

HCl⁺ X vibrational states investigated from the HCl threshold photoelectron spectrum

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The threshold photoelectron spectrum of HCl has been investigated in the 980–760-Å region. The various autoionization processes leading to the observed resonances are discussed. From the resonance positions located at the successive vibrational thresholds, spectroscopic constants of the X²Π state of HCl⁺ have been determined.

I. INTRODUCTION

Threshold photoelectron spectroscopy (TPES) has long been recognized as a tool for the study of molecular spectroscopy [1,2]. It has already been pointed out that ion states that cannot be produced by He I photoelectron spectroscopy can be observed by TPES due to the importance of autoionization.

Photoionization of HCl is known to produce HCl⁺ ions in the ground state X²Π v=0 (90%) and v=1 (10%) and at much higher energy in the excited state A²Σ. The region lying between the X²Π v=1 state and the A²Σ v=0 level is known as the Franck-Condon gap. The vibrational levels of the X²Π state of HCl⁺ lying in the Franck-Condon gap were first observed through resonant autoionization using the Ne(I) resonance lines, in a photoelectron spectroscopy experiment [3].

The TPE spectrum of HCl gives resonances for all the vibrational levels v=0–14. Their intensity variations are due to the relative importances of the excitation and autoionization of the Rydberg levels; their positions locate the various ionization thresholds. We made a careful reexamination of the X²Π vibrational progression of HCl⁺ extending over one more vibrational level than the 14 reported previously [3]. From the present data we were able to determine new spectroscopic constants of the X²Π state of HCl⁺.

II. EXPERIMENTAL

The experiment was done using the pulsed synchrotron radiation from ACO storage ring at the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE). The double-electron-ion time-of-flight spectrometer has been described previously [4,5] and we will only briefly recall its characteristics. The synchrotron radiation dispersed by a 1-m McPherson monochromator equipped with a 2400 l/mm Jobin Yvon holographic

grating is focused on an effusive beam of HCl gas at room temperature (99.9% purity supplied by Air Liquide Co. without any further purification). Electrons are extracted at right angles from both the photon and gas beams. They are accelerated by a 1-V/cm electric field.

The threshold electron signal is obtained by gating the arrival of the electrons (duration of 4 ns) at the detector with respect to the ACO light pulse, which allows further rejection of fast electrons which are not completely rejected by angular discrimination alone. The threshold photoelectron (TPE) spectrum was obtained with a 0.4-Å photon bandwidth and an electron-energy band pass of 8 meV. The incident light flux varied strongly with the wavelength due to the grating and the mirror responses and decreased slowly during any recording due to the lifetime of the electron bunch in the storage ring. The spectra were numerically corrected for both effects (see Ref. [6]).

III. RESULTS

The TPE spectrum observed in the 980–760-Å region is displayed in Figs. 1 and 2 with the ionization cross section. The two spin-orbit components ²Π_{3/2} and ²Π_{1/2} of the v⁺=0 and 1 levels present a striking difference in intensity; they are asymmetrical and display structures. The v⁺=0 resonances had been studied previously [5]. We have been able to reproduce the observed signal using a fairly simple model: the signal due to both direct ionization of the ²Π_{3/2} and ²Π_{1/2} states and spin-orbit autoionization of the ²Π_{1/2} Rydberg states in the ²Π_{3/2} continuum. The overall shape of the resonance is due to the rotational transfer in the processes. The TPE calculated signal is the sum of the various J⁺ contributions (J⁺ being the total angular momentum of the ion) convoluted by the electron transmission function T(ε), approximated by a half Lorentzian. We applied the same model to the v⁺=1 resonances. The relative positions of the

TABLE I. Vibrational energy terms (in cm^{-1}) for the $X^2\Pi$ state of HCL^+ . E_v refers to the $\text{HCl } X^1\Sigma v''=0$ level, T_v to the $\text{HCl}^+ {}^2\Pi v'=0$ level. The numbers in parentheses are the uncertainty in the last digits.

v	E_v^a (-304cm^{-1})	E_v^b	T_v^c	T_v^b
0	102 810 (16)	103 094 (20)	0	0
1	105 400 (40)	103 662 (20)	2568.6198 (33)	2 568 (25)
2	107 876 (40)	108 126 (20)	5032.1666 (95)	5 032 (25)
3	110 263 (40)	110 494 (20)		7 400 (25)
4	112 538 (40)	112 752 (20)		9 658 (25)
5	114 715 (40)	114 906 (20)		11 812 (25)
6	116 804 (40)	116 940 (25)		13 846 (30)
7	118 772 (40)	118 937 (25)		15 843 (30)
8	120 643 (40)			
9	122 434 (40)	122 615 (25)		19 521 (30)
10	124 144 (40)	124 335 (25)		21 240 (30)
11	125 749 (40)	125 964 (25)		22 870 (30)
12	127 265 (40)	127 537 (50)		24 443 (50)
13	128 741 (40)	128 995 (50)		25 901 (50)
14		130 366 (50)		27 272 (50)

^aFrom Ref. [3] [the quoted values refer to the ${}^2\Pi_{3/2} J=3/2$ energy differing from the term value by $304 \text{ cm}^{-1} (-A/2+B)$].

