LA-UR -86-1423

CONF-8603127--1

RECEIVED BY OSTI MAY 12 1986

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

TITLE **VACUUM ULTRAVIOLET PHOTOLYSIS OF ACETYLENE IN THE 110-135 nm REGION**

LA-UR--86-1423

DE86 010202

AUTHOR(S) Joe J. Tiee, CHM-4
Robert K. Sander, CHM-4
Charles R. Quick, CHM-4
Ron Estler, Fort Lewis College

SUBMITTED TO American Institute of Physics Proceedings

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

By acceptance of this article the publisher recognizes that the U S Government retains a nonexclusive royalty-free license to publish or reproduce the published form of this contribution or to allow others to do so, for U S Government purposes

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U S Department of Energy

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

FORM NO 836 R4
ST NO 2629 5/81

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Vacuum Ultraviolet Photolysis of Acetylene in the 110-135-nm Region

J. J. Tiee, R. K. Sander, and C. R. Quick

Los Alamos National Laboratory, Los Alamos, NM 87545

R. Estler
Fort Lewis College, Durango, Colorado

Abstract

State-specific photofragmentation of acetylene in the 110- to 135-nm region has been studied using vuv laser and synchrotron sources. Investigations have been focused on learning the spectroscopic identity of the excited photoproducts by examining their time-resolved fluorescence. Results of the quenching of the excited photofragment emission and the emission polarization measurements are presented. An interpretation of these results in relating the observed photoproducts to the vuv photodissociation process is discussed.

Introduction

Vacuum ultraviolet photolysis of acetylene has been studied first by Stief et al.[1] at 1236 nm. An visible emission was reported by this work to be due to C_2 Swan band. Becker et al.[2] later attributed the emission to be from an excited state of C_2H_2 or that of the C_2H (designed here as C_2H^*) because the emission appeared to be broad covered the 400- to 580-nm region, unlike the diatomic spectrum of the C_2 radical. Similar works[3,4] on the vuv photolysis of C_2H_2 and C_2HBr have provided strong evidences that excited ethynyl radicals, C_2H^* are indeed the photoproducts. Very recently, additional experimental evidences were provided by other workers using a fast discharge vuv light source[5] and synchrotron radiation.[6] There seems to be little doubt that the broad emission is due to C_2H^*. However, a controversy has arisen over the mechanism of the observed long decay time: does it represent the radiative lifetime of the excited radical or a dark intermediate state that rapidly produces the emitting photoproducts. A proposal[7,8] for the dark intermediate state is that it is the lowest triplet state of vinylidene, CCH_2,[9-11] since it has been observed in flash photoexcitation of acetylene. The triplet state of the acetylene isomer, CCH_2 has been calculated to be at 14,700 cm^{-1} above the ground state.[9]

With the availability of the laser-based high-resolution vuv light sources, a state-specific photofragmentation study of C_2H_2 can be implemented to address these issues. The intention is to examine the collision-free fluorescence lifetime and quenching efficiency of the observed emission in a state selective manner. In addition, using the fluorescence polarization measurements to learn about the excited state symmetry.

Experimental

Both a synchrotron light source and a laser-based coherent vuv source are used for these experiments. The synchrontron light source is used for providing a low-resolution survey of excitation spectra over a broad wavelength range (110 to 140 nm). With the large time-window and the high-spectral resolution of the laser source. The coherent light is used for obtaining time-resolved measurements of fluorescence decay and vibronically state-specific excitation spectra.

The synchrotron light source is a windowed (LiF) beam port (U9A) at the Brookhaven National Laboratory, National Synchrotron Light Source (NSLS). A 0.5-M monochromator is used to disperse the vuv light. Excited species emission is detected at right angles with a 0.2-M monochromator and a cooled photomultipler tube (PMT). The broadband synchrotron radiation is used to calibrate the spectral efficiency of the detection system. NIM photon counting electronics in conjunction with a LeCroy 3500 multichannel analyzer and a mini-computer (LS-11) are used for data acquisition and reduction.

