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Nascent Vibrational Distribution of $CO^+(A^2\Pi)$ Resulting from the $He(2^3S)$ + CO Penning Ionization in a Low-pressure Apparatus

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Nascent vibrational distribution of $CO^+(A^2\Pi)$ produced from the $He(2^3S)$ + CO Penning ionization has been determined by optical emission spectroscopy. Experiments were performed by using a new low-pressure apparatus utilizing a mild expansion of helium metastable atoms generated in a flow tube.

The $He(2^3S)$ + CO reaction has been studied by Penning ionization electron spectroscopy (PIES)[1,2] and Penning ionization optical emission spectroscopy (PIOS).[3-6] The $He(2^3S)$ + CO reaction provides the three electronic states of CO^+:

$$He(2^3S) + CO \longrightarrow CO^+(B^2\Sigma^+, A^2\Pi, X^2\Sigma^+) + He + e^- \quad (1)$$

The relative vibrational populations of each state and the electronic branching ratio have been determined by PIES.[1,2] On the other hand, PIOS studies on the $He(2^3S)$ + CO reaction provide data which complement PIES. PIOS studies have been performed by several authors in He flowing afterglows at He pressure between 0.3 and 16 Torr (1 Torr≈133.32 Pa).[3-6] Richardson and Setser[3] and Piper et al.[4] measured the relative vibrational populations of $CO^+(A)$ under the conditions where the effect of the vibrational relaxation could not be neglected. It is well known that the $CO^+(A)$ state undergoes extensive vibrational relaxation in the He flowing afterglow owing to collisions with He atoms during its radiative lifetime (3.1-4.6 μs).[5,7] Marcoux et al.[5] and Endoh et al.[6] obtained the nascent vibrational

populations of $CO^+(A)$ by non-linear extrapolation. We have determined the relative vibrational populations of $CO^+(A, v'=0-10)$ without the effect of vibrational relaxation for the first time by using a new low-pressure apparatus.

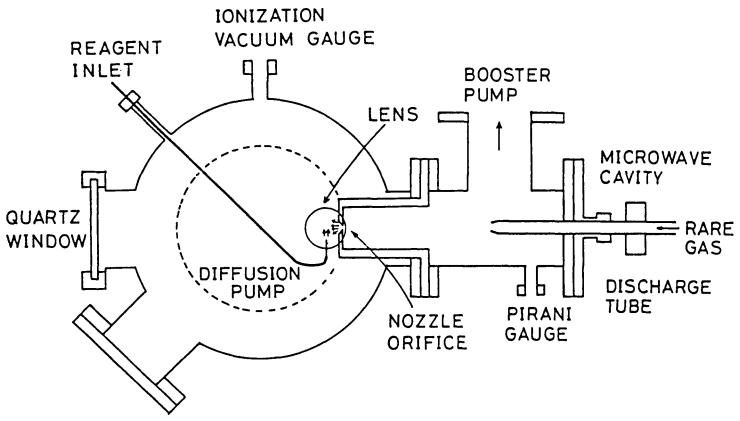

Fig. 1. Schematic diagram of the apparatus.

In Fig. 1 is shown the low-pressure apparatus. It consists of a flowing afterglow source for the production of thermalized rare gas atoms and a high vacuum chamber. The discharge tube is evacuated by a 10000 l/min mechanical booster pump. The interaction chamber is 25 cm in diameter and is evacuated by a 6 inch diffusion pump. The $He(2^3S)$ atoms are produced by a 2450 MHz microwave discharge and are expanded into a high vacuum chamber through a nozzle orifice centered on the flow tube axis. Since the diameter of the orifice is relatively large (3 mm), it forms a mild expansion of helium metastable atoms. The reagent gas is injected by a stainless steel gas inlet placed about 5 mm downstream from the orifice. Resulting chemiluminescences are collected by a lens, reflected by a plane mirror, and focused on a slit of a Nippon Jarrell Ash M2 monochromator (f=1 m) equipped with a cooled photomultiplier (HTV R376). Experiments were performed under the conditions where the contribution of the $He_2^+ + CO$ charge transfer reaction is insignificant.[6] Under typical operating conditions, the He pressure measured in the flow tube is 0.45-0.5 Torr. The total pressure and the partial pressure of CO in the interaction chamber are $0.8-1.2\times10^{-3}$ Torr and $1-2\times10^{-4}$ Torr, respectively. The average center-of-mass interaction energy of $He(2^3S)$ in the expansion with the added CO is estimated to be 0.025 eV, which is obtained by calculating the terminal Mach number M_T in a helium gas expansion.[8]

