  Bull. Chem. Soc. Jpn., 56, 3033—3036 (1983) 

# Production of $C_2(d^3\Pi_g)$ by Controlled Electron Impact on Acetylene, Ethylene, and Ethane

Teiichiro OGAWA,* Yasuhiro UEDA,† and Morihide HIGO††
*Department of Molecular Science and Technology, Kyushu University 39, Kasuga, Fukuoka 816*
(Received January 20, 1983)

The emission spectra produced by controlled electron impact on $C_2H_2$, $C_2H_4$, and $C_2H_6$ have been analyzed to gain insight into the production mechanisms of $C_2(d^3\Pi_g)$ from the three molecules. There are four thresholds on the excitation function of $C_2(d^3\Pi_g)$ from $C_2H_2$. Its vibrational temperatures are 22000 K for $C_2H_2$, 30000 K for $C_2H_4$ and 56000 K for $C_2H_6$ at an electron energy of 100 eV. Doubly-excited states are involved in the dissociative excitation of $C_2H_2$.

The observation of the diatomic $C_2$ radicals can be traced back to the nineteenth century. The intense emission bands of $C_2$ are prominent in all kinds of flames and electrical discharges of carbon compounds. Laser photolysis combined with laser-induced fluorescence detection is an efficient method to produce and to monitor this radical, and has been applied for studying elementary processes of $C_2$.[1] The mechanism of $C_2$ production in the infrared multiphoton dissociation has been investigated under collisionless conditions.[2,3] This radical has been produced by excimer laser photolysis;[4,5] the vibrational and the rotational temperatures of $C_2(d^3\Pi_g)$ from acrylonitrile have been determined to be 7150 and 4960 K, respectively.[5]

The molecular excitation process by electrons is somewhat different from that by photons; excitation into a triplet state and into a doubly-excited state is more feasible for the former. The $C_2(d^3\Pi_g)$ radical has been observed by controlled electron impact on acetylene,[6,7] ethylene,[8] and benzene;[9] however, no detailed discussion on their production mechanism has been carried out.

In the present paper, the emission spectra of $C_2H_2$, $C_2H_4$, and $C_2H_6$ produced by controlled electron impact have been measured under higher resolution than those in the previous papers, and the vibrational distributions and excitation functions of $C_2(d^3\Pi_g)$ have been analyzed to elucidate its production mechanisms.

## Experimental

The details of the apparatus have been described.[10,11] In brief, the sample gas jet ($10^{-4}$ Torr, 1 Torr≈133.322 Pa) was made to collide with an electron beam and the photoemission was measured with a Spex 1269 monochromator. The photons were detected with an HTV R585 photomultiplier and were counted with an NF PC545A photoncounter. The wavelength response was corrected with an Ushio JC-24-150 halogen lamp.[12] All the spectra were measured in a region where the intensity was proportional to both the electron-beam current and to the gas pressure. The sample gases were used as supplied ($C_2H_2$, Fuji Gas Ind.; $C_2H_4$, Seitetsu Chemicals; $C_2H_6$, Takachiho Chemicals); bulb-to-bulb distillation did not induce any change on the spectrum.

† Present address: Atsugi Plant, Sony Corporation Atsugi, Kanagawa 243.

†† Present address: Faculty of Engineering, Kagoshima University, Korimoto, Kagoshima 890.

