ELECTRONIC-VIBRATIONAL EMISSION SPECTRUM OF HYDROGEN CHLORIDE EXCITED BY AN ELECTRON BEAM

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The electron-beam method for measuring the temperatures and populations of the internal degrees of freedom is based on recording the radiation excited by the electron beam in the gas under study. Thus far this method has been developed in detail for nitrogen [1, 2], and attempts have been made to use it for carbon monoxide [3], carbon dioxide [4], hydrogen [5], and water vapor [6]. The development of the method requires a study of the mechanism of excitation of the upper radiative state of the selected electronic transition, construction of a model of excitation-radiation processes, and determination of the transition probabilities for electronic excitation.

This work is devoted to the study of the radiation excited by a beam of 10-keV electrons for the purpose of developing a method of electron-beam diagnostics of hydrogen chloride. The radiation spectrum of hydrogen chloride has been studied in many works (see [7, 8]). The spectra were obtained there in discharge tubes, where the state of the gas prior to excitation is unknown and it is therefore difficult to determine the mechanism of the excitation-radiation processes. The use of a beam of fast electrons substantially simplifies the problem of analysis of the excitation mechanisms. In this paper only the electronic-vibrational transitions, neglecting the rotational structure of the bands, are studied.

Results of Measurements. A diagram of the experiment is shown in Fig. 1a. The electron beam 2, generated by the electron gun 1, was injected through a differential evacuation system into the vacuum chamber and struck the electron collector 3. Conditions with stationary pressure were maintained in the vacuum chamber by continuously injecting hydrogen chloride and evacuating the vacuum chamber with vapor—oil pumps. Technically pure hydrogen chloride was employed. The radiation excited by the electron beam was observed in a direction perpendicular to the beam. This radiation was transmitted by the lens 4 through the window of the vacuum chamber onto the input slit of a SPM-2 monochromator 5 with a quartz prism. The spectrometer slit was placed parallel to the electron beam. The radiation was recorded with FEU-39A 6 and recorded on the record strip of an ÉPPV-60 potentiometer 7. The pressure in the vacuum chamber was measured with a VIT-3 ionization vacuummeter with an MI-10 transducer. The factor scaling the indications of the ionization transducer from air to hydrogen chloride was set equal to 2.65.

The spectra were recorded at wavelengths ranging from $2.2\cdot10^{-4}$ to $1\cdot10^{-3}$ mm. Radiation at wavelengths exceeding $6.0\cdot10^{-4}$ and shorter than $2.8\cdot10^{-4}$ mm was not recorded. The emission spectrum at wavelengths ranging from $2.6\cdot10^{-4}$ up to $6.5\cdot10^{-4}$ mm is shown in Fig. 2. It was obtained with a gas temperature of 295 K, pressure of 10.6 Pa, beam current of 8.8-9.0 mA, energy of electrons in the beam equal to 10 keV, and the input and output monochromator slit widths equal to 0.15 mm. The spectrum was recorded in three ranges of sensitivity of the ÉPPV-60 potentiometer. To compare the intensities the readings must be multiplied by 100 in the most coarse range and by 10 in the least coarse range. These numbers are shown on the spectrogram. The spectrum was identified following [7, 8]. In the range studied primarily the $A^2\Sigma+ - X^2\Pi_i$ bands of the electronic transition (the scheme of the electronic states is shown in Fig. 1b) were recorded. Because of the large distance between $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ substates (644 cm^{-1} [7, 8]) two groups of bands (G_1 and G_2) are observed. The values of the vibrational quantum numbers are indicated in the spectrogram in parentheses: the first number is for the $A^2\Sigma+$ state and the second is for the $X^2\Pi_i$ state. The wavelengths of the transition, marked by an asterisk and not indicated in [7, 8], were calculated using the formulas

$$G(v') = T_e + \omega_e^A\left(v' + \frac{1}{2}\right) - \omega_e x_e^A\left(v' + \frac{1}{2}\right)^2,$$

