest excited triplet state of acetylene to be cis bent. Subsequently Lundberg et al[30], noticed some anomalous vibronic states in the stimulated emission pumping spectra of C_2D_2. The authors postulated that one plausible explanation would be to lower the excitation energy T_0 for the cis-bent triplet state of acetylene to $\leq$ 25820 cm^{-1}. This was inconsistent with the best ab-initio results available at that time. The same authors carried out new higher level ab-initio calculations and found to their surprise that instead of lowering the term energy values of the cis–bent $\tilde{a}$ $^3B_2$ to match the experimental results, they had to raise it by 3000 cm^{-1}. Their best estimate for T_0 was 30500 ± 1000 cm^{-1} [30,31].

If we assume that the slow H atoms formed in the 243 nm photodissociation of the vinyl radical comes through the C_2H_2 ($\tilde{a}$ $^3B_2$) + H channel, we can derive an upper limit for the heat of formation for the triplet species. Using the known heats of formation for C_2H_3 (71.48 kcal/mol)[11], and H(^{2}S) (52.11 kcal/mol)[11] we derive the heat of formation for C_2H_2($\tilde{a}$ $^3B_2$) ΔH_f^0 to be 82.65 kcal/mol. This is the first direct experimental derivation

of the heat of formation for the triplet state of acetylene. Using this value we derive the electronic excitation energy for C_2H_2 ($\tilde{a}\ ^3B_2$) (relative to the X $^1\Sigma_g^+$ ground state), T_0, to be 28904 cm^{-1}. This experimental value is consistent within error limits with the earlier ab-initio value of 28200 cm^{-1} [28], but is somewhat outside the quoted error limits for the latest value of 30500 cm^{-1} [30,31].

Aside from possible shortcomings in the ab-initio calculations, one reason for this discrepancy could be that the vinyl radicals in our beam may not be internally cold. Examination of the $P(E_T)$ in Fig. 3(a), shows that the translational energy distribution extends out to 45 kcal/mol, beyond the limit for ground state vinylidene formation which is at 36.6 kcal/mol. This can arise from either ground state acetylene being formed with substantial internal energy, or from 'hot band' contributions from internally excited vinyl radicals in the beam. The latter could then account for our observation of triplet acetylene being formed below the calculated ab-initio threshold. The fact that the contribution beyond the threshold for vinylidene is a very small fraction of the total gives us reason to believe this 'hot band' contribution is fairly small. Nevertheless, if it were the only means to produce the triplet product, its contribution might show up clearly. If indeed this contribution arises from vibrationally excited radicals in the beam, then we expect this channel leading to the formation of triplet acetylene to become more important as we increase the photon energy for dissociation. There are other low lying triplet states of acetylene (^3B_u, ^3A_u, and $^3A_2$) and vinylidene ($^3B_2$ and $^3A_2$) near the C_2H_2 ($\tilde{a}\ ^3B_2$) state[7]. Increasing the photon energy to access these states will allow us to probe the dynamics of these little-studied states. This work is underway.

Conclusion:

We have measured the translational energy release of H atoms formed in the photodissociation of the vinyl radical (C_2H_3) at 243.2 nm in a molecular beam. The primary product is singlet vinylidene (H_2CC ($\tilde{X}$ $^2A'$)) or singlet acetylene at energies where interconversion between the H_2CC and HCCH geometries is sufficiently rapid to make the distinction meaningless. The translational energy distributions are consistent with a barrier of at least 9.5 kcal/mol to dissociation for the vinylidene channel which may arise from twisting on the excited state surface necessary to lead to electronic symmetries that can couple to products. In addition, a minor contribution is seen which is assigned to triplet acetylene (C_2H_2 ($\tilde{a}$ $^3B_2$)). The heat of formation of vinylidene is derived to be 100.3±4.0 kcal/mol in agreement with literature values. We have also identified the C-H symmetric stretch in the vinylidene fragment. From the translational energy release, we derive the T_0 for triplet acetylene C_2H_2 ($\tilde{a}$ $^3B_2$) to be 28900 cm^{-1}.

