Title: Dissociative Excitation of C₂H₂ and C₂D₂ at Ne(I) Resonance Lines

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Dissociative Excitation of C$_2$H$_2$ and C$_2$D$_2$

at Ne(I) Resonance Lines

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The electronically excited states of photofragments in the photolyses of C$_2$H$_2$ and C$_2$D$_2$
at neon resonance lines ($h\nu=16.85$ and 16.63 eV) were C$_2$(D$^2\Sigma^+$, C$^2\Pi$, B$^2\Pi$, A$^2\Delta$) and CH
and CD(D$^2\Sigma^+$, B$^2\Sigma^-$, A$^2\Delta$) radicals observed by dispersing fluorescence. They are produced
through a neutral superexcited state of acetylene but not via ionic species. A large isotope
effect was observed in the emissions intensities between C$_2^*/$CH$^*$ and C$_2^*/$CD$^*$ ratios. The
emission cross sections determined at Ne(I) lines were 2.3 Mb in both C$_2$H$_2$ and C$_2$D$_2$, indicating that about 40% of the superexcited state decomposes into the electronically excited C$_2^*$
and CH$^*$ (and CD$^*$) radicals.

KEY WORDS: VUV photolysis/ Fluorescence/ Isotope effect/ Superexcited state/ Emission cross section/

1. INTRODUCTION

Acetylene is one of the simplest polyatomic molecules and its photochemistry
has been extensively studied in a wide energy region of the exciting primary beam:
below LiF cutoff (<11.8 eV)$^{1-6}$, windowless VUV (<70.85 eV)$^7-17$, and electron
energy loss spectroscopy encompassing the range of 5–180 eV.$^18-20$

The total photoabsorption cross section and the partial cross sections for the
molecular and dissociative photoionization of C$_2$H$_2$ have been discussed in detail.$^{20}$
The dipole induced breakdown for the ionic photofragmentation of C$_2$H$_2$ has also
been proposed in relation to the electronic states of C$_2$H$_2$$^+$ cation.$^{20}$

At $h\nu <18$ eV, the quantum yield of ionization ($\eta_i$) defined by the ratio of the
number of ions produced to that of photons absorbed is less than unity.$^3,20$ The
ionization yield curve shows two minima of $\eta_i \approx 0.65$ and 0.67–0.81 at 13.5 and 16.3
eV, respectively$^3,20$, suggesting the formation of a superexcited C$_2$H$_2$$^{+*}$ molecule
which lies at the potential energy level higher than the first ionization energy and
decomposes into neutral fragments without autoionization. In this work electronically
excited radicals which come from VUV photodecomposition of C$_2$H$_2$ and
C$_2$D$_2$ are detected by optical emission spectroscopy, and the isotope effect is reported.

2. EXPERIMENTAL

The experimental setup is identical to the one described previously.$^{21}$ In brief,
Dissociative Excitation of C$_2$H$_2$ and C$_2$D$_2$

the electronically excited radical was generated by Ne(I) (73.59 and 74.37 nm or 16.85 and 16.67 eV, respectively) irradiation. The lamp was a 10 mm inner diameter quartz tube, through which high purity neon gas (Mitsui-Toatsu Chemical Co., 99.999%) was flowed and powered by a 2.45 GHz microwave discharge. The emission spectra were observed through a quartz lens attached at right angles to the Ne(I) resonance lines, and dispersed by a Nikon G250 monochromator with a grating blazed at 250 or 500 nm. A low spectral resolution of ~6 nm was employed because of the weak emission intensity. Dispersed fluorescence was detected by a photomultiplier tube (Hamamatsu R585 or a cooled R649) and a multichannel analyzer.

The relative response of the optical system on photon energy was calibrated with a standard bromine lamp (Ushio Electronic Co., JPD-100-500CS). The absolute fluorescence cross sections were determined by normalizing the fluorescence intensities of acetylene measured at 73.6 nm with that of the CO$^+$(\$A^2\Pi$→$X^2\Sigma^+$) fluorescence, for which the fluorescence excitation spectrum has been measured up to 17.5 nm.

High purity C$_2$H$_2$ and C$_2$D$_2$ were commercially purchased from Takachiho Shoji Co., and CEA in France, respectively. The minimum isotopic purity of C$_2$D$_2$ is stated to be 99 atom % and used without further purification.

3. RESULTS AND DISCUSSION

The quantum yield of ionization of C$_2$H$_2$ is shown in Fig. 1 where the data are taken from Refs. 3 and 20. The quantum yield at 16.85 eV is estimated to be 0.85, indicating the superexcited state is substantial. Figs. 2 and 3 show the dispersed fluorescence of C$_2$H$_2$ and C$_2$D$_2$ in the wavelength regions of 200-600 nm.

