Ultraviolet laser-induced fluorescence of the C₂H radical

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In the spectral range 34500–40000 cm⁻¹, two molecular species were detected by means of laser-induced fluorescence in the 193 nm photolysis of acetylene: one is C₂(a ³Π_u), the other is most likely C₂H($\tilde{X}$). The identification of C₂H is based upon the rotational constants ($B'' = 1.4397$ – 1.4534 cm⁻¹), the deuterium isotope effect on the vibronic bands, and the wavelength-resolved fluorescence.

1. Introduction

The photochemistry of acetylene has been extensively investigated. Several laboratories have observed emissions from C₂ (A ¹Π_u, d ³Π_g, C ¹Π_g) and CH (A ²Δ) produced by multiphoton dissociation of acetylene [1–3]. The presence of C₂H in the 193 nm photolysis of acetylene has been proved by the time-of-flight mass spectrometric technique [4] and time-resolved Fourier transform infrared emission [5]. However, no C₂H band has been identified in the visible and ultraviolet (UV) spectral region. It has been reported [6,7] that the continuous emission spectrum between 400 and 600 nm is most likely associated with electronically excited C₂H.

Although much experimental (refs. [8–16], and references therein) and theoretical (refs. [17–22], and references therein) work has been done on the microwave and infrared spectra of the C₂H radical, some problems remain unsolved. For example, the frequency ν_1 of the CH stretching mode [14,16] and the $\tilde{A}$ – $\tilde{X}$ energy separation [13,17–19] are not yet definitively established. Major difficulties arise from large vibronic coupling between the $\tilde{A}$ and $\tilde{X}$ states [11,13,14]; the energy of the $\tilde{A}$ ²Π state is about 3650 cm⁻¹ above that of the $\tilde{X}$ ²Σ⁺ state. According to ab initio calculations [19,20], when the C–C bond is elongated from the equilibrium position of the $\tilde{X}$ state, complicated vibronic interactions between the

$\tilde{A}$ and $\tilde{X}$ states are expected due to the Renner–Teller effect and the avoided curve crossing.

Little is known about the visible or UV spectrum of the ethynyl radical. Its UV spectrum has been studied only by matrix isolation [23] and multiphoton ionization [24]. No definite assignment of the $\tilde{B}$ (²Σ⁺) state has yet been made [23,25]. Here, we report the laser-induced fluorescence (LIF) spectra of C₂H and C₂(e←a) observed in the 193 nm photodissociation of acetylene.

2. Experiment

An ArF laser (Lambda Physik LPX 110i) was used to photolyze the precursor, acetylene. The power density of the photolysis light source was kept as small as possible to suppress some multiphoton processes of acetylene. With varied time delay (2–10 μs), a tunable UV laser was used to probe the photofragments by means of the LIF technique. The tunable UV radiation of 34500–40000 cm⁻¹ was produced by frequency doubling the output of a commercial dye laser pumped by an excimer laser (Lambda Physik EMG 202). The induced fluorescence signal in the wavelength range of 400–600 nm was collected to record the excitation spectrum of the monitored species. In our high-resolution (0.12 cm⁻¹) experiments, line frequencies were calibrated against the

absorption spectrum of iodine with an estimated accuracy of $\pm 0.02 \text{ cm}^{-1}$. The excitation spectrum due to the acetylene $\tilde{A} \leftarrow \tilde{X}$ band [26] near 40000 cm^{-1} can be identified by comparing the spectrum obtained with/without the photolysis laser.

To record the wavelength-resolved emission, the induced fluorescence was dispersed by a 0.3 m monochromator (JY HR360) and detected by an optical multichannel analyzer (OMA PAR 1461); the gate of the OMA was chosen to be 80 ns wide and was opened at the rising edge of the pulse (20 ns) of the probe laser to minimize the relaxations occurring in the excited state of the emitter. The best resolution of the dispersed emission obtained in this work is 12 cm^{-1} . Because the emission intensity decreased substantially at frequencies above the excitation frequency, the dispersed fluorescence spectrum in the higher frequency region could be recorded at only 50 cm^{-1} resolution. The absolute frequency of the dispersed fluorescence was referred to the emission lines of an iron-neon hollow-cathode lamp with estimated accuracy $\pm 2.0 \text{ cm}^{-1}$.