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References:

1. W.C. Gardiner Jr. (Ed.), Combustion Chemistry, Springer, New York, 1984.
2. B.A. Balko, J. Zhang and Y.T. Lee, J. Chem. Phys. **97**, 935 (1992).

3. D.A. Blank, W. Sun, A.G. Suits, Y.T. Lee, S.W. North and G.E. Hall, J. Chem. Phys. **108**, 5414 (1998).

4. A. Sevin, H.T. Yu and E.M. Evleth, J. Molec. Structure. (Theochem) **104**,163 (1983).

5. M. N. Paddon-Row and J. A. Pople, J. Phys. Chem. **89**, 2768 (1985).

6. J-H Wang, H-C Chang, and Y-T Chen, Chem. Phys. **206**, 43 (1996).

7. A. M. Mebel, Y-T Chen, and S-H Lin, Chem. Phys. Lett. **275**, 19 (1997).

8. K.A. Peterson, and T.H. Dunning, Jr. J. Chem. Phys. **106**, 4119 (1997).

9. M.N. Glukhovtsev and R.D. Bach, Chem. Phys. Lett. **286**, 51 (1998).

10. K.M. Ervin, S. Gronert, S.E. Barlow, M.K. Giles, A.G. Harrison, V.M. Bierbaum, C.H. Depuy, W.C. Lineberger, and G.M. Ellison, J. Am. Chem. Soc. **112**, 5750 (1990).

11. H.Y. Afeefy, J.F. Liebman, and S.E. Stein, "Neutral Thermochemical Data" *in NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, Eds. W.G. Mallard and P.J. Linstrom, March 1998, National Institute of Standards and Technology, Gaithersburg MD, 20899 (http://webbook.nist.gov).

12. S.G. Lias, J.E. Bartmess, J.L. Holmes, R.D. Levin, W. G. Mallard, J. Phys. Chem. Ref. Data **17** (1988) Supp. 1.

13. H.E. Hunziker, H. Kneppe, A.D. McLean, P. Siegbahn, and H.R. Wendt, Can. J. Chem. **61**, 993 (1983).

14. A. Fahr and A.H. Laufer, J. Phys. Chem. **92**, 7229 (1988).

15. A. Fahr, P. Hassanzadeh and D. B. Atkinson, Chem. Phys. **236**, 43 (1998).

16. R.G.W. Norrish, Int. Symp. on Combustion **10**, 1 (1965).

17. We propose the euphonious acronym VELMI for the velocity map imaging technique pioneered by Eppink and Parker (A.T.J.B. Eppink and D.H. Parker, Rev. Sci. Instrum., **68**, 3477 (1997)) , as this method is rapidly coming into widespread use.

18. J.C. Whitehead, Rep. Prog. Phys. **59**, 993 (1996).

19. M. Ahmed, D. Blunt, D. Chen, and A.G. Suits, J. Chem. Phys. **106**, 7617 (1997).

20. D. Proch and T. Trickl, Rev. Sci. Instrum. **60**, 713(1989).

21. D.P. Baldwin, M.A. Buntine, and D.W. Chandler, J. Chem. Phys. **93**, 6578 (1990).

22. M.J. Berry, J. Chem. Phys. **61**, 3114 (1974).

23. L.J. Rogers, M.N.R. Ashfold, Y. Matsumi, M. Kawasaki, and B.J. Whitaker, J. Chem. Soc. Faraday. Trans. **92**, 5181 (1996).

24. K.M. Ervin, J. Ho, and W.C. Lineberger, J. Chem. Phys. **91**, 5979 (1989).

25. C.S. Burton and H.E. Hunziker, J. Chem. Phys. **57**, 339 (1972).

26. W.E. Kammer, Chem. Phys. Lett. **6**, 529 (1970).

27. D. Demoulin, Chem. Phys. **11**, 329 (1975).

28. R.W. Wetmore and H.F. Schaefer, J. Chem. Phys. **69**, 1648 (1978).

29. H.R. Wendt, H. Hippler, and H.E. Hunziker, J. Chem. Phys. **70**, 4044 (1979).

30. J.K. Lundberg, R.W. Field, C.D. Sherill, E.T. Seidl, Y. Xie and H.F. Schaefer III, J. Chem. Phys. **98**, 8384 (1993).

