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Tsuji, Masaharu
Institute of Advanced Material Study Kyushu University

Shimada, Shin-Ichi
(Present address) Toshiba Co.

Mizukami, Kazumi
(Present address) Nippon Steel Co.

Obase, Hiroshi
(Present address) Department of Industrial Chemistry Towa University

他

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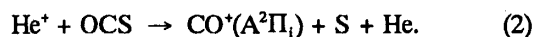
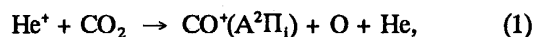
Vibrational Distributions of $CS^+(B^2\Sigma^+)$ Produced from Dissociative Charge-Transfer Reactions of He^+ with CS_2 and OCS at Thermal Energy

Masaharu TSUJI, Shin-ichi SHIMADA*¹, Kazumi MIZUKAMI*²,
Hiroshi OBASE*³, and Yukio NISHIMURA

The $CS^+(B^2\Sigma^+-A^2\Pi_i)$ emissions have been observed from dissociative charge-transfer reactions of He^+ with CS_2 and OCS in a helium afterglow. The vibrational distribution of $CS^+(B)$ has a peak at $v'=1$ or 2 for both reactions. The average fraction of the total excess energy deposited into vibration of $CS^+(B)$ was estimated to be $\leq 13\%$, indicating that almost all excess energy is partitioned into the relative translational energy of the products. The higher vibrational excitation than the statistical prediction led us to conclude that $CS^+(B)$ is formed directly through short lived intermediates.

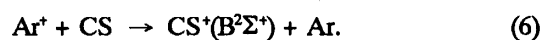
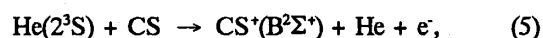
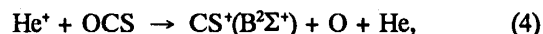
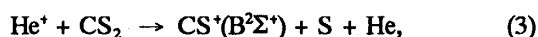
Introduction

The flowing-afterglow method is an ideal technique for studying charge-transfer (CT) reactions at thermal energy.¹⁾ We have previously applied this method to optical spectroscopic studies of dissociative CT reactions of He^+ with CO_2 and OCS leading to the $CO^+(A^2\Pi_i)$ state:^{2,3)}



From the analysis of the $CO^+(A-X)$ emission, the vibrational distributions of $CO^+(A)$ in reactions (1) and (2) have been determined. The dissociation mechanism is discussed from the vibrational distributions of $CO^+(A)$.

We have reported that $CS^+(B^2\Sigma^+-A^2\Pi_i)$ emissions are formed from the following CT reactions and Penning ionization:⁴⁻⁸⁾



On the basis of the vibrational analysis, vibrational constants of $CS^+(B^2\Sigma^+)$ and Franck-Condon factors and r -centroids of the $CS^+(B-A)$ transition have been determined.⁹⁾ Although the vibrational distributions of $CS^+(B)$ in Penning ionization (5) and CT reaction (6) have been determined,^{7,8)} those in dissociative CT reactions (3) and (4) have not been estimated.

In this study, the vibrational distributions of $CS^+(B)$ in dissociative CT reactions (3) and (4) are estimated from the analysis of the visible $CS^+(B-A)$ emission. The results obtained are compared with those predicted from a simple statistical theory in order to obtain dynamical features of the reaction processes.

Experimental

The flowing-afterglow apparatus used in this study was similar to that reported previously.¹⁻⁵⁾ In brief, the metastable $He(2^3S)$ atoms and He^+ ions were generated by a microwave discharge of high purity He gas. The contribution of ionic active species to the

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*1 Present address: Toshiba Co., Kawasaki

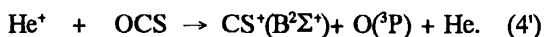
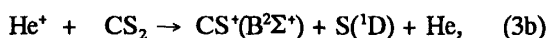
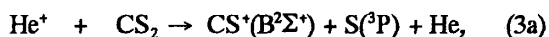
*2 Present address: Nippon Steel Co., Kimitsu, Chiba