The coherent vuv light is generated by frequency tripling in inert gas mixtures (Xe, Kr, and Ar). The apparatus is shown in Fig. 1. A Nd:YAG laser-pumped dye laser system is employed. The dye laser output of 40 to 70 mJ/pulse at the 550- to 600-nm region is mixed with residual 1.06-μm light from the YAG laser to produce 5 to 10 mJ of the 365- to 385-nm light. A 10-cm f.l. lens is used to focus the near uv light into the third harmonic generation (THG) section. A bandwidth of 1.5 cm^{-1} for the vuv light is approximated for the vuv light. A LiF lens (10 cm f.l. at 400 nm) is used to collimate or focus the vuv light to the sample cell section. A nitric oxide ionization cell with two plates biased at 200 V is utilized a detector for the vuv light.

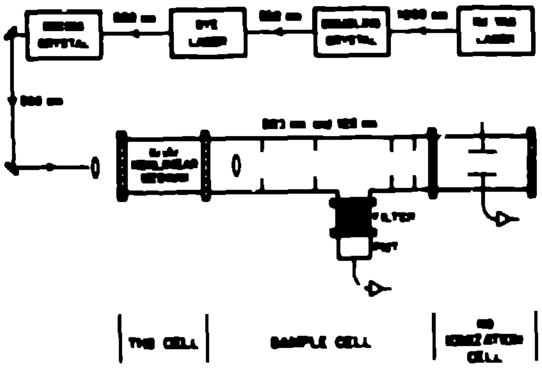

Figure 1. A schematic diagram of the experimental apparatus.

Since the THG process is only typically generated at a 10^{-6} efficiency, near uv scattered light is large compared to the desired photoproduct emission resulting from vuv photolysis. A number of light baffles are inserted along the beam path. A liquid filter (5-g/l hydrated $Fe_2(SO_4)_3$ and other interference filters are used to block the scattered fundamental laser light. The filtering system transmits emission from 400 to 940 nm with a transmission dip from 550 to 620 nm. In some experiments, a pinhole (~0.3 mm in diameter) is inserted into the midsection of the sample chamber. Because of the very large difference in the refractive index of the LiF lens, the vuv and near uv laser beams are focused at very different focal lengths. This allows the pinhole to discriminate much of the near uv light. A better than two orders of magnitude of reduction in the scattered light is attained. A gated PMT, which can be turn on/off for preset time delays and windows, is used for observing the emission. The output of the PMT is sent to either a boxcar averager or a transient digitizer/minicomputer system for signal averaging and data reduction.

Results and Discussion

The photoproduct emission spectra are obtained at different excitation wavelengths. The spectra are observed to be broad with no detectable structure, covering the entire visible region, similar to previous observations.[2,3,5] However, the observed spectra differ from the previous work in that the emission extending farther to the red, essentially to the cut-off wavelength of our PMT's, around 900 nm. This is most likely due to the broader spectral response of the PMT's used in the present work. The synchrotron excitation spectrum, and the laser absorption and excitation spectra are shown in Fig. 2. The synchrotron excitation spectrum shows peaks due to a combination of vibrational progression in Rydberg states and valence states. The spectrum agrees with the previous work,[6] which indicates a cut-off wavelength of emission at 136.5 nm, rather than 130 nm.[3] The laser spectra are scans of one vibronic band (Rydberg series, n = 4, $v_2 = 1$) which demonstrate the relatively high resolution of the laser source. However, since the laser linewidth is comparable to the rotational spacing of C_2H_2, it is not determined whether the actual bandwidth is smeared out due to the predissociation process.

