SiCl_4^+(C^2T_2-X^2T_1, C^2T_2-A^2T_2) Emissions Produced from the He(2^3S), Ne(^3P_<2,0>)/SiCl_4 Penning Ionization and Ar^+(^2P_<3/2>)/SiCl_4 Charge-Transfer Reaction at Thermal Energy

Tsuji, Masaharu
Institute of Advanced Material Study, Kyushu University

Nakamura, Masafumi
Department of Molecular Science and Technology, Graduate School of Engineering Sciences, Kyushu University

Mizuguchi, Toshinori
(Present address)Nippon Steel Corp.

Kaneko, Nobuo
(Present address) Sanken Electronic Co.

他

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$SiCl_4^+(\tilde{C}^2T_2-\tilde{X}^2T_1, \tilde{C}^2T_2-\tilde{A}^2T_2)$ Emissions Produced from the $He(2^3S)$, $Ne(^3P_{2,0})/SiCl_4$ Penning Ionization and $Ar^+(^2P_{3/2})/SiCl_4$ Charge-Transfer Reaction at Thermal Energy

Masaharu TSUJI, Masafumi NAKAMURA,* Toshinori MIZUGUCHI,**
Nobuo KANEKO***, and Yukio NISHIMURA

The bound-free $SiCl_4^+(\tilde{C}^2T_2-\tilde{X}^2T_1, \tilde{C}^2T_2-\tilde{A}^2T_2)$ emissions resulting from the $He(2^3S)$, $Ne(^3P_{2,0})/SiCl_4$ Penning ionization and $Ar^+(^2P_{3/2})/SiCl_4$ charge-transfer reaction have been observed in the rare gas flowing afterglows. A comparison of the observed spectral features with those in a reported electron-impact spectrum suggested that $SiCl_4^+(\tilde{C})$ is formed through a vertical Franck-Condon type process in the $He(2^3S)$, $Ne(^3P_{0,2})/SiCl_4$ Penning ionization, while the $Ar^+(^2P_{3/2})/SiCl_4$ charge-transfer reaction preferentially populates near-resonant highly vibrationally excited levels with small Franck-Condon factors for ionization.

1. Introduction

In general, large molecular ions do not give fluorescence, because competitive non-radiative transitions become significant with increasing the number of atoms in a molecular ion. Therefore, little optical spectroscopic study has been carried out on Penning ionization and charge-transfer (CT) reactions of large polyatomic molecules. According to a recent systematic study of Tuckett and co-workers,$^{1-3)}$ the group IV tetrahalide cations are exceptional large molecular ions which decay by fluorescence in the ultraviolet and visible region. The fluorescence quantum yield of $SiCl_4^+(\tilde{C}^2T_2)$ has been measured to be unity.$^{3)}$ In the present study, a comparative spectroscopic study was conducted on the $He(2^3S)$, $Ne(^3P_{2,0})/SiCl_4$ Penning ionization and the $Ar^+(^2P_{3/2})/SiCl_4$ CT reaction leading to the emitting $SiCl_4^+(\tilde{C})$ state. The observed $SiCl_4^+(\tilde{C}-\tilde{X}, \tilde{C}-\tilde{A})$ spectra are compared with the reported spectra obtained under fast electron impact$^{1)}$ in order to examine whether ionization takes place via a vertical Franck-Condon (FC) process or not.

2. Experimental

The flowing afterglow apparatus used in the present study was similar to that reported previously.$^{4,5)}$ In brief, the metastable $He(2^3S)$, $Ne(^3P_{2,0})$, or $Ar(^3P_{2,0})$ atom and He^+, He_2^+, Ar^+, or $(Ar^+)^*$ ion were generated by a microwave discharge of the high purity He, Ne, or Ar gas. It was found that all of the Ar^+ ion in the ground state was located in the lower $^2P_{3/2}$

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*Department of Molecular Science and Technology, Graduate School of Engineering Sciences, Kyushu University.