*3 Present address: Department of Industrial Chemistry, Tohwa University, Minami-ku, Fukuoka

observed emissions was examined by using an ion-collector grid placed between the discharge section and the reaction zone. A sample gas, CS₂ or OCS, was admixed with the He discharge flow operated at a He buffer gas pressure range of 0.5-1.5 Torr (1 Torr=133.3 Pa). The emission spectra were dispersed with a Jarrell Ash 1 m monochromator equipped with a 1180 lines/mm grating blazed at 300 nm.

Results and Discussion

Figures 1 and 2 show typical emission spectra in the 390-420 nm region obtained by the addition of CS₂ or OCS into the He flowing afterglow. The most prominent band is the CS⁺(B²Σ⁺-A²Π_i) transition on which the present study focuses. The Δv=0 and 1 sequences for the v'=0-2, 4, and 5 levels are identified in both spectra. The lack of the CS⁺(B-A) emission from the v'=3 level may be due to vibrational perturbation.⁵⁾ Partially overlapping with the CS⁺(B-A) emission, the (5,1) and (3,0) bands of CO⁺(A²Π_i-X²Σ⁺) and the 3₀⁰ band of OCS⁺(A²Π_i-X²Π) are observed in Fig. 2. When ionic active species were removed by using the ion collector grids, the CS⁺(B-A) and CO⁺(A-X) bands disappeared completely, while no appreciable change in the intensity of the OCS⁺(A-X) band was found. On the basis of these findings, He⁺ is the excitation source of CS⁺(B) and CO⁺(A), while He(2³S) is responsible for the formation of OCS⁺(A). Possible formation mechanism of CS⁺(B) is as follows:



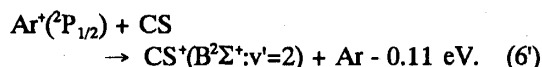
The H⁰ values for the formation of CS⁺(B;v'=0) in processes (3a)-(3c) and (4') are 4.27, 3.12, 1.52, and 1.91 eV, respectively. Although the spin-conservation rule is held in processes (3a) and (3b), it must be violated in process (3c). It is therefore reasonable to assume that process (3c) is insignificant for the formation of CS⁺(B).

The relation between the emission intensity of a (v',v'') band [I_{v',v''}] and the population of the upper vibrational state [N_{v'}] is given by

$$I_{v',v''} = K N_{v'} \text{Re}^2(\bar{r}) q_{v',v''} v_{v',v''}^3 \quad (7)$$

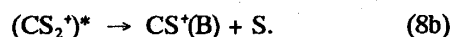
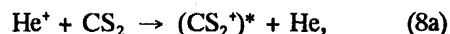
where K is a constant depending on the units and geometry of the system, and Re(\bar{r}), q_{v',v''}, and v_{v',v''} are the electronic transition moment, the Franck-Condon factor, and the transition frequency, respectively.⁹⁾

The N_{v'} values were calculated by using reported q_{v',v''} and v_{v',v''} values⁵⁾ assuming Re(\bar{r}) to be constant. The results obtained are shown in Table 1 together with our previous results on the He(2³S)/CS Penning ionization⁷⁾ and the Ar⁺/CS CT reaction.⁸⁾ The N_{v'} values were independent of the He buffer gas pressure over the range of 0.5-1.5 Torr, indicating that the vibrational relaxation of CS⁺(B) due to collisions with the buffer He gas is insignificant during its radiative lifetime of 425 ns.¹⁰⁾ It is clear from Table 1 that the vibration of CS⁺(B) produced in the He⁺/CS₂ reaction is slightly more excited than that in the He⁺/OCS reaction. One reason for this may be higher total excess energies released in the processes (3a) and (3b) than that in process (4'). The CS⁺(B) ions produced through the dissociative He⁺/CS₂ and He⁺/OCS CT reactions are much more vibrationally excited than those in the He(2³S)/CS Penning ionization and the Ar⁺/CS CT reaction. The low vibrational excitation of CS⁺(B) in the He(2³S)/CS reaction can be explained as due to perturbation of CS potential by an access of the reactant He(2³S) atom,⁷⁾ while the lack of CS⁺(B) above v'=2 in the Ar⁺/CS reaction is attributed to the energy restriction:⁸⁾