A small amount of acetylene (13–33 Pa) in hy-

drogen (MG 99.9%) or argon (MG 99.99%) was constantly flowed through the observation zone to prevent further reactions of C_2H . The system was studied at a total pressure 0.04–2.7 kPa, which was monitored by a capacitance manometer (MKS 0–1.3 kPa or 0–13.3 kPa). Acetylene (MG 99.6%) was prepurified by passage successively through two dry-ice/acetone traps. To study deuterium isotope effects, C_2D_2 (Cambridge Isotope Laboratories, >98%) was used without further purification.

3. Results and discussion

We have identified two molecular species by the LIF technique in the photolysis products of acetylene. We found that C_2 ($a^3\Pi_u$) molecules were dominant in the high-pressure regime by increasing the pressure above 80 Pa or lengthening the time interval (4–20 μs) between the photolysis and probe lasers. This result indicates that most observed $\text{C}_2(a)$ molecules are not the primary product, in agreement with the previous report [4]. The observed LIF spectrum of C_2 in fig. 1 is assigned as the Fox–Herz-

Fig. 1. LIF excitation spectrum of $\text{C}_2 e \leftarrow a$ transition observed in a mixture of C_2H_2 (80 Pa) in H_2 (2.6 kPa). Values in the parentheses represent the vibrational assignments (v' , v'').

berg system ($e^3\Pi_g \leftarrow a^3\Pi_u$) [27]. When deuterated acetylene C_2D_2 was photolyzed instead of C_2H_2 , an identical spectrum was obtained, consistent with this assignment.

The LIF spectrum of the other molecular species was detectable only at smaller pressure (27–53 Pa) and shorter delay (1–8 μ s). About fifteen bands have been observed in the spectrum interval 34500–40000 cm^{-1} with the deuterium isotopic effect. An excerpt of the spectrum is shown in fig. 2, indicating that the spectral carrier is a molecular species containing hydrogen atom(s). Transition of parallel type (i.e. $\Pi-\Pi$ and $\Phi-\Phi$) have been observed. We have also studied the emission spectrum at the bandhead of some of the observed transitions. The result due to the band at 37010 cm^{-1} is shown in fig. 3; two vibrational frequencies, $\nu_2=448-502$ cm^{-1} and $\nu_3=1568-1623$ cm^{-1} were deduced under the assumption of an anharmonic oscillator-rigid rotor. All these results support the assignment that the spectral carrier of fig. 2 is a polyatomic species with hydrogen atom(s).

Table 1 lists molecular species which might be

present in the photolysis process of acetylene at 193 nm and their rotational parameters previously reported [8,28–33]. After excluding the assignments CH and C_2 , we simulated the spectra of C_2H_3 (vinyl radical), H_2CC (vinylidene) and C_4H_2 (1,3-butydiyne) using the rotational constants in table 1 and the $B'-B''$ value estimated from the observed P branch. However, no simulated rotational contours were similar to the spectrum in fig. 4. Moreover, alternating intensities of rotational lines are expected for the molecules H_2CC or C_4H_2 .

One distinct feature seen in fig. 4 is that, with increasing J , the splitting of the doublets in the P branch increases, indicating that at least one of the states has either Λ - or K-type doubling. As the 37010 cm^{-1} band is a parallel-type transition, a $^2\Pi-^2\Pi$ transition is thus assigned. To describe the rotational levels in a $^2\Pi$ vibronic state, the effective Hamiltonian of Brown et al. [34] was transformed into the basis sets of Hund's case (b). Rotational assignments in the 37010 cm^{-1} band are indicated in fig. 4. Values of parameters obtained by a standard nonlinear least-

Fig. 2. Top trace is the LIF excitation spectrum obtained by photolysis of C_2D_2 , lower trace due to the photolysis of C_2H_2 .

Fig. 3. Wavelength-resolved emission resulting from the excitation at 37018 cm^{-1} , near the head of the 37010 cm^{-1} band. The spectral resolution in the region (a) is 50 cm^{-1} and that of the region (b) is 12 cm^{-1} . Values in parentheses represent the vibrational assignments (ν_1, ν_2, ν_3).

Table 1

Rotational constants ^{a)} of possible species involved in the photodissociation of acetylene

	CH ^{b)}	C ₂ (a ³ Π _u) ^{c)}	C ₂ H ^{d)}	H ₂ CC(ã ³ B ₂) ^{e)}	C ₂ H ₃ ^{f)}	C ₄ H ₂ ^{g)}
<i>B</i>	14.192330	1.623964	1.4568249	1.24	1.083026	0.14641
<i>C</i>				1.09	0.948643	
<i>A</i>				9.57	7.90934	

^{a)} In units of cm^{-1} . ^{b)} Ref. [28]. ^{c)} Ref. [29]. ^{d)} Ref. [7]. ^{e)} Calculated from the molecular geometry reported in ref. [30].

