

STRUCTURE OF THE ELECTRON-ROTATION-VIBRATION SPECTRUM OF AN HCl⁺ ION IN AN ELECTRON BEAM

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The present paper continues studies on the processes that occur in the interaction of hydrogen chloride (HCl) molecules with the electrons of a diagnostic beam. In analysis of electron-vibration spectra, Karelov and his coworkers [1, 2] have shown that, under low pressures ($P < 1$ Pa), the vibrational levels in $A^2\Sigma^+$ HCl⁺ are excited by direct electron impact in accordance with optical selection rules, and deactivation is performed by means of spontaneous radiation. As the vapor pressure rises, additional processes that lead to a relative overpopulation of the lower vibrational states in $A^2\Sigma^+$ and also to an increase of their rotational temperature begin to work. These processes were initially interpreted as selective quenching. However, the significant difference between the measured quenching constants of a level with $v' = 0$ and the constants of the higher levels allows one to assume that the mechanism is more complicated and, to examine it, it is necessary to analyze the line-intensity distributions in the rotational-band structure.

The goal of the present paper is to analyze the intensity distribution in the electron-vibration-rotation radiation spectrum of an HCl⁺ ion and to clarify the potentialities of electron-beam diagnostics of internal HCl states.

Experiments were performed on the low-pressure research unit of the Institute of Thermal Physics, Siberian Division of the Russian Academy of Sciences using the conventional scheme of electron-beam experiments [3] under static pressure conditions. The HCl vapor pressure in the chamber was varied within the range 1–60 Pa. To avoid the accumulation of gas–electron beam interaction products, a continuous equilibrium gas flow through the chamber was ensured. Passing through the gas, a 10-keV focused electron beam with current of 1–10 mA excited and ionized the gas molecules and was collected by an electron collector. The electron-generated radiation was focused by a quartz lens to the entrance slit of an SPM-2 monochromator. The photomultiplier signal was recorded by a self-recorder. In the experiments, the electron-vibration-rotation radiation spectra of the ($A^2\Sigma^+$)–($X^2\Pi$; HCl⁺) transition were recorded at various values of the HCl vapor pressures and the electron-beam current.

Figure 1 shows the spectrum of the (0–0) G_2 band, which was taken for the HCl vapor pressure $P = 8$ Pa and an 11-mA electron-beam current (curve 1) and the spectrum (curve 2) calculated with allowance for the spread function of the monochromator (the calculational procedure will be given below). One should note that because of the low dispersion of the monochromator, we managed to resolve only the peaks that consist of several lines (their positions are indicated at the top of the figure) rather than separate rotational lines. A great number of branches in the radiation spectrum, which are superimposed on one another, complicates greatly the identification of the spectra and the calculation of the intensity distributions. Good agreement between the calculated and measured spectra is observed both in the structure and in the intensity distributions of the peaks to be resolved (the deviation of the calculated normalized intensity peaks from the experimentally measured one is less than 10% within the wavelength range $\lambda = 360.5$ – 366.5 nm), which offers the possibility of carrying out a further investigation through an analysis of the band contours.

Owing to λ -doubling, the principal state of an $X^2\Pi_{1/2,3/2}$ ion is divided into two substates $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$, which are 630 cm^{-1} distant from each other. In addition, spin splitting is significant in the $A^2\Sigma^+$ and

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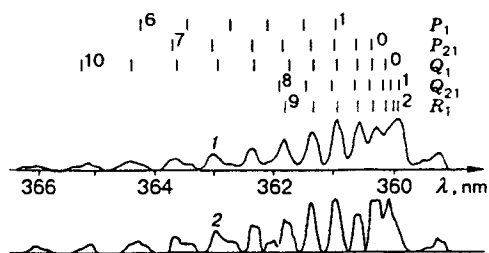


Fig. 1

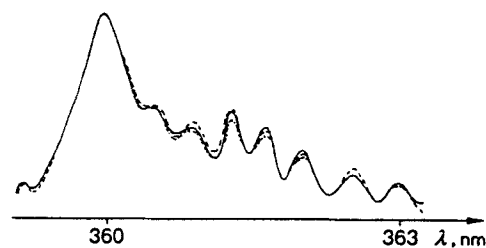


Fig. 2

$X^2\Pi_i$ states. With allowance for the selection rules $\Delta j = 0$ and ± 1 , we, therefore, have, in the spectrum of each vibrational band, two groups, with six superimposed branches in each. The wavelengths of rotational lines in radiation were calculated by the usual formulas [4]. The constants B_e , α_e , D_e , β_e , and γ for the states $A^2\Sigma^+$ HCl^+ and $X^2\Pi_i$ HCl^+ were taken from [5].