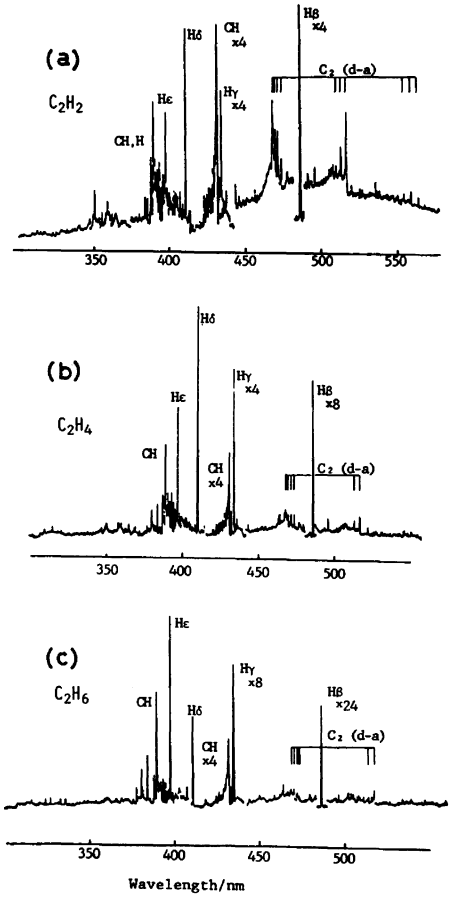


Fig. 1. Emission spectra of acetylene (a), ethylene (b), and ethane (c) by controlled electron impact.
Electron energy 100 eV; electron-beam current 100 μA (a, b), 1000 μA (c); gas pressure $3\times10^{-4}$ Torr; optical resolution 3.2 Å.

## Results and Discussion

*Spectra.* The emission spectra of acetylene, ethylene, and ethane by controlled electron impact show the Balmer lines of the excited hydrogen atom and bands of the CH radical (the A–X and B–X transition) and of the $C_2$ radical (the Swan system: the d–a transition),[13] as are shown in Fig. 1. The detailed spectra of the Swan system of $C_2$ from acetylene are shown in Fig. 2. The weak intensity of this system, especially for ethane, makes a quantitative analysis difficult. The band shape was independent of pressure

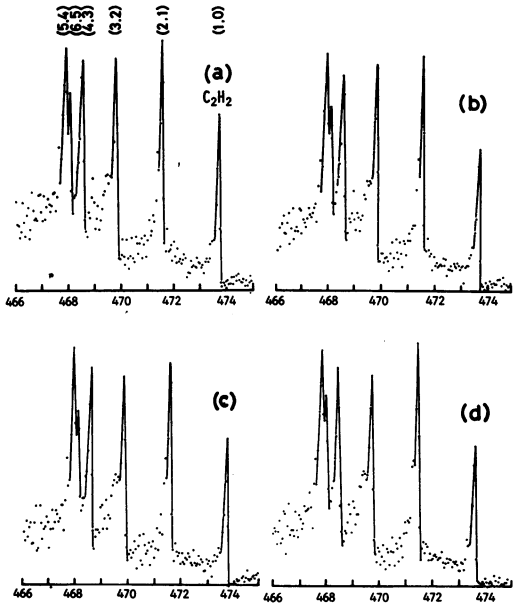


Fig. 2. The detailed spectra of the Swan system of acetylene at 100 eV (a), 50 eV (b), 30 eV (c), and 20 eV (d).
Electron-beam current 200—400 μA; optical resolution 0.8 Å.

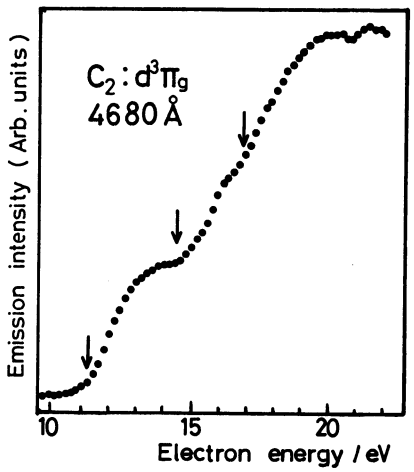


Fig. 3. The excitation function of $C_2(d^3\Pi_g)$ from acetylene at 4680 Å.
Electron-beam current 2 μA; electron energy resolution 0.6 eV; gas pressure $3\times10^{-4}$ Torr.

$(6—50)\times10^{-5}$ Torr. The Swan bands are slightly polarized (1—2%) for electron energies from the threshold to 100 eV: this finding indicates that direct dissociation processes are involved in the dissociative excitation of the three molecules.

