BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (11), 3226—3228 (1979)

Vibrational Distribution of CS($X^1\Sigma^+$) Fragments Formed in the UV Flash Photolysis of CS_2

Takayuki Ebata, Masahiro Kawasaki†, Kin-ichi Obi, and Ikuzo Tanaka*
Department of Chemistry, Tokyo Institute of Technology, Ohokayama, Meguro-ku, Tokyo 152

(Received April 26, 1979)

The vibrational distribution of the CS(X) fragment has been studied by the UV flash photolysis and kinetic spectroscopic technique. The CS fragment was generated by the flash photolysis of CS_2 at ≈200 nm. The vibrational distribution is well represented by a sum of two modified Poisson distributions with different mean values. This distribution is explained by assuming the following two photodissociation processes of CS_2; one is a predissociation through a triplet state and the other is a direct photodissociation.

$$CS_2 + h\nu \longrightarrow \begin{cases} CS_2(\tilde{A}^1B_2) \rightarrow CS_2(T) \rightarrow CS(X^1\Sigma^+, v'') + S(^3P), \\ CS(X^1\Sigma^+, v'') + S(^1D). \end{cases}$$

The photodissociation dynamics of triatomic molecules has been of theoretical interest and simple models for the vibrational distribution have been developed.[1] The vibrational distribution of CS fragments in the photodissociation of CS_2 is a good test for these models. Early works[2–4] reported that the vibrationally excited CS($X^1\Sigma^+$) radicals are formed in the flash photolysis of CS_2. Lee and Judge[5] pointed out that the vibrational population of CS($A^1\Pi$) produced in the vacuum-UV photolysis of CS_2 is approximately represented by a modified Poisson distribution. Bersohn and colaborators[6] measured the translational energy distribution of photofragments, CS and S, by photodissociating a CS_2 molecular beam with a pulsed ArF excimer laser at 193 nm. They observed that the translational energy distribution can be represented by a sum of two distributions.

In this study, using the flash photolysis and kinetic spectroscopic technique, the vibrational distribution of CS($X^1\Sigma^+$) has been determined in the photolysis of CS_2 at quartz UV region.

Experimental

The set-up of quartz UV flash photolysis and kinetic spectroscopic system has been described previously.[7] In brief, the mixture of CS_2 (0.2 Torr) and Ar (5.0—200 Torr) was flash-photolyzed in a quartz cell which contained a multiple reflection mirror system. The 1000 J photolysis and 50 J spectroscopic flash lamps gave 8 and 5 μs light pulses, respectively. The absorption spectra of CS were photographed with a Nikon G-500 spectrograph on Kodak 2475 recording films in the wavelength range between 255 and 275 nm. We assumed that in this wavelength range the spectral sensitivity of the film was constant. The absorption intensity of each vibrational band at "no delay" was obtained by extrapolating the decay curve to $t=0$.

CS_2 (Wako Chemical) was degassed under vacuum and Ar (Takachiho Chemical Ind., 99.99%) was used without further purification. The mixture was left in a 20-1 glass bulb for 4 h before photolysis. Under our experimental conditions, the absorption spectrum of CS ($A^1\Pi$, $v'=0 \leftarrow X^1\Sigma^+$, $v''=0$) could be observed even a few minutes after one flashing because of its stability. Therefore after each flashing, the mixture was pumped out.

Results and Discussion

Vibrational Distribution of the CS($X^1\Sigma^+$) Photofragment. Figure 1 shows relative excited population density which is determined by folding the lamp spectral irradiance into the absorption spectrum of the CS_2 molecule. The population density is centered at ≈200 nm. The FWHM is ≈1700 cm^{-1} which corresponds to less than two vibrational quanta of CS ($X^1\Sigma^+$).

