Formation of $CO(d^3\Delta_i, a'^3\Sigma^+)$ by Dissociative Ion-Ion Neutralization Reaction of CO_2^+ with $C_6F_6^-$ in the Helium Flowing Afterglow

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The ion-ion neutralization reaction of CO_2^+ with $C_6F_6^-$ has been spectroscopically studied in a He flowing afterglow. The CO($d^3\Delta_i$-$a^3\Pi_r$) transition from v'=0-3 and the CO($a'^3\Sigma^+$-$a^3\Pi_r$) transition from v'=3-7 were observed with a CO(a'-a)/CO(d-a) ratio of 3.9. The vibrational distributions of CO(d,a') indicated that 43 and 62 % of the total excess energies are deposited into vibrational modes of CO(d) and CO(a'), respectively.

Compared with an extensive optical study on ionization processes of CO_2, little information has been obtained on its inverse recombination process of CO_2^+. We have recently studied recombination processes of CO_2^+ with electrons by observing emission spectra of excited products in a He flowing afterglow.[1,2] We found that the CO_2^+/e^- recombination reaction gives the CO($A^1\Pi$,$d^3\Delta_i$,$e^3\Sigma^-$,$a'^3\Sigma^+$) states:[1,2]

$$CO_2^+(X^2\Pi_g{:}0,0,0) + e^- \rightarrow CO(A^1\Pi,d^3\Delta_i,e^3\Sigma^-,a'^3\Sigma^+) + O(^3P). \quad (1)$$

The formation rate constants of the CO(A,d,e,a') states and their vibrational and rotational distributions were determined.

In the present study, the ion-ion neutralization reaction of CO_2^+ with $C_6F_6^-$ has been spectroscopically studied in a He flowing afterglow. This is the first spectroscopic study on the dissociative ion-ion neutralization reaction of CO_2^+ with a negative ion leading to excited CO* states.

The flowing-afterglow apparatus used in this study was the same as that reported previously.[1-3] In brief, the positive CO_2^+ ions were produced from the He(2^3S)/CO_2 Penning ionization by the addition of CO_2 into the He afterglow 10 cm downstream from the center of the discharge, while the negative $C_6F_6^-$ ions were formed by a fast nondissociative electron attachment to C_6F_6 10 cm further downstream from an inlet of CO_2.

The partial pressure in the reaction zone was 0.5-1.5 Torr (1 Torr = 133.3 Pa) for He, 50-300 mTorr for CO_2, and 3-10 mTorr for C_6F_6. Under the operating conditions, the density of $C_6F_6^-$ was estimated to be ~10^{10}/cm^3 by using a single Langmuir probe. The emission spectrum near the C_6F_6 gas inlet was dispersed in the 400-1000 nm region with a Spex 1250 M monochromator. All spectra presented here were corrected for the wavelength response of the detection system.

When emission spectra resulting from the He afterglow reaction of CO_2 were observed 10 cm downstream from the inlet of CO_2, CO(A-X:v'=0-2,d-a:v'=0-7,e-a:v'=0,1,a'-a:v'=3-11) emissions due to CO_2^+/e^- recombination process (1) were observed in the 140-1000 nm region.[1,2] Figure 1(a) shows a typical emission spectrum of the CO_2^+/e^- reaction in the 480-820 nm region, where the CO(d-a) emission from v'=1-3 and the CO(a'-a) emission from v'=5-7 are observed. When C_6F_6 was added to the He afterglow, the same vibronic bands are observed,