^bPresent work.

^cFrom Ref. [7].

$v^+=0$ and 1 resonances are in perfect agreement with spectroscopic data [7,8]. The relative intensities are in the ratio 5/1, quite far from the ratios observed by photoelectron measurements: 12/1 [3,9] or calculated from the potential values: 18/1 [10].

In the model used in Ref. [5], direct ionization was described by the rotation-spectator model [11] (rotation is a very slow process compared to ionization), the out-going electron takes the angular momentum from the incident photon and leaves the rotating core with an electronic hole. In that case the change of total angular momentum between the molecule in its ground state and the ion core

$$|J'' - J^+| \leq 3/2. \quad (1)$$

Direct ionization is a very fast process; on the contrary, autoionization occurs in a time similar to or longer

than a rational period. The only governing law is total angular-momentum conservation. The ejected electron is mainly in a "d" orbital [12], its maximum angular momentum is then 5/2, leading to an angular-momentum change [13] of

$$|J'' - J^+| \leq 7/2. \quad (2)$$

The autoionized states are for $v^+=0$ and 1, the Rydberg states converging to ${}^2\Pi_{1/2} v^+=0$ and 1, respectively, autoionizing through spin-orbit interaction in the ${}^2\Pi_{3/2}$ continua. They can be described in an "e" coupling scheme [14].

Due to a very low Franck-Condon (F) factor, the $v^+=2-14$ continua cannot be reached directly. Only autoionization can explain the observed resonances.

At wavelengths shorter than 940 Å, the structures observed in absorption or in ionization are very broad [6,11,15]; the individual position and the width of each rotational level is unknown. We described them as a quasicontinuum. Equation (2) gives the allowed momentum change. We tried first to determine the spectroscopic position of the resonances, i.e., the T_v values. The position of the rotational levels of the ion are according to Refs. [7] and [8],

$$E({}^2\Pi_{3/2}, v, J) = T_v + B(J-1/2)(J+3/2) - [(A-2B)^2/4 + B^2(J-1/2)(J+3/2)]^{1/2}, \quad (3)$$

$$E({}^2\Pi_{1/2}, v, J) = T_v + B(J-1/2)(J+3/2) + [(A-2B)^2/4 + B^2(J-1/2)(J+3/2)]^{1/2}, \quad (4)$$

where B and A are the rotational and spin-orbit constant,

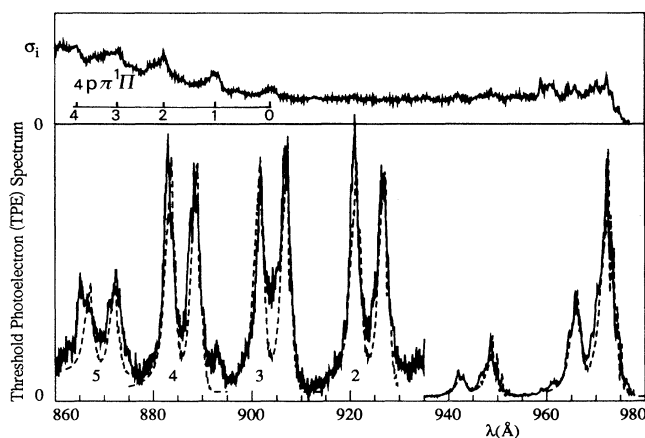


FIG. 1. TPE spectrum (lower curve) and total ionization cross section (upper curve) in the 860–980-Å spectral range. Dashed lines are the simulated resonances (see text).

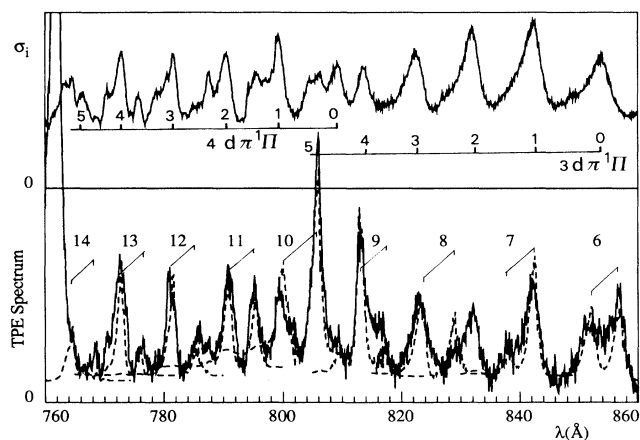


FIG. 2. TPE spectrum (lower curve) and total ionization cross section (upper curve) in the 760–860-Å region. Dashed lines are the simulated resonances (see text). The TPES peak located at 762 Å corresponds to the $A^2\Sigma v'=0$ excitation.

respectively, and are from Ref. [7]; all other terms can be neglected here. [The A constant was not observed to vary (within our precision) from $v^+=0-14$.]