The absorption spectra of the CS($X^1\Sigma^+$) fragment formed in the photodissociation of CS_2 by quartz flash lamp were observed up to five vibrational quanta. The pressure effect of Ar buffer gas was not observed under our experimental conditions. In order to obtain the vibrational population of CS($X^1\Sigma^+$) at $t=0$, the optical density of each vibrational band is plotted against delay time as shown in Fig. 2, where $OD_t(0, 0)$ is normalized to unity. The plots show good linear relations between $\log[OD_t(v', v'')/OD_t(0, 0)]$ and delay time. Using the extrapolated values of the optical

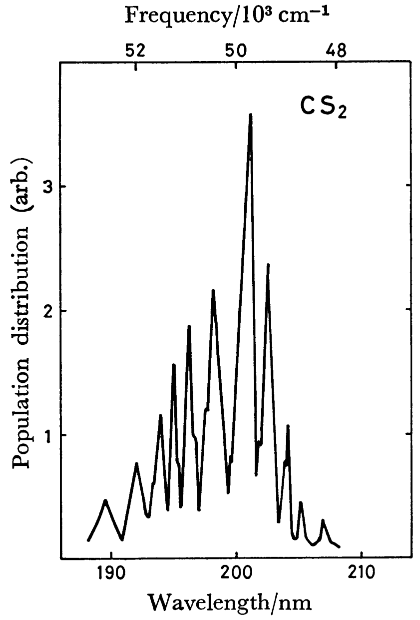

Fig. 1. Population density which is obtained by multiplying the absorption spectra of CS_2 by the lamp spectral irradiance.

---

† Present address: Chemistry Department of Industry and Resources, Faculty of Engineering, Mi'e University, Kamihama-cho, Tsu 514.

TABLE 1. VIBRATIONAL DISTRIBUTION OF $CS(X^1\Sigma^+)$ FORMED BY PHOTODISSOCIATION OF CS_2

v'-v''	λ/nm	$OD_0(v', v'')/OD_0(0, 0)$	$q_{v'v''}$[a]	$N_{v''}$(rel.)	$q_{v'v''}$[b]	$N_{v''}$(rel.)	$N_{v''}$(rel.)
0-0	257.7	1.00	0.830	1	0.75	1	1
0-1	266.4	0.43	0.151	2.9	0.17	2.2	2.1±0.4
1-1	259.1	1.08	0.514	1.8	0.59	1.4	
1-2	267.9	0.38	0.268	1.5	0.23	1.5	1.5±0.1
2-2	260.7	0.57	0.261	1.9	0.35	1.2	
2-3	269.4	0.43	0.306	1.5	0.34	1.2	1.3±0.2
3-4	271.0	0.32	0.292	1.2	0.35	0.8	1.0±0.2
4-5	272.7	0.22	0.242	1.0	0.36	0.6	0.8±0.2

a) Ref. 8. b) Corrected for the change of the electronic transition moment according to Ref. 5. c) Averaged population relative to $v''=0$.

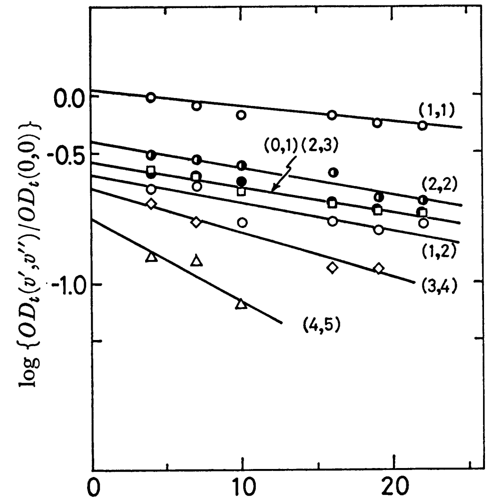

Fig. 2. Time variation of the relative absorption intensity of CS, $A^1\Pi(v')\leftarrow X^1\Sigma^+(v'')$ bands. The (0, 0) band is normalized to unity.

density at $t=0$, the vibrational population $N_{v''}$ is obtained by,

$$\frac{N_{v''}}{N_0}=\frac{OD_0(v',v'')}{OD_0(0,0)}\,\frac{q_{00}}{q_{v'v''}}\,\frac{R_e^2(\bar r_{00})}{R_e^2(\bar r_{v'v''})} \qquad \text{(I)}$$

where $q_{v'v''}$ is the Franck-Condon factor of CS(A-X) and R_e is the electronic transition moment which is given by $R_e(\bar r_{v'v''})=c(1-0.39\bar r_{v'v''})$ with the r-centroid in Ångstrom units. In order to evaluate the ratio $N_{v''}/N_0$, we used the Franck-Condon factors which were calculated by Coxon *et al.*[8] with the RKR potential and obtained experimentally by Lee and Judge[5] with correction for the change of the electronic transition moment (Table 1). The averaged values of $N_{v''}/N_0$ against vibrational quantum numbers are plotted in Fig. 3. A population inversion between $v''=0$ and 1 levels is evident. The FWHM is approximately four vibrational quanta which is wider than that of the population density of the parent molecule of Fig. 1, indicating vibrational excitation of CS in photodissociation processes.

