Rotational Distribution of CO($b^3\Sigma^+$) Produced in Energy Transfer Reaction from Ar($^3P_2$) to CO

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(Received February 20, 1992)

Synopsis. The rotational energy disposal of CO($b^3\Sigma^+$) in the Ar($^3P_2$)+CO reaction has been measured by observing CO($b^3\Sigma^+$-$a^3\Pi_r$) emission in an Ar flowing afterglow. The initial rotational distribution of CO($b:v'$=0,1) was expressed by a single Boltzmann temperature of 7000±700 K. The fraction of available energy deposited into rotational mode of CO(b), $\langle f_r \rangle$, was estimated to be 32±2%.

Carbon monoxide is an ideal molecule for studying state selectivity in excitation transfer from metastable rare gas atoms because there are many emitting excited singlet and triplet states in the energy range of 6—11 eV.[1,2] We have recently made a systematic optical spectroscopic study on the electronic excitation transfer from the metastable Ar($^3P_2$: 11.55 eV), Kr($^3P_2$: 9.92 eV), and Xe($^3P_2$: 8.32 eV) atoms to CO at thermal energy (39 meV) by using flowing-afterglow (FA) and beam apparatus.[3–8] For the Ar($^3P_2$)+CO system, the following exit channels have been identified:[4]

$$\mathrm{Ar}(^3P_2) + \mathrm{CO} \xrightarrow{k_{1a}} \mathrm{CO}(c^3\Pi : v' = 0) + \mathrm{Ar}, \qquad (1a)$$

$$\xrightarrow{k_{1b}} \mathrm{CO}(b^3\Sigma^+ : v' = 0\text{—}2) + \mathrm{Ar}, \qquad (1b)$$

$$\xrightarrow{k_{1c}} \mathrm{CO}(a'^3\Sigma^+ : v > 23) + \mathrm{Ar}. \qquad (1c)$$

The reaction rate constants for each product channel have been determined to be $k_{1a}=1.3\times10^{-14}$, $k_{1b}=7.0\times10^{-14}$, and $k_{1c}=9.9\times10^{-13}$ cm^3 s^{-1}. The energy level diagram of Ar($^3P_2$) and CO(c,b) is shown in Fig. 1. It is clear from the diagram that the energy of CO($b:v'$=0) is lower than that of CO($c:v'$=0) by 1.02 eV, and the CO($b:v'$=0—2) levels are lying below the C(^{3}P)+O(^{3}P) dissociation limit. The rotational distribution of the near-resonant CO($c:v'$=0) level has been expressed by a single Boltzmann temperature of 800±150 K.[6] Although the relative vibrational population of CO($b:v'$=0—2) has been estimated, no information on the rotational distribution has been obtained.

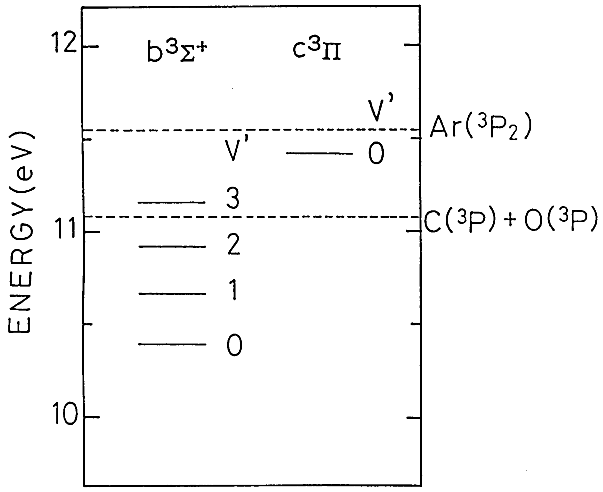

Fig. 1. Energy level diagram of Ar($^3P_2$), CO($b^3\Sigma^+$, $c^3\Pi$), and C(^{3}P)+O(^{3}P). Thermochemical and spectroscopic data are obtained from Refs. (1,2, and 11).

In the present study, the rotational distributions of CO($b:v'$=0,1) are determined from a spectral simulation. A component arising from the c→b radiative cascade is found in the rotational distribution of CO($b:v'$=0). Taking account of this contribution, the initial vibrational population of CO($b:v'$=0—2) is reexamined. The observed rotational distributions are compared with those predicted from a simple statistical theory for characterizing the dynamical features of the E–E reaction.

