Electron-Impact Dissociation of Acetylene, Ethylene and Ethane to Produce Excited C$_2$ Radical

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Electron-Impact Dissociation of Acetylene, Ethylene and Ethane to Produce Excited C₂ Radical

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The emission spectra of the Swan system of C₂ have been analyzed in order to discuss the production mechanism of C₂ from the three molecules. The vibrational distribution of this system looked like a Boltzman distribution and semi-logarithmic plots gave the vibrational temperatures of 22000-30000 K (C₂H₂), 30000-46000 K (C₂H₄) and 56000-92000 K (C₂H₆). The excitation functions have shown four thresholds, which indicate coexistence of four major processes of C₂ production. Doubly-excited Rydberg states are concluded to play important roles in these processes.

1. Introduction

The Swan system is one of the most intense emission bands of C₂ and appears in all kinds of flames and electrical discharges of carbon compounds. In spite of its importance in gas dynamics, combustion, astronomy and atmospheric chemistry, little is known on its production and reaction. The production mechanism of C₂ in the IR and UV multiphoton dissociation has been recently investigated. The C₂ Swan band emission follows a cubic power dependence in the ArF excimer laser excitation of C₂H₄CN and its vibrational and rotational temperatures are 7150 and 4960 K, respectively.

Electron impact excitation is another useful technique in the investigation of molecular dissociation dynamics. Since electrical discharge processes are complicated, excitation by controlled electron impact is more advantageous for an investigation on a primary process.

The production mechanism of C₂ from acetylene has been reported in the previous paper. Detailed results on the emission spectra, the vibrational distribution and temperatures, and excitation functions of C₂ from the three molecules are described in the present paper for the understanding of its production mechanism.

2. Experimental

The apparatus consists of a stainless-steel collision chamber, a 1.26m monochromator and a photon counting system. The sample gas was collided with the electron beam and photoemissions from the excited species were observed. The details have been published previously.

3. Results

The emission spectra by controlled electron impact on acetylene, ethylene
Dissociation of C\(_2\)H\(_2\), C\(_2\)H\(_4\) and C\(_2\)H\(_6\)

**Fig. 1.** Emission spectra of the Swan system of C\(_2\) by controlled electron impact on (a) acetylene, (b) ethylene and (c) ethane.

Electron energy 100 eV; electron-beam current 200-400 nA; optical resolution 0.8 Å.

and ethane show the Balmer lines of the excited hydrogen atom and bands of the CH and C\(_2\) radicals.\(^6\) The detailed spectra of the Swan system (\(\Delta v = +1\)) are shown in Fig. 1. The band shape was independent of the gas pressure for 6-50×10\(^{-5}\) Torr. The Swan band was slightly polarized and this finding indicates importance of the direct dissociation process.

The excitation functions of C\(_2\) (\(d^3\Pi_u\)) from the three molecules have four thresholds, as are shown in Fig. 2. Those for C\(_2\)H\(_4\) are 18.5±1.2, 23.3±1.2, 32.8±1.2 (?), and 39.7±2.4 eV and are consistent with the previous results.\(^7\) The existence of the four thresholds indicates that there are four major processes for the formation of C\(_2\) (\(d^3\Pi_u\)) from the three molecules.

The high resolution spectrum can disclose the vibrational distribution of the emitting species. The vibrational band intensity of the \(\Delta v = +1\) transition of C\(_2\) (\(d^3\Pi_u\)) were analyzed by the method of Danylewych and Nicholls.\(^8\) The band intensity \((I_{\nu',\nu})\) is related with the vibrational population \((N_{\nu'})\) for a photon counting measurement:

\[
I_{\nu',\nu'} = k N_{\nu'} \nu_{\nu'\nu'} R \Omega_{\nu'\nu'} g_s
\]

where \(\nu_{\nu'\nu'}\) is the frequency of the band origin, \(R\) is the electronic transition moment, \(\Omega_{\nu'\nu'}\) is the Franck-Condon factor and \(g_s\) is the statistical weight. This equation allows an estimation of \(N_{\nu'}\), for each \(\nu'\) level from the observed band intensity \((I_{\nu',\nu})\).

The relation between the band intensity and the experimentally measured band head intensity was given for the optical resolution of 3.325 Å and the rotational temperature of 1225 K.\(^9\) The experimental conditions in the present study are not identical with theirs. However, their formula and their correlation factors have been carried over here, mainly because the experimental
Fig. 2. The excitation function of $C_2 \left( d^{3}\Pi_u - a^{3}\Pi_u \right)$ (4680 Å) from (a) acetylene, (b) ethylene and (c) ethane.

The upper curves in (a) and (c) are enlarged one in the low energy region and should be read with the upper energy scale.

Electron-beam current (a) 2 μA, (b, c) 40 μA; electron energy resolution 0.6 eV; pressure 3-4.5×10^{-4} Torr.