In order to describe the TPE spectrum we have to consider the direct excitation of the continuum for $v=0$ and 1 and the excitation of Rydberg states, from the various rotational levels of the X fundamental state of HCl, populated according to a Boltzmann distribution. For a particular ground-state level J'' , one can excite a set of final J^+ levels of the ion according to the above rules. The TPE signal is then the sum of the various J^+ contributions, convoluted by the electron transmission function $T(\epsilon)$, approximated by a half Lorentzian. The remaining parameter is the energy T_v of the spectroscopic term, i.e., the position of the double peak. The T_v values were fitted for each vibrational pair of spin-orbit resonances, the values are gathered in Table I. Figures 1 and 2 display such fits.

IV. DISCUSSION

For the $v^+=2$ threshold, no structure appears in the absorption nor the ionization cross section, no Rydberg level is observed located nearby. The only possible autoionizing levels lying there are those belonging to the B state, which is partly of a valence type at short distance and an ion pair ($H^+ + Cl^+$) at large distance [10]; at such an energy, the vibrational quantum may be of the order of 90 (from a calculation using the *ab initio* potential curve of Ref. [10]). The vibrational energy difference between two successive levels is about 40 cm^{-1} , much smaller than the rotational spread of the initial state. Its absorption spectrum may thus appear as a continuum. To simulate the resonances, the autoionizing levels were described as a flat quasicontinuum. It works quite well for $v^+=2-6$ (see Fig. 1). The B -state limit lies below the $v^+=6$ resonances (860 Å). The $v^+=3-5$ have very little correlation with the $(A, 4p\pi)^1\Pi$ resonances observed in ionization spectrum. The $v^+=2-5$ resonances may well be one evidence of the B state. If the B state is also

efficient for the $v^+=0$ and 1 resonance, it would explain the observed ratio between the $v^+=0$ and 1 resonances.

The $v^+=7-14$ resonances are strongly correlated to the $(A, 3d\pi)^1\Pi$ and $(A, 4d\pi)^1\Pi$ resonances [6] observed on the total ionization cross section. To simulate these resonances, the autoionizing levels amplitude was described by the structured part of the observed ionization cross section. This approach is similar to the procedure proposed by Spohr *et al.* [1], who suggested to normalize the TPES signal by the total ionization signal. We know that the continuum cannot be efficient here due to poor F factors. According to Bardsley and Smith [16], under these conditions the autoionization into one particular v^+ channel depends on the total ionization resonance amplitude and for an electrostatic interaction on the Franck-Condon factor between the v' Rydberg state and the v^+ ionic state. The calculated peaks fit the observed resonances well (see Fig. 2). Their intensities have been adjusted for each pair of resonances. The $v^+=9$ and 10 resonances are more intense than the neighbors. They are due to the autoionization of the $v=4$ and 5, $3d\pi^1\Pi$ levels, respectively. In this case, the calculated F factors are particularly high. The F factors were calculated using the Numerov method; the X potential curve was from Ref. [10], the A one from Ref. [7]. The results are gathered in Table II. The correlation between the F factors and the observed weight gives a strong assumption for electrostatic autoionization [16].

From fitting the calculated peak profiles, i.e., the rotational band contours of a pair of resonances to the TPE spectrum, we measured the T_v values (see Table I). The indicated error bars reflect the uncertainties due to the fit on the relative position of the v^+ and 0 band. They are smaller than the peak widths. Some of the values obtained here are slightly different from those of Natalis *et al.* [3]. For $v^+\geq 7$, the values are systematically higher than the extrapolated spectroscopic values, i.e., the values obtained from the ω_e and $\omega_e x_e$ values determined from $v^+=0, 1$, and 2 at high resolution [8]. This has to be due to a positive value of $\omega_e y_e$.