Experimental

The FA apparatus and the experimental procedure used in this study have been described previously.[4] The Ar($^3P_{0,2}$) metastable atoms were produced by a microwave discharge of high purity Ar gas. All experiments were carried out under the condition where the relative concentration of the upper Ar($^3P_0$) spin-orbit state to that of Ar($^3P_2$) was insignificant. The pressure in the reaction zone was 0.1—0.25 Torr for Ar and 1—10 mTorr for CO (1 Torr=133.3 Pa) as measured by an MKS Baratron gauge. The UV emission in the 200—350 nm region was dispersed by using a Jarrell Ash 1 m monochromator equipped with a cooled Hamamatsu Photonics R376 photomultiplier. The sensitivity of the monochromator and the optical detection system was calibrated by using standard D_2 and halogen lamps.

Results and Discussion

Figure 2(a) shows a typical emission spectrum resulting from the Ar($^3P_2$)+CO reaction. The (2,0), (1,0), (0,0), and (0,1) bands of CO($b^3\Sigma^+$-$a^3\Pi_r$) and the (0,2), (0,3), and (0,4) bands of CO($c^3\Pi$-$a^3\Pi_r$) are identified in this spectral range. For comparison, in Fig. 2(b) is given a CO(b–a) emission spectrum obtained by adding CO into the Ar discharge flame, where electrons and rare gas active species such as metastable atoms and ionic species were present. It should be noted that the CO(b–a) emission by the Ar($^3P_2$) reaction appears in much wider spectral range than that in the discharge spectrum due to a higher rotational excitation. The spectral features of CO(b–a) by the Ar($^3P_2$) reaction

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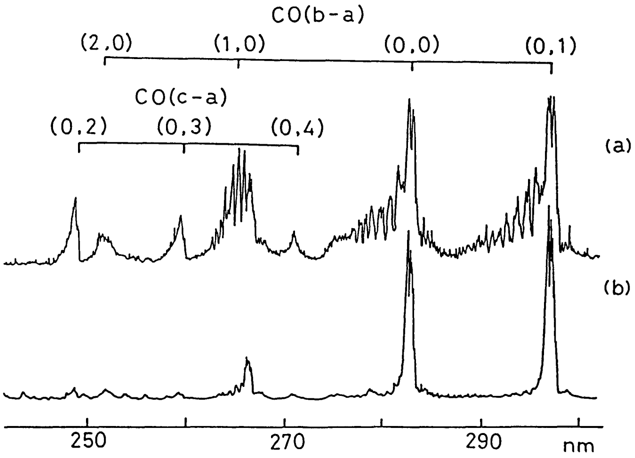

Fig. 2. CO($b^3\Sigma^+$-$a^3\Pi_r$, $c^3\Pi$-$a^3\Pi_r$) emissions produced (a) from the Ar($^3P_2$)+CO reaction in the Ar flowing afterglow (b) in the Ar discharge. The optical resolution is 0.115 nm (FWHM). In spectrum (b), the CO(b-a) emission from $v'=0$ can be well reproduced by a single Boltzmann rotational temperature of 300 K.

were independent of the Ar gas pressure over the range of 0.1—0.25 Torr. From this fact and a short radiative lifetime of $\tau=56\pm1$ ns for CO(b: $v'=0,1$),[9] collisional relaxation was expected to be insignificant under the operating conditions.

The rotational distribution was estimated from the computer simulation of the observed spectrum. The procedure used for the spectral simulation was identical with that reported previously.[8] The spectroscopic data of CO(b,a) in Refs. (1, 2, 10, and 11) were employed for the calculation. The observed and simulated spectra of the (0,1) and (1,0) bands of CO(b-a) are compared in Fig. 3. The observed spectra can be reproduced assuming a double Boltzmann distribution with a branching ratio of 0.70(7000±500 K) and 0.30(700±100 K) for $v'=0$ and a single Boltzmann distribution of 7000±700 K for $v'=1$. It was difficult to evaluate the rotational distribution of $v'=2$ because of predissociation in high rotational levels.

Since the $c^3\Pi \rightarrow b^3\Sigma^+$ transition has recently been discovered,[12] the c→b radiative cascade as well as direct excitation can take part in the formation of the b state. The rotational temperature of the minor component in CO(b: $v'=0$) is in good agreement with that of CO(c: $v'=0$), 800±150 K.[6] It is, therefore, reasonable to assume that the minor cold component arises from the radiative cascade, while the major hot component is populated directly. The absence of a cold component for $v'=1$ is probably a consequence of a small Franck-Condon factor for the (0,1) transition of CO(c-b). We have previously determined the relative vibrational distribution of CO(b: $v'=0$—2) to be $N_0:N_1:N_2=0.55:0.37:0.08$.[6] Taking into account of the c($v'=0$)→b($v'=0$) radiative cascade, the initial vibrational population should be corrected as $N_0:N_1:N_2=0.46:0.44:0.10$. The significant decrease in the N_2 population is probably due to a fast predissociation in excited rotational levels of $v'=2$.

