

Infrared photochemistry of ethylene clusters

Michael P. Casassa,^{a)} David S. Bomse,^{b)} J. L. Beauchamp, and Kenneth C. Janda

Division of Chemistry and Chemical Engineering^{c)}, California Institute of Technology, Pasadena, California 91125

(Received 26 March 1980; accepted 15 April 1980)

Considerable experimental¹⁻⁴ and theoretical^{5,6} effort has been applied to the study of decomposition processes of electronically and vibrationally excited van der Waals molecules. These are relatively simple systems for studying dynamics of intramolecular energy transfer. When high-power pulsed CO₂ lasers are used to dissociate (C₂H₄)₂, a broad spectrum is observed in the region of the ν_7 vibrational mode of the monomer.¹ We report direct observation of efficient infrared photodissociation of ethylene clusters using low-power cw laser radiation. When low-power radiation is used, the homogeneous linewidth observed is significantly narrower than suggested by the pulsed laser experiments of Gentry *et al.*¹

Ethylene clusters are formed in a molecular beam by supersonic expansion of ethylene mixed with helium. The molecular beam composition is monitored with a quadrupole mass spectrometer positioned 65 cm from the nozzle. An unfocused infrared CO₂ laser beam is directed coaxially to the molecular beam through the ionizer of the mass spectrometer. Photodissociation is detected as the laser-induced change in the molecular beam mass spectrum.

A typical infrared photodissociation spectrum is shown in Fig. 1. In this case, the molecular beam is formed by expansion of an 11% C₂H₄-He mixture at 7 atm pressure using a 35 μ m nozzle. Data are given for fractional attenuation of C₃H₅⁺ (*m/e* 41) and C₄H₈⁺ (*m/e* 56) signal intensities as a function of laser wavelength. At the maximum laser power available at 951 cm⁻¹ (laser

linewidth < 10⁻² cm⁻¹) 80% of the van der Waals molecules are dissociated without saturating the transition. In both cases the spectra exhibit Lorentzian line shapes with maxima at $\nu_0 = 953$ cm⁻¹ and linewidths (FWHM) of 16 \pm 3 cm⁻¹. The observed photodissociation line shapes are invariant to changes in laser power. Furthermore, the position and width of the bands are independent of changes of ethylene concentration (3.6%–100%) in the expansion even though this is equivalent to altering the molecular beam temperature and the distribution of ethylene cluster sizes. Within the CO₂ laser wavelength region, monomeric ethylene has a single absorption band, $\nu_7 = 949.2$ cm⁻¹, due to an out-of-plane bending vibration of *b*_{2u} symmetry.⁷ The photoacoustic spectrum of ethylene at 1 atm pressure, obtained using a CO₂ laser, shows appreciable intensity at a single laser line, 949.48 cm⁻¹, with no significant absorption at other CO₂ laser lines.⁸ The above results indicate a homogeneously broadened absorption by the van der Waals molecules. We attribute this to a vibrationally predissociative lifetime of 0.33 psec. This lifetime corresponds to ~10 vibrational periods prior to dissociation.

We have also studied the 10 μ m photodissociation spectra of clusters derived from C₂D₄ (10% in He). A line is observed at 1074 cm⁻¹ with a cross section an order of magnitude lower than for C₃H₅⁺ and which indicates a minimum lifetime of 0.7 psec. In comparison, the C₂D₄ infrared absorption spectrum shows a maximum at 1077.9 cm⁻¹ due to an in-plane bending vibration of *b*_{3u} symmetry.⁷ The difference in lifetimes obtained for ethylene clusters and ethylene-*d*₄ clusters can be under-

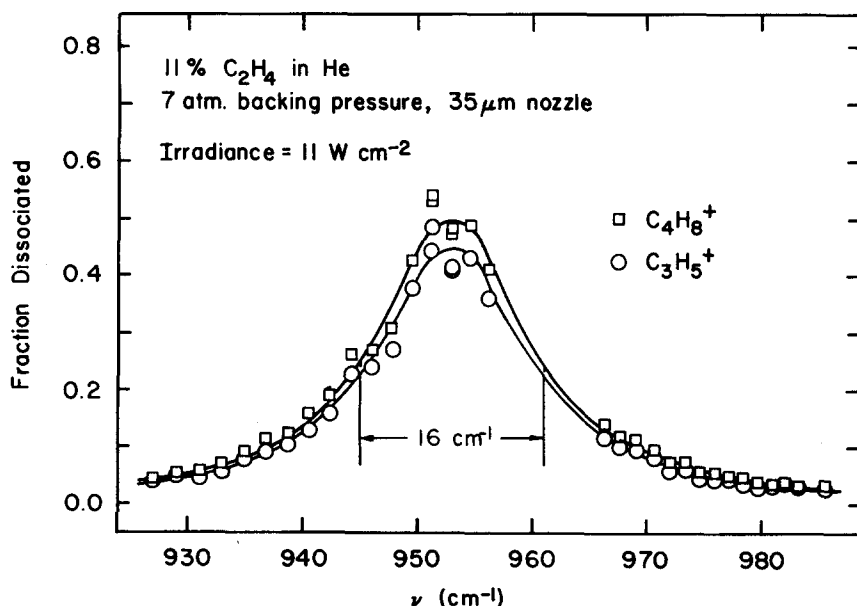


FIG. 1. Infrared photodissociation spectra of ethylene clusters. The solid curves are Lorentzian profiles.