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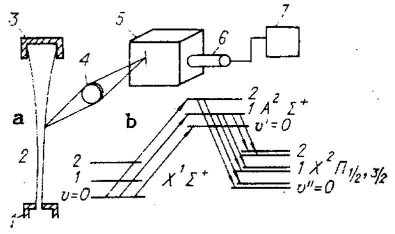

Fig. 1

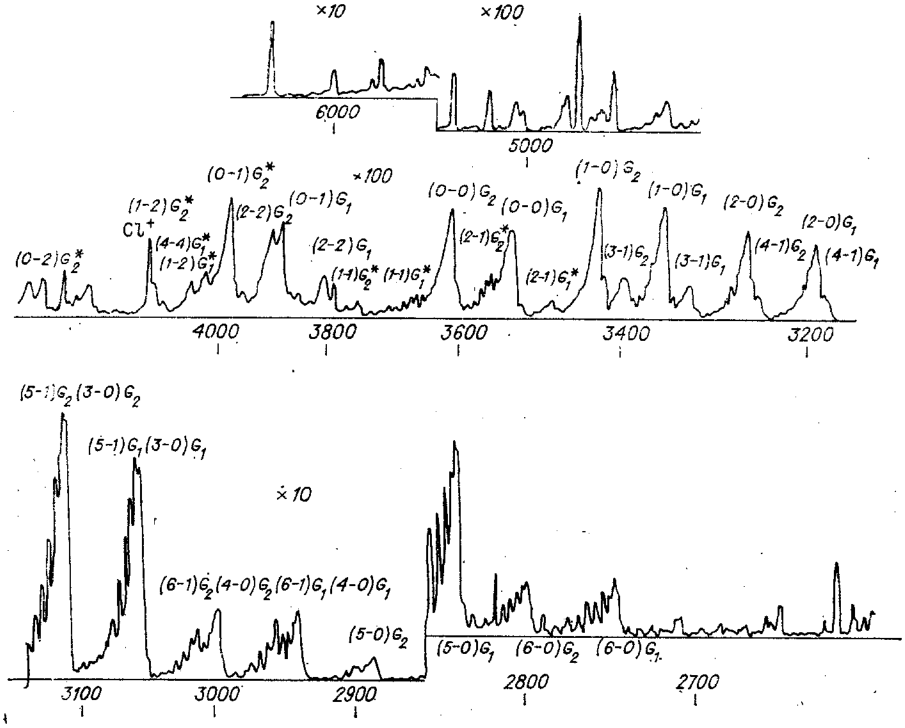

Fig. 2

$$G(v'') = \omega_e^{\Pi}\left(v''+\frac{1}{2}\right) - \omega_e x_e^{\Pi}\left(v''+\frac{1}{2}\right)^2 \pm \frac{A_e}{2},$$

$$\lambda = [G(v') - G(v'')]^{-1}.$$

The quantities $\omega_e{}^A = 1606.4\ \text{cm}^{-1}$, $\omega_e{}^{II} = 2673.7\ \text{cm}^{-1}$, $\omega_e x_e{}^{II} = 39.6\ \text{cm}^{-1}$, $\omega_e x_e{}^A = 53.5\ \text{cm}^{-1}$, $T_e = 28628.1\ \text{cm}^{-1}$, $A_e = 643.7\ \text{cm}^{-1}$ are taken from [9]. The lines and bands in the regions $\lambda > 4.5 \cdot 10^{-4}$ and $< 2.7 \cdot 10^{-4}$ mm were not identified, since a careful identification of the spectrum was not part of the problem addressed in this work. All transitions given in the table of [7] were recorded in the spectrum. The bands in the spectrum overlap strongly. Only the (0–0), (1–0), and (3–1), as well as the subbands (0–1) G_2 and (2–2)G_1 are free of overlapping.