If reaction (1b) proceeds throug a long-lived complex of ArCO*, the rotational energy of CO(b) is expected to be distributed statistically. According to a statistical theory for the two-body dissociation model,[13,14] the population of a given ($v'J'$) level is given by the relation

$$[\mathrm{CO}(\mathrm{b}:v'J')] \propto (2J'+1)\,[E_{\mathrm{avl}} - E(\mathrm{b}:v'J')]^{1/2}, \qquad (2)$$

where E_{avl} is the total available energy of reaction (1b) including rotational and kinetic energies of the reactants and $E(\mathrm{b}:v'J')$ is the internal energy of the final state. The prior rotational distributions are more excited than the observed ones for both the $v'=0$ and 1 levels, as shown in Fig. 4. The deviation from the prior rotational distributions suggests that the rotational energy disposal is not governed by a statistical manner. The deviation from the prior distribution can be represented by a linear surprisal $-\ln[(P(v'J')/P^{\circ}(v'J')]$.[13,14] Linear surprisal parameters of $\theta=1.37$ for $v'=0$ and $\theta=0.91$ for $v'=1$ are obtained.

Having established rovibrational distribution of CO(b), it is possible to estimate average rotational energy and the average fraction of the total available energy deposited into rotational mode of CO(b) by using the relations

$$\langle E_r\rangle = \sum_{v'}\sum_{J'} N_{v'J'}E_{v'J'} \Big/ \sum_{v'}\sum_{J'} N_{v'J'}, \qquad (3a)$$

$$\langle f_r\rangle = \langle E_r\rangle / E_{\mathrm{avl}}. \qquad (3b)$$

Assuming that the contribution of $v'=2$ is negligible because of the small vibrational population, the average rotational energy of CO(b) is evaluated to be 0.39±0.02

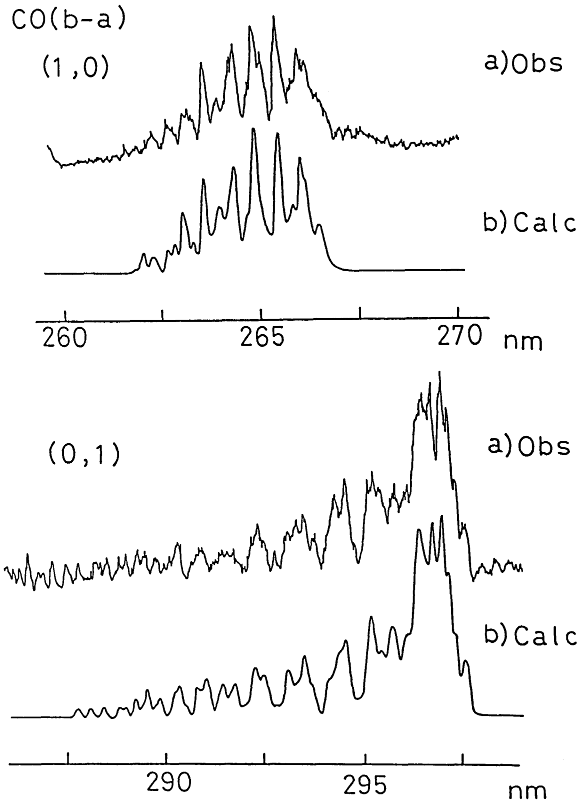

Fig. 3. (a) Observed and (b) simulated spectra of the (0,1) and (1,0) bands of CO($b^3\Sigma^+$-$a^3\Pi_r$) excited by the Ar($^3P_2$)+CO reaction. The optical resolution is 0.115 nm(FWHM).

