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COLLISIONAL QUENCHING OF THE $A^2\Sigma^+(v' = 2)HF^+$ STATE BY He ATOMS

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Results of an experimental study of the process of quenching of excited states of HF^+ *ions in a hydrofluoride–helium electron-beam plasma are reported. The rate constant of quenching of* $A^2\Sigma^+(v' = 2)HF^+$ *by helium atoms is measured. The ions were excited by activation of the rarefied gas mixture by an electron beam. Diagnostics of internal states of the ions was performed using the electron-vibration-rotation spectrum of their spontaneous emission.*

Introduction. The process of collisional of quenching of excited states of molecular ions is actually a separate class of gas-phase reactions. This is due primarily to the fact that ions experience strong electrostatic attraction, described by the long-range part of the interaction potential. For gases at room temperature, this effect largely determines the course of vibrational relaxation [1, 2]. As a result, quenching of molecular ions proceeds at a high rate: for almost all neutral quenchers, except for rare gases and molecular hydrogen, the probability of quenching exceeds 10^{-3}. In addition, as the relative kinetic energy increases, the rate constant of quenching of vibrational levels of the ions decreases. Unlike ions, the process of quenching of neutral molecules is characterized by low rate and direct temperature dependence of the quenching rate constant [3].

In the present work, the population and deactivation of vibration–rotation levels of the short-lived electron state $A^2\Sigma^+$ is studied using HF^+ ions because of the necessity of studying kinetic processes in a plasma containing hydrogen halides (including processes in the upper layers of the Earth's atmosphere) and also because of the practical problem of developing a method of electron-beam diagnostics of hydrogen halides [4, 5]. In addition, the HF^+ ion is one of the simplest systems with a hydrogen bonding possessing a considerable dipole moment.

Experimental Equipment and Measuring Procedure. The experimental technique and the procedure of electron-beam measurements are described in [6, 7]. Analysis of the electron-beam emission spectra of a mixture of hydrogen fluoride with helium (5% HF + 95% He) showed that the 2–0 band of the $A^2\Sigma^+$–$X^2\Pi_i HF^+$ transition is most free from overlaps of the peaks of atomic hydrogen and fluorine and also from the bands due to residual nitrogen. Figure 1 gives experimentally obtained emission spectra of the mixture of HF and He excited by an electron beam at pressures $P = 130$, 5, and 2.3 Pa, and a calculated spectrum at an equilibrium rotational temperature of the ion $T_R = 290$ K (in the calculation, the spread function of the spectra-recording system was taken into account). The positions of the rotational bands of the HF^+ ion are shown at the bottom of the figure (each recorded peak of the ion consists of several unresolved bands).

Comparison of the experimental and calculated spectra allowed us to distinguish nonoverlapping peaks of the HF^+ ion (they are hatched). The ratio of the intensities of these peaks recorded at low pressure corresponds to the calculated ratio at a temperature $T_R = 290$ K (Table 1). Comparison of the spectra in Fig. 1 shows that as the pressure is changed, the intensities of the peaks of impurities (primarily, of the second positive system of bands of molecular nitrogen) increase and the ratio of the peak intensities of the hydrogen fluoride ion changes.

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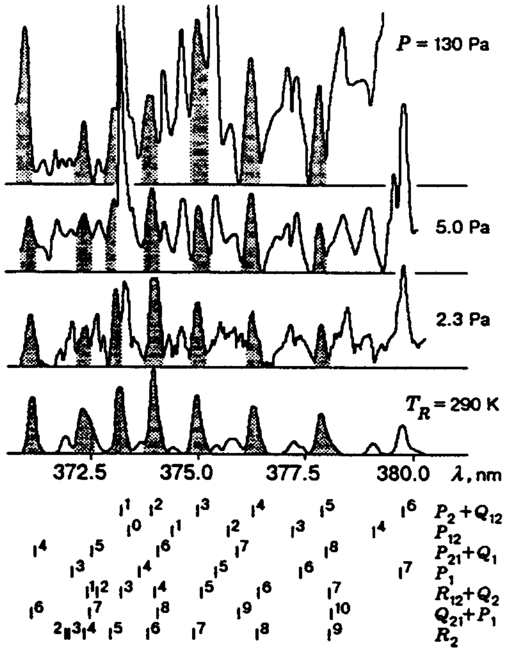

Fig. 1. Segment of the spectrum of the 2–0 band of the $A^2\Sigma^+$–$X^2\Pi_i$HF$^+$ transition.

