

Emission Spectrum of Acetylene by Controlled Electron Impact

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Emission spectra of C_2H_2 and C_2D_2 excited by collisions with electrons of 7–20 eV show a broad and diffuse band in the 240–400 nm region and this band was assigned to the S_1 (lower vibrational levels)– S_0 transition of acetylene on the basis of its wavelength, excitation function (threshold: 5.5 eV) and lifetime (323 ± 30 ns). Their emission cross sections are on the order of 10^{-19} cm². Among intense fragment emissions at higher electron energies, band of C_2H has also been observed and its lifetime is 3.9 ± 0.8 μ s.

Fluorescence of acetylene is very weak. A discrete fluorescence was observed in a high frequency discharge,¹⁾ in a matrix²⁾ and in the gas phase under a laser excitation.^{3,4)} These fluorescence was assigned to the transition from the lowest excited state to the ground state. The fluorescence quantum yield in the gas phase was estimated to be 10^{-4} , and it decreased sharply with decreasing exciting wavelength.⁵⁾

The electron is an efficient excitation source and is able to excite both optically-allowed and forbidden transitions.⁶⁾ Aromatic molecules exhibit characteristic emission upon excitation by electrons similar to optical fluorescence.⁷⁾ However, their vibrational structure is different and optically-forbidden vibrational levels are predominant in the benzene spectrum.⁸⁾ Meanwhile, emission spectrum of acetylene excited by electrons showed only bands of fragments and no parent emission was detected in the previous investigation.⁹⁾

In order to clarify spectroscopic properties of acetylene, we have again measured emission spectrum of acetylene under controlled electron-impact excitation and analyzed its decay curve.

Experimental

The apparatus is similar with the one described previously.⁷⁾ In brief, the collision chamber (8") was evacuated with a 4" oil-diffusion pump with a liquid nitrogen trap. The base pressure was of the order 10^{-6} Torr (1 Torr=133 Pa) and the operating pressure was about 1×10^{-3} Torr. The sample gas was jetted into the collision region through a mass flow controller (Standard Tech. 400MKII) and a multi-channel nozzle, and was collided with the electron beam from a tungsten filament.

The optical emission was observed through a quartz window at an angle of 45° with respect to the electron beam. The spectrum was obtained with a SPEX 1670 monochromator equipped with a 1200 grooves/mm grating blazed at 300 nm and a Hamamatsu R585 photomultiplier and with an NF PC545 photoncounter. The electron beam was pulsed so as to subtract the stray radiation from the hot filament.

The instrumental response of the optical system was calibrated with a Hamamatsu L591 standard deuterium lamp. The corrected spectrum was expressed in units of relative number of photons per wavenumber. The electron energy

was calibrated with the peak of N_2^* (337.1 nm) at 14.5 eV and its energy resolution was 0.8 eV at 10 eV.

Fluorescence decay was measured with an Ortec 457 time-to-amplitude converter, an Ortec 473A constant-fraction discriminator, a Norland Ino-tech 5300 multichannel analyzer, and an NEC PC 9801VF microcomputer. The pulse width of the electron beam was 1 μ s, and its repetition rate was 50 kHz. The system was calibrated with the lifetime (1.7 ns) of the 3^1P – 2^1S transition of He (501.4 nm).

C_2H_2 was commercially obtained (Eto Sanso, 99.6%) and was used as supplied. C_2D_2 was prepared from CaC_2 and D_2O , and its isotopic purity was $> 96\%$ according to a mass spectrometric analysis.

Results and Discussion

There are bands of H (Balmer lines), CH (the A–X and B–X transitions), CH^+ (the B–A and b–a transitions) and C_2 (the d–a transition) on the emission spectrum by controlled electron impact on acetylene, as are reported previously.^{9,10)} But no feature assignable to C_2H_2 was observed previously,⁹⁾ partly because measurements were carried out at higher electron energies. Typical emission spectra of C_2H_2 and C_2D_2 excited at electron energies of 14 and 7 eV are shown in Fig. 1;