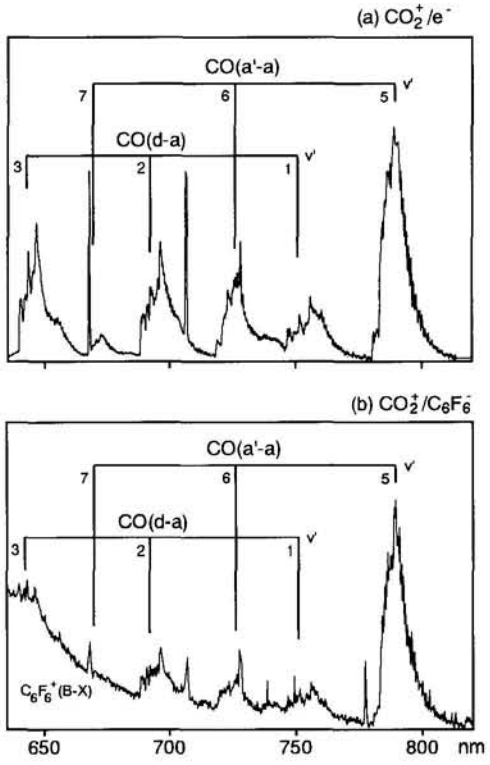

Figure 1. CO(d-a, a'-a) emissions obtained from the (a) CO_2^+/e^- and (b) $CO_2^+/C_6F_6^-$ reactions in the He afterglow.

partially overlapping with the intense $C_6F_6^-$(B-X) emission due to the He(2^3S)/C_6F_6 Penning ionization [Figure 1(b)]. A comparison between Figures 1(a) and 1(b) indicates that the CO(a'-a)/CO(d-a) ratio in Figure 1(b) is higher than that in Fig. 1(a) and the relative intensities of high v' bands in shorter-wavelength region become weak in Figure 1(b). When emission spectra in the 820-1000 nm region were measured using a red sensitive photomultiplier, CO(d-a) emission from v'=0 and CO(a'-a) emission from v'=3,4 were identified.

Figure 2 shows the energy-level diagram of CO_2^+ and CO($A^1\Pi$,$d^3\Delta_i$,$e^3\Sigma^-$,$a'^3\Sigma^+$) + O(^3P) obtained using reported thermochemical and spectroscopic data.[4-6] Since a sufficient amount of CO_2 was added to the He afterglow, $CO_2^+(X^2\Pi_g{:}v_1'',v_2'',v_3'')$ ions are expected to be completely relaxed to the ground vibrational level by collisions with the CO_2 molecules. It is clear from Figure 2 that the formation of CO(d:v'≤2) and CO(a':v'≤7) are energetically accessible in the $CO_2^+(X^2\Pi_g{:}v_1''=0,v_2''=0,v_3''=0)/C_6F_6^-$ reaction at thermal energy taking account of the relative kinetic energy and the rotational energy of CO_2^+ at 300 K (5/2RT). The highest observed v'

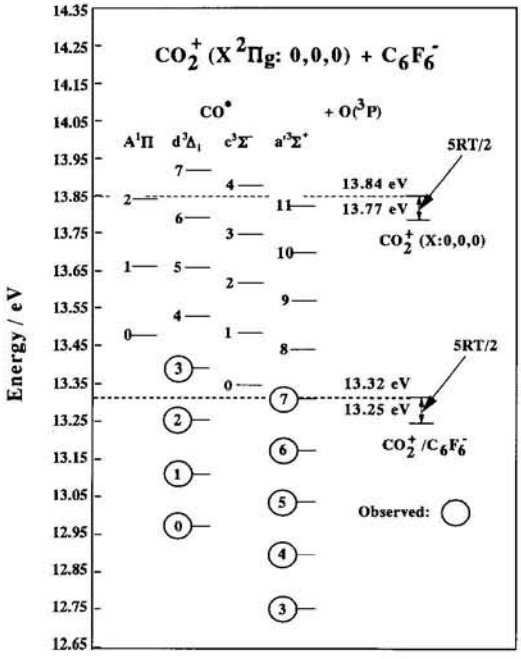

Figure 2. Energy-level diagram of CO(A,d,c,a') + O(^{3}P).

levels of the CO(d, a') states observed here are close to those predicted energetically for the $CO_2^+(X^2\Pi_g{:}0,0,0)/C_6F_6^-$ reaction. This led us to conclude that the CO(d-a,a'-a) emissions are produced from the following $CO_2^+/C_6F_6^-$ dissociative ion-ion neutralization reaction:

$$CO_2^+(X^2\Pi_g{:}0,0,0) + C_6F_6^- \rightarrow CO(d^3\Delta_i{:}v'=0\text{-}3, a'^3\Sigma^+{:}v'=3\text{-}7) + O(^3P) + C_6F_6. \quad (2)$$

The endoergic energy of 0.14 eV for the formation of CO(d:v'=3) must be supplied from the relative kinetic energy of the reactants, which occupy 1.3 % assuming a Boltzmann distribution at 300 K.