Having the established N_{v'} values, the average vibrational energy of CS⁺(B), <E_{v'}>, was evaluated to be 0.27 eV for the He⁺/CS₂ reaction and 0.25 eV for the He⁺/OCS reaction. The average fraction of the total excess energy deposited into the vibrational energy of CS⁺(B), <f_{v'}>, was determined to be only 9% for the He⁺/CS₂ reaction and 13% for the He⁺/OCS reaction. The major part of the excess energy must be released into the rotational mode of CS⁺(B) and/or the relative translational energy of the products. Since the spectral appearance of CS⁺(B-A) emissions shows no significant rotational excitation in CS⁺(B), the major part of the energy will be partitioned into the relative kinetic energy of the products.

The recombination energy of He⁺, 24.59 eV, is expected to be transferred near resonantly to CS₂ or OCS during the passage through a transition state; the excited CS₂⁺* or OCS⁺* ions dissociate into CS⁺(B) + S or CS⁺(B) + O, while the He atom departs the system without a significant change in its kinetic energy. In such a case, the following two-body dissociation model can be assumed for the formation of the CS⁺(B) fragment: e.g.,



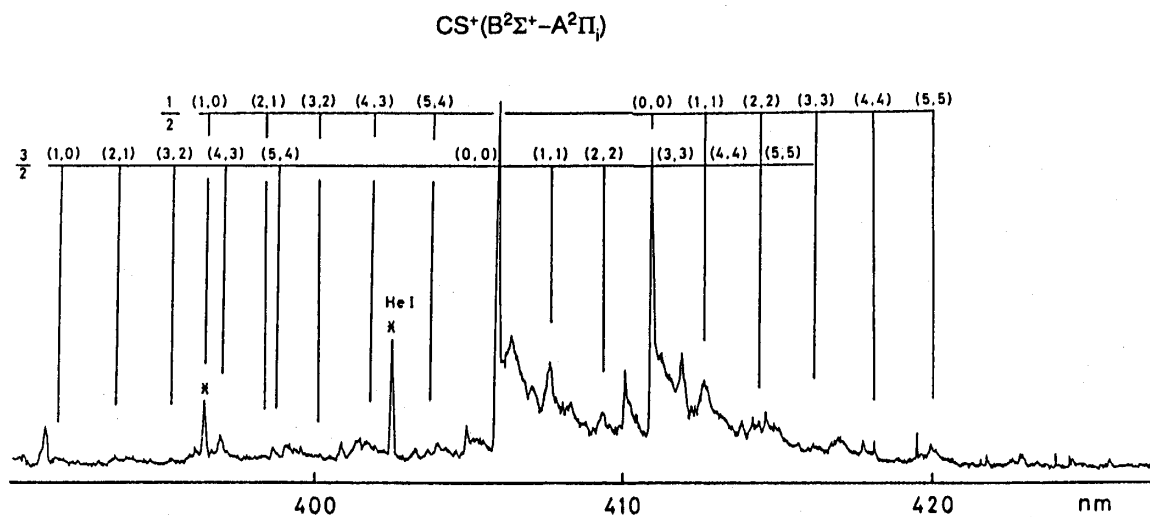


Fig. 1. $CS^+(B^2\Sigma^+-A^2\Pi_i)$ emission produced from the He afterglow reaction of CS_2 .