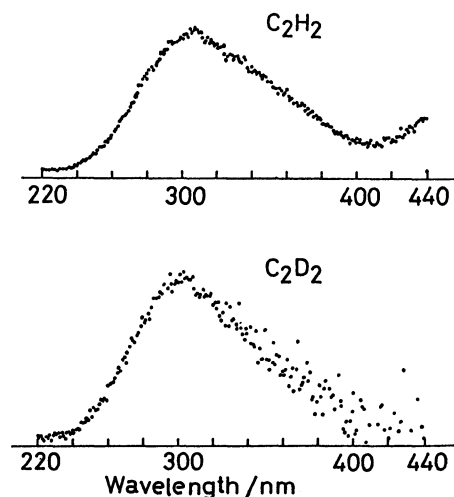


Fig. 1. Emission spectra of C_2H_2 and C_2D_2 by controlled electron impact. Electron energy: 14 eV (C_2H_2) and 7 eV (C_2D_2). Optical resolution: 5 nm.

the optical resolution was 5 nm and the optical response of the instrument was corrected. The spectra are broad and diffuse, and the peak appears at 307 nm for C_2H_2 and at 300 nm for C_2D_2 .

The similarity of the observed spectra with those by the optical excitation²⁻⁴⁾ shows that the observed emission is due to the transition from the lowest excited state ($^1\Sigma_u$) to the ground state ($^1\Sigma_g$), as is optical fluorescence. However, the present spectrum was measured at a much lower pressure than that in the laser excitation and collisional effects can be ignored. The spectrum of C_2H_2 shifts to the red than that of C_2D_2 , probably because the vibrational spacing of the latter in the ground electronic state is smaller.

There is no contribution of any fragment species at 7 eV and only C_2H and $CH(C)$ may appear at 14 eV, because the calculated dissociation limits of $C_2H(B)$ and $CH(C)$ are 9.29^{11,12)} and 13.91^{11,13)} eV, respectively. The increase at 400 nm region toward longer wavelength in the C_2H_2 spectrum can be assigned to the band of C_2H^* .

The excitation function of C_2H_2 measured at 280 nm is shown in Fig. 2. A peak at 14.5 eV is due to N_2 (the C-B transition) measured together for a calibration of the electron energy. The rise toward higher electron energy is due to fragments such as C_2H^* and $CH(C-X)$. The excitation function above 9.0 eV was obtained by subtracting the contribution from the fragment emission, and is shown by triangles. It has a maximum at about 10 eV and decreases smoothly to higher electron energies. The $C_2H_2^*$ emission was not distinguishable from the fragment emissions at higher electron energies. The threshold energy is found to be 5.5 ± 0.6 eV. The 0-0 transition of C_2H_2 is located at 5.23 eV,¹⁴⁾ and this agreement is consistent with the assignment. Because this threshold energy is much lower than the dissociation limit of any fragment, the

observed emission is certainly not due to any fragment species.

The electron excitation is nonresonant in principle and many vibrational levels may be excited together. Thus, the acetylene spectra may be diffuse, though it exhibits banded fluorescence under a dye-laser excitation. The peak of the spectra seems to locate in the identical region with that excited at the 0-0 transition by the laser,³⁾ if we take instrumental response into consideration. However, the present spectrum is broader than the 0-0 fluorescence by the laser excitation, and this finding indicates that not only the 0 level but also some lower vibrational states are also excited by controlled electron impact.

The 0-0 transition is forbidden due to the geometry change between the ground and the excited states, and excitation to the higher vibrational levels had larger intensity in the optical excitation.^{3,14)} Nevertheless, the 0-0 transition seems to be prominent under electron excitation. This is also the case in benzene.⁸⁾ The higher intensity of the 0-0 transition should be due to a specific interaction between the molecule and the electron.

The emission cross sections of acetylene emission were determined by measuring the band areas relative to that of the C-B transition of N_2 ; the emission cross section of the latter was determined to be $1.6 \times 10^{-18} \text{ cm}^2$ at 12.4 eV.¹⁵⁾ They were $2.2 \times 10^{-19} \text{ cm}^2$ for C_2H_2 and $3.2 \times 10^{-19} \text{ cm}^2$ for C_2D_2 at the incident electron energy of 12.4 eV. Uncertainty of these values would be 50% mainly due to uncertainty in the pressure measurements; however, relative values of C_2H_2 and C_2D_2 should be more accurate.