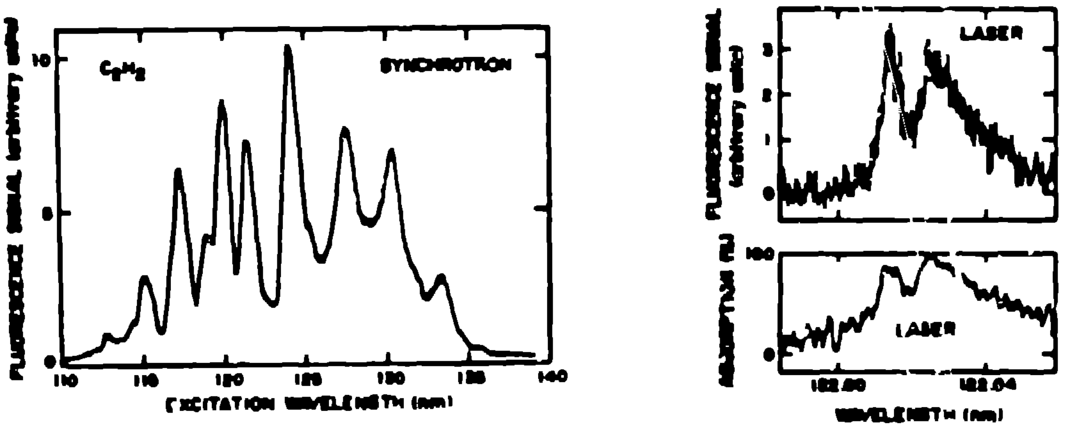

Figure 2. A synchrotron fluorescence excitation spectrum, a vuv laser fluorescence excitation spectrum, and a vuv laser absorption spectrum of C_2H_2.

The excitation spectra are also taken at different emission wavelength regions. Two excitation spectra obtained with bandpass filters (with a half-width of 40 nm) centered at 440 and 850 nm are shown in Fig. 3. There is a distinct shift in the amplitudes of vibronic peaks in the two spectra. This seems to indicate that higher excitation photon energy tends to produce more excited photoproducts The temporal characteristics of the emission are also investigated in detail. It is found that single exponential decays give good fits to emission curves. It should be noted, however, since the emission is broad, the observing decay is not a state-selected decay. Collision-free fluorescence lifetimes of the emission are determined to be varied between 6 to 10 µs and are wavelength dependent. It appears that the shorter the emission wavelength the shorter the lifetime. The implication is then the more excited the photoproducts are, the shorter their fluorescence lifetimes are. This is consistent with the observation that the broadband emission lifetime is shortened at shorter excitation wavelengths.

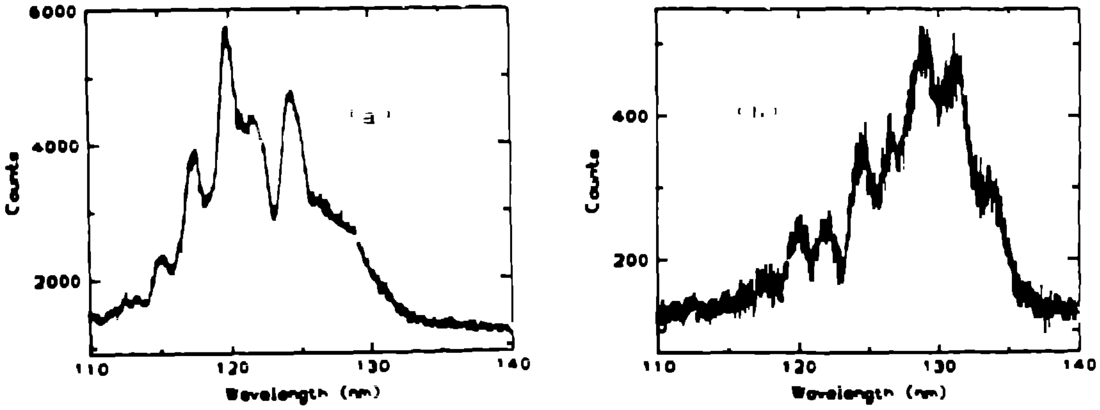

Figure 3. A fluorescence excitation spectrum of C_2H_2 obtained with (a) 440-nm and (b) 850-nm bandpass filters.

In the emission quenching measurements, a number of gases are used as quenchers. Several quenching rate constants are determined and listed in Table 1 for the emission resulted from the photolysis of either C_2H_2 or C_2D_2. Overall, no isotope effect is observed between these two sets of quenching rate constants. This is not surprising since the observed emission contains presumably large number of excited vibronic states, no state specificity is preserved within the photoproducts. The quenching data are fit to a simple quenching model, namely the harpoon model,[12] which assumes a crossing of a neutral repulsive potential energy curve with an attractive ionic potential energy curve to cause the quenching process This model works well for molecules which have low ionization potentials or large electron affinities. In this case, C_2H does have a fairly large electron affinity (~3 ev). It is found that most of the calculated quenching cross-sections using this model to be in reasonable agreement to the measured cross-sections. The exceptions are the quenching cross-sections for C_2H_2, CF_4, and SF_6, which are measured to be much fast than the model predicts. In the C_2H_2 case, this can be explained to be the result of a reactive channel. As for CF_4 and SF_6, we believe that fast vibrational relaxation is probably the pathway, due to the high internal degree of freedom of the quenchers. One very important result is that no noticeably faster quenching rate constants are determined for heavy atoms or for fast triplet quenchers such as O_2. The implication is that the emitter can not be a triplet intermediate.