TABLE 1

λ, nm	$I/\Sigma I$	
	Experiment (P_H = 2 Pa)	Calculation (T_R = 290 K)
371.1	0.13	0.14
372.5	0.12	0.11
373.2	0.17	0.17
374.0	0.21	0.21
375.0	0.15	0.15
376.3	0.12	0.12
377.8	0.10	0.10

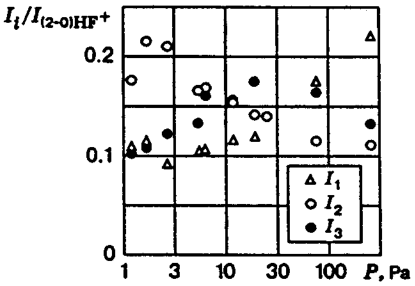

Fig. 2. Intensities of individual peaks of the 2–0 band normalized by the intensity of the entire band versus pressure: peaks I_1, I_2, and I_3 correspond to λ = 371.1, 374.0, and 377.8 nm, respectively.

The change in the relative contribution of individual peaks to the intensity of the 2–0 band is illustrated in Fig. 2, which shows the dependences of intensities on pressure for peaks I_1–I_3, which correspond to the following wavelengths: peak I_1 corresponds to $\lambda = 371.1$ nm (lines $4P_{21}$, $4Q_1$, $6Q_{21}$, and $6R_1$ make the major contribution); peak I_2 to $\lambda = 374.0$ nm (lines $2P_2$ and $2Q_{12}$), and peak I_3 to $\lambda = 377.8$ nm (lines $5P_2$ and $5Q_{12}$). The intensities are normalized by the intensity of the entire I_{2-0} band. Thus, as the pressure increases, the intensities of transitions from high-lying levels, and hence, their occupancies increase.

Analysis of Results. The integral intensity of the 2–0 HF$^+$ band versus pressure is shown in Fig. 3a. On the initial segment ($P < 10$ Pa), the intensity of the band increases linearly. With a further increase in pressure, the slope of the curve decreases, indicating the processes of deactivation of the radiating state $A^2\Sigma^+(v' = 2)\,$HF$^+$, which are competitive with spontaneous radiation. These processes can be described by introducing an integral quenching rate constant that takes into account purely collisional deactivation, leading

TABLE 2

Ion	Damper	K_q, cm^3/sec	Source
HF^+	He	$33.0 \cdot 10^{-12}$	Present work
HF^+	HF	$28.5 \cdot 10^{-10}$	[8]
HCl^+	He	$< 0.3 \cdot 10^{-12}$	[9]
HCl^+	HCl	$34.0 \cdot 10^{-12}$	[10]
HCl^+	Ar	$3.5 \cdot 10^{-10}$	[9]

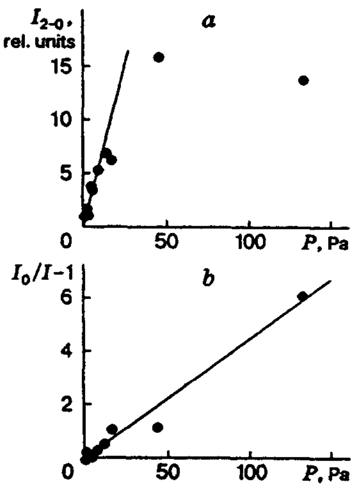

Fig. 3

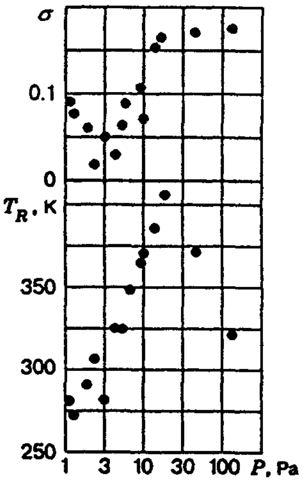

Fig. 4

Fig. 3. Integral intensity of the 2–0 HF^+ band versus pressure (a) and the Shtern–Volmer dependence for the intensity of the 2–0 HF^+ band (b).

Fig. 4. Rotational temperature T_R of the $A^2\Sigma^+(v' = 2)HF^+$ state and the degree of departure from equilibrium σ versus the pressure of the mixture.

to exit of the ion from the $A^2\Sigma^+HF^+$ state, and vibration–rotation relaxation inside the excited state. For the dependence of the band intensity on pressure, quenching of fluorescence is described by the Shtern–Volmer relation: $I_0/I = 1 + K_q\tau_{v'}n_0$, where I is the measured intensity of the band at a certain pressure, I_0 is the band intensity in the absence of quenching, K_q is the quenching constant of the vibrational state, $\tau_{v'}$ is the lifetime of the state, and n_0 is the gas density. To determine I_0, we used a linear approximation (the straight line in Fig. 3a), constructed by the least-square method from the band intensities measured under conditions where the contribution of collision processes was negligibly small.