Uncertainty would be larger than errors caused by such assumptions. The electronic transition moment, $R_{\alpha}$, is assumed to be constant for all vibrational transitions studied.
The vibrational populations thus obtained decrease as \( v' \) becomes large, and their semi-logarithmic plots are shown in Figs. 3 and 4. These plots show that the vibrational distributions are approximately Boltzman distributions, though there are fairly large scatterings. The calculated vibrational temperatures are summarized in Table 1. Those of the larger parent molecule are larger than those of the smaller one.

### 4. Discussion

The observed excitation functions show that there are four major processes for the formation of \( \text{C}_2 \left( d^3 \Pi_g \right) \) from acetylene and ethylene, and probably also from ethane. It has been found that there are a few major dissociative excitation processes of the excited hydrogen atom from several hydride molecules.\(^{11-14}\) Existence of a few processes seems to be common for electron excitation, since an electron can excite a molecule into any excited states simultaneously of which excitation energies are below the electron energy.

The core-ion model of molecular dissociation predicts that production mechanism of a ion and corresponding high-Rydberg fragments are identical.\(^{15}\) This model may be extended to the low-Rydberg fragment.\(^{11-14}\) If this is also true for \( \text{C}_2 \) production, dissociative ionization \( \left( \text{C}_2^+ \right) \) should be correlated with dissociative excitation \( \left( \text{C}_2^* \right) \).

The assignment of production mechanism of \( \text{C}_2 \left( d^3 \Pi_g \right) \) from acetylene was given previously.\(^{14}\) That of ethylene is discussed here. The ionization potentials (IP) of ethylene were measured by photoelectron\(^{11,12}\) and double charge transfer\(^{13}\) spectroscopy. Minimum energies for the formation of \( \text{C}_2 \left( d^3 \Pi_g \right) \) (DL) can be calculated from known dissociation energies into fragments and excitation energies of \( \text{C}_2 \). The energy diagram of ethylene is shown in Fig. 5.

The most probable process for the formation of the first component (threshold: 18.5 eV) is the excitation to the Rydberg states converging to the \( (2b_1)^{-1} \) ionized state and the successive dissociation to \( \text{C}_2 \left( d^3 \Pi_g \right) + \text{H}_2(X) + 2\text{H} \) or

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**Table 1. Vibrational temperatures of \( \text{C}_2 \left( d^3 \Pi_g \right) \)**

<table>
<thead>
<tr>
<th>( \text{C}_2\text{H}_2 )</th>
<th>( \text{C}_2\text{H}_4 )</th>
<th>( \text{C}_2\text{H}_6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 eV 22000 K</td>
<td>100 eV 30000 K</td>
<td>100 eV 50000 K</td>
</tr>
<tr>
<td>50</td>
<td>30000</td>
<td>50</td>
</tr>
<tr>
<td>15</td>
<td>25000</td>
<td>15</td>
</tr>
<tr>
<td>13</td>
<td>39000</td>
<td>13</td>
</tr>
</tbody>
</table>

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**Fig. 5. Energy diagram of ethylene.** The ionization potentials, the observed threshold energies and the calculated dissociation limits are shown. The width of the threshold energy represents its uncertainty.
to $\text{C}_2(d^3\Pi_g) + 2\text{H}_2$; both of them are possible, since the vibrational energy of $\text{C}_2$ is about 3.5 eV. The second component has the threshold energy around the $(2a_e)^{-1}$ ionized state. The Rydberg states converging to this ionized state may play an important role in the formation of this component. Around the threshold energies of the other two components, there are several doubly ionized states and doubly excited states converging to them. Excitation to some of these states, which are optically-forbidden, results in the dissociation into $\text{C}_2 + 4\text{H}$. These assignments correspond to those for acetylene. Thus, we can conclude that the singly and doubly excited Rydberg states play important roles in the molecular dissociation.

The highly-excited $\text{C}_2\text{H}_4$ decomposes mainly into $\text{C}_2 + n\text{H}$. It is an interesting question to ask whether $\text{C}_2(d^3\Pi_g)$ comes to appear in one step (explosively\textsuperscript{10}) or in several steps (quasi-equilibrium). The vibrational distribution should be correlated with the bond length of the parent molecule according to the Franck-Condon principle, if the dissociative excitation would proceed in one step. Calculated vibrational temperatures of $\text{C}_2(d^3\Pi_g)$ by using a modified Morse potential and an approximated formula\textsuperscript{14} are 3500 K ($\text{C}_2\text{H}_2$) and 4000 K ($\text{C}_2\text{H}_4$). The disagreement with the experimental results may be due to the existence of several competing processes.

Electron is an efficient source of molecular excitation and has a distinct advantage in comparison with photon. The detailed discussion of molecular dissociation dynamics are especially important and interesting because of this difference.

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References

Dissociation of C$_2$H$_2$, C$_2$H$_4$ and C$_2$H$_6$