The vibrational and rotational levels in $A^2\Sigma^+$ HCl^+ can be populated:

- by direct impact of primary and secondary electrons (mechanism 1.1),
- by excitation through an intermediate state (mechanism 1.2),
- upon vibration-rotation heating by slow (below the ionization threshold) secondary electrons with subsequent ionization (mechanism 1.3),
- by slow (but above the ionization threshold) secondary electrons with violation of the optical selection rules (mechanism 1.4),
- owing to the relaxation from high-lying levels (mechanism 1.5).

Depopulation of the levels can be caused (a) by spontaneous radiation, (b) by quenching owing to the recombination by slow secondary electrons or in collisions of the excited ions with the background gas molecules, i.e., in collision processes that lead to the escape of the excited ion from the state $A^2\Sigma^+$, and (c) owing to vibration-rotation relaxation inside $A^2\Sigma^+$.

The basic excitation and deactivation mechanisms described above are different in the character of the dependences of their velocities on the interaction parameters: gas density and electron current. In the excitation by direct electron impact, the population rate $R_{1.1}$ is proportional to the molecule density and the electron current: $R_{1.1} \sim in$. For mechanism 1.2, the excitation rate in $A^2\Sigma^+$ is proportional to the population of the intermediate state and the current of exciting electrons: $R_{1.2} \sim (in)i = i^2n$. Upon vibration-rotation heating of the principal state with subsequent excitation in $A^2\Sigma^+$, the rate $R_{1.3}$ is proportional to the secondary electron density in , the density of gas molecules n , and the current of fast electrons i : $R_{1.3} \sim (in)ni = i^2n^2$. In direct excitation by slow electrons, the excitation rate $R_{1.4}$ is proportional to the secondary electron and gas densities: $R_{1.4} \sim (in)n = in^2$. For relaxation population, the rate $R_{1.5}$ is proportional to the population of the high-lying level in and the gas density n : $R_{1.5} \sim (in)n = in^2$. Thus, the experimental determination of the dependence of the intensity distribution inside the band on the electron current and the HCl vapor density make it possible to reveal the working excitation and deactivation mechanisms.

The line-intensity distributions on the beam current were examined within the current range 1–10 mA. Figure 2 shows the results of such an experiment for the (0–0) G_2 subband at an electron energy of 10 keV and an HCl vapor pressure $P = 8$ Pa (the dashed, solid, and dot-and-dashed curves refer to the subband contours for the beam currents $i = 1.1$, 3.1, and 9.0 mA, respectively). Since the intensity distribution inside the band is not current-dependent, the effect of mechanisms 1.2 and 1.3 (excitation via the intermediate state and vibration-rotation heating in the principal state) in the current range indicated above can be ignored.

The intensity distribution in the spectrum on the HCl vapor density was studied within the pressure range 1–60 Pa. As the pressure varies, the spectrum was found to begin restructuring, both the intensity relation of vibrational bands and the line-intensity distribution inside the band vary. Figures 3 and 4 show the results for the (0–0) G_2 and (1–0) G_2 bands, respectively, which were taken under various pressures and were reduced to the same scale. Curves 1–6 are the experimentally measured radiation-intensity distributions

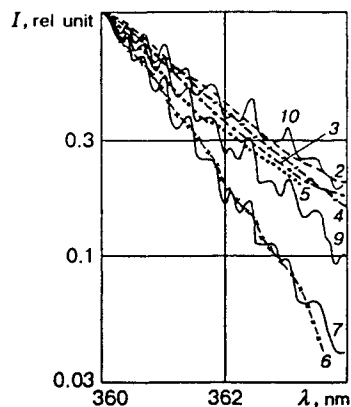


Fig. 3

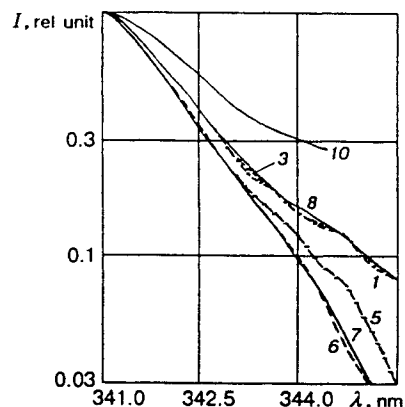


Fig. 4

inside the bands for the HCl vapor pressures $P = 60, 41, 22, 13.3, 7.2,$ and 1.33 Pa. Since in the bands of the $(A^2\Sigma^+) - (X^2\Pi; \text{HCl}^+)$ transition, to larger λ values correspond larger numbers of rotation levels involved, one can conclude that, on all bands, an increase is observed in the intensities of high-lying rotational lines inside the band, which becomes an asymptote, as the HCl vapor pressure increases.