The degree of departure of experimentally measured intensities from the approximating straight line allowed us to determine the value of $K_q\tau_{v'}$. For this, we plotted the Shtern–Volmer dependence in the coordinates $(I_0/I - 1)$ and P (Fig. 3b). By linear approximation of the points in Fig. 3b using the value $\tau_{v'} = 5.7$ μsec from [8], we obtained a value of $K_q = 3.3 \cdot 10^{-11}$ cm^3/sec for the constant of quenching of the $A^2\Sigma^+(v' = 2)\,HF^+$ state by helium atoms. The constant of quenching of the same state HF^+ by neutral hydrogen fluoride molecules measured in [8] is $2.85 \cdot 10^{-9}$ cm^3/sec. According to the data of [9], the constants of quenching of the ground state $X^2\Pi_i$ of the hydrogen chloride ion by helium and argon are smaller than $0.3 \cdot 10^{-12}$ cm^3/sec and $3.5 \cdot 10^{-10}$ cm^3/sec, respectively. The integral constants of quenching of the vibrational levels in $A^2\Sigma^+HCl^+$ by hydrogen chloride molecules are given in [10]. Comparison of the constants (Table 2) shows that the rate of quenching of the vibrational levels of both hydrogen fluoride and chloride ions by their neutral molecules is two orders of magnitude higher than the rate of quenching by helium atoms. In both cases, the quenching rate of the heavier hydrogen chloride ion is two orders of magnitude lower than that of the hydrogen fluoride ion.

The results given in Figs. 1 and 2 and similar results show that an increase in the density of the gas mixture leads to relative overpopulation of the high rotational levels of the HF^+ ion. The intensity distribution in the spectrum recorded at a minimum pressure agrees well with a calculation in which the rotational temperature is assumed to be equal to the gas-kinetic temperature. For spectra recorded at elevated pressures, it is of interest to determine the rotational temperature T_R that most closely corresponds to the given distribution of peak intensities and the degree of departure of σ of this distribution from equilibrium. The latter quantity was defined as $\sigma = \sum_i |I^i_{\text{calc}}/I^i_{\text{exp}} - 1|$, where the subscripts calc and exp mean the calculated and experimental intensities, respectively.

Figure 4 shows the degree of departure from equilibrium σ (the upper graph) and the calculated rotational temperature of the $A^2\Sigma^+(v' = 2)\,HF^+$ state (the lower graph) versus the pressure of the mixture. An increase in the density of the gas mixture leads to an increase in both the temperature and the degree of nonequilibrium of the occupancies of the rotational levels of the radiating state, so that at pressures above 10 Pa, the occupancies have a non-Boltzmann distribution ($\sigma > 0.1$). The slight increase in σ at pressures below 2 Pa is explained by an increase in the measurement error, because the amplitude of the signal measured at these pressures is small and noise begins to manifest itself.

Such behavior of the occupancies and rotational temperatures of the levels of the HF^+ ion differs from similar dependences for the hydrogen chloride ion [11], probably because the rotational quantum for HF^+ is twice as large as that for HCl^+. As a result, the probability of rotational transitions in collisions decreases exponentially, and this limits the rate of redistribution of the energy transferred to the rotational degrees of freedom in collisional relaxation of vibration-excited ions. Barbeau et al. [12] also came to the same conclusions. They explained the nonequilibrium distribution of the occupancies of the high rotational levels of excited hydrogen molecules in a low-temperature plasma by the large magnitude of the rotational quantum.

Conclusions. It is shown that in vibrational relaxation of excited states of the hydrogen fluoride ion, part of the energy is transferred to the rotational degrees of freedom. This agrees with the conclusions of [13], made within the framework of the model of isolated binary collisions. The rate constant of quenching $A^2\Sigma^+(v' = 2)$ of the vibrational state of the HF^+ ion by helium atoms is measured.

Results of the study of the mechanisms determining the occupation of the internal degrees of freedoms of the hydrogen fluoride ion in the short-lived electron state $A^2\Sigma^+$ populated by means of electron impact in collisions of excited ions with background gas can be used in modeling gas-phase processes in plasmachemical reactors, the upper layers of the Earth's atmosphere, and also in spectral measurements of parameters of media containing molecular hydrogen fluoride.

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