The excitation function of $C_2(d^3\Pi_g)$ from acetylene is shown in Fig. 2. There are four thresholds; their values are $11.2\pm0.8$, $14.5\pm1.1$, $16.9\pm0.8$, and $24.0\pm1.0$ eV. Those of ethylene and probably of ethane also have four thresholds.[14] These findings indicate that there are four major processes for the formation of $C_2$ from acetylene and ethylene, and probably also from ethane. The existence of two or more processes for dissociative excitation is usual for electron impact dissociations.[15]

*Vibrational Population.* The Vibrational distribution of the fragments produced in a collision process has much to do with the kinematics. The intensity of each vibrational band of the $\Delta v=+1$ transition of $C_2(d^3\Pi_g)$ has been obtained from its peak intensity, following the method of Danylewych and Nicholls.[16] The vibrational population thus obtained are shown in Fig. 3 for the three molecules excited by an electron beams of 100 eV. The values are relative to that $v'=0$, which is set to 1.0. The error bars shown are due to random experimental fluctuations. The observed distribution represents the nascent one, since the pressure is so low that the collisional deactivation can be ignored over the lifetime of the emitting level (≈119 ns[4]).

The vibrational population of $C_2$ decreased as $v'$ increased. If the excess energy of the primarily excited species are distributed randomly over various freedoms of motions, the vibrational population may be a Poisson distribution. This is not the case, as is shown in Fig. 4.

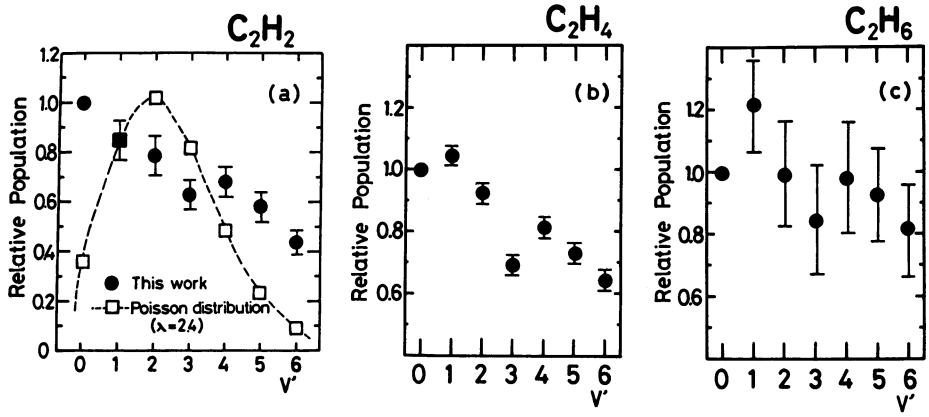


Fig. 4. Vibrational populations of $C_2(d^3\Pi_g)$ from $C_2H_2$ (a), $C_2H_4$ (b), and $C_2H_6$ (c) at an excitation energy of 100 eV.
The error bars represent random scatterings. A poisson distribution is shown for the case of $C_2H_2$, where $\lambda$ is determined as a parameter for the least-square fitting with the observed values.

Table 1. Vibrational temperature ($T_{vib.}$) of $C_2$ at various electron energies ($E_{el}$)

| $C_2H_2$ | | $C_2H_4$ | | $C_2H_6$ | |
|---|---|---|---|---|---|
| $E_{el}$/eV | $T_{vib}$/K | $E_{el}$/eV | $T_{vib.}$/K | $E_{el}$/eV | $T_{vib.}$/K |
| 100 | 22000 | 100 | 30000 | 100 | 56000 |
| 50 | 26000 | 50 | 32000 | | |
| 16 | 25000 | 30 | 46000 | | |
| 13 | 30000 | 21 | 36000 | | |

Estimated errors: $C_2H_2$ and $C_2H_4$ at 100—50 eV; ±10%, the others; ±20%.