![Fig. 1. Ionization efficiency of C$_2$H$_2$. □: Ref. 3 and ●: Ref. 20.](249)
using a grating blazed at 250 nm, respectively. In these figures the relative band intensity is normalized by the CH (A^2 \Pi \rightarrow X^2 \Sigma_g^+) emission intensity at 430 nm, and is displayed after correcting the fluorescence detection efficiency of the optical system employed. The emission bands are assigned as shown in the figures. Except the C(2^3 \Pi_g \rightarrow 2^3 \Pi_a) transition at ~250 nm which shows a vibrational progression, the electronic transitions have been observed in the VUV photolysis of C_2H_2.

When the fluorescing photofragments are produced through an ionic intermediate, thermochemically possible processes to form the CH (A) and C_2 (d) states, which are the lowest excited levels in the present observation, are supposed to be

\[ \text{C}_2\text{H}_2 \rightarrow \text{CH (A)} + \text{CH}^+ + e^-, \quad \Delta H = 20.9 \text{ eV} \]  
\[ \text{C}_2\text{H}_2 \rightarrow \text{C}_2 (d) + 2 \text{H} + e^-, \quad \Delta H = 24.2 \text{ eV} \]  

where the standard heats of formation are \( \Delta H^\circ (\text{C}_2\text{H}_2) = 2.35 \), \( \Delta H^\circ (\text{C}_2) = 8.59 \), and \( \Delta H^\circ (\text{CH}) = 4.95 \text{ eV} \). The potential energy levels of CH (A) and C_2 (d) above the ground state are taken from Ref. 24. It is clear that the photon energy of Ne(I) is insufficient for Reactions (3a) and (3b), and thus the emitting species should be formed from the superexcited state(s) of acetylene.

The fluorescence cross sections were obtained as follows: The absolute fluorescence cross section for the N_2^+(B^3 \Sigma_u^+ \rightarrow X^3 \Sigma_g^+) transition has been reported to be 2.4 Mb (1 Mb = 10^{-18} \text{ cm}^2) independent of the primary photon energy in the range of 19-24 eV. We measured the dispersed spectra of the N_2^+(B \rightarrow X) and CO^+(B, A \rightarrow X) transitions at He(I) resonance line of 58.4 nm or 21.22 eV under the same optical conditions. By comparing the emission intensities of the CO^+(A) with that of N_2^+(B) ions, we obtained the emission cross section of 5.7 Mb for the CO^+ emission at 58.4 nm. Non-dispersed fluorescence excitation spectrum of CO^+ ion has been measured using synchrotron radiation, which gives a value of 0.29 as the relative emission intensity from the excited CO^+ at 16.85 eV to that at 21.22 eV. Thus, the absolute fluorescence cross section for CO^+(A \rightarrow X) at 16.85 eV can be deduced to be 1.6 Mb. Adopting the CO^+(A) fluorescence cross section at 16.85 eV, the total emission cross sections of C_2H_2 and C_2D_2 are obtained to be 2.3 \pm 0.1 Mb at the Ne(I) excitation. On the other hand, the total photoabsorption cross section of C_2H_2 is 37.0 Mb, and the ionization efficiency is \( \eta = 0.85 \) at 16.85 eV. By multiplying these two values, the total cross section to produce the superexcited state(s) is calculated to be 5.6 Mb. This means that 40% of molecules in the superexcited state(s) of C_2H_2 decomposes into CH (C, \tilde{B}, \tilde{A}) and C_2 (\tilde{D}, \tilde{C}, \tilde{E}, \tilde{D}) electronically excited radicals.

The fluorescence cross section for C_2H_2 presently obtained is larger than the value of ~1.5 Mb at 73.6 nm reported previously. This discrepancy mainly comes from the correction of the efficiency to detect fluorescing photons. In the previous works, it seems that no correction was made for the optical system used. The total photoabsorption cross section of C_2D_2 has not been reported. However, we suppose the situations of C_2D_2 are similar to those of C_2H_2.
Dissociative Excitation of C2H2 and C2D2

Table 1 shows the observed emission intensity from the electronically excited state of CH and C2 radicals. The highest emission peak is CH (A→X) at 430 nm, and the strongest transition probability is C2 (d→a) as judged from the accumulated area of the emission bands.

Table 1. Relative Fluorescence Intensities.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Observed Wavelength (nm)</th>
<th>Relative Intensity (%)</th>
<th>C2H2</th>
<th>C2D2</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2 radical</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Δ^1Σ_g^+ → Δ^3Σ_g^+</td>
<td>225 - 238</td>
<td>1.5</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>eΠ_g → eΠ_u</td>
<td>240 - 318</td>
<td>3.8</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>CΠ_g → AΠ_u</td>
<td>322 - 413</td>
<td>20.8</td>
<td>19.3</td>
<td></td>
</tr>
<tr>
<td>Δ^1Π_g → Δ^3Π_u</td>
<td>445 - 650</td>
<td>54.1</td>
<td>48.5</td>
<td></td>
</tr>
<tr>
<td>CH and CD radicals^a</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O^3Σ_g → O^3Π_u</td>
<td>310 - 320</td>
<td>1.0</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>A^3Π_d → A^3Π_u</td>
<td>413 - 445</td>
<td>18.8</td>
<td>25.9</td>
<td></td>
</tr>
</tbody>
</table>

^a. CH(Δ ≡ C→A) transition at 389 nm is overlapped by the Δb=0 of C2(C→A).