The $CO^+(B-X)$, $CO^+(A-X)$, and $CO^+(B-A)$ emission systems were identified in the low-pressure apparatus. The observation of these emission systems agrees with the results of flowing afterglow experiments.[3-6] A typical emission spectrum observed in the 320-520 nm wavelength region is shown in Fig. 2a. In Fig. 2b is shown

an emission spectrum observed in the flowing afterglow at a He pressure of 1.0 Torr, which was measured under the same resolution as the spectrum shown in Fig. 2a for comparison. The flowing afterglow apparatus employed was basically the same as that described previously.[6] It is clear from Fig. 2 that the relative intensities of the $CO^+(A,v'-X,v")$ transitions from $v'\geq 3$ to those from $v'\leq 2$ are stronger in Fig. 2a than those in Fig. 2b. The $CO^+(A)$ vibrational distribution was independent of the variation of CO pressure over the range of $1x10^{-4}$-$1x10^{-3}$ Torr and total pressure between $8x10^{-4}$ and $5x10^{-3}$ Torr in the low-pressure apparatus. This indicates that the vibrational relaxation is insignificant in the low-pressure apparatus.

The relative vibrational populations of $CO^+(A)$ were determined directly from the observed emission spectrum by using a procedure described previously.[6] Corrections

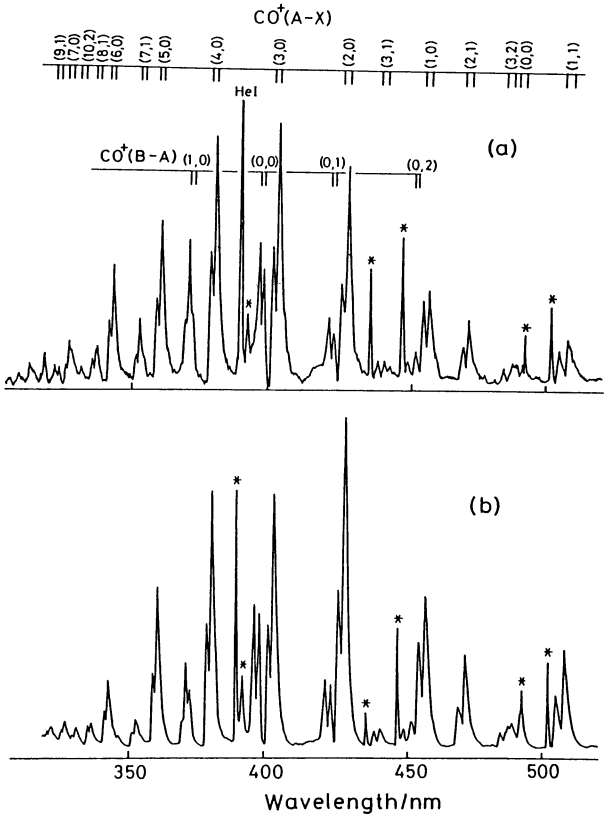

Fig. 2. The $CO^+(A-X,B-A)$ emission spectrum detected in the low-pressure apparatus (a) and that detected in the flowing afterglow apparatus (b). For (a) the total pressure and the partial pressure of CO were $1.2x10^{-3}$ and $2x10^{-4}$ Torr, respectively. For (b) the He and CO pressures were 1.0 and $5x10^{-3}$ Torr. Spectral resolution was 0.4 nm.

Table 1. Relative vibrational populations of $CO^+(A)$

	Vibrational level										
	0	1	2	3	4	5	6	7	8	9	10
PIOS (this work)	48±6	86±6	100	81±4	49±4	35±4	26±4	13±2	8±2	5±1	3±1
PIOS (Marcoux)[5]	63	83	100	71	46	33	21				
PIOS (Endoh)[6]	77	87	100	88	58	49	34	19	11	8	7
PIES (Hotop)[1]	47±4	80±5	100	85±5	55±5	33±5	20±5				
PIES (Yee)[2]	63±9	90±9	100	92±9	58±9	37±9	16±9				
FCF(Albritton)[9]	37.3	82.1	100	89.5	66.0	42.6	25.0	13.7	7.15	3.59	1.75

were made to $CO^+(A,v'=0-3)$ populations for the $CO^+(B-A)$ cascade. The results are summarized in Table 1. The vibrational populations of $CO^+(A)$ determined in this work are in good agreement with those determined by PIES[1,2] to within the experimental errors, and are very similar to theoretical Franck-Condon factors (FCF) for the $CO(X)-CO^+(A)$,[9] suggesting that there is little modification of the initial $CO^+(A)$ vibrational distribution resulting from transversal of the exit channel. The $CO^+(A)$ vibrational distribution determined in this work is also in agreement with those determined by Marcoux et al.[5] and Endoh et al.[6] with the use of non-linear extrapolation. However, large uncertainties would be involved in the relative vibrational populations of $CO^+(A)$ obtained by non-linear extrapolation since significant vibrational relaxation still occurs at He pressures below 0.3 Torr.

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