**Present address: Nippon Steel Corp., Yahata-Higashi-ku, Kitakyushu 805.

***Present address: Sanken Electronic Co., Niiza City, Saitama 352.

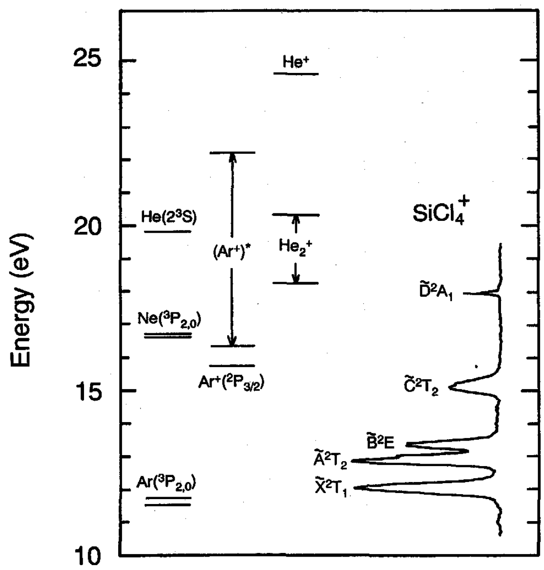

Fig. 1 Photoelectron spectrum of $SiCl_4^+$ reported by Green et al.[7] and energies of rare gas active species involved in the He, Ne, and Ar afterglows.

spin-orbit state by observing the ArF* excimer resulting from the $Ar^+(^2P_{1/2,3/2})/SF_6^-$ ionic-recombination reaction.[6] The contribution of ionic active species to the observed emissions was examined by using a pair of ion-collector grids placed between the discharge section and the reaction zone. The sample $SiCl_4$ gas was admixed with the rare gas discharge flow operated at a buffer gas pressure range of 0.03-0.5 Torr for Ar, 0.04-0.07 Torr for Ne, and 0.5-1.5 Torr for He (1 Torr=133.3 Pa). The emission spectra were dispersed in the 200-700 nm region with a Jarrell Ash 1 m monochromator.

3. Results and discussion

Figure 1 shows the photoelectron spectrum (PES) of $SiCl_4$ measured by Green et al.[7] along with the available energies of rare gas active species involved in the He, Ne, and Ar afterglows. There are five electronic states of $SiCl_4^+$ in the 11-18 eV region. Among them, the $\tilde{C}^2T_2$ state with adiabatic and vertical ionization potentials of 15.09 and 15.27 eV, respectively,[8] decays by fluorescence into the $\tilde{X}^2T_1$ and $\tilde{A}^2T_2$ states. The ionization energies of the $\tilde{C}^2T_2$ state are lower than the available energies of He^+(24.58 eV), He(2^3S: 19.82 eV), Ne($^3P_0$: 16.72 eV), Ne($^3P_2$: 16.62 eV), Ar^+ ($^2P_{3/2}$: 15.76 eV), and $(Ar^+)^*$(16.41-22.19 eV),[5] while it is higher than those of Ar($^3P_2$: 11.55 eV) and Ar($^3P_0$: 11.75 eV). The intensity distribution of the HeI PES spectrum reflects the relative magnitudes of the FC factors for the ionization of $SiCl_4$. From an inspection of Fig. 1, it can be seen that the FC factor for $SiCl_4^+(\tilde{C})$ has a maximum at ~15.3 eV, and rapidly decreases with increasing the vibrational energy.