The vibrational excitation of the CS fragment is explained both in terms of the comparison of the CS internuclear distance of CS_2^* with that of the electronically ground state of CS radical and in terms of the dynamical energy transfer during photodissociation.[9] If we assume that both the vibrational levels $i=0$ and 1, are *initially* populated and the energy transferred by dynamical interaction is the same for two vibrational states, the population in the vibrational level v'' is given by "modified Poisson distribution" in the impulsive half-collision model[1]

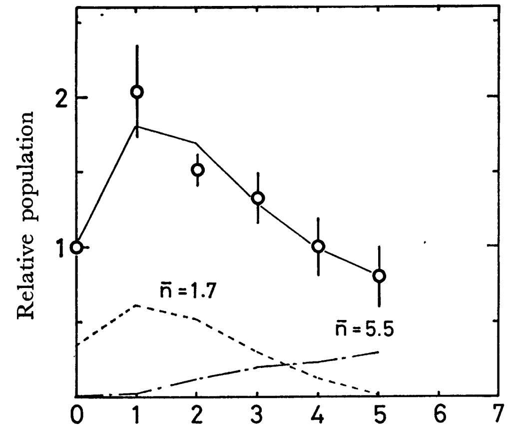

Fig. 3. The vibrational population of the $CS(X^1\Sigma^+)$ state formed in photodissociation. The solid line shows the best fit curve obtained by summing up the two distributions. See text.

$$N_{v''}=(\bar n)^{v''}\frac{(\bar n)^2+(\alpha-2v'')\bar n+v''^2}{v''![(\bar n)^2+(\alpha-2)\bar n+1]}\exp(-\bar n) \qquad \text{(II)}$$

where α is the ratio of the population in the $i=0$ state to that in the $i=1$ state, and $\bar n$ is the averaged vibrational state.[5] Assuming two photodissociation processes, *i.e.*, two vibrational distributions, the result of the best fit to the observed populations using Eq. II is shown in Fig. 3. The best fit curve was obtained by summing up two distributions of the ($\bar n$, α) values of (1.7, ∞) and (5.5, 19.0) almost equally weighted. The former means that CS fragments are not *initially* vibrationally excited, while the latter indicates the *initial* vibrational excitation of the CS photofragments.

Photodissociation Processes. The vibrationally hot CS fragments may be directly produced by the photolysis of CS_2. Since the absorption of light is centered at ≈200 nm in this experiment, photolysis occurs with sufficient energy to leave an excess of ≈40 kcal/mol after production of electronically ground state fragments. In the photolysis of the CS_2 molecular beam at 193 nm,[6] the translational energy distribution of the fragments consists of two distributions; one peaks sharply at $\approx$8 kcal/mol and the other extends broadly with its peak at $\approx$15 kcal/mol. From both these data and ours, it is expected that there are two photodissociation processes of CS_2 at $\approx$200 nm and that the CS fragment is vibrationally and/or rotationally excited.

The absorption spectrum of gaseous CS_2 around at 200 nm consists of a single progression of bands superimposed on the continuum. The variation of the contours of the bands may result from varying degrees of predissociation.[10] The maximum quantum yield of $\approx 10^{-3}$ has been reported for the fluorescence of CS_2 and it is concluded that the main fate of $CS_2{}^*$ is photodissociation.[11]

The following two processes are energetically possible in the photolysis at $\approx$200 nm,

$$\Delta H_0^\circ \text{ (kcal/mol)}$$

$$CS_2 \left[\begin{array}{ll} \rightarrow CS(X^1\Sigma^+) + S(^3P), & 102.9 \quad (1) \\ \rightarrow CS(X^1\Sigma^+) + S(^1D). & 129.3 \quad (2) \end{array}\right.$$