The radiation intensity of the rotational line $j' - j''$ can be calculated by the formula [2, 4, 6]

$$I_{\nu' \nu''}^{j' j''} = C(64\pi^4 c/3)(\nu_{j' j''})^4 \sigma_e^{AX} q_{\nu' \nu''} P_{j' j''} n_{j'}, \quad (1)$$

where C is the spread function, c is the velocity of light in vacuum, $\nu_{j' j''}$ is the line frequency, σ_e^{AX} is the square of the matrix element of the electron transition $(A^2\Sigma^+) - (X^2\Pi;)$, $q_{\nu' \nu''}$ and $P_{j' j''}$ are the Franck-Condon and Hanle-London coefficients in radiation [7], and n_j is the population of the rotation level in $A^2\Sigma^+ \text{HCl}^+$, which results from the balance between the excitation and depopulation of the radiating state. The calculation results of the radiation-intensity distribution inside the bands are given in Figs. 3 and 4 by solid curves 7-10 for rotational temperatures $T_R = 300, 450, 500,$ and 800 K under the assumption of the equilibrium population of rotational levels in a radiating state. It follows from a comparison of the calculated and experimentally measured intensity distributions that

(1) for each pressure, the radiation-intensity distribution in a band is well described by a calculation that assumes the equilibrium population of rotational levels in a radiating state;

(2) at low densities, the experimental radiation-intensity distributions for all bands are approximated with good accuracy by the calculated ones in which the rotational temperature of a radiating state is assumed to be equal to the gas temperature (curves 7 in Figs. 3 and 4, $T_R = 300$);

(3) the higher the density of the gas in which a spectrum is taken, the higher the rotational temperature used in the calculation should be;

(4) for some pressure, the line-intensity distribution inside the band becomes an asymptote described by the equilibrium calculation, but the T value used in these calculations is different for different bands. For example, for the (0-0) band, the asymptotic temperature is $T(v' = 0) = 800$ K (curve 10 in Fig. 3), and, for the (1-0) band, we have $T(v' = 1) = 450$ K (curve 8 in Fig. 4). It is worth noting that, for the band (3-1) measured in the present study with large error (omitted in the figures), we have $T(v' = 3) = 550-800$ K.

The coincidence of the real gas temperature with the rotational temperature used for calculation under the HCl vapor pressure $P = 1$ Pa allows us to state that, for $P < 1$ Pa, the rotational levels in $A^2\Sigma^+ \text{HCl}^+$ are excited by direct electron impact of the primary and secondary electrons of the beam with the observance of optical selection rules. The deviation of the asymptotic calculational temperature from the gas temperature as the density grows cannot be explained by excitation by slow (above the ionization threshold) secondary electrons, since, with the growth of v' , a monotone decrease of the asymptotic temperature T_R , which should be expected because of an abrupt decrease of the excitation cross section by secondary electrons as their

TABLE 1

v'	K^q , cm ³ /sec	K_{10} , cm ³ /sec	K^q [2], cm ³ /sec	v'	K^q , cm ³ /sec	K_{10} , cm ³ /sec	K^q [2], cm ³ /sec
0	$1.9 \cdot 10^{-11}$	$1.4 \cdot 10^{-11}$	$0.6 \cdot 10^{-11}$	3	$1.4 \cdot 10^{-11}$	—	$2.1 \cdot 10^{-11}$
1	$4.7 \cdot 10^{-11}$	—	$2.6 \cdot 10^{-11}$	4	$3.0 \cdot 10^{-11}$	—	$2.0 \cdot 10^{-11}$
2	$4.1 \cdot 10^{-11}$	—	$3.4 \cdot 10^{-11}$				

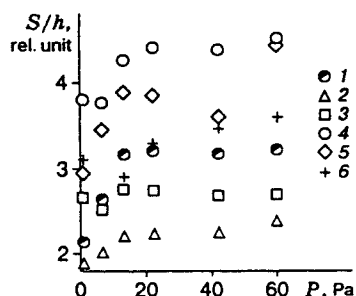


Fig. 5

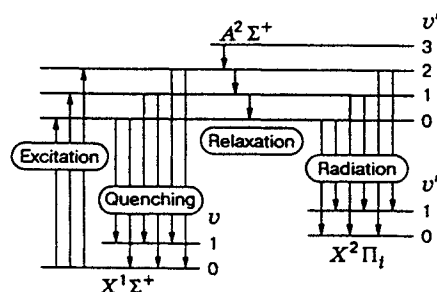


Fig. 6

energy becomes greater than the ionization threshold, is not observed.