To determine the mechanism of excitation of the $A^2\Sigma+$ state of the ion it is necessary to determine the dependence of the ratio of the band intensities in the spectrum on the beam current and the gas pressure. The dependence on the beam current was studied under a constant HCl vapor pressure of 3.2 Pa and is shown in Fig. 3. The intensities of the $I_{v'v''}$ are normalized to the sum $\sum_{v'}\sum_{v''} I_{v'v''}$. The integral of the band contour was taken as the band intensity; 1-8 corresponds to (0–0)G_1, (0–0)G_2, (1–0)G_2, (3–1)G_2, (2–0)(4–1)G_2, (3–0)(5–1)G_2, (4–0)(6–1)G_2, (5–0)G_1. For currents ranging from 1 to 10 mA no dependence of the ratios of the band intensities on the beam current was observed, and the spread observed in the experimental points for the bands (0–0), (1–0), (2–0)(4–1) lies within the error limits of the measurements and the data analysis.

The effect of the pressure on the radiation spectrum was studied in the pressure range from 1.3 to 60 Pa. The spectrograms for the extreme pressures are compared in Fig. 4. The

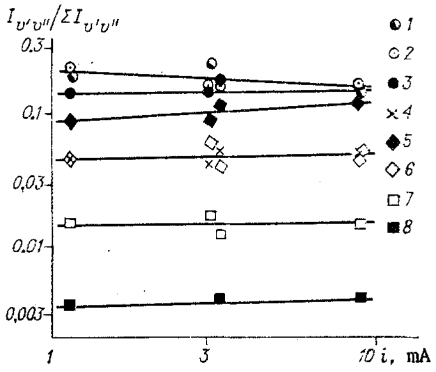

Fig. 3

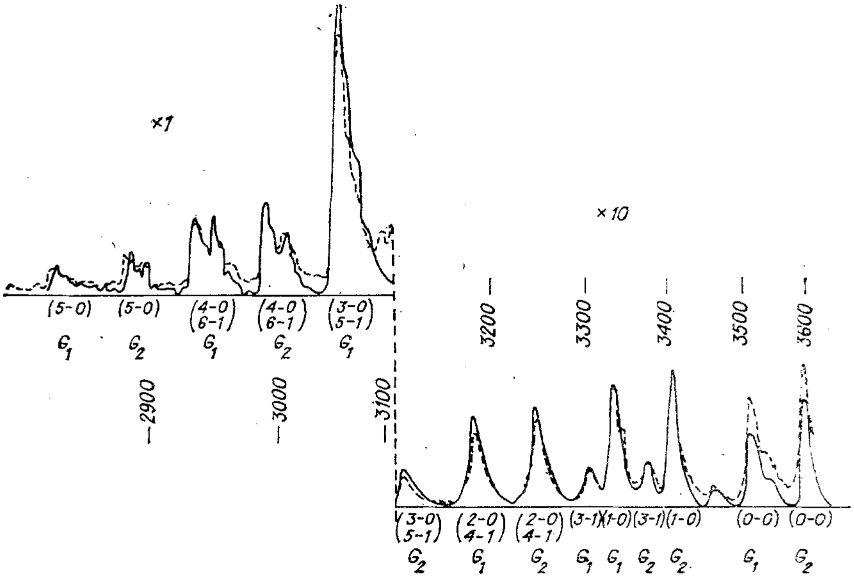

Fig. 4

spectrum shown by the solid line was obtained at a pressure of 1.3 Pa, and the spectrum shown by the broken line was obtained at a pressure of 60 Pa. The other conditions are the same for all spectrograms: the beam energy equals 10 keV and the input and output slit widths equal 0.15 mm. The notation is the same as that used in Fig. 2. For convenience of comparison the spectrograms are scaled to the same scale by normalization to the intensity of the (1–0) G_2 subband. One can see that as the gas pressure increases all bands are broadened owing to the extension of the tails, as if the gas temperature rises. The intensity of most bands relatively decreases as the pressure increases; the subbands (0–0) G_2 and (0–0) G_1 are exceptions.

