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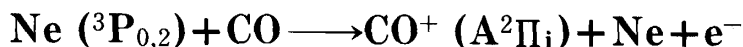Institute of Advanced Material Study Kyushu University

A Flowing Afterglow Study of Penning Ionization

Ne ($^3P_{0,2}$)+CO ——→CO$^+$ (A$^2\Pi_i$)+Ne+e$^-$

Masaharu TSUJI, Hiroshi OBASE and Yukio NISHIMURA

Dedicated to Professor Otohiko Tsuge on the occasion of his retirement

Penning ionization of CO by metastable Ne($^3P_{0,2}$) atoms has been investigated by observing UV and visible emission from excited products in the Ne flowing afterglow. The CO$^+$(A$^2\Pi_i$−X$^2\Sigma^+$) emission system from the $v'=0$ and 1 vibrational levels was identified. The vibrational population ratio, N_1/N_0, was estimated to be 0.33±0.02 at thermal energy.

Chemiionization of CO by collisions with Ne($^3P_{0,2}$) has been studied by mass spectrometry[1] and Penning ionization electron spectroscopy (PIES).[2] A reasonable agreement of the total ionization cross section observed by mass spectrometry[1] with the total quenching cross section determined by the flowing afterglow technique[3] suggests that ionization channels are the major reaction pathway of the Ne($^3P_{0,2}$) system. Based on the measurements of the branching ratio of the ionic products,[1] main product is CO$^+$, which occupies 92.5% of all products. According to the PIES study,[2] most CO$^+$ ions resulting from the Ne($^3P_{0,2}$)/CO reaction lie in the ground state with a significant enhancement of vibrational excitation. Although a PIES peak probably corresponding to the ionization into the A$^2\Pi_i$ ($v'=0$) state is found in the low energy region, structureless feature of the spectrum disturbs the detailed analysis. A great advantage of emission spectroscopy in comparison with the electron spectroscopy is that emitting products can be monitored with high resolution. Recently, Bel Bruno and Krenos[4] have spectroscopically studied the formation of CO$^+$(A) in the Penning ionization between Ne ($^3P_{0,2}$) and CO by using beam-gas apparatus. They found the CO$^+$(A−X) emission system from the $v'=0$ and 1 levels. The dependence of emission cross-section ratio σ($v'=1$)/σ($v'=0$) has been measured as a function of the collision energy from thermal energy to 0.56 eV$_{c.m.}$. In order to obtain information about the Ne($^3P_{0,2}$) Penning ionization into the CO$^+$(A) state at thermal energy, we have measured the optical fluorescence from the excited state in the flowing Ne afterglow.

Experimental

The flowing-afterglow apparatus used in the present study was essentially identical with that reported previously.[5] The flow reactor, which consisted of a quartz flow tube (11mm i.d.) and a stainless steel reaction chamber (60mm i.d.), was continuously evacuated by means of a 10,000 L·min^{-1} mechanical booster pump combined with a 1600 L·min^{-1} oil rotary pump. Active species of neon atoms were generated by a microwave discharge (2450 MHz, power 70W) of high purity Ne (Osaka Sanso Co. purity $\geq$ 99.99%), further purified by passage through a molecular sieve trap. Ionic active species which may be involved in the discharge flow were prevented from entering the reaction zone by the application of a suitable electrostatic potential to an ion-collector grid (20 nickel mesh, transparency $\sim$90%). Although we have attempted to produce the Ne($^3P_{0,2}$) atoms by the discharge through a variety of Ne/He mixtures, it was difficult to distinguish the responsible active species (Ne* or He*). Since Ne gas is expensive, spectroscopic measurements were made at the lowest Ne pressure to maintain the Ne discharge. The Ne gas pressure ranged from 60 to 100 mTorr, corresponding to a Ne flow of 0.03–0.05 mole·min^{-1}. The sample CO gas (Seitetsu Kagaku Ind. Co. purity$\geq$ 99.95%) was introduced from a nozzle (0.6mm i.d.) at about 12 cm downstream from the center of the discharge. The CO pressure in the reaction zone was about 30 mTorr. The photoemission in the 200–500 nm region was observed through a quartz window by a Jarrell Ash 1 m monochromator equipped with a 1200 groove·mm^{-1} grating blazed at 300 nm. A Hamamatsu Photonics R376 photomultiplier and a Burr-Brown 3521J OP amplifier were used for the photometric measurements.