Concerning the photodissociation process (1) which is spin-forbidden, it is postulated that CS_2 is decomposed through a triplet excited state[4]

$$CS_2 + h\nu \rightarrow CS_2(\tilde{A}^1B_2) \rightarrow CS_2(T) \rightarrow CS(X^1\Sigma^+) + S(^3P). \qquad (1a)$$

The CS_2 absorption band near 200 nm has been assigned to the transition to the $\tilde{A}^1B_2$ state[10] which is nonlinear with a C–S bond distance of $r_e = 1.66$ Å. Once this singlet state crosses over to the repulsive triplet state, CS_2 will simultaneously decompose to the fragments. If this is the case, the CS fragment is vibrationally excited before photodissociation because the CS equilibrium bond distance of the excited $CS_2(\tilde{A}^1B_2)$ is longer than that of $CS(X^1\Sigma^+)$ by 0.13 Å. Furthermore, during dissociation the fragment is vibrationally excited by the actual repulsive force, *i.e.*, dynamical excitation. Because the $\tilde{A}^1B_2$ state has the S–C–S angle of 153°, the CS fragments are thought to be rotationally excited. The spectator model predicts that the rotational energy will be one fourth of the vibrational energy.[12]

Concerning the photodissociation process (2), Donovan *et al.*[13] reported the preliminary results which showed the yields of $S(^1D_2)$ in the photolysis of CS_2 at 200 nm. As the process (2) is thought to be the direct photodissociation, the singlet excited state must have very short lifetime in which the linear structure of the ground state of $CS_2(\tilde{X}^1\Sigma^+)$ is retained during the decomposition. Although no rotational excitation is possible in this case, $\bar{n}$ is smaller because available energy for the process (2) is smaller than that for (1) by 26.4 kcal/mol.[14] Because the CS bond distance (1.55 Å) of $CS_2(\tilde{X})$ is almost same as that of CS(X) (1.53 Å), the value of α in Eq. II is expected to be infinite, *i.e.* only $i=0$ is *initially* populated. From the above discussion it is concluded that the vibrational distribution with the lower vibrational quanta $(\bar{n}, \alpha) = (1.7, \infty)$ corresponds to the process (2), while that with $(\bar{n}, \alpha) = (5.5, 19.0)$ corresponds to the process (1) because of the *initial* excitation of the CS fragment.

References

1) (a) Y. Band and K. F. Freed, "Excited States," ed by E. C. Lim Academic Press, New York (1977); b) W. M. Gelbart, *Ann. Rev. Phys. Chem.*, **28**, 323 (1977).

2) G. Porter, *Proc. R. Soc. London, Ser. A*, **200**, 284 (1950).

3) A. B. Callear and R. G. W. Norrish, *Nature*, **188**, 53 (1960).

4) A. B. Callear, *Proc. R. Soc. London, Ser. A*, **276**, 401 (1963).

5) L. C. Lee and D. L. Judge, *J. Chem. Phys.*, **63**, 2782 (1975).

6) R. Bersohn, *J. Photochem.*, **9**, 87 (1978); A. Freedman, S. Yang, M. Kawasaki, and R. Bersohn, to be published.

7) K. Shibuya, T. Ebata, K. Obi, and I. Tanaka, *J. Phys. Chem.*, **81**, 2292 (1977).

8) J. A. Coxon, P. J. Marcoux, and D. W. Setser, *Chem. Phys.*, **17**, 408 (1976).

9) M. J. Berry, *Chem. Phys. Lett.*, **29**, 329 (1974).

10) A. E. Douglas and I. Zanon, *Can. J. Phys.*, **42**, 627 (1964).

11) K. Hara and D. Phillips, *Trans. Faraday Soc.*, **74**, 1441 (1978).

12) G. E. Bush and K. R. Wilson, *J. Chem. Phys.*, **56**, 3626 (1972).

13) M. C. Addison, C. D. Byrne, and R. J. Donovan, *Chem. Phys. Lett.*, **64**, 57 (1979).

14) H. Okabe, "Photochemistry of Small Molecules," Wiley-Interscience (1978).