31. Y. Yamaguchi, G. Vacek, and H.F. Schaefer III, Theor. Chim. Acta. **86**, 97 (1993).

Captions:

Fig. 1. Schematic view of the velocity map imaging machine.

Fig. 2. Data images for H atoms from photodissociation of the vinyl (C_2H_3) radical at 243.2 nm. (a) Image of total distribution; 0-limit for cold ground state vinylidene and 1-one quanta of C-H symmetric stretch in vinylidene. The bright spot is H atoms formed by photodissociation of C_2H_3Cl at the nozzle (see text). (b) 5x magnified image showing slow H atom distribution (see text).

Fig. 3. (a) Translational energy distributions for H atoms obtained from the image in Fig. 2 (a). (b) same but from image shown in Fig. 2(b).

Fig. 4. Energy diagram for ground and excited states of C_2H_3 and the dissociation channels to low lying states of vinylidene and acetylene + H. Downward arrows indicate coupling to ground state surface.

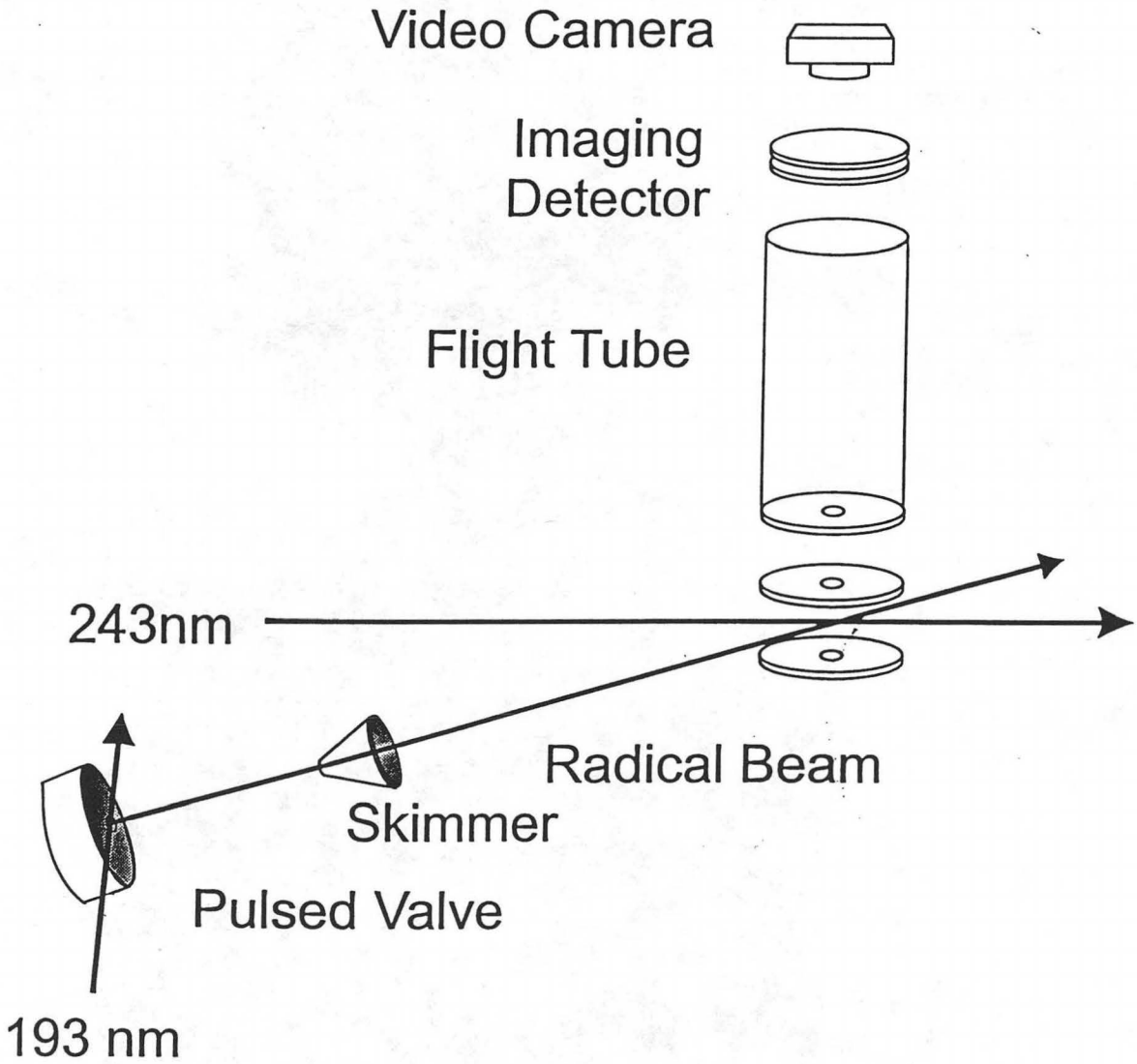
Video Camera
Imaging
Detector
Flight Tube
243nm
Radical Beam
Skimmer
Pulsed Valve
193 nm