Results and Discussion

The emission spectrum resulting from the Ne($^3P_{0,2}$) + CO reaction consists entirely of the CO$^+$(A$^2\Pi_i$−X$^2\Sigma^+$) comet-tail system from v'=0 and 1 as shown in Fig. 1(a). In Fig. 1(b) is presented the He(2^3S) + CO spectrum for comparison in which CO$^+$(A−X) emission from the v'=0−3 levels is identified. In Table 1 are listed the energetics of Ne in the $^1P_1$, $^3P_0$, $^3P_1$, and $^3P_2$ levels and the ionization potentials of CO leading to CO$^+$(A$^2\Pi_{1/2, 3/2}$). In order to examine the contribution of the Ne $^1P_1$ and $^3P_1$ levels, which has been known to produce CO$^+$ (A:v'=0,1) by radiating 744 and 736 Å photons,[6-8] respectively, a light trap and a right angle bend were installed between the discharge source and the mixing region. Although the intensity of CO$^+$(A−X) was reduced by a factor of 3, no significant change in the vibrational distribution was observed, indicating that the contribution of photoionization to the observed emission was negligible. Thus, the responsible active species for the production of CO$^+$(A) in the Ne afterglow were attributed to the metastable Ne($^3P_{0,2}$) atoms.

On the basis of the energetics, both the metastable Ne($^3P_2$) and Ne($^3P_0$) atoms can produce the CO$^+$(A) ions in the v'=0 level.
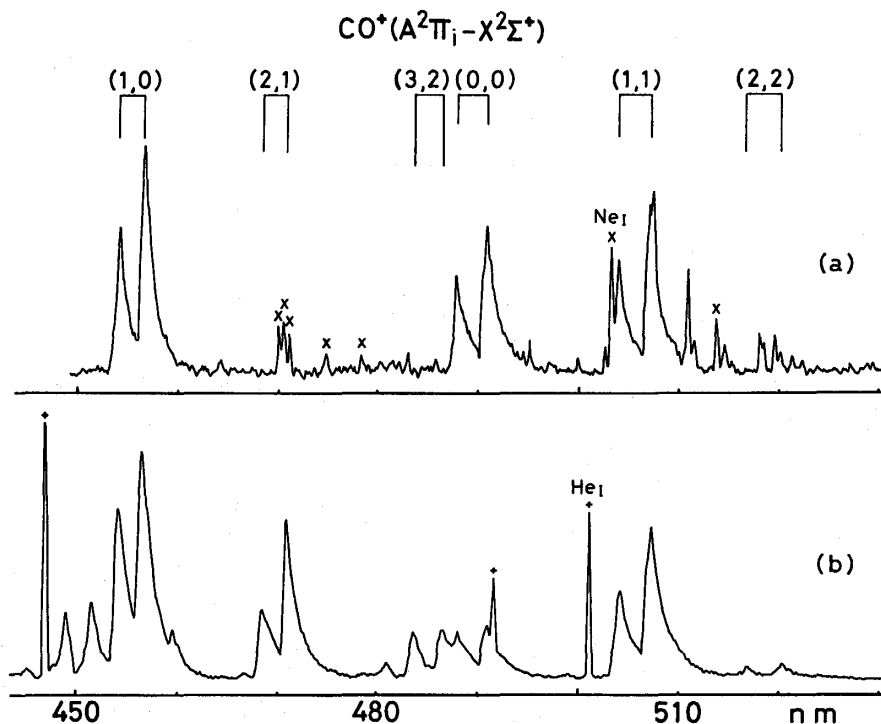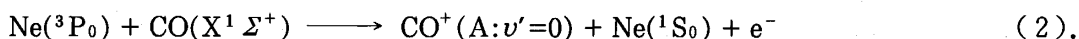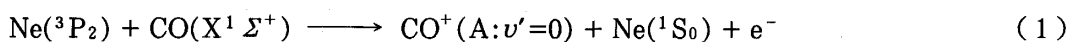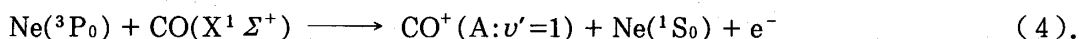
Fig. 1 The $CO^+(A^2\Pi_i - X^2\Sigma^+)$ emission spectra produced from the (a) $Ne(^3P_{0,2})$ + CO and (b) He (2^3S) + CO Penning ionization in the flowing afterglows.

