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Vibrational Distributions of CO^+ (A) Produced from the Charge-transfer Reactions of Ne^+ and He^+ with OCS at Thermal Energy

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Synopsis. The Ne^++OCS and He^++OCS charge-transfer reactions have been studied by emission spectroscopy in a flowing afterglow. The relative vibrational populations of $CO^+(A^2\Pi)$ were determined by observing the $CO^+(A^2\Pi-X^2\Sigma^+)$ emission system produced from the above reactions. The populations decrease approximately exponentially with the vibrational quantum number.

Optical spectroscopic studies on the thermal-energy charge-transfer (CT) reactions between Ne^+ and small molecules are limited,[1,2] although those on the reactions between He^+ and small molecules have been made extensively.[3,4] Previously we have reported on the $CO^+(A^2\Pi-X^2\Sigma^+)$ emission produced from the Ne^++OCS CT reaction in a flowing afterglow.[1] The $CO^+(A\text{-}X)$ emission arises also from the He^++OCS CT reaction.[5] In order to understand the overall CT process, it is important to determine the internal energy state distribution of the products resulting from the thermal-energy CT reactions between rare gas ions and small molecules. In this Note we describe the vibrational distribution of $CO^+(A)$ produced from the Ne^++OCS reaction in comparison with that produced from the He^++OCS reaction. To our knowledge, this is the first report on the vibrational distribution of a product resulting from the Ne^+ CT reaction.

Experimental

The flowing afterglow apparatus is essentially identical to that described previously.[1] Active species of Ne and He were generated in a 2450 MHz microwave discharge. The Ne and He pressures ranged from 80 to 87 Pa (1 Pa=7.5×10^{-3} Torr). Emission spectra were observed on a Nippon Jarrell Ash 1-m monochromator equipped with either a HTV R376 or a HTV R585 photomultiplier. The relative sensitivity of the detection system was calibrated by a halogen lamp.

Results and Discussion

The $CO^+(A\text{-}X)$ emission system was observed in both Ne and He afterglows together with numerous emission systems which have been reported in the earlier papers.[1,5] The $CO^+(A\text{-}X)$ emission systems observed in the above two afterglows arise from the following CT reactions, respectively:

$$\begin{aligned} Ne^+ + OCS &\longrightarrow CO^+(A) + S + Ne, \\ CO^+(A) &\longrightarrow CO^+(X) + h\nu. \qquad (1) \\ He^+ + OCS &\longrightarrow CO^+(A) + S + He, \\ CO^+(A) &\longrightarrow CO^+(X) + h\nu. \qquad (2) \end{aligned}$$

The recombination energies of $Ne^+(^2P_{1/2,3/2})$ are 21.66 and 21.56 eV, while that of the ground-state $He^+(^2S)$ is 24.58 eV.[6] Meanwhile, the calculated minimum energy required for the formation of $CO^+(A)$ from OCS is 19.73 eV, which is obtained on the assumption that sulfur atoms are formed in the ground ^3P state.[7] In Fig. 1 is shown a typical emission spectrum of the $CO^+(A\text{-}X)$ in the He afterglow, where a pulsed modulation system[5,8] was employed to eliminate the emissions due to the $He(2^3S)$+OCS Penning ionization. The $CO^+(B\text{-}A)$ emission has been observed in the $He(2^3S)$+CO Penning ionization.[9] However, no $CO^+(B\text{-}A)$ emission could be identified in the He^++OCS reaction, although weak $CO^+(B\text{-}X)$ emission could be identified.[5] Accordingly, the contribution of the $CO^+(B\text{-}A)$ cascade to the production of $CO^+(A)$ is very small in the He^++OCS reaction. The identified vibrational levels of $CO^+(A)$ range from $v'=0$ to $v'=5$ in the Ne^++OCS reaction[1] and from $v'=0$ to $v'=11$ in the He^+ +OCS reaction. In the Ne^++OCS reaction, as a partner of $CO^+(A)$ for $v'=0$—4, sulfur atoms in the ^3P and ^1D states are energetically possible, while sulfur atoms only in the ^3P state are energetically possible as a partner of $CO^+(A)$ for $v'=5$. On the other hand, in the He^++OCS reaction sulfur atoms in the ^3P, ^1D, and ^1S states are energetically accessible as a partner of $CO^+(A)$ for $v'=0$—11.

The relative vibrational populations were obtained from the emission spectra by means of a procedure reported in the previous paper.[8] The contribution of the vibrational relaxation of $CO^+(A)$ has been examined in the He pressures ranging from 80 to 800 Pa: Little difference has been found between the vibrational populations observed at 80 Pa and those extrapolated to zero He pressure. In the Ne^++OCS reaction, no pressure dependence of the vibrational populations of $CO^+(A)$ could be examined owing to the low intensity of the $CO^+(A\text{-}X)$ emission. We regarded the vibrational distribution of $CO^+(A)$ measured at 80 Pa as an approximate initial distribution in both Ne^++OCS and He^++OCS reactions. The relative vibrational populations of $CO^+(A)$, $N_{v'}$, thus obtained are shown in Fig. 2. It should be

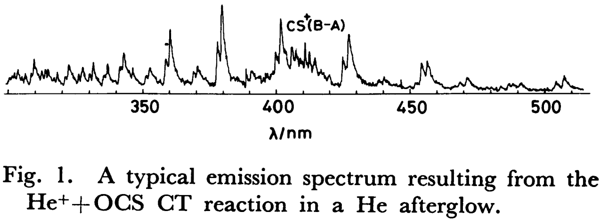

Fig. 1. A typical emission spectrum resulting from the He^++OCS CT reaction in a He afterglow.

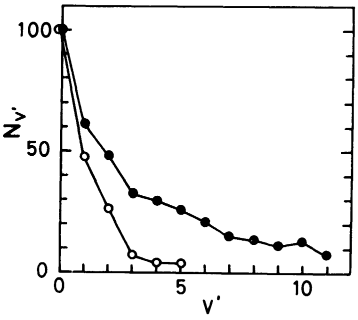

Fig. 2. Relative vibrational distribution of CO^+ (**A**). ○: Produced from the $Ne^+ + OCS$ reaction, ●: Produced from the $He^+ + OCS$ reaction.

noted that $N_{v'}$ decreases approximately exponentially with v' not only in the He^++OCS reaction but also in the Ne^++OCS reaction. Assuming a Boltzmann distribution for the vibrational levels, the effective vibrational temperatures are estimated to be 3400±400 K and 10100±1000 K for the Ne^++OCS and He^++OCS reactions, respectively. No photoelectron spectroscopic experiment has been reported on the excited electronic states of OCS^+ lying above 20 eV, which would be optically inaccessible states. The precursor states leading to the $CO^+(A)$ state in the Ne^++OCS and He^++OCS reactions would be optically forbidden multiple-electron-transition states of OCS^+ lying above 20 eV, which have been identified by Carnovale *et al.*[9] through electron-ion coincidence.

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