Table 1. Quenching Rate constants of C_2H and C_2D emission

	Rate Constants (sec^{-1} $torr^{-1}$)	
	C_2H	C_2D
He	4.71 ± 0.08 (+5)	4.9 ± 0.1 (+5)
Ar	7.7 ± 1.1 (+5)	7.9 ± 0.6 (+5)
Kr	6.25 ± 0.35 (+5)	7.3 ± 0.3 (+5)
Xe	1.30 ± 0.04 (+6)	1.13 ± 0.10 (+6)
H_2	1.65 ± 0.04 (+6)	1.36 ± 0.10 (+6)
D_2	1.36 ± 0.08 (+6)	1.26 ± 0.08 (+6)
O_2	1.43 ± 0.26 (+6)	1.30 ± 0.06 (+6)
N_2	9.8 ± 0.7 (+5)	1.01 ± 0.05 (+6)
CO	1.39 ± 0.90 (+6)	1.38 ± 0.20 (+6)
CO_2		2.58 ± 0.15 (+6)
CF_4		2.42 ± 0.18 (+6)
SF_6		3.70 ± 0.25 (+6)
C_2H_2 (122 nm)	5.03 ± 0.15 (+6)	
C_2H_2 (118.2 nm)	4.79 ± 0.15 (+6)	
C_2D_2		5.02 ± 0.14 (+6)

Since the excited C_2H_2 state symmetry is $^1\pi_u$, the exit channel of the predissociation must also be $^1\pi_u$; the H atom is ^2S, so the photoproduct must be produced in states correlating with π electronic symmetry. By examining the C_2H electronic state calculation of Shih et al.,[13] it is believed that $3^2A'$ is the most likely candidate emitting state of C_2H on the basis of energy spacing correlated with $^2\pi$ at its equilibrium C-C bond spacing. In addition, fluorescence polarization measurements are made with the vuv laser light polarized parallel with respect to the detector. A positive polarization ratio of ~6% is measured. This indicates a perpendicular transition to be the main contributor in the emission process and is in agreement with our tentative assignment of the $3^2A'$ --> $2^2A'$ transition as the one responsible for the observed emission.

Acknowledgment

Collaboration with J. Presses and R. E. Weston, Jr., in use of the Brookhaven National Laboratory Synchrotron beam line is grate-fully acknowledged, as well as technical support by R. Romero and M. Ferris. Financial support by DOE is also acknowledged.

References

1. L. J. Stief, V. J. Decarico, and R. J. Mataloni, J. Chem. Phys. 42. 3113(1965).
2. K. H. Becker, D. Haaks, and M. Schurgers, Z. Naturforsch. Teil A 26, 1770 (1971).
3. H. Okabe, J. Chem. Phys. 62, 2782 (1975).
4. H. Okabe, Photochemistry of Small Molecules, (Wiley, New York, 1978), p.262.
5. Y. Saito, T. Hikida, T. Ichimura, and Y. Mori, J. Chem. Phys. 80, 31 (1984).
6. M. Suto and L. C. Lee, J. Chem. Phys. 80, 4824 (1984).
7. A. H. Laufer, J. Chem. Phys. 73, 49 (1980).
8. A. H. Laufer and Y. L. Yung, J. Chem. Phys. 87, 181 (1983).
9. Y. Osamura and H. F. Schaefer III, Chem. Phys. Lett. 79, 412 (1981).
10. R. Krishnan, M. J. Frisch, J. A. Pople, and P. Von R. Schleyer, Chem. Phys. Lett. 79, 408 (1981).
11. K. A. White and G. C. Schatz, J. Phys. Chem. 88, 2049, (1984).
12. R. D. Levine and R. B. Bernstein, Molecular Reaction Dynamics (Oxford University Press, New York, 1974) pp.86-87.
13. S. K. Shih, S. D. Peyerimhoff, and R. J. Buenker, J. Mol. Spectrosc. 74, 124 (1979).