^{f)} Ref. [31]. ^{g)} Ref. [32].

squares fit to the observed line frequencies are given in table 2. Large deviations at $J'' \geq 12.5$ in one of the Λ -doubling components are probably due to local perturbations. Rotational parameters B'' (for the 36075 cm^{-1} band, $B'' = 1.4397(13)\text{ cm}^{-1}$, $B' = 1.2132(12)\text{ cm}^{-1}$; for the 36224 cm^{-1} band, $B'' = 1.4516(4)\text{ cm}^{-1}$, $B' = 1.2294(4)\text{ cm}^{-1}$; for the 37946 cm^{-1} band, $B'' = 1.4543(9)\text{ cm}^{-1}$, $B' = 1.2435(9)\text{ cm}^{-1}$; for the 38108 cm^{-1} band,

$B'' = 1.4434(4)\text{ cm}^{-1}$, $B' = 1.2348(7)\text{ cm}^{-1}$) obtained from analysis of the other four bands are also consistent with the previously reported values for the ethynyl radical [8,10,11,13,14], indicating that the spectral carrier is C₂H. Detailed rotational analysis of the observed bands will be published in a forthcoming paper.

The small effective spin-orbit constant, $A'' = -(2.19 \pm 0.18)\text{ cm}^{-1}$, of the 37010 cm^{-1} band

Fig. 4. LIF excitation spectrum of C_2H of the 37010 cm^{-1} band measured with 0.12 cm^{-1} resolution.

Table 2
Molecular constants of the 37010 cm⁻¹ band ^{a)}

	Lower state	Upper state
<i>B</i>	1.44944(93)	1.2433(11)
<i>D</i> × 10 ⁴	-2.160(27)	-2.335(34)
<i>A</i>	-2.19(18)	-1.97(18)
<i>q</i> × 10 ²	-1.49(19)	-0.94(22)
<i>q</i> ₀ × 10 ⁵	-2.46(54)	-0.7 ^{b)}

^{a)} Values are in units of cm⁻¹, numbers in parentheses denote one standard deviation in terms of the last digit.

^{b)} Constrained value.

indicates that its lower state has about 90% $\tilde{X}$ -state character [13,22]. Based upon the wavelength-resolved fluorescence of the 37010 cm⁻¹ band, we assign the lower state of the 37010 cm⁻¹ band to be $\tilde{X}$ (0, 3¹, 5) or $\tilde{X}$ (0, 5¹, 3) by assuming that $x_{33} = -14$ cm⁻¹ and $x_{23} = -31$ cm⁻¹ for the vibrational levels of the $\tilde{X}$ state [9,15]. One tentative assignment is made in fig. 3. This result places the upper state of the 37010 cm⁻¹ band at ≈ 46390 or 43960 cm⁻¹. That only lines with even Δv_2 have prominent intensities in fig. 3 indicates that the geometries of its upper and lower electronic states are linear, consistent with the $2^2\Pi-2^2\Pi$ assignment.

Ab initio calculations [21,25] have shown that the vertical excitation energies required for transitions from the $\tilde{X}^2\Sigma^+$ state to the $2^2\Sigma^+$ and $2^2\Pi$ states are near 6.8 and 7.3 eV. It has also been shown that as the C-C bond increases to 0.141 nm, the energies of the $3^2A'$ and $2^2A''$ states, which are correlated to the $2^2\Sigma^+$ and $2^2\Pi$, states respectively, decrease by 1 eV or more. Moreover, $2^2\Pi$ can be even below $2^2\Sigma^+$ [25] (but no optimized geometry has been given [25]). Taking into account the observed small value of B' , we interpret our spectrum as a transition from a vibrationally excited state of the $\tilde{X}$ state to the $2^2\Pi$ ($3^2A'$) state, which has a large C-C bond length (≈ 0.135 nm). Nevertheless, it has been predicted that the geometry of $3^2A'$ is bent [25], which cannot explain our results. In order to resolve the nature of the observed transitions, more experimental work and ab initio calculations on the high-lying electronic states of the ethynyl radical are necessary.

4. Concluding remarks

In the range 34500–40000 cm⁻¹ of excitation energy, LIF spectra of two types were identified in the products of the 193 nm photodissociation of acetylene. One is due to $C_2(a \rightarrow e)$; the other is tentatively assigned as the transition from a high vibrational level of $C_2H(\tilde{X})$ to the high-lying $2^2\Pi$ vibronic state. The latter assignment is supported by the determined rotational constants, the observed deuterium isotope effect and the wavelength-resolved emission.

