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$CF_2(^1B_1)$ FORMATION BY VACUUM ULTRAVIOLET PHOTOLYSIS OF C_2F_4

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An emission due to the $^1B_1 \rightarrow {^1A_1}$ transition of CF_2 radical was observed during the vacuum ultraviolet photolysis of tetrafluoroethylene with Xe and Kr resonance lamps. The extent of vibrational excitation of the $CF_2(^1B_1)$ evidenced that the dissociation process $C_2F_4 + h\nu \rightarrow CF_2(^1A_1) + CF_2(^1B_1)$ is responsible.

The ultraviolet emission of the CF_2 radical due to its $^1B_1 \rightarrow {^1A_1}$ transition has been studied by a number of researchers, and the observation of the emission during the vacuum ultraviolet (vuv) photolysis of CF_2Br_2 is reported.[1)] Tetrafluoroethylene is expected to be a good starting material for producing $CF_2(^1B_1)$ radicals with well-defined internal energy. This compound has a weak C=C bond (70 kcal mol^{-1} [2)]), and in fact its mercury photosensitized decomposition is reported to yield $CF_2(^1A_1)$ in good yield.[3)] Moreover, it absorbs light in a longer wavelength range than CF_2Br_2. The following dissociation processes into CF_2 radicals are possible on the basis of energetics.[2,4,5)]

$$C_2F_4 + h\nu \longrightarrow \begin{array}{lll} CF_2(^1A_1) + CF_2(^1A_1) & \lesssim 412\ \text{nm} & (1) \\ CF_2(^1A_1) + CF_2(^1B_1) & \lesssim 163\ \text{nm} & (2) \\ CF_2(^3B_1) + CF_2(^3B_1) & \lesssim 156\ \text{nm} & (3) \end{array}$$

The apparatus for the vuv photolysis and the materials were described previously.[4,6)] The spectral sensitivity of the system was determined by the use of a halogen lamp (Philips 7027), the emission spectrum of which was kindly calibrated by Dr. Suzuki of Electrotechnical Laboratory.

During the vuv photolysis at 147.0 nm (Xe lamp with a CaF_2 window) and at 123.6 nm (Kr lamp with a LiF window), an emission was observed in the wavelength range 230 - 400 nm, as shown in Fig. 1. The excitation of C_2F_4 is probably to its $^1(\pi\pi^*)$ state, though Rydberg type transitions may occur to a certain extent.[7)]

In the case of Xe lamp irradiation, the $CF_2(^1B_1)$ is produced at 1400 K under the equipartitioning assumption that $(1/2)\underline{s}kT = \underline{E}$. Here $\underline{s}$ is the number of degrees-of-freedom for internal motion and molecular rotation of C_2F_4. The total available energy $\underline{E}$ is equal to the photon energy at 147.0 nm plus the thermal energy of C_2F_4 minus the bond dissociation energy after the process (2). We tried to simulate the observed spectrum according to the following procedure. The vibrational and rotational distributions of the $CF_2(^1B_1)$ were assumed to be a Boltzmann distribution at 1400 K. At first the band contour for the (040) → (000) transition was calculated on the basis of the rotational constants reported by Mathews.[5)] The profile was

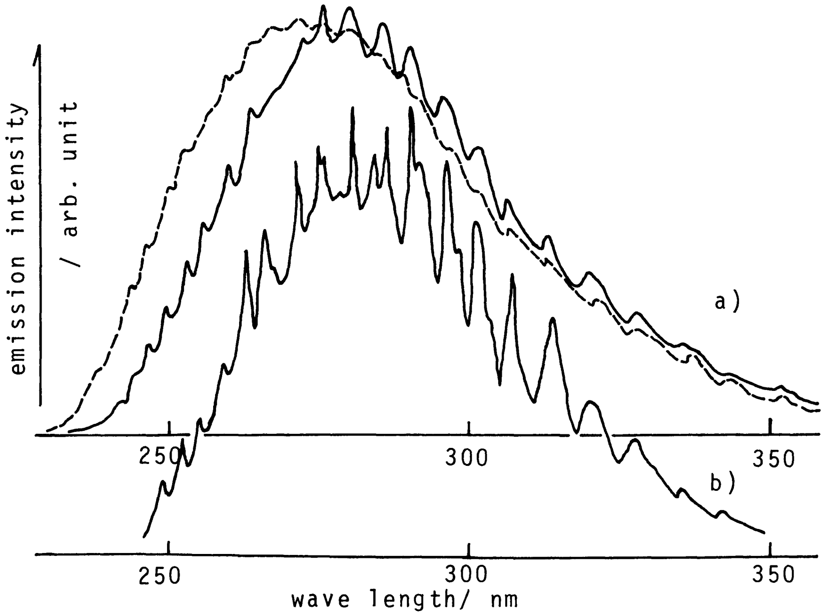

Fig. 1 Observed and simulated spectra for $^1B_1 \rightarrow {}^1A_1$ transition of CF_2

a) observed spectra

C_2F_4 : 0.3 torr

—— : Xe lamp, band pass width, 0.6 nm

---- : Kr lamp, band pass width, 0.24 nm

b) simulated spectrum for 147.0 nm irradiation

then convoluted with the triangular slit function estimated experimentally. The band profiles for other transitions were assumed to be identical with that for the (040) → (000) transition. The bands were then superposed by the use of appropriate Franck-Condon (FC) factors and line positions.$^{8)}$ Only the contributions from $v_1'v_2' \rightarrow v_1''v_2''$ ($v_1' \leq 2$, $v_2' \leq 6$) transitions were taken into account, because FC factors are not determined for other transitions. The equilibrium geometry of the $^1A_1$ and $^1B_1$ states differs appreciably in the ∠FCF angle alone, and the above simplification should be permitted so long as the internal excitation is small (≤ 1500 K). We employed the library programs of Computer Center - University of Tokyo prepared by Drs. Nakagawa and Hirakawa (DB06, DB16).

Relatively good agreement of the calculated spectrum (b) in Fig. 1) with the observed one shows that the emission is due to the $CF_2(^1B_1)$ radical. Moreover, the process (2) is evidenced by the fact that the extent of the internal excitation is that expected from the equipartitioning of the available energy for the process. The much higher internal excitation in the case of Kr lamp irradiation which is shown by the blue shift of the emission is reasonable, though we did not try to simulate the spectrum from lack of data on FC factors necessary for these highly-excited $CF_2(^1B_1)$ radicals as mentioned before.

References

1) C. A. S. Johnson and H. J. Ross, J. Chem. Soc. Faraday Trans. I., 74, 2930 (1978).
2) JANAF Thermochemical Tables, Natl. Stand. Ref. Data Ser. No. 37 (1971).
3) B. Atkinson, J. Chem. Soc., 1952, 2684.
4) S. Koda, Chem. Phys. Lett., 55, 353 (1978).
5) C. W. Mathews, Can. J. Phys., 45, 2355 (1967).
6) S. Koda, Bull. Chem. Soc. Jpn., 50, 1683 (1977).
7) G. Belanger and C. Sandorfy, J. Chem. Phys., 55, 2055 (1971).
8) D. S. King, P. K. Schenck, and J. C. Stephenson, J. Mol. Spectrosc., to be published. We are grateful to the authors for sending their manuscript before the publication.

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