The decay curve of the C_2H_2 emission at 300 nm is

Table 1. The Lifetime of $C_2H_2^*$ by Controlled Electron Impact at an Electron Energy of 17 eV

Wavelength/nm	Lifetime/ns
280	313 ± 26
290	322 ± 20
300	336 ± 30
315	319 ± 41

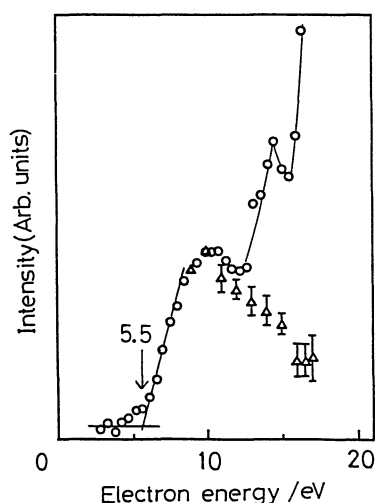


Fig. 2. Excitation function of C_2H_2 at 280 nm.
O: Total optical emission. Δ : $C_2H_2^*$ above 10 eV.
Total optical emission should be due to $C_2H_2^*$ below 9.5 eV.

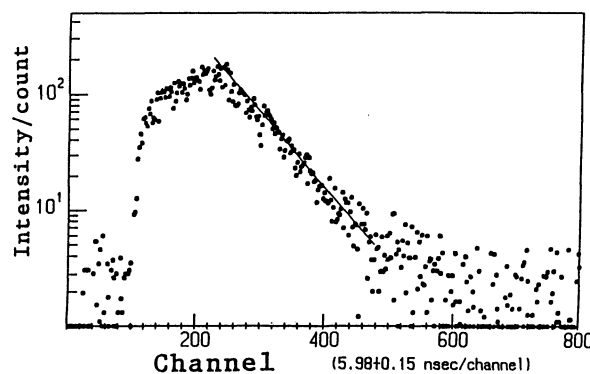


Fig. 3. Fluorescence decay curve for C_2H_2 at 300 nm.
The electron energy: 10 eV.

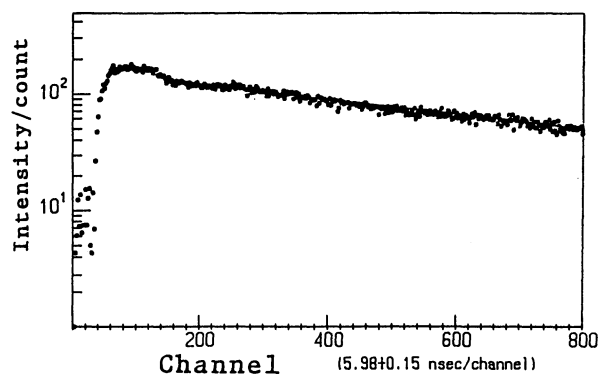


Fig. 4. Fluorescence decay curve for C₂H at 500 nm. The electron energy: 50 eV.

Table 2. The Lifetime of C₂H* by Controlled Electron Impact

Wavelength /nm	Lifetime at 19eV/ μ s	Lifetime at 50 eV/ μ s
300		3.5 \pm 0.5
450	3.6 \pm 1.0	3.9 \pm 0.7
500	3.9 \pm 0.8	4.4 \pm 0.7

shown in Fig. 3; the incident electron energy was 10 eV. The lifetime of the excited state was determined to be 328 \pm 50 ns by a least-square fitting of the decay curve. The results of the decay curve analysis is shown in Table 1. The lifetime was independent of the electron energy between 10 and 50 eV and of the wavelength between 280 and 315 nm within experimental uncertainties. Then, we can conclude that the lifetime of C₂H₂* is 323 \pm 30 ns by taking the average of all data. This lifetime agrees with that to lower vibrational levels measured by laser excitation³⁾ within experimental uncertainties, and disagree with that to higher vibrational levels.⁴⁾ This finding confirms the assignment that the observed emission arises mainly from the lower vibrational levels of the A state of acetylene.

There is another band above 410 nm in Fig. 1(a). This band is also broad and diffuse and is extended to longer wavelength region. Since its threshold is about 10 eV and the calculated threshold for C₂H is 9.29 eV, this band can be assigned to C₂H*, as was reported by a VUV photolysis of acetylene.¹⁶⁾ The decay curve of the C₂H emission at 500 nm is shown in Fig. 4 and the lifetime was determined to be 4.4 \pm 0.7 μ s. The lifetimes measured are shown in Table 2; lifetime does not

vary with wavelength within experimental uncertainties. The lifetime of C₂H was determined to be 3.9 \pm 0.8 μ s by taking an average of these results. This lifetime is approximately in agreement with those obtained in a VUV photolysis;¹⁶⁾ however, the latter values were measured at higher pressures by extrapolating observed lifetime to zero pressure. Since the present measurements were carried out at 10⁻³ Torr, our values should be more accurate.

The electron excitation is a useful technique to investigate the molecular excited state at a very low pressure where collisional effect can be ignored.

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