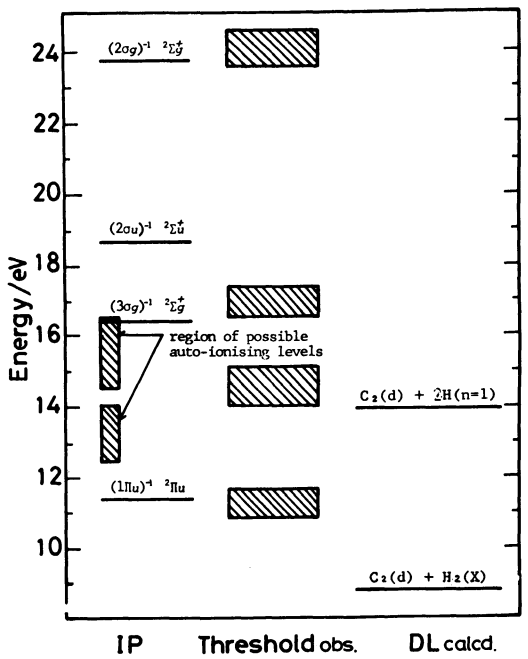


Fig. 5. Energy diagram of acetylene.
The ionization potentials, the observed threshold energies and the calculated dissociation limits are shown. The width of the threshold energy represents its uncertainty.

The vibrational distributions of $C_2$ are rather similar to a Boltzmann distribution. Semi-logarithmic plots of the vibrational populations give the vibrational temperatures of $C_2(d^3\Pi_g)$, as are shown in Table 1. The vibrational temperatures tend to increase for a larger parent molecule. This finding seems to be inconsistent with a statistical prediction,[17] which has been successfully applied to multiphoton dissociation of benzene.[18] This means either that the three molecules are too simple to be treated statistically or that there are some predominant processes.

*Assignments for Acetylene.* The core-ion model of molecular dissociation may be extended to the low-Rydberg fragments.[15] If this is also the case for the production of $C_2$, dissociative ionization to produce $C_2^+$ should be correlated with dissociative excitation. The electron configuration of acetylene is $KK(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4$. The energy diagram for dissociation is shown in Fig. 5.

The first component of $C_2$, which has the threshold at 11.2 eV, is assigned to be produced from dissociative excitation through Rydberg states converging to the $(1\pi_u)^{-1}$ ionized state, which lies in this region.[19] The final state should be $C_2(d^3\Pi_g)+H_2(X)$ from energy considerations. The excess energy of this process is about 2.6 eV and is almost equal to the vibrational energy of $C_2$ excited at 13 eV (30000 K=2.6 eV); thus, the excess energy mostly goes into the vibrational freedom of $C_2$ in this process.

There are auto-ionizing levels[20] near the second threshold (14.5 eV), Rydberg states converging to the $(2\sigma_u)^{-1}$ and $(3\sigma_g)^{-1}$ ionized states[19] near the third threshold (16.9 eV), and Rydberg states converging to the $(2\sigma_g)^{-1}$ ionized state[19] near the fourth threshold (24.0 eV). The $(3\sigma_g)^{-1}$ state dissociates into $C_2H^+$ and then into $C_2^+$ quickly.[21] The $(2\sigma_u)$ orbital is strongly bonding for the C–H bonds and the $(2\sigma_u)^{-1}$ state is expected to dissociate into $C_2^+$. Thus, these states are expected to be important for the formation of $C_2(d^3\Pi_g)$ in the respective energy regions.

Assignments of $C_2$ production mechanism may be carried out similarly for ethylene and ethane; however, insufficient information on their highly-excited states and larger experimental fluctuations made any detailed discussion difficult.

*Concluding Remarks.* An electron is a very efficient source for molecular excitation in the 10—1000 eV range, and an electron source is much easily operated than a synchrotron orbital radiation facility. Furthermore, the electron has a distinct advantage; it is able to excite optically forbidden processes, which are often important in the dissociation dynamics.[15] The vibrational distributions of $C_2(d^3\Pi_g)$ produced by IR multiphoton dissociation of $C_2H_3CN$ concentrate in the lower vibrational level,[3] whereas those produced by UV multiphoton dissociation of $C_2H_3CN$ have a vibrational temperature of 7150 K.[5] These results disclose differences in the excitation mechanisms. Recent demands for the dynamics and kinetics of $C_2$ from combustion engineering, atmospheric and environmental sciences warrant further investigation on this subject.