A typical emission spectrum resulting from the He(2^3S)/$SiCl_4$ reaction is shown in Fig. 2(a). The spectrum consists of two broad continuous bands in the 350-500 nm region with a peak at ~410 nm and in the 510-650 nm region with a peak at ~560 nm. Since the observed spectral features are very similar to those measured by Lambert et al. under electron-impact at 200 eV,[1] the shorter and longer wavelength bands are ascribed to the bound-free $\tilde{C}^2T_2$-$\tilde{X}^2T_1$ and $\tilde{C}^2T_2$-$\tilde{A}^2T_2$ transitions of $SiCl_4^+$, respectively,

$$He(2^3S) + SiCl_4 \xrightarrow{k_1} SiCl_4^+(\tilde{C}) + He + e^-. \qquad (1)$$

A weak band with a peak at ~620 nm must not be associated with $SiCl_4^+$ because the same peak has been found in the He(2^3S)/$GeCl_4$ reaction.[9] The measurements of the relative sensitivity of the optical detection system by using a standard halogen lamp suggested that it arises from a rapid change in the optical sensitivity. Partially overlapping with the $SiCl_4^+$ ($\tilde{C}$-$\tilde{X}$) transition, weak discrete bands, which have been ascribed to $SiCl_2^*$ by Sameith et al.,[10] are found in the 360-390 nm region.

When emission spectrum resulting from the He(2^3S),He^+,He_2^+/$SiCl_4$ reactions was observed without applying a retarding potential to the ion-collector grids, no appreciable change in emission intensities was found for the $SiCl_4^+(\tilde{C}$-$\tilde{X}$, $\tilde{C}$-$\tilde{A})$ bands. The absence of the $SiCl_4^+(\tilde{C}$-$\tilde{X}$, $\tilde{C}$-$\tilde{A})$ emissions due to the $He^+/SiCl_4$ and $He_2^+/SiCl_4$ reactions is attributed to the fact that the formation of $SiCl_4^+(\tilde{C})$ by these CT reactions are highly exoergic,