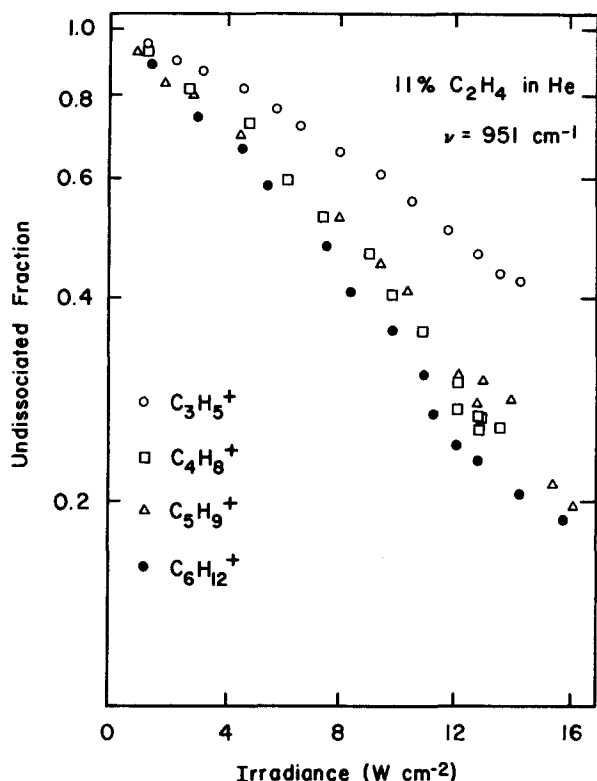


FIG. 2. Power dependences of the photodissociation yield. The supersonic expansion conditions are 7 atm backing pressure and 35 μm nozzle diameter.

stood by examination of the vibrational modes excited.¹ Assuming ethylene clusters form with molecular planes parallel, as is observed in the crystal,⁹ then the out-of-plane bending mode should be more efficient than an in-plane vibration at leading to dissociation.

Figure 2 shows the variation of the logarithm of photodissociation yield, monitored at four ion masses, as a function of laser power at fixed wavelength. The ions are C_3H_5^+ (m/e 41), C_4H_8^+ (m/e 56), C_5H_9^+ (m/e 69), and $\text{C}_6\text{H}_{12}^+$ (m/e 84). In each case data points fall on a straight line indicating that the undissociated fraction of molecules, F , follows $F = \exp(-\Phi\sigma t)$, where Φ is the photon flux, σ is the photodissociation cross section, and t is the irradiation time. No saturation is observed at irradiances up to 17 Wcm^{-2} . The four apparent cross sections are unequal and depend on the ethylene concentration in the expansion indicating that photodissociation of several cluster sizes is detected as intensity loss at a single mass peak. For example, electron impact ionization of ethylene trimers, $(\text{C}_2\text{H}_4)_3$, forms fragment ions C_3H_5^+ , C_4H_8^+ and C_5H_9^+ as well as the parent ion $\text{C}_6\text{H}_{12}^+$. Analysis of the changes in infrared photodissociation

cross section with molecular beam composition yields an upper bound value for the ethylene dimer cross section of $\sigma_2 = 9.2 \times 10^{-19} \text{ cm}^2$ and a lower bound value for the ethylene trimer cross section of $\sigma_3 = 1.7 \times 10^{-18} \text{ cm}^2$.

In the power regime of these experiments, photodissociation spectral linewidths are dominated by lifetime broadening providing valuable information on intramolecular energy transfer rates. Differences in observed lifetimes of ethylene clusters and ethylene- d_4 clusters show relaxation rates vary with the vibrational mode initially excited. Dimers and trimers of ethylene exhibit similar photodissociation maxima and lifetimes.

The narrow linewidths and efficient cross sections of low-power IR photodissociation enhance prospects of isotope-selective dissociation at greatly reduced photon expense compared to standard techniques. Similarly, these results suggest that cluster intensities can be conveniently modulated for phase sensitive detection in spectroscopic or scattering experiments. There are many aspects of this process which merit further investigation.

This work was supported by the Research Corporation and the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy under contract No. DE-AS03-76SF00767. Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

^aNational Science Foundation Predoctoral Fellow.

^bJosephine de Karman Fellow and Monsanto Fellow.

^cContribution number 6183.

¹W. R. Gentry, *XI International Conference on the Physics of Electronic and Atomic Collisions* (North-Holland, Amsterdam, 1979).

²J. E. Kenney, K. E. Johnson, W. Sharfin, and D. H. Levy, *J. Chem. Phys.* **72**, 1109 (1980); and references contained therein.

³T. E. Gough, R. E. Miller, and G. Scoles, *J. Chem. Phys.* **69**, 1588 (1978).

⁴A. Sudbø, P. A. Schultz, Y. T. Lee, and Y. R. Shen, *Proceedings of the First International School on Laser Applications to Atoms, Molecules and Nuclear Physics* (Vilnius, USSR, 1978).

⁵J. A. Beswick and J. Jortner, *J. Chem. Phys.* **68**, 2277 (1978); *ibid.* **69**, 512 (1978); G. Ewing, *J. Chem. Phys.* **29**, 253 (1978).

⁶R. Ramakrishna and A. E. DePristo, *J. Chem. Phys.* **72**, 770 (1980).

⁷G. Herzberg, *Infrared and Raman Spectra* (Van Nostrand Reinhold, New York, 1966).

⁸L. B. Kreuzer, *Anal. Chem.* **46**, 235A (1974).

⁹C. Brecher and R. S. Halford, *J. Chem. Phys.* **35**, 1109 (1961).