More complete information about the changes in the spectrum accompanying an increase in the pressure is given in Fig. 5, which shows the band intensities normalized to their sum as a function of the pressure. As in Fig. 3, the band intensities were obtained by integrating the band contour. In Fig. 5 the points 1-6 correspond to (0–0) G_2, (1–0) G_2, (2–0)(4–1) G_2, (3–1) G_2, (3–0)(5–1) G_2, (4–0)(6–1) G_2. It is evident that the normalized intensities of the bands emitted from the zeroth vibrational level in the $A^2\Sigma+$ state increase substantially, while the remaining bands decrease insignificantly as the pressure increases. The lines show the calculation taking into account the extinction of the fluorescence. In the experiments on determining the effect of the pressure on the spectrum the pressure dependence of the band intensities was also measured. For this the monochromator was placed on a selected section of the spectrum and the band intensities were recorded at different pressures. The results are presented in Fig. 6 for the bands (0–0) and (1–0) in the form $I_{v'v''}/p \sim p$. The data are normalized to unity by extrapolating $I_{v'v''}/p$ to zero pressure. The lines show the calculation according to the model described below.

Analysis. The intensity of a band is given by

$$I_{v'v''} = Chc\nu_{v'v''}A_{v'v''}n_{v'}, \tag{1}$$

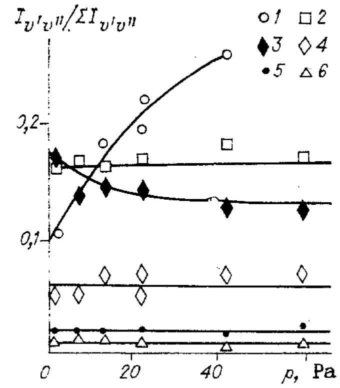

Fig. 5

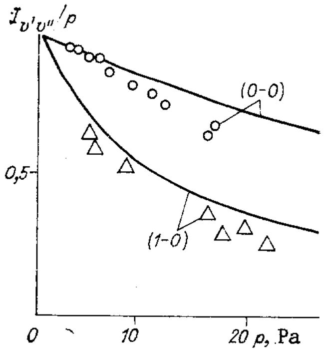

Fig. 6

where C, h, c, $\nu_{v'v''}$, $A_{v'v''}$ are the instrumental constants, Plank's constant, the velocity of light, the transition frequency, and Einstein's coefficient for the given electronic-vibrational transition. The population of the level $n_{v'}$, in the $A^2\Sigma^+$ state is established by the balancing of the pumping and annihilation processes:

$$\sum_{v''} A_{v'v''} n_{v'} + n_{v'} n K_{v'}^{q} = \Sigma R_i .$$

In this expression the first term on the left determines the rate of annihilation of the v' level in $A^2\Sigma+$ by spontaneous emission, the second term is the rate of annihilation of the v' level owing to nonradiative transitions in collisional excitations of HCl^+ ions with neutral molecules; $K_{v'}{}^q$ is the fluorescence extinction constant; n is the density of the gas; the sum on the right is the rate of excitation of the $A^2\Sigma+$ state. The processes leading to excitation of the $A^2\Sigma+$ state can be as follows:

$$\mathrm{HCl}X^1\Sigma + e_b \rightarrow \mathrm{HCl}^+A^2\Sigma^+ + e_s; \qquad (2a)$$

$$\mathrm{HCl}X^1\Sigma + e_s \rightarrow \mathrm{HCl}^+A^2\Sigma^+ + e_s; \qquad (2b)$$

$$\mathrm{HCl}^* + e_{b,s} \rightarrow \mathrm{HCl}^+A^2\Sigma^+ + e_s; \qquad (2c)$$

$$\mathrm{HCl}^* + \mathrm{HCl}^* \rightarrow \mathrm{HCl}^+A^2\Sigma^+ + \mathrm{HCl}. \qquad (2d)$$

Here e_b and e_s are the primary and secondary electrons; HCl^* denotes HCl molecules in different electronic as well as vibrationally excited states, as well as the molecular ion in the $X^2\Pi_i$ state. The actual process that leads to the excitation of the $A^2\Sigma+$ state can be determined by comparing the dependences of the radiation intensities on the beam current and the gas pressure according to the proposed process with those obtained in the experiment.