Table 1. Energy levels of Ne and $CO^+(A)$.

Ne (eV)		$CO^+(A^2\Pi_i)$ (eV)	
$^1P_1$ 16.848	$v'=1$	$^2\Pi_{1/2}$	16.742
$^3P_0$ 16.715		$^2\Pi_{3/2}$	16.727
$^1P_1$ 16.671	$v'=0$	$^2\Pi_{1/2}$	16.551
$^3P_2$ 16.619		$^2\Pi_{3/2}$	16.537

$$Ne(^3P_2) + CO(X^1\Sigma^+) \longrightarrow CO^+(A:v'=0) + Ne(^1S_0) + e^- \qquad (1)$$

$$Ne(^3P_0) + CO(X^1\Sigma^+) \longrightarrow CO^+(A:v'=0) + Ne(^1S_0) + e^- \qquad (2).$$

On the other hand, the formation of $CO^+(A^2\Pi_{3/2}: v'=1)$ is required in excess of electronic energies of $Ne(^3P_0)$ and $Ne(^3P_2)$ by 0.027 and 0.123 eV, respectively:

$$Ne(^3P_2) + CO(X^1\Sigma^+) \longrightarrow CO^+(A:v'=1) + Ne(^1S_0) + e^- \qquad (3)$$

$$Ne(^3P_0) + CO(X^1\Sigma^+) \longrightarrow CO^+(A:v'=1) + Ne(^1S_0) + e^- \qquad (4).$$
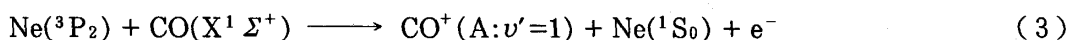
Taking account of the relative kinetic energy of colliding particles at thermal energy (0.039 $eV_{c.m.}$ at 300K), process (4) is expected to take place easily. On the other hand, high relative kinetic and/or rotational energies must be supplied for process (3); fractions of kinetic and rotational energies higher than 0.123 eV are evaluated to be only 2.4 and 0.6%, respectively,

assuming a Boltzmann distribution at 300K. Therefore, the contribution of process (3) is expected to be unimportant at 300K.

The vibrational population ratio, N_1/N_0, was estimated from relative band intensities of $CO^+(A-X)$. The total emission intensities of vibronic bands from individual v' level correspond to the population ratio, because the electronic transition moment of $CO^+(A-X)$ is independent of the r-centroid.[9,10] The $\sum_{v''} I_{0,v''} / \sum_{v''} I_{1,v''}$ value was estimated by summing up the intensity of each progression. The band which emits outside the observation region was calculated by reference to the intensity distribution reported by Richardson and Setser.[11] The ratio was found to be constant at 0.33 ± 0.02 within our experimental conditions. This value is in reasonable agreement with a beam result of about 0.3 at 0.039 eV$_{c.m.}$ which is estimated from the extrapolation of the excitation function to low energy.[4] Bel Bruno and Krenos[4] found that the cross section ratio between $v'=0$ and $v'=1$ is consistent with that predicted from Franck-Condon (FC) factors for the $CO(X:v''=0) \rightarrow CO^+(A:v')$ vertical ionization at high collisional energies above 0.2 eV$_{c.m.}$. It is difficult to discuss whether the $Ne(^3P_0) + CO$ Penning ionization is still FC like at thermal energy from the present data, because the $^3P_2/^3P_0$ ratio is not determined. A state selective work is, therefore, required at low pressures where the vibrational relaxation from $v'=1$ to $v'=0$ is negligible.

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