Fig. 1

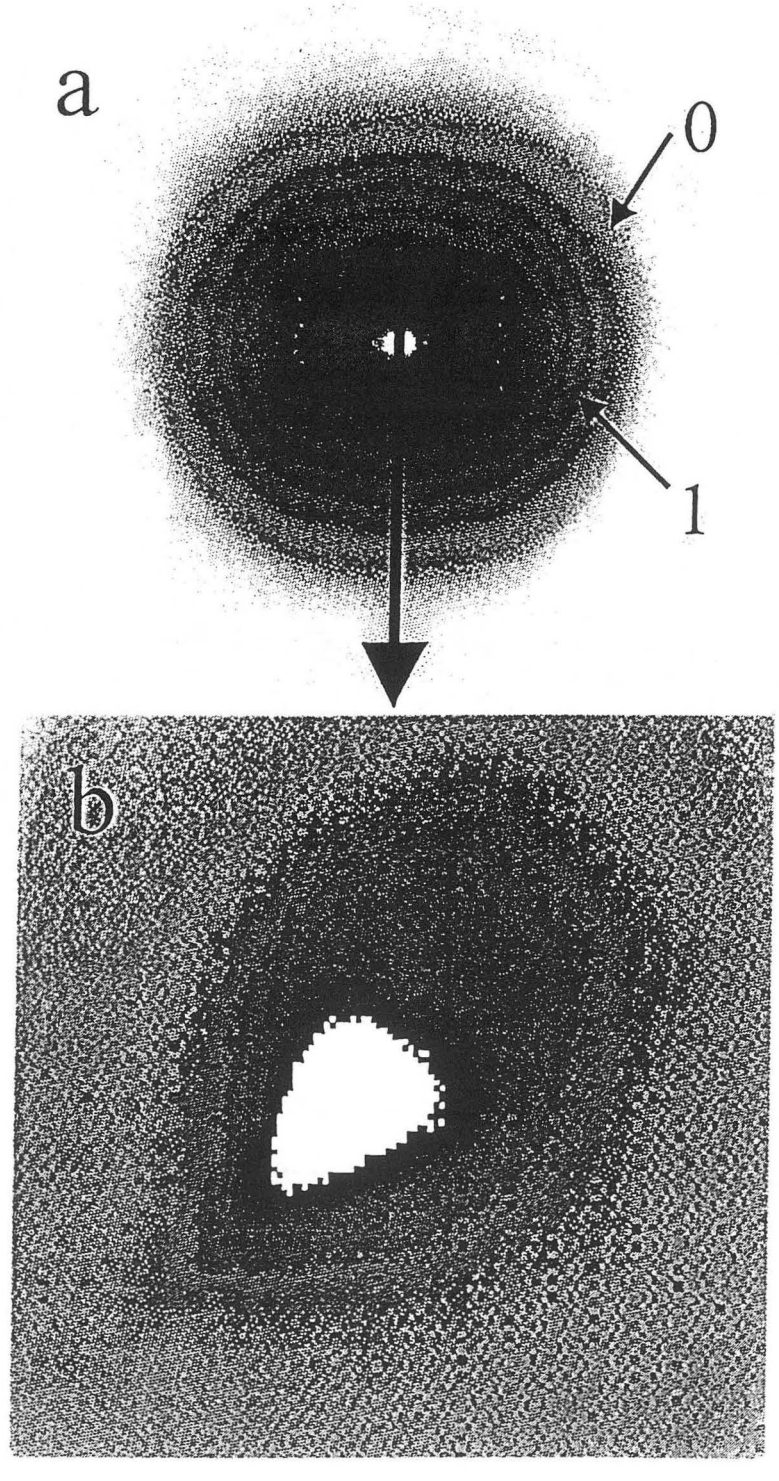

Fig. 2.

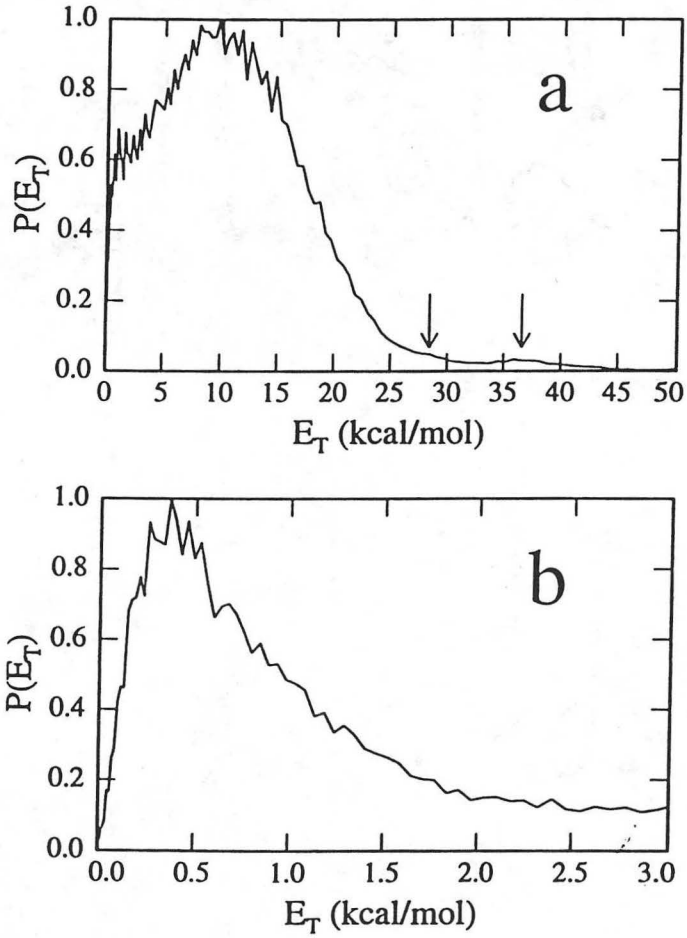
a
b
P(E_T)
E_T (kcal/mol)
1.0
0.8
0.6
0.4
0.2
0.0
0
5
10
15
20
25
30
35
40
45
50
0.5
1.5
2.0
2.5
3.0