The excitation by primary electrons

$$R_a \sim n n_b v_b \sigma,$$

where n_b, v_b, and σ are the density, the velocity, and the cross section for the excitation of the $A^2\Sigma+$ state by primary electrons; the product $n_b v_b$ is proportional to the beam current. Therefore,

$$I_{v'v''}/R_a \sim I_{v'v''}/i_b n = \mathrm{const}.$$

The excitation of neutral molecules by secondary electrons is given by

$$R_b \sim \int_V \int_{v_s} n n_s \sigma v_s f(v_s) dv_s dV.$$

Here n_s, v_s, and $f(v_s)$ are the density, velocity, and the velocity distribution function (normalized to V) of secondary electrons. The contribution of the secondary electrons also depends strongly on the observation volume [10]. Since the flux of secondary electrons is proportional to the beam current and the gas pressure

$$I_{v'v''}/i_b n \sim n.$$

Since the density of excited particles is proportional to the current and density, according to the excitation mechanisms (2c) and (2d)

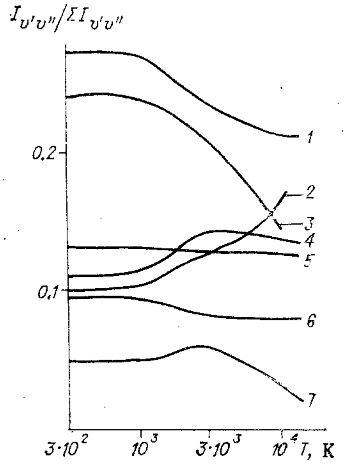

Fig. 7

TABLE 1

v'	$q_{0v'}$	
	Theory	Experiment
0	0.1528	0,202
1	0,2462	0,240
2	0,2293	0,258
3	0.1632	0.109
4	0,0992	0,079
5	0.0545	0.090
6	0,0281	0,022

TABLE 2

Transition	$\sigma^{XA}_{HCl}/\sigma^{XB}_{N_2}$
(1—0) G_1	0,198
(1—0) G_2	0.237
(3—1) G_2	0.223
(0—0) G_1	0,257
(0—0) G_2	0,287

$$I_{v'v''}/i_b n \sim i_b n.$$

The fact that the intensity distributions for the bands in the spectrum are independent of the beam current (see Fig. 3) indicates that the $A^2\Sigma+$ state of HCl^+ is excited by direct electron impact on neutral molecules HCl. At the same time the nonlinearity of the pressure dependences of the band intensities I_{00} and I_{10} in Fig. 6 and the redistribution of the band intensities depending on the pressure in Fig. 5 indicate that secondary electrons can contribute to the excitation of the $A^2\Sigma+$ states and the fluorescence can be extinguished in collisions of the excited ion with neutral molecules. In the case when the excitation occcurs by direct electron impact of the primary and secondary electrons, while the annihilation of the vibrational levels occurs via spontaneous emission and extinction, the intensity of the bands from the chosen volume in the electron beam gives the expression [11]

$$I_{v'v''} = C(\lambda)\frac{\tau_{v'}hc\nu_{v'v''}A^{A\Pi}_{v'v''}\left[n_b v_b \sum\limits_{v} \sigma_{vv'} n_v + \int\limits_{v_s} n_s v_s \sum\limits_{v} \sigma_{vv'} n_v dv_s\right]}{1+\tau_{v'} n_{v'} K^q_{v'}}, \tag{3}$$

where $\tau_{v'}^{-1} = \sum\limits_{v''} A_{v'v''}$ is the lifetime of the v' level and C(λ) is the instrumental constant. In the derivation of this expression it was assumed that the vibrational relaxation in the $A^2\Sigma+$ state and the changes in the population of the levels owing to radiation accompanying vibrational transitions from the $A^2\Sigma+$ state are insignificant. At low pressures extinction and the contribution of secondary electrons can be neglected, so that when the gas is at room temperature and the zeroth vibrational level in the $X^1\Sigma$ is primarily populated, the expression for the band intensity simplifies:

$$I_{v'v''} = C_1(\lambda) n_b v_b hc\nu^4_{v'v''} q_{v'v''} q_{0v'} \sigma^{XA} n_0.$$