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References

- [1] J.R. McDonald, A.P. Baronavski and V.M. Donnelly, Chem. Phys. 33 (1978) 161.
- [2] H. Okabe, R.J. Cody and J.E. Allen Jr., Chem. Phys. 92 (1985) 67.
- [3] Y.-C. Hsu, M.-S. Lin and C.-P. Hsu, J. Chem. Phys. 94 (1991) 7832.
- [4] A.M. Wodtke and Y.T. Lee, J. Phys. Chem. 89 (1985) 4744.
- [5] T.R. Fletcher and S.R. Leone, J. Chem. Phys. 90 (1989) 871.
- [6] H. Okabe, J. Chem. Phys. 62 (1975) 2782.
- [7] Y. Saito, T. Hikida, T. Ichimura and Y. Mori, J. Chem. Phys. 80 (1984) 31.
- [8] K.V.L.N. Sastry, P. Helminger, A. Charo, E. Herbst and F.C. DeLucia, Astrophys. J. 251 (1981) L119.
- [9] M.E. Jacox and W.B. Olson, J. Chem. Phys. 86 (1987) 3134.
- [10] J.M. Brown and K.M. Evenson, J. Mol. Spectry. 131 (1988) 161.
- [11] H. Kanamori and E. Hirota, J. Chem. Phys. 89 (1988) 3962.
- [12] M. Vervloet and M. Herman, Chem. Phys. Letters 144 (1988) 48.
- [13] W.-B. Yan, C.B. Dane, D. Zeitz, J.L. Hall and R.F. Curl, J. Mol. Spectry. 123 (1987) 486.
- [14] J.W. Stephens, W.-B. Yan, M.L. Richnow, H. Solka and R.F. Curl, J. Mol. Struct. 190 (1988) 41.
- [15] K.M. Ervin and W.C. Lineberger, J. Phys. Chem. 95 (1991) 1167.
- [16] W.-B. Yan, H.E. Warner and T. Amano, J. Chem. Phys. 94 (1991) 1712.
- [17] G. Fogarasi, J.E. Boggs and P. Pulay, Mol. Phys. 50 (1983) 139.

- [18] W.P. Kraemer, B.O. Roos, P.R. Bunker and P. Jensen, *J. Mol. Spectry.* 120 (1986) 236.
- [19] H. Thümmel, M. Peric, S.D. Peyerimhoff and R.J. Buenker, *Z. Physik D* 13 (1989) 307.
- [20] M. Peric, S.D. Peyerimhoff and R.J. Buenker, *Mol. Phys.* 71 (1990) 693.
- [21] A.G. Koures and L.B. Harding, *J. Phys. Chem.* 95 (1991) 1035.
- [22] M. Peric, W. Reuter and S.D. Peyerimhoff, *J. Mol. Spectry.* 148 (1991) 201.
- [23] K.W. Chang and W.R.M. Graham, *J. Chem. Phys.* 76 (1982) 5238.
- [24] T.A. Cool and P.M. Goodwin, *J. Chem. Phys.* 94 (1991) 6978.
- [25] S.-K. Shih, S.D. Peyerimhoff and R.J. Buenker, *J. Mol. Spectry.* 74 (1979) 124.
- [26] J.K.G. Watson, M. Herman, J.C. Van Craen and R. Colin, *J. Mol. Spectry.* 95 (1982) 101.
- [27] J.L. Hardwick and D.H. Winicur, *J. Mol. Spectry.* 115 (1986) 175.
- [28] P.F. Bernath, C.R. Brazier, T. Olsen, R. Hailey, W.T.M.L. Fernando, C. Woods and J.L. Hardwick, *J. Mol. Spectry.* 147 (1991) 16.
- [29] T. Suzuki, S. Saito and E. Hirota, *J. Mol. Spectry.* 113 (1985) 399.
- [30] K.M. Ervin, J. Ho and W.C. Lineberger, *J. Chem. Phys.* 91 (1989) 5974.
- [31] H. Kanamori, Y. Endo and E. Hirota, *J. Chem. Phys.* 92 (1990) 197.
- [32] J.L. Hardwick and D.A. Ramsay, *Chem. Phys. Letters* 48 (1977) 399.
- [33] C. Amiot, J. Chauville and J.-P. Maillard, *J. Mol. Spectry.* 75 (1979) 19.
- [34] J.M. Brown, E.A. Colbourn, J.K.G. Watson and F.D. Wayne, *J. Mol. Spectry.* 74 (1979) 294.