Fig. 3

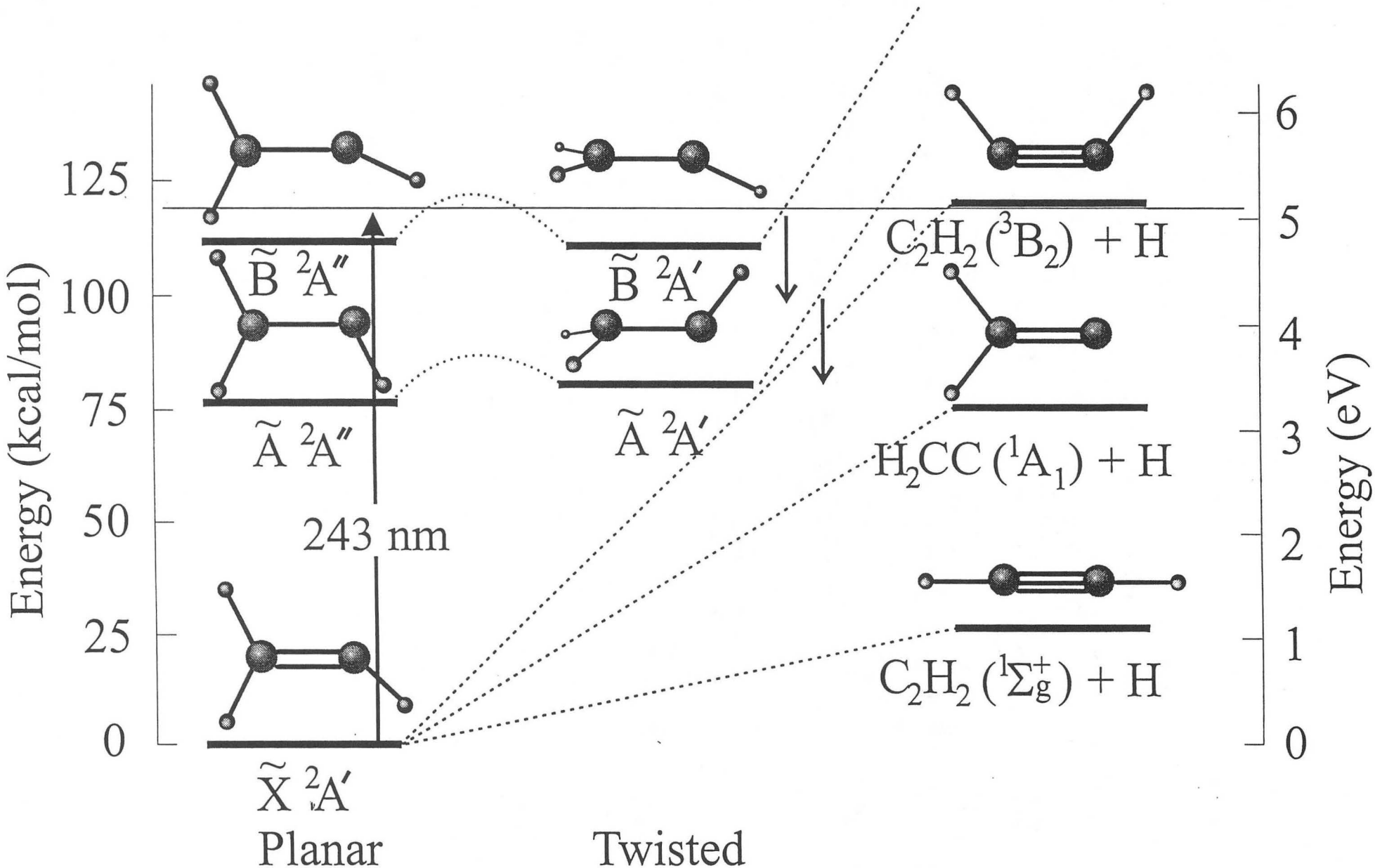
Energy (kcal/mol)
125
100
75
50
25
0
Energy (eV)
6
5
4
3
2
1
0
$\tilde{B}\ ^2A''$
$\tilde{A}\ ^2A''$
243 nm
$\tilde{X}\ ^2A'$
Planar
$\tilde{B}\ ^2A'$
$\tilde{A}\ ^2A'$
Twisted
$C_2H_2\ (^3B_2)$ + H
$H_2CC\ (^1A_1)$ + H
$C_2H_2\ (^1\Sigma_g^+)$ + H

Fig. 4

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