Here $C_1(\lambda) = C(\lambda)\sigma^{A\Pi} 64\pi^4 c/3$; $A^{A\Pi}_{v'v''} = \frac{64\pi^4\sigma^{A\Pi}\nu^3_{v'v''}q_{v'v''}}{3h}$; $\sigma_{0v'} = q_{0v'}\sigma^{XA}$. After normalization to the sum of the band intensities

TABLE 3

v'	$\tau_{v'} K^q_{v'}$, cm^3	$\tau_{v'}\cdot 10^5$, sec	$K^q_{v'}$, cm$^3\cdot$sec^{-1}	v'	$\tau_{v'} K^q_{v'}$, cm^3	$\tau_{v'}\cdot 10^5$, sec	$K^q_{v'}$, cm$^3\cdot$sec^{-1}
Σ	$3.73\cdot 10^{-16}$	0.26	$1,43\cdot 10^{-10}\pm 40\%$	3	$3,40\cdot 10^{-16}$	1,64	$2,08\cdot 10^{-11}\pm 40\%$
0	$8,11\cdot 10^{-17}$	1,26	$6,42\cdot 10^{-12}\pm 40\%$	4	$3,73\cdot 10^{-16}$	1.83	$2,05\cdot 10^{-11}\pm 70\%$
1	$3.59\cdot 10^{-16}$	1,37	$2.63\cdot 10^{-11}\pm 40\%$	5	$3,73\cdot 10^{-16}$	2.05	$1.82\cdot 10^{-11}\pm 90\%$
2	$5.14\cdot 10^{-16}$	1,50	$3,42\cdot 10^{-11}\pm 40\%$				

$$\frac{I_{v'v''}}{\sum\limits_{v'v''} I_{v'v''}} = \frac{C_1(\lambda)\, \nu^4_{v'v''} q_{v'v''} q_{0v'}}{\sum\limits_{v'v''} C_1(\lambda)\, \nu^4_{v'v''} q_{v'v''} q_{0v'}}. \tag{4}$$

Bands with v' ≤ 6 were recorded in the spectrum, and summation up to v' = 6 does not take $\sum\limits_{v'v''} I_{v'v''}$ into account exactly, but as the calculation of the Franck–Condon factors shows [12], $\left(1-\sum\limits_{0}^{6} q_{0v'}\right) = 0.027$; this error is less than the experimental error and the error in the analysis of the experiment, and can be neglected. After the equality (4) is normalized to the expression for the intensity of the (0–0) band we obtain the working formulas for the Franck–Condon factors:

$$\frac{q_{0v'}}{q_{00}} = \frac{I_{v'v''} C_1(\lambda)\, \nu^4_{0v''} q_{0v''}}{I_{0v''} C_1(\lambda)\, \nu^4_{v'v''} q_{v'v''}}.$$

From the normalization rule $\sum\limits_{v'} q_{0v'} = 1$ we obtain

$$\sum_{v'} q_{0v'}/q_{00} = 1/q_{00}.$$

The values of the intensities needed for the calculation are measured experimentally, the instrumental constant $C_1(\lambda)$ is determined by the conditions of the experiment, and the frequencies of the quanta in the bands $\nu_{v'v''}$ and the Franck–Condon factors in the radiation $q_{v'v''}$ are taken from [7, 8]. To calculate the Franck–Condon factors spectrograms obtained with minimum pressure in the chamber (1.3 Pa), when the effect of extinction of fluorescence and excitation of $A^2\Sigma^+$ by secondary electrons is small, were analyzed. The spectral sensitivity of the apparatus was taken into account based on the spectra of the first negative system of bands of nitrogen, for which the ratio of the band intensities is quite well-known [1]. The results of the analysis of the experiments are presented in Table 1, which also gives the results of the calculations of $q_{0v'}$ from [12]. As one can see, theory and experiment agree satisfactorily for all v' except v' = 0, which could be linked with the large error in the calculation of q_{00}.