The relative formation ratio of CO(a'-a)/CO(d-a) was determined to be 3.9 from the total emission intensities of CO(d-a) and CO(a'-a). This value is much larger than that in the CO_2^+/e^- reaction, 1.5,[2] indicating that the formation of CO(a') is more favorable in the $CO_2^+/C_6F_6^-$ reaction.

The vibrational distributions of the CO(d, a') levels in the $CO_2^+/C_6F_6^-$ reaction were evaluated from the emission intensity of a (v',v") transition of CO*, $I_{v'v"}$, using the following relation:

$$P_{v'} = N_{v'}/\tau_{v'} \propto \sum_{v"} I_{v'v"} \propto k_{v'}(CO^*). \quad (3)$$

where, $P_{v'}$ is the /initial vibrational distribution, which is proportional to the relative formation rate of a v' level of CO*, $N_{v'}$ is the steady-state vibrational distribution, and $\tau_{v'}$ is the radiative lifetime of the v' level. Since $\tau_{v'}$ values of the CO(d:v'=0) and CO(a'=3) levels have not been measured,[7] they were estimated by linearly extrapolating known $\tau_{v'}$ data in the evaluation of $N_{v'}$ values.

The vibrational distributions obtained from the above analyses are given in Table 1 together with the reported $\tau_{v'}$ values. The vibrational distributions of CO(d, a') were independent of buffer He gas pressure in the 0.5-1.5 Torr range and CO_2 pressure in the 50-300 mTorr range. It was therefore concluded that the collisional relaxation was insignificant and the observed

Table 1. Vibrational distributions of CO($d^3\Delta_i$,$a'^3\Sigma^+$) produced from the $CO_2^+/C_6F_6^-$ reaction at 300 K[a]

v'	$d^3\Delta_i$			$a'^3\Sigma^+$		
	$\tau_{v'}$ (μs)	$P_{v'}$	$N_{v'}$	$\tau_{v'}$ (μs)	$P_{v'}$	$N_{v'}$
	Ref. 7	This work		Ref. 7	This work	
0	(7.68)	0.99	1.00			
1	7.30	0.97	0.93			
2	6.62	1.00	0.87			
3	5.75	0.26	0.20	(10.76)	0.50	0.53
4				10.24	1.0	1.00
5				9.12	0.99	0.88
6				8.82	0.16	0.14
7				8.15	0.016	0.013

[a]Uncertainties of the $P_{v'}$ values are ±6 %.

vibrational distributions reflected the nascent populations. The average vibrational energies, $\langle E_v \rangle$, and the average fractions of the total available energy deposited into vibrational modes of CO(d, a'), $\langle f_v \rangle$, were estimated from the observed vibrational distributions of CO(d, a') by using the same relations as reported previously:[1]

CO(d): $\langle E_v \rangle = 0.15$ eV, $\langle f_v \rangle = 0.43$,
CO(a'): $\langle E_v \rangle = 0.62$ eV, $\langle f_v \rangle = 0.62$.

These $\langle E_v \rangle$ values are smaller than those in the CO_2^+/e^- reaction: 0.29 eV for CO(d) and 0.66 eV for CO(a').[2] However, the $\langle f_v \rangle$ values are larger than those in the CO_2^+/e^- reaction: 0.33 for CO(d) and 0.43 for CO(a'),[2] because of the lower total available energy of the $CO_2^+/C_6F_6^-$ reaction, as shown in Figure 2.

The rotational distributions of CO(d, a') were determined by a computer simulation of the observed spectra. They were expressed by low Boltzmann rotational temperatures of 300-450 K. Since radiative lifetimes of CO(d, a') are long, as shown in Table 1, the possibility of collisional rotational relaxation cannot be excluded. A further study at a low pressure is required to obtain initial rotational distributions.

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References and Notes

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