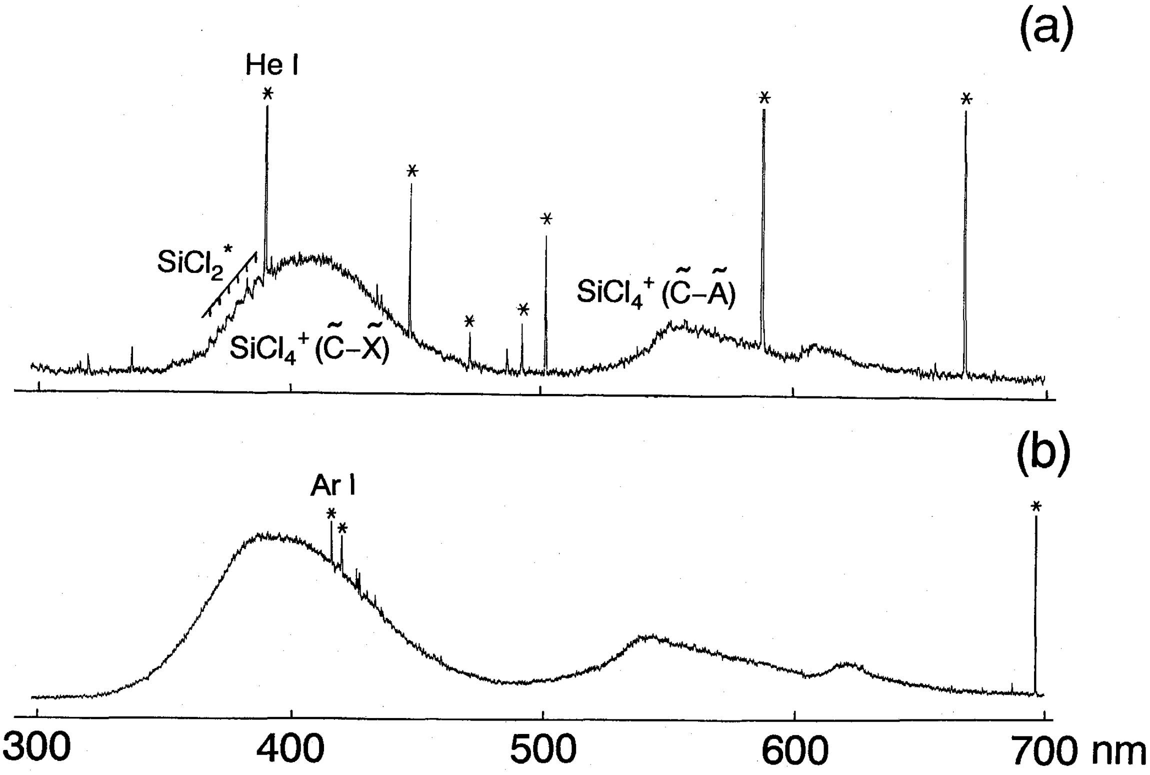

Fig. 2 $SiCl_4^+(\tilde{C}-\tilde{X}, \tilde{C}-\tilde{A})$ emissions produced from (a) the $He(2^3S)/SiCl_4$ Penning ionization and (b) $Ar^+(^2P_{3/2})/SiCl_4$ charge-transfer reaction at thermal energy (uncorrected for relative sensitivity). A weak peak at ~620 nm is not a real peak but it arises from a rapid change in the relative sensitivity.

$$He^+ + SiCl_4 \xrightarrow{k_2} SiCl_4^+(\tilde{C}) + He + 9.3\ eV, \qquad (2)$$

$$He_2^+ + SiCl_4 \xrightarrow{k_3} SiCl_4^+(\tilde{C}) + 2He + 3.0\sim5.0\ eV, \qquad (3)$$

where the ΔH values are calculated by using a vertical ionization potential of $SiCl_4^+(\tilde{C})$. Thus, significant energy transfer from the internal energy of the reactant ion to the relative translational energy of the products is required. Such an energy transfer process is generally unfavorable. The relative concentrations of $He(2^3S)$, He^+, and He_2^+ at a He pressure of 1 Torr were estimated to be 1, 1.5, and 0.25, respectively, by comparing the total intensities of the $N_2^+(B^2\Sigma_u^+-X^2\Sigma_g^+)$ emissions resulting from the reactions of $He(2^3S)$, He^+, and He_2^+ with N_2.[5] Taking account of these ratios, the k_2/k_1 and k_3/k_1 ratios were evaluated to be less than 0.002 and 0.07, respectively. The lack of the $SiCl_4^+(\tilde{C}-\tilde{X}, \tilde{C}-\tilde{A})$ emissions due to the $He^+/SiCl_4$ reaction is consistent with a small formation rate of $SiCl_4^+$ in the $He^+/SiCl_4$ reaction $[(4\pm2)\times10^{-11}\ cm^3s^{-1}]$.[11]

The $SiCl_4^+(\tilde{C}-\tilde{X}, \tilde{C}-\tilde{A})$ emissions due to the $Ne(^3P_{2,0})/SiCl_4$ reaction were also found in the Ne afterglow reaction of $SiCl_4$. The observed spectral features were the same as those in the $He(2^3S)/SiCl_4$ reaction, indicating that the $Ne(^3P_{2,0})/SiCl_4$ Penning ionization proceeds through a similar mechanism. The $SiCl_4^+(\tilde{C}-\tilde{X})$ emission starts from ~350 nm and gives a peak at ~410 nm. On the other hand, the $SiCl_4^+(\tilde{C}-\tilde{A})$ emission starts from ~510 nm and the main peak is observed at ~560 nm. These spectral features in the $He(2^3S)/SiCl_4$ and $Ne(^3P_{2,0})/SiCl_4$ Penning ionization are very similar to those obtained under fast electron -impact ionization,[1] where ionization is expected to proceed through a vertical FC mechanism. It is therefore concluded that the $He(2^3S)/SiCl_4$ and $Ne(^3P_{2,0})/SiCl_4$ Penning ionization leading to $SiCl_4^+(\tilde{C})$ takes place through a vertical FC mechanism.