The cross sections for excitation from $X^1\Sigma$ into $A^2\Sigma^+$ by electron impact can be calculated from the intensities of the bands in the spectra of hydrogen chloride and nitrogen:

$$\frac{\sigma^{XA}_{\mathrm{HCl}}}{\sigma^{XB}_{\mathrm{N}_2}} = \frac{I^{\mathrm{HCl}}_{v'v''}}{I^{\mathrm{N}_2}_{v'v''}} \left(\frac{\nu^{\mathrm{HCl}}_{v'v''}}{\nu^{\mathrm{N}_2}_{v'v''}}\right)^4 \frac{q^{\mathrm{HCl}}_{v'v''}}{q^{\mathrm{N}_2}_{v'v''}} \frac{q^{\mathrm{HCl}}_{0v'}}{q^{\mathrm{N}_2}_{0v'}} \frac{C_1^{\mathrm{HCl}}(\lambda)}{C_1^{\mathrm{N}_2}(\lambda)} \frac{i_b^{\mathrm{N}_2} p_{\mathrm{N}_2}}{i_b^{\mathrm{HCl}} p_{\mathrm{HCl}}} \left(1+\tau_{v'} n_{v'} K^q_{v'}\right)_{\mathrm{HCl}}.$$

Here the indices HCl and N_2 denote the corresponding quantities in the experiments with HCl and N_2; i_b and p are the current and pressure. The results of the calculation of the cross section ratios are presented in Table 2. The average value equals 0.24 ± 20%. The relative error equals 30% and is determined primarily by the uncertainty of the gas pressure.

It follows from the expression (3) that the sum-normalized band intensities for arbitrary gas density are given by

$$\frac{I_{v'v''}}{\Sigma I_{v'v''}} = \frac{1+K^q_{\Sigma}\tau^{\Sigma} n_0}{1+K^q_{v'}\tau_{v'} n_0} \left(\frac{I_{v'v''}}{\Sigma I_{v'v''}}\right)_0,$$

where $(I_{v'v''}/\Sigma I_{v'v''})_0$ are the normalized band intensities in those cases when the extinction of fluorescence can be neglected; $K_{v'}q$ are the extinction constants for the v' vibrational levels in $A^2\Sigma+$;

$$K_{\Sigma}^{q}=\frac{\Sigma K_{v'}^{q} n_{v'}}{\Sigma n_{v'}};\ \tau_{v'}=\frac{1}{\sum\limits_{v''} A_{v'v''}};\ \tau^{\Sigma}=\frac{1}{\sum\limits_{v'}\sum\limits_{v''} A_{v'v''}}.$$

The extinction constants can be found from the experimentally determined pressure dependences of the band intensities (see Fig. 5). For this the experimentally measured pressure dependences of the band intensities were approximated by the computed dependences, and the coefficients were determined by the method of least squares. The results of calculations of $\tau_{v'}K_{v'}{}^{q}$, $\tau_{v'}$, and $K_{v'}{}^{q}$ and the errors in $K_{v'}{}^{q}$ are given in Table 3. The computed values of the band intensities are presented in Fig. 5 (the lines). One can see that the experimental data are satisfactorily described with the help of the constants obtained. The data on the pressure dependences of the band intensities I_{00} and I_{10} (see Fig. 6) are also satisfactorily described by the extinction of fluorescence. The disagreement between the calculation (solid lines) and experiment at high pressures is caused by incomplete trapping of radiation from the aureole around the beam. As one can see from Table 3, the extinction constants $K_{v'}{}^{q}$ depend on the vibrational quantum number v'. This dependence of the extinction constants on v' is also observed for nitrogen [13]. The quantum number selective extinction of fluorescence leads to the fact that the inversion distribution of the vibrational level populations, observed in [12], is destroyed as the gas pressure is raised.

The experimental confirmation of the direct mechanism of excitation of the $A^2\Sigma+$ state and the Franck–Condon principle for excitation of the $A^2\Sigma+$ state of HCl^+ makes it possible to measure the populations of the vibrational levels and the vibrational temperatures in the ground state of HCl from the radiation excited by the electron beam. The extent to which the distribution of the band intensities is sensitive to the gas pressure can be judged from the calculation of the intensities shown in Fig. 7. It was obtained from the formula (1) with a Boltzmann population distribution of the vibrational levels in the $X^1\Sigma$ state of HCl and using the Franck–Condon factors from [12]; curves 1-7 correspond to (2–0)(4–1)G_2, (3–0)(5–1)G_2, (1–0)G_2, (0–0)G_1, (0–0)G_2, (3–1)G_2, (4–0)(6–1)G_2. Fluorescence extinction can be taken into account based on the constants of this work, and in addition, as follows from [13], the temperature dependence of the extinction constants is insignificant. Figure 7 shows that at 10^3 K the ratio of the band intensities begins to depend quite strongly on the temperature of the gas, and the vibrational temperatures can be calculated based on these ratios.