As the T_1 and T_2 values had been determined with very high precision [8], we used the following relation to determine $\omega_e y_e$ (easily deduced from the vibrational expansion formula using T_0 as origin):

$$(T_1 - T_0/v)/(v-1) = \omega_e x_e - \omega_e y_e(v + 5/2), \quad (5)$$

as illustrated in Fig. 3. The experimental error on each T_v value is included in the $\omega_e y_e$ determination, with the $1/v(v-1)$ factor, allowing a satisfactory determination of $\omega_e y_e$. The $\omega_e x_e$, ω_e , and T_e values are then determined from T_1 and T_2 . The whole set of vibrational constants of the $X^2\Pi$ state is then (the uncertainty is on the last digit)

$$\begin{aligned} \omega_e y_e &= 0.40(\pm 4) \text{ cm}^{-1}, \\ \omega_e x_e &= 54.3(\pm 2) \text{ cm}^{-1}, \\ \omega_e &= 2676.0(\pm 3) \text{ cm}^{-1}, \\ T_e &= -1324.46(\pm 8) \text{ cm}^{-1}. \end{aligned} \quad (6)$$

TABLE II. Calculated Franck-Condon (F) factors involved in the observed resonances compared with the weight used in the fit (normalized for $v^+ = 7$).

v^+	v'	F	Weight
7	1	8×10^{-4}	1.0
7	2	1.2×10^{-2}	
8	2	3.5×10^{-3}	2.0
8	3	2.4×10^{-2}	
9	4	5.6×10^{-2}	3.6
10	5	8.0×10^{-2}	3.6

The positive value of $\omega_e y_e$ gives a positive curvature to the $\Delta G(v)$ curve making a Birge-Spencer extrapolation to determine the dissociation energy of the $^2\Pi$ state $D_p(^2\Pi)$ meaningless. The $X^2\Pi$ state is correlated to $H(1S) + Cl(^3P)$, and its dissociation energy can be determined through

$$D_0(^2\Pi) = D_0(HCl) + V_{IP}(Cl) - T_0(^2\Pi), \quad (7)$$

where $D_0(HCl) = 4.433$ eV [17], $V_{IP}(Cl) = 13.017$ eV [18].

We can point out here, the error slipped into Ref. [6] where T_0 was assimilated to the V_{IP} from Eq. (3),

$$\begin{aligned} V_{IP} &= E(^2\Pi_{3/2}, v^+ = 0, J^+ = 3/2) \\ &= T_0 + 3B - [(A - 2B)^2/4 + 3B^2]^{1/2} \\ &\simeq T_0 + 2B + A/2, \end{aligned}$$

A being negative. This gives, according to our V_{IP} value [5],

$$\begin{aligned} T_0 &= (103\,094 \pm 20) \text{ cm}^{-1} \\ &= (12.782 \pm 0.002) \text{ eV}. \end{aligned}$$

This leads to $D_0(^2\Pi) = 4.668$ eV and $D_e = 4.833$ eV. Such values are much higher than the value obtained through a Birge-Spencer extrapolation performed with previous constants [7]: $D_0 = 4.05$. A negative sign of $\omega_e y_e$ would have decreased the D_0 extrapolated value. The above D_0 and D_e values are slightly more precise

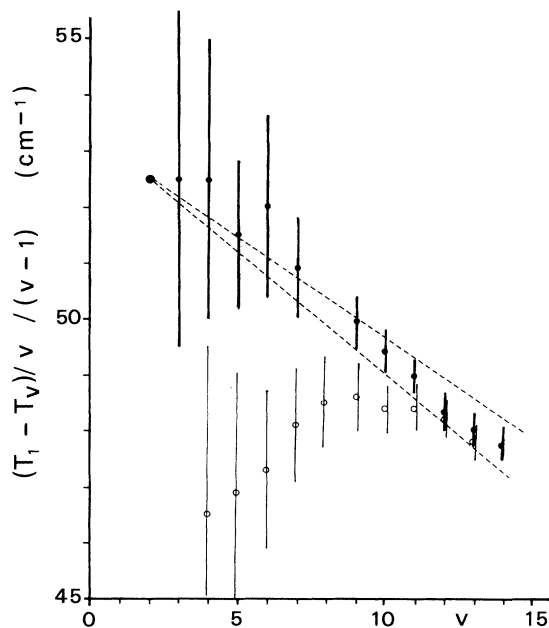


FIG. 3. The function used for the $\omega_e y_e$ determination. The bars represent the experimental error for each value. The slashed lines correspond to the extreme accepted values of $\omega_e y_e$. Full circles are our measurements, open circles are values determined from Ref. [3].

than the values reported previously by Huber and Herzberg [17].

V. CONCLUSION

The TPE spectrum of HCl, performed in the 980–760-Å spectral range allowed us to interpret the autoionization observed and to locate the $v^+ = 0-14$ progression of the $X^2\Pi$ state of HCl^+ . The vibrational $\omega_e y_e$ spectroscopic constant had then been determined.

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