Fluorescence Spectra of HCl⁺ in the Photoionization of HCl by 58.4-Nanometer Radiation (Commemoration Issue Dedicated to Professor Yoshimasa Takezaki on the Occasion of his Retirement)

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Fluorescence Spectra of HCl$^+$ in the Photoionization of HCl by 58.4-Nanometer Radiation

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The emission spectra of HCl$^+$ ions in the excited $A^3\Sigma^+$ state was observed in the photoionization of HCl molecules by HeI (58.4-nm) photon impact. The vibrational populations determined from the emission spectra are basically in accord with the photoabsorption Franck-Condon factors.

KEY WORDS: Excited state/ Vacuum ultraviolet photolysis/ Vibrational populations/

The determinations of vibrational population of HCl$^+$ ions have been obtained by the photoelectron spectroscopy (PhES),$^{1-3}$ Penning ionization electron spectroscopy (PIES),$^{4-6}$ Penning ionization optical emission spectroscopy (PIOS),$^{7,8}$ and the collision of HCl with He$^+$ ions.$^9$ The PhES, PIES and HCl-He$^+$ collision data showed that the excitation is a Franck-Condon process in which the target molecules are ionized in a vertical process. On the contrary, the PIOS data showed a nonvertical process in HCl$^+$ ($A^3\Sigma^+$) formed by He(2$^3$S) metastables.$^{13}$ It has been pointed out that the PIOS detects the states of HCl$^+$ in about $10^{-7}$ sec after the act of ionization and the electron and the electron spectroscopical methods detect the moment of ionization.$^{4,5}$ However, the significant differences between the PIOS and PIES data are not explained clearly.

Fluorescence from HCl$^+(A^3\Sigma^+)$ state, the vibrational populations of which were not determined by the photoionization optical emission spectroscopy (PhOS), was observed in the ionization of HCl by HeI (58.4-nm) radiation. The observation carried out through a fluorescence cell made of stainless steel. The chamber was filled with hydrogen chloride supplied by Takachiho Co. Ltd. with a purity of 99.5%. The gas pressure was monitored with a Baratron capacitance manometer. The experimental cell with a 2-mm ID entrance slit for the exciting beam was isolated by differential pumping from a light source consisted of 8-mm ID quartz tube through which high purity helium flowed at a pressure near 1.3 Torr. The helium was excited by a 2450 MHz discharge. The fluorescence was dispersed at right angles to the primary photon beam through a 0, 2-m monochromator (Jobin Yvon, H-20 UV) with a resolution of 1 or 2-nm. The dispersed fluorescence was measured by a photomultiplier (Hamamatsu TV, R585). The photon pulses from the photomultiplier were fed to a multichannel analyzer. A standard bro-

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A mine lamp with a known spectral irradiance (Ushio Electronic Co., type JPD-100-500 GS) was used for a calculation of the monochromator and the associated photomultiplier system.

Typical fluorescence spectra of HCl* are shown in Fig. 1. The potential energy curves of HCl and HCl* depicted in Fig. 2 are selected from Refs. 4, 10 and 11. Identifications mark bandheads of HCl*($A^2Σ^*→X^2Π_L$) transitions. The main bands are identified by Sheasley and Mathews\(^{11}\) and Norling.\(^{12}\) Some weak bands in Fig. 1 have not been identified in earlier works. The bands have been tentatively identified as 1→1 at 374, 0-nm, 2→1 at 346, 5-nm, 0→2 at 439, 5 and 427, 1-nm, and 1→2 at 411, 9-nm. The bands of 4→1, 5→1 and 6→1 are unresolved. However, their intensities are small\(^{11}\) and hence the contributions to the intensities of 2→0, 3→0 and 4→0 would be negligible.

The number of particles per unit volume in the various vibrational levels of the electronic state is given the following relation,\(^{12}\)

$$N_\nu = K \sum \frac{i_{\nu', \nu''}}{e_{\nu', \nu''}}$$

where K is a constant of proportionality, $i_{\nu', \nu''}$ is the peak photomultiplier current corresponding to fluorescence transition from some vibrational level $\nu'$ to a lower level $\nu''$, and $e_{\nu', \nu''}$ is the relative efficiency of the fluorescence analyzing system.

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Figure 2. Potential energy curves for the electronic states involved in the present observation.

Figure 3 shows the results obtained by several measurements at the gas pressure of 40-80 mTorr. There was no pressure effect on the populations. The distribution shows decreased population of levels with high quantum number \( \ell' \geq 4 \). The depopulations owe parity to the unresolved spectra as mentioned above and hence they should be the minimum values.

Although the vibrational populations determined in the present work are a post-ionization distribution, they have a similar tendency to the electron spectroscopical data which are close to the Franck-Condon factors of photoabsorption process of \( \text{HCl}^* (A^3\Sigma^+) \leftarrow \text{HCl}(X^1\Sigma^+) \). This implies that relaxation such as by collision of the excited \( \text{HCl}^* \) with parent molecules or by radiationless transition is ruled out within the lifetime of \( \text{HCl}^* (A^3\Sigma^+) \) estimated to be \( 0.5-1 \times 10^{-6} \) sec.\(^6\) This observation is in agreement with the result obtained by the collision of \( \text{HCl} \) with 2.5 keV \( \text{He}^+ \) carried out by Haugh.\(^9\) He dispersed the emission from \( \text{HCl}^* (A^3\Sigma^+) \) and found similar population to the Franck-Condon factors up to \( \ell' = 4 \).

Unfortunately it is impossible to find a suitable explanation by the present work about the difference between the PhOS and PIES populations. However, one can suppose that in the case of Penning ionization of \( \text{HCl} \) there must be a strong interaction
between the formed HCl* and He atom after the ionization and within the lifetime of HCl*(A2Σ+).

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REFERENCES

(6) C. E. Brion and P. Crowley, ibid., 11, 399 (1977).
(9) W. J. Haugh, ibid., 56, 4001 (1972).