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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 $A^2\Sigma^+$ 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^+ ($A^2\Sigma^+$) formed by $\text{He}(2^3\text{S})$ metastables.^{7,8)} 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 $\text{HCl}^+(A^2\Sigma^+)$ 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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mine lamp with a known spectral irradiance (Ushio Electronic Co., type JPD-100-500 CS) was used for a calculatuion of the monochromator and the associated photomultiplier system.

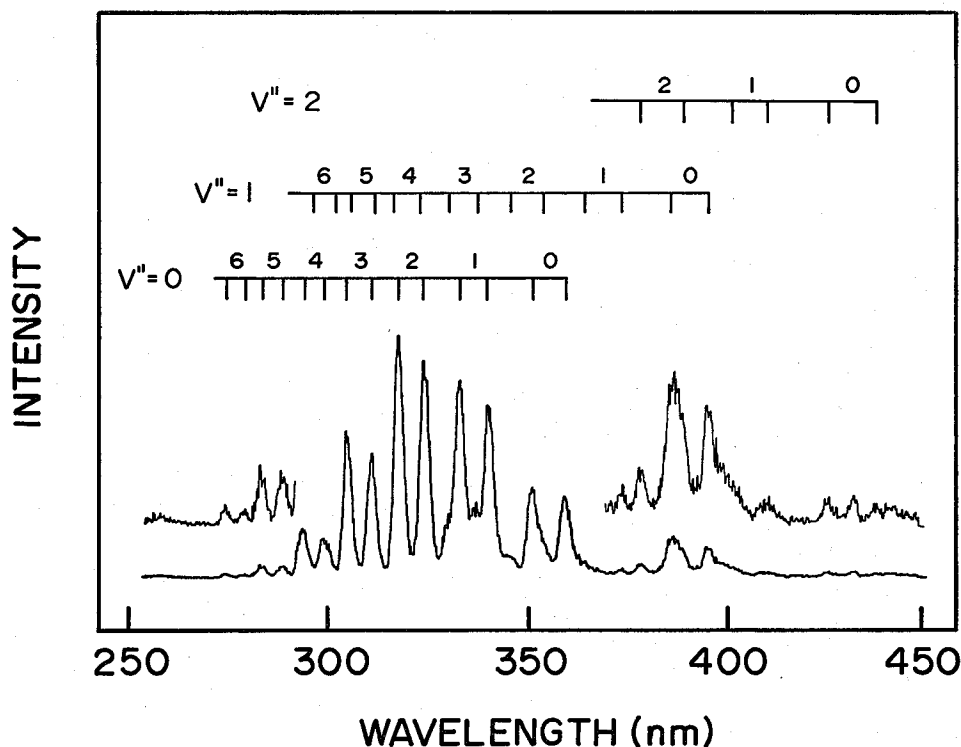


Fig. 1. Fluorescence spectra of $\text{HCl}^+(A^2\Sigma^+ \rightarrow X^2\Pi_i)$ system at a resolution of 2-nm.

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 $\text{HCl}^+(A^2\Sigma^+ \rightarrow X^2\Pi_i)$ transitions. The main bands are identified by Sheasley and Mathews¹¹⁾ and Norling.¹²⁾ Some weak bands in Fig. 1 have not been identified in earlier works. The bands have been tentatively identified as $1 \rightarrow 1$ at 374.0-nm, $2 \rightarrow 1$ at 346.5-nm, $0 \rightarrow 2$ at 439.5 and 427.1-nm, and $1 \rightarrow 2$ at 411.9-nm. The bands of $4 \rightarrow 1$, $5 \rightarrow 1$ and $6 \rightarrow 1$ are unresolved. However, their intensities are small¹¹⁾ and hence the contributions to the intensities of $2 \rightarrow 0$, $3 \rightarrow 0$ and $4 \rightarrow 0$ would be negligible.

The number of particles per unit volume in the various vibrational levels of the electronic state is given the following relation,¹³⁾