The authors thank Professor Nobuhiko Ishibashi for his encouragement. The present study was partially supported by a Grant-in-Aid from the Ministry of Education, Science and Culture.

## References

1) H. Reisler, M. Mangir, and C. Witting, "Chemical and Biochemical Applications of Lasers," ed by C. B. Moore, Academic Press, New York (1980), Vol. 5, p. 139.

2) R. V. Anbartzumian, N. V. Chekalin, V. S. Letoknov, and E. A. Ryabov, *Chem. Phys. Lett.*, **36**, 301 (1975); N. V. Chekalin, V. S. Letoknov, V. N. Lokhman, and A. N. Shibanov, *Chem. Phys.*, **36**, 415 (1979).

3) J. D. Campbell, M. H. Yu, M. Mangir, and C. Wittig, *J. Chem. Phys.*, **69**, 3854 (1978); M. H. Yu, M. R. Levy, and C. Wittig, *ibid.*, **72**, 3789 (1980).

4) J. R. McDonald, A. P. Baronavski, and V. M. Donnelly, *Chem. Phys.*, **33**, 161 (1978).

5) N. Nishi, H. Shinohara, and I. Hanazaki, *J. Chem. Phys.*, **77**, 246 (1982).

6) C. I. M. Beenakker and F. J. de Heer, *Chem. Phys.*, **6**, 291 (1974).

7) M. Tsuji, T. Ogawa, Y. Nishimura, and N. Ishibashi, *Bull. Chem. Soc. Jpn.*, **49**, 2913 (1976).
8) D. E. Donobue, J. A. Schiavone, and R. S. Freund, *J. Chem. Phys.*, **67**, 769 (1977).
9) M. Tsuji, T. Ogawa, T. Imasaka, Y. Nishimura, and N. Ishibashi, *Bull. Chem. Soc. Jpn.*, **49**, 53 (1976).
10) T. Ogawa and M. Higo, *Chem. Phys.*, **52**, 55 (1980).
11) T. Ogawa, N. Yamami, M. Tsuji, and Y. Nishimura, *Bull. Chem. Soc. Jpn.*, **54**, 1203 (1981).
12) The authors are indebted to Dr. M. Suzuki of the Electrotechnical Laboratory for his determination of the spectral irradiance of this lamp.
13) R. W. B. Pearse and A. G. Gaydon, "The Identification of Molecular Spectra," 4th ed, Chapman and Hall, London (1976).
14) T. Ogawa, Y. Ueda, and M. Higo, *Eng. Sci. Repts. Kyushu Univ.*, **5**, 1 (1983).
15) T. Ogawa, J. Kurawaki, and M. Higo, *Chem. Phys.*, **61**, 181 (1981); M. Higo, S. Kamata, and T. Ogawa, *ibid.*, **66**, 243 (1982).
16) L. L. Danylewych and R. W. Nicholls, *Proc. R. Soc. London, Ser. A*, **339**, 197, 213 (1974).
17) J. Silberstein and R. D. Levine, *Chem. Phys. Lett.*, **74**, 6, (1980).
18) N. Ohmichi, J. Silberstein, and R. D. Levine, *Chem. Phys. Lett.*, **84**, 228 (1981).
19) K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata, "Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules," Japan Sci. Soc. Press, Tokyo (1981).
20) R. Botter, V. H. Dibeler, J. A. Walker, and H. M. Rosenstock, *J. Chem. Phys.*, **44**, 1271 (1966); T. Hayaishi, S. Iwata, M. Sasanuma, E. Ishiguro, Y. Morioka, Y. Iida, and M. Nakamura, *J. Phys. B*, **15**, 79 (1982).
21) R. S. Lehrle and R. S. Mason, *Int. J. Mass Spectrom. Phys.*, **21**, 165 (1976).