A large isotope effect can be seen in the ratios of C2*/CH*=4.06 and C2*/CD*=2.54. Since the total fluorescence cross sections of C2H2 and C2D2 are 2.3±0.1 Mb at 16.85 eV, the partial fluorescence cross sections of CH*, CD*, C2*(H), and C2*(D) radicals are deduced to be 0.45, 0.65, 1.85, and 1.65 Mb, respectively, where C2*(H) and C2*(D) denote the emitting C2* radicals which come from the C2H2 and C2D2 photolyses. The C2* radicals should be formed by the direct C-H and C-D bond

Table 2. Calculated Thresholds for Photodissociative Excitations of C2H2.

<table>
<thead>
<tr>
<th>Process</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) C2(Δ)+H2</td>
<td>8.72</td>
</tr>
<tr>
<td>(2) CH(Δ)+CH</td>
<td>10.4</td>
</tr>
<tr>
<td>(3) C2(C)+H2</td>
<td>10.5</td>
</tr>
<tr>
<td>(4) CH(Δ)+CH</td>
<td>10.7</td>
</tr>
<tr>
<td>(5) C2(Δ)+H2</td>
<td>11.3</td>
</tr>
<tr>
<td>(6) CH(C)+CH</td>
<td>11.5</td>
</tr>
<tr>
<td>(7) C2(Δ)+H2</td>
<td>11.6</td>
</tr>
<tr>
<td>(8) C2(Δ)+2H</td>
<td>13.2</td>
</tr>
<tr>
<td>(9) C2(C)+2H</td>
<td>15.0</td>
</tr>
<tr>
<td>(10) CH(Δ)+C+H</td>
<td>15.2</td>
</tr>
<tr>
<td>(11) CH(Δ)+C+H</td>
<td>15.5</td>
</tr>
<tr>
<td>(12) C(Δ)+2H</td>
<td>15.8</td>
</tr>
<tr>
<td>(13) C(Δ)+2H</td>
<td>16.1</td>
</tr>
<tr>
<td>(14) CH(C)+C+H</td>
<td>16.2</td>
</tr>
</tbody>
</table>

^a. For electronic energy levels and the heats of formation, see Refs. 24 and 25, respectively.
fissions. Since the C-H bond energy is weaker than that of C-D, it seems normal that the emission cross section of the $C_2^*(H)$ is larger than that of $C_2^*(D)$. The calculated onsets to form the fluorescing radicals are listed in Table 2. Reaction

![Graph 2](image-url)

Fig. 2. Dispersed fluorescence from excitation of $C_2H_2$ at Ne(I). The electronic transitions of $CH(C, B, A \rightarrow X)$, $C_2(d \rightarrow a)$, $C_2(e \rightarrow a)$, $C_2(d \rightarrow a)$, and $C_2(D \rightarrow X)$ are indicated.

![Graph 3](image-url)

Fig. 3. Dispersed fluorescence from excitation of $C_2D_2$ at Ne(I).
Dissociative Excitation of C$_2$H$_2$ and C$_2$D$_2$

(8) of C$_2$H$_2$(C$_2$D$_2$)$\rightarrow$C$_2$(d) +2H(2D) in the table has a normal isotope effect of C$_2^*$(H)/C$_2^*$(D) = 1.12 as seen in Figs. 2 and 3. On the other side, the partial fluorescence cross sections for the CH* and CD* suggest that the bond fission of C≡C is strongly affected by the D atom substitution, i.e., the secondary hydrogen isotope effect exceeds 40% and has an inverse tendency against the normal isotope effect.\textsuperscript{28}

When we call it in mind that the secondary isotope effects are usually quite small\textsuperscript{28}, another decomposing channel to produce non-radiative species should play an important role. That is,

$$C_2H_2 \rightarrow 2C + H_2, \Delta H = 12.5 \text{ eV}. \quad (3c)$$

Reaction (3c) contains a C≡C bond fission and should compete with the CH* producing processes such as Reactions (6) and (10) in Table 2. In C$_2$H$_2$ molecule the intramolecular H atom migration through Reaction (3c) can occur more easily than D in C$_2$D$_2$ since the tunneling effects in C$_2$H$_2$ are superior to C$_2$D$_2$. Therefore we think the intramolecular H atom migration in the superexcited C$_2$H$_3$ molecule suppresses the CH* formation and results in the large inverse isotope effect of C$_2^*$/CH*>C$_2^*$/CD*. Similar isotope effects have been observed in the dissociative excitations of CH$_3$CN and CD$_3$CN\textsuperscript{29}, CH$_3$OH and CD$_3$OD\textsuperscript{20}, and CHCl$_3$ and CDCl$_3$\textsuperscript{31} in which non-radiative decompositions through tunnelings are suggested as discussed in the present work.

REFERENCES