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TRANSPORT PROCESSES IN VIBRATIONALLY EXCITED MOLECULAR GASES

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UDC 539.196

There has recently been significantly increased interest in studies and applications of molecular gases in conditions far from equilibrium when the amount of vibrational energy of the molecules markedly exceeds the equilibrium value corresponding to the temperature of the gas. Such conditions occur in gaseous discharges, in outflow of a very hot gas from a nozzle, in relaxation zones behind shock waves, etc. The distribution of molecules in the vibrational states can be of a non-Boltzmann character in these conditions and therefore the transport processes in a vibrationally excited nonequilibrium gas differ from the equilibrium case. For a small difference between the vibrational and translational temperature when the Boltzmann distribution of vibrational degrees of freedom is realized via fast V–V processes, the transport coefficients are calculated in [1, 2]. Here we analyze the case of a large difference between the vibrational and translational temperature when the regime of quasiresonance exchange is realized [3]. Moreover, for low vibrational levels ($i \le i_*$) the distribution of molecules on the vibrational levels is of the Treanor type with a characteristic vibrational temperature T_V determined by the full margin of the vibrational energy; on higher levels ($i_* < i \le i_{**}$) the distribution of molecules forms a plateau which for $i > i_{**}$ becomes the equilibrium Boltzmann distribution with the gas temperature T via a strong V–T exchange. We will limit ourselves to the case when the spatial inhomogeneities only slightly perturb the above distribution. For weak variations of the parameters in space and time one obtains a quasistationary and quasihomogeneous regime when the distribution preserves its form and is determined by its local parameters – gas and vibrational temperatures. This approximation holds when the flow of molecules in vibrational levels is much larger than the flow due to spatial diffusion [4].

The kinetic equation for the distribution function of molecules in velocities and nonequilibrium populations has the form of Wang Chang–Uhlenbeck equations [5]

$$\varepsilon\left(\partial f_{\alpha i}/\partial t + \mathbf{v}_\alpha \nabla f_{\alpha i}\right) = J_{\alpha i}^{TT} + \eta J_{\alpha i}^{R}, \quad J_{\alpha i}^{R} = J_{\alpha i}^{VV} + J_{\alpha i}^{VT} + J_{\alpha i}^{l}. \tag{1}$$

Here $f_{\alpha i}(\mathbf{v}_\alpha, \mathbf{r}, t)$ is the distribution function in velocities of particles of type α in vibrational state i with velocity $\mathbf{v}_\alpha$; on the right-hand side we have the collisional integrals taking into account the processes of elastic $J_{\alpha i}^{TT}$ and inelastic $J_{\alpha i}^{R}$ collisions including V–V ($J_{\alpha i}^{VV}$) and V–T ($J_{\alpha i}^{VT}$) exchanges and sources $J_{\alpha i}^{\ell}$ of population of the vibrational levels due to external interaction (excitation by electron impact, infrared radiation, laser-chemical reactions, etc.); $\varepsilon \ll 1$ is the Knudsen number; $\eta = \sigma_R/\sigma_{TT}$ is the ratio of the cross sections of the inelastic and elastic processes. In contrast to the equilibrium Boltzmann population of the vibrational levels when $\eta \ll 1$, in the considered conditions the effects of vibrational anharmonicity are substantial when the cross sections of the inelastic processes on upper vibrational levels equal the cross sections of the elastic processes and therefore $\eta \le 1$. To obtain the solution of the kinetic equation in this case we will use the generalized Chapman–Enskog method [6] developed for arbitrary ratios of elastic and inelastic processes (i.e. the

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