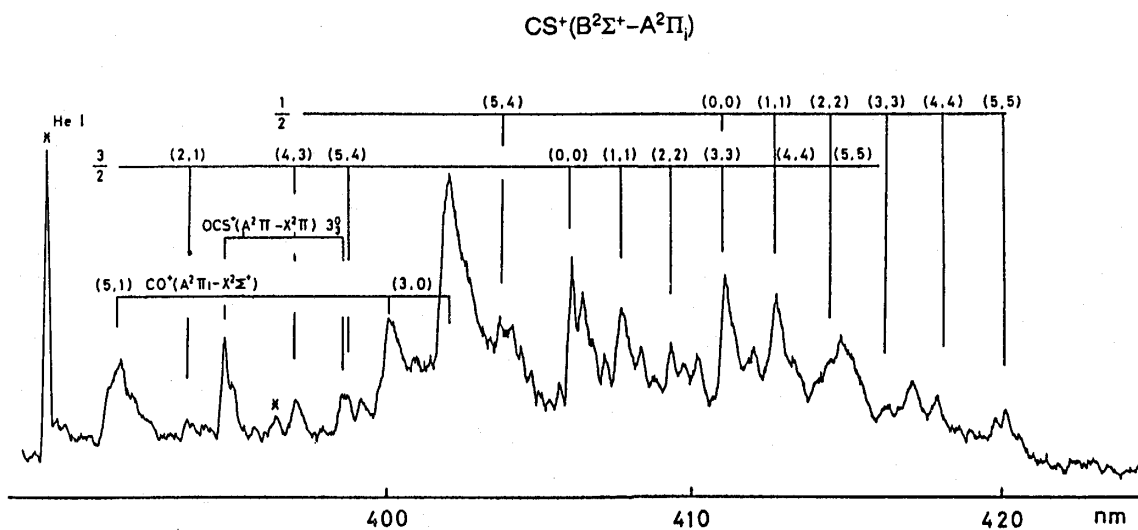


Fig. 2. $CS^+(B^2\Sigma^+-A^2\Pi_i)$, $CO^+(A^2\Pi_i-X^2\Sigma^+)$, and $OCS^+(\widetilde{A}^2\Pi_i-\widetilde{X}^2\Pi)$ emissions produced from the He afterglow reaction of OCS.

Under the assumption of a simple statistical mechanism, the prior vibrational distribution, N_v^0 is evaluated from the relation:¹¹⁾

$$N_v^0 \propto (1-f_v)^{3/2}, \quad (9)$$

where, $f_v = E_v/E_{tot}$. The N_v^0 values are calculated for processes (3a), (3b), and (4'). The results obtained are

given in Table 1. The statistical model predicts much lower vibrational excitation than the experimental observation in both reaction systems. This finding led us to conclude that the formation of $CS^+(B)$ in the He^+/CS_2 and He^+/OCS CT reactions occurs through a direct mechanism where the precursor ionic states have not enough lifetimes to randomize the excess energy statistically to the products.

Vibrational Distributions of CS+(B)

 Table 1. Observed and statistical vibrational distributions of CS⁺(B) produced from dissociative He⁺/CS₂ and He⁺/OCS CT reactions, He(2³S)/CS Penning ionization, and Ar⁺/CS CT reaction in the flowing afterglow.

	He ⁺ /CS ₂		He ⁺ /OCS		He(2 ³ S)/CS	Ar ⁺ /CS
	This work	This work	This work	This work	Ref. 7	Ref. 8
	N _v ^a	N _v ^b	N _v ^a	N _v ^b	N _v ^a	N _v ^a
v'=0	1.00	1.00 ^a	1.00	1.00	1.00	1.00
v'=1	1.13±0.05	0.96 (0.95) ^b	1.05±0.01	0.91	0.65	0.28±0.02
v'=2	1.36±0.08	0.92 (0.89)	1.05±0.01	0.83	0.53	
v'=3	~0	0.89 (0.84)	~0	0.75	~0	
v'=4	1.26±0.02	0.85 (0.80)	0.86±0.16	0.68	0.35	
v'=5	1.01±0.09	0.82 (0.75)	0.91±0.18	0.60	0.31	

^aValues for process (3a).

^bValues for process (3b).

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