Obase et al.[12] have found that vibrational distributions of $HCl^+(A^2\Sigma^+)$ and $HBr^+(A^2\Sigma^+)$ in the $He(2^3S)/HCl,HBr$ Penning ionization were different from those predicted from FC factors for ionization. The deviations from FC like distributions have been explained as due to a $He(2^3S)-HX$ ($X=Cl$ or Br) interaction in the incoming half collision and/or a $HX^+(A)-He(1^1S)$ interaction in the outgoing half collision. The present study demonstrates that such interactions are insignificant in the $He(2^3S)/SiCl_4$ and $Ne(^3P_{2,0})/SiCl_4$ reactions leading to $SiCl_4^+(\tilde{C})$.

When $SiCl_4$ was introduced into the Ar afterglow operated at Ar gas pressures above 0.25 Torr, where $Ar(^3P_{2,0})$, $Ar^+(^2P_{3/2})$, and $(Ar^+)^*$ were present as active species,[5] the $SiCl_4^+(\tilde{C}-\tilde{X}, \tilde{C}-\tilde{A})$ transitions are found in the 310-650 nm region, as shown in Fig. 2(b). The $SiCl_4^+(\tilde{C}-\tilde{X},\tilde{C}-\tilde{A})$ emissions disappeared completely when ionic active species were removed from the discharge flow. This implies that $Ar^+(^2P_{3/2})$ and/or $(Ar^+)^*$ are the responsible excitation source of $SiCl_4^+(\tilde{C})$. The dependence of the emission intensity of $SiCl_4^+(\tilde{C}-\tilde{X}, \tilde{C}-\tilde{A})$ on the Ar buffer gas pressure was different from that of the Kr^* lines from the $(Ar^+)^*/Kr$ reaction.[13] However, it was identical to that of the $OCS^+(\tilde{A}^2\Pi-\tilde{X}^2\Pi)$ emission due to the Ar^+/OCS CT reaction,[14] indicating that the same active species participates in the excitation of $SiCl_4^+(\tilde{C})$. Thus, it is concluded that $Ar^+(^2P_{3/2})$ is the responsible active species for the excitation of $SiCl_4^+(\tilde{C})$,

$$Ar^+(^2P_{3/2}) + SiCl_4 \longrightarrow SiCl_4^+(\tilde{C}) + Ar + 0.49\ \mathrm{eV}. \tag{4}$$