$$N_{v'} = K \sum_{v''} i^{v',v''} / \epsilon^{v',v''}$$

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

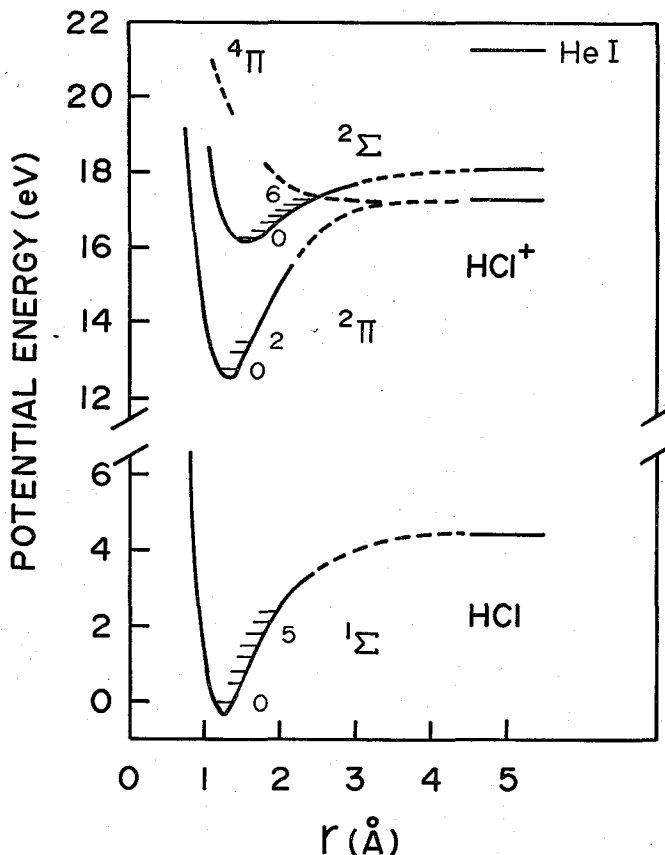


Fig. 2. Potential energy curves for the electronic states involved in the present observation.

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 ($v' \geq 4$). 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 $\text{HCl}^+(A^2\Sigma^+) \leftarrow \text{HCl}(X^1\Sigma^+)$.¹⁴⁾ This implies that relaxation such as by collision of the excited HCl^+ with parent molecules or by radiationless transition is ruled out within the lifetime of $\text{HCl}^+(A^2\Sigma^+)$ estimated to be $0.5\text{--}1 \times 10^{-6}$ sec.⁸⁾ This observation is in agreement with the result obtained by the collision of HCl with 2.5 keV He^+ carried out by Haugh.⁹⁾ He dispersed the emission from $\text{HCl}^+(A^2\Sigma^+)$ and found similar population to the Franck-Condon factors up to $v'=4$.

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 HCl there must be a strong interaction

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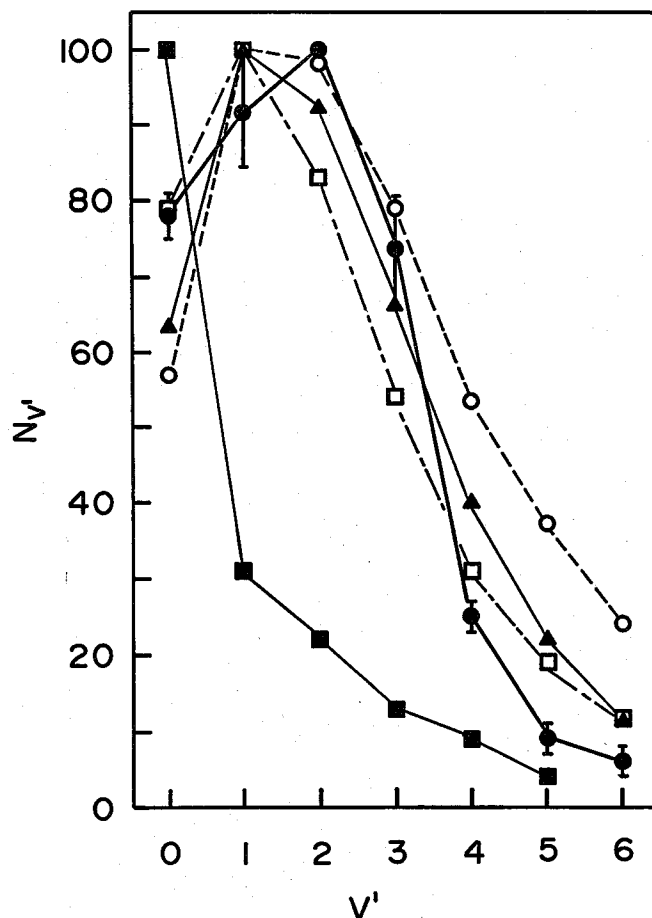


Fig. 3. Relative population of vibrational levels of $\text{HCl}^+(A^2\Sigma^+)$ determined in: ○ photoionization electron spectroscopy (Ref. 4), ▲ Franck-Condon factors (Ref. 14), □ Penning ionization electron spectroscopy (Ref. 4), ■ Penning ionization optical emission spectroscopy (Ref. 7), and ● phototonization fluorescence measurement (this paper).

between the formed HCl^+ and He atom after the ionization and within the lifetime of $\text{HCl}^+(A^2\Sigma^+)$.

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