Thus, the experimentally observed variations in the shapes of vibration bands in varying the pressure can be accounted for either by vibration-rotation relaxation in the $A^2\Sigma^+$ state, or j' -selective quenching of rotational levels in $A^2\Sigma^+$. In the latter case, the asymptotic character of rotational-level population distribution should be observed for different bands under different pressures; note that, for any pair of bands, the ratio of these pressures should be inversely proportional to the ratio of the selective-quenching constants of the corresponding vibrational states [2], because the rotational-level selective-quenching constants are normalized to the quenching constant of an appropriate vibrational state.

To check this assumption, we constructed, for a number of bands, the pressure dependence of the parameter S/H having the sense of the half-width of a band and being equal to the ratio of the integral under the band contour to its maximum intensity. The results are shown in Fig. 5, where points 1–6 correspond to the S/H values for the (0–0), (1–0), (2–0) (4–1), (3–1), (4–0) (6–1), and (5–0) bands. All the bands became asymptotic in a narrow interval of HCl vapor pressures ($P \sim 10$ – 15 Pa), which does not support the assumption of the j' -selective quenching of rotational levels in $A^2\Sigma^+$.

Thus, as the density grows, vibration-rotation relaxation in $A^2\Sigma^+$ is the most probable mechanism of measurements of the ratio between the band intensities [2] and the radiation-intensity distribution inside a band.

A detailed analysis of this mechanism calls for further consideration with the use of high-resolved spectral equipment. Here we confine ourselves to the vibrational structure alone.

We write the level-by-level balances as follows:

$$dn_{v'}/dt = (i/e)\sigma n_0 - \sum_{v''} (A_{v'v''} n_{v'}) - K_{v'}^q n_{v'} n_0 + K_{v'+1, v'} n_{v'+1} n_0 - K_{v', v'-1} n_{v'-1} n_0, \quad (2)$$

where $n_{v'}$ is the population of the v' -level in $A^2\Sigma^+$, n_0 is the gas density, σ is the cross section of $A^2\Sigma^+$ excitation by diagnostic electrons, i is the beam current, e is the electron charge, $A_{v'v''}$ is the Einstein coefficient in radiation, $K_{v'}^q$ is the rotational-level quenching constant, and $K_{v'+1, v'}$ is the relaxation-rate constant (only single-quantum transitions are taken into account). Expressing the level population through band intensities in formula (2), we obtain

$$(I^{v'v''}/I_0^{v'v''}) = [1 + (K_{v'}^q + K_{v', v'-1})\tau_{v'} n_0]^{-1} + (I_0^{v'+1, v''}/I_0^{v', v''})(I^{v'+1, v''}/I_0^{v'+1, v''})$$

$$\times \tau_{v',n_0} K_{v'+1,v'} (\nu_{v',v''}^4 / \nu_{v'+1,v''}^4) (q_{v',v''} / q_{v'+1,v''}) [1 + (K_{v'}^q + K_{v',v'-1}) \tau_{v',n_0}]^{-1}. \quad (3)$$

Note that relation (3) describes the ratio of the band intensities and the pressure, which were given in [2] (see Fig. 5). One can estimate the quenching and relaxation constants in the simplest way under the assumption that the relaxation constants are related by the relation $K_{v'+1,v'} = v' K_{1,0}$ [8]. From the experimental data in [2], we then obtain the values of the relaxation constants (see Table 1), which describe fairly well the experimental results and agree with the integral values of the vibrational-level selective-quenching constants [2].

Thus, the transition pattern in the excitation or deactivation of the $A^2\Sigma^+$ HCl⁺ vibrational-rotational levels upon electron-beam probing looks like that in Fig. 6; here excitation is performed by direct electron impact according to the optical selection rules, whereas quenching is selective only relative to the vibrational quantum number (the quenching constants were estimated using experimental data). The vibration-rotation relaxation in $A^2\Sigma^+$ HCl⁺ can be given in detail up to the level of rotational constants in experiments with better resolution of the rotational band structure.

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