The observation of $SiCl_4^+(\tilde{C}-\tilde{X}, \tilde{C}-\tilde{A})$ emissions due to the above CT reaction is consistent with a large formation rate constant of $SiCl_4^+$ $[(8.5\pm2.6)\times10^{-10}\ cm^3s^{-1}]$.[11] Since the radiative lifetime of the $\tilde{C}$ state is short ($\tau=38$ ns),[2] vibrational and rotational relaxation by collisions with a buffer rare gas is expected to be negligible under the operating pressures. It should be noted that the $\tilde{C}-\tilde{X}$ and $\tilde{C}-\tilde{A}$ transitions due to the $Ar^+(^2P_{3/2})/SiCl_4$ reaction appear from ~320 and ~490 nm, respectively. These value are shorter than those due to the $He(2^3S)/SiCl_4$ and $Ne(^3P_{2,0})/SiCl_4$ reactions by ~20 nm. The peak positions of the $\tilde{C}-\tilde{X}$ and $\tilde{C}-\tilde{A}$ transitions in the $Ar^+(^2P_{3/2})/SiCl_4$ reaction also shift to blue by ~20 nm in comparison with those in the $He(2^3S)/SiCl_4$ and $Ne(^3P_{2,0})/SiCl_4$ reactions. These spectral shifts suggest that much higher rovibrational levels in $SiCl_4^+(\tilde{C})$ are populated in the $Ar^+(^2P_{3/2})$ reaction than those in the $He(2^3S)$ and $Ne(^3P_{2,0})$ Penning ionization. It is highly likely that $SiCl_4^+(\tilde{C})$ around 15.3 eV with favorable FC factors is dominantly formed in the $He(2^3S)/SiCl_4$ and $Ne(^3P_{2,0})/SiCl_4$ Penning ionization. On the other hand, $Ar^+(^2P_{3/2})/SiCl_4$ CT reaction preferentially populates $SiCl_4^+(\tilde{C})$ around 15.5 eV with small FC factors based upon the observed spectral shifts. The maximum excitation energies of the $\tilde{X} \longrightarrow \tilde{C}$ transition were estimated from the observed shortest wavelength of the $SiCl_4^+(\tilde{C}-\tilde{X})$ transition to be 3.9 eV for the $Ar^+(^2P_{3/2})$ CT reaction and 3.5 eV for the $He(2^3S)$ and $Ne(^3P_{2,0})$ Penning ionization. Adding these energies to an adiabatic ionization potential of $SiCl_4^+(\tilde{X})$, 11.79 eV,[8] the highest excitation level of the $\tilde{C}$ state is evaluated to be 15.7 eV for the $Ar^+(^2P_{3/2})$ reaction, whereas 15.3 eV for the $He(2^3S)$ and $Ne(^3P_{2,0})$ reactions. A good agreement of the former value with the recombination energy of $Ar^+(^2P_{3/2}$: 15.76 eV) suggests that the $Ar^+(^2P_{3/2})/SiCl_4$ populates the $\tilde{C}$ state up to near-resonant levels with a high probability. Based upon the HeI PES shown in Fig. 1, FC factors for ionization of $SiCl_4^+(\tilde{C})$ at ~15.7 eV are very small. The population of such near-resonant levels in the $Ar^+(^2P_{3/2})/SiCl_4$ reaction may be interpreted by the distortion of the nuclear geometry of $SiCl_4$ due to a slowly approaching $Ar^+(^2P_{3/2})$ ion field during the reaction.[15]

The ionization mechanism of molecules by thermal CT reactions has been discussed in terms of energy-resonance and FC factors for ionization.16) According to our recent mass spectroscopic studies on thermal ion-molecule reactions, energy-resonant requirement takes precedence over FC factors for the CT reactions of $Ar^+(^2P_{3/2})$ with polyatomic molecules such as CH_4, C_2H_4, and C_2H_6.17) The present finding led us to conclude that the $Ar^+(^2P_{3/2})/SiCl_4$ CT reaction also takes place through a near-resonant process where FC factors do not play a significant role.

Radiationless transitions of polyatomic ions have been classified into three cases: (a) resonance limit, (b) statistical limit, and (c) intermediate case, which are characterized by the structure of the vibronic levels of a lower electronic state which are coupled to isoenergetic vibronic levels of a higher electronic state.18) In case (a) for small cations, the density of vibrationally excited levels of a lower state is small, so that an initially excited level decays only radiatively and the fluorescence quantum yield is equal to unity. On the other hand, the density of vibrationally excited levels of a lower state is large in case (b) for large cations, so that non-radiative decay occurs to a quasi-continuum of isoenergetic lower levels and the fluorescence quantum yield becomes small. Since the fluorescence quantum yield of $SiCl_4^+(\tilde{C})$ is close to unity,2) the relaxation process of low vibrational levels of $SiCl_4^+(\tilde{C})$ in the FC region can be classified into case (a). In general, not only internal conversion described above, but also intramolecular vibrational redistribution and predissociation become significant for large cations with increasing the excess vibrational energy. The observation of $SiCl_4^+(\tilde{C}-\tilde{A}, \tilde{C}-\tilde{X})$ emissions from the near-resonant levels suggests that case (a) probably holds for $SiCl_4^+(\tilde{C})$ up to high vibrationally excited levels near ~15.76 eV. The slow non-radiative decay rate of the large $SiCl_4^+$ ion can be attributed to the high symmetry of $SiCl_4^+$ which reduces the density of vibrational levels and a large energy gap between the $\tilde{C}$ state and the lower $\tilde{B}$ state which reduces the internal conversion rate from $\tilde{C}$ to $\tilde{B}$.

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