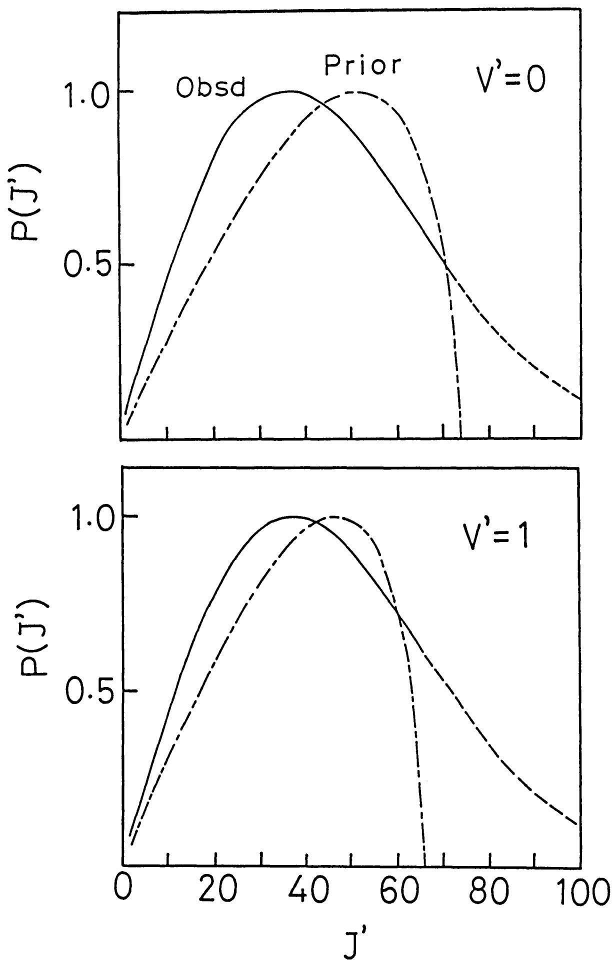

Fig. 4. Observed and prior rotational distributions of $CO(b^3\Sigma^+$: $v'=0,1)$ produced from the $Ar(^3P_2)+CO$ reaction.

eV. Thus, about 32±2% of the total available energy is deposited into the rotational energy of CO(b). This value is comparable with that of CO(c), 38±10%, produced in reaction (1a).[6]

The electronic configuration of the ground state of CO is $K^2K^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2$. The $CO(b^3\Sigma^+)$ state is formed by promotion of a 5σ electron to the $3s\sigma$ Rydberg state.[1,2] This takes place by an electron exchange process; an electron from 5σ fills the space of the 3p orbital of Ar, while the 4s electron enters the $3s\sigma$ Rydberg orbital. Since there is only one half-filled p orbital on $Ar(^3P_2)$, the potential surface of the entrance channel splits into three distinct branches upon approach of the $Ar(^3P_2)$ atom toward the CO molecule. If the half-filled p orbital is oriented perpendicular to the molecular plane, a surface with $^3A''$ symmetry ($^3\Pi$ in $C_{\infty v}$) arises, whereas the two remaining branches are characterized by an in-plane orientation of the p orbital and thus correlate to $^3A'$ symmetry ($^3\Sigma^+$, $^3\Pi$ in $C_{\infty v}$ symmetry). Among three possible surfaces, the formation of $CO(b^3\Sigma^+)+Ar(^1S_g)$ is allowed both through the $^3\Sigma^+$ surface in a collinear approach and through a $^3A'$ surface in an off-axis approach. A relatively high rotational excitation leads us to conclude that reaction (1b) proceeds dominantly through the latter $^3A'$ surface in bent configuration.

This work was partially supported by a Grant-in-Aid for Scientific Research No. 02555170 from the Ministry of Education, Science and Culture, the Asahi Glass Foundation, the Ito Science Foundation, and the Shimadzu Science Foundation.

References

1) P. H. Krupenie, "The Band Spectrum of Carbon Monoxide," National Standard Reference Data Series, Natl. Bur. Stand., Vol. 5, 1966.
2) K. P. Huber and G. Herzberg, "Constants of Diatomic Molecules," Van Nostrand Reinhold, New York (1979).
3) M. Tsuji, K. Yamaguchi, S. Yamaguchi, and Y. Nishimura, *Chem. Phys. Lett.*, **143**, 482 (1988).
4) M. Tsuji, K. Yamaguchi, and Y. Nishimura, *Chem. Phys.*, **123**, 151 (1988).
5) M. Tsuji, K. Yamaguchi, and Y. Nishimura, *Chem. Phys.*, **125**, 337 (1988).
6) M. Tsuji, K. Yamaguchi, H. Obase, and Y. Nishimura, *J. Chem. Phys.*, **90**, 5891 (1989).
7) M. Tsuji, K. Yamaguchi, H. Obase, and Y. Nishimura, *Chem. Phys. Lett.*, **161**, 41 (1989).
8) M. Tsuji, K. Yamaguchi, H. Kouno, and Y. Nishimura, *Jpn. J. Appl. Phys.*, **30**, 1281 (1991).
9) H. A. van Sprang, G. R. Möhlmann, and F. J. de Heer, *Chem. Phys.*, **24**, 429 (1977).
10) L. Gerö, *Z. Phys.*, **101**, 311 (1936).
11) C. V. V. Prasad, G. L. Bhale, and S. P. Reddy, *J. Mol. Spectrosc.*, **121**, 261 (1987).
12) I. Dabrowski, M. Vervloet, and D. C. Wang, *Can. J. Phys.*, **65**, 1171 (1987).
13) R. D. Levine, *Ann. Rev. Phys. Chem.*, **29**, 59 (1978).
14) R. D. Levine and J. L. Kinsey, in "Atom-Molecule Collision Theory," ed by R. B. Bernstein, Plenum, New York (1979).