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ELECTRON-BEAM DIAGNOSTICS OF HYDROGEN FLUORIDE. OPTICAL MODEL AND ITS LIMITATIONS

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In the study of many molecular systems by means of electron-beam diagnostics (EBD) using the Muntz method [1], one observes differences from the optical model that show up at densities above $1 \cdot 10^{15}$ particles/cm^3. It was found that these deviations may be due to the presence of secondary processes, nonlinear in pressure, in the excitation and deactivation of the molecules: multiquantum transitions [2], excitation by secondary electrons [3], fluorescence (possibly, selective) quenching during oscillations of excited ions with molecules of the background [4], etc. Therefore, use of the EBD method in the study of new molecular systems is impossible without the development of an adequate excitation–radiation model with a detailed analysis of the probable channels of population and emptying of the radiating states. Such a model becomes more complicated, the more complex the structure of the electronic states. An EBD method has now been developed, and models for the N_2, CO_2, CO, and HCl molecules have been constructed [5-8].

This paper presents the results of a study of the emission spectra of hydrogen fluoride excited by an electron beam, results obtained from constructing a model of the excitation–deactivation processes of HF^+ ion, and results of determination of the scope of applicability of the EBD technique to hydrogen fluoride mixtures. The spectra of HF are of major interest in connection with the extensive use of hydrogen halides as optical media for high-power chemical lasers.

1. Let us examine the process of electron-impact excitation–radiation of HF. The radiation intensity of a rotational line is [9]

$$I_{v'v''}^{j'j''} = Chc\nu_{v'v''}^{j'j''}A_{v'v''}^{j'j''}n_{j'},$$

where C is the instrument function; h is Planck's constant; c is the speed of light in a vacuum; $\nu_{v'v''}^{j'j''}$ is the frequency of the rotational transition; $A_{v'v''}^{j'j''}$ is Einstein's coefficient for spontaneous emission; $n_{j'}$ is the population of the rotational level in the $A^2\Sigma^+$ state of HF^+, established as a result of a balance between the processes of population and emptying of the radiant state.

The main channels of population of the levels are: direct impact of primary and fast secondary electrons — mechanism 1.1, excitation via an intermediate state — 1.2, vibrational-rotational heating by slow secondary electrons (below the ionization threshold) followed by ionization — 1.3, excitation by low secondary electrons (but higher than the ionization threshold) with violation of optical selection rules — 1.4, relaxation from higher-lying levels — 1.5.

Emptying of the levels can occur as follows: by spontaneous emission — mechanism 2.1, by fluorescence (possibly, selective) quenching during collisions of excited ions with molecules of the background, resulting in the ion leaving the $A^2\Sigma^+$ state — 2.2, and by vibrational-rotational relaxation of the $A^2\Sigma^+$ state — 2.3.

When the population process is determined by mechanism 1.1 and the emptying process by 2.1, i.e., when $R_{11} \gg (R_{12}R_{13}R_{14}R_{15})$ and $R_{21} \gg (R_{22}R_{33})$, it is easy to construct a model by means of which, using the recorded emission spectrum, one can determine the populations of the energy levels (vibrational or rotational populations) in the ground state, and by measuring the parameters of the gaseous medium (studies in supersonic flow) — the kinetics of the relaxation process. In practice, the process of electron impact excitation is not quite as ideal.

Experimental determination of the influence of certain secondary processes makes it necessary to know the dependence of their rates on the density of the gas and of the electron-beam current. During excitation by direct electron impact (mechanism 1.1), the population rate R_{11} is proportional to the density of the molecules and electron-current density ($R_{11} \sim in$). For mechanism 1.2, the rate of excitation to $A^2\Sigma^+$ is proportional to the product of the population of the intermediate state by the

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current density ($R_{12} \sim (in)i = i^2n$). During vibrational-rotational heating of the ground state followed by excitation to $A^2\Sigma^+$ (mechanism 1.3), $R_{13} \sim (in)ni = i^2n^2$. In direct excitation by slow secondary electrons with violation of optical selection rules (mechanism 1.4), $R_{14} \sim (in)n = in^2$. Finally, for relaxation population (mechanism 1.5), the rate of the process is proportional to the population of the higher-lying level ni and to the gas density n, i.e., $R_{15} \sim (in)n = in^2$. Thus, a check of the dependence of the band strengths and of the distribution of the strengths within a band on the electron beam current and HF vapor density makes it possible to determine the excitation channels of the levels in $A^2\Sigma^+$ of HF^+.

2. In the course of the studies, we recorded the emission spectra of the $A^2\Sigma^+ - X^2\Pi_i$ transition of HF^+ ion and of atomic hydrogen and fluorine. The experiments were carried out in accordance with the standard EBD scheme on a stand specially designed for work with hydrogen halides. We used a DFS-12 spectrometer with an FÉU-118 photomultiplier cooled with liquid nitrogen. The photomultiplier signal was fed to an IMT-05 amplifier and recorded with a KSP-4 potentiometer. The measurements were taken under pressure-static conditions determined by a continuous supply of the gas to the chamber and continuous evacuation, so that a weak equilibrium flow was maintained. In order to provide for the predominance of collisions of HF molecules with structureless particles, an HF−He mixture containing 6-8% of HF by volume was used. The technique of the electron-beam measurements in HF and a review of the spectra over a wide spectral range are given in [10]. The wavelengths of the rotational lines were calculated by use of the formulas given in [11].

The dependence of the band strength ratio in the emission spectrum of HF^+ ion on current was determined in the range i = 3.35-18 mA. The lack of data at lower i values is due to the fact that the emission strengths of the lines in the (1−0), (2−0), and (3−0) bands at pressures optimal for such measurements were low, and the signal could not be reliably recorded at lower currents. However, as is known from the data of [3], deviations from linear curves should be expected at high values of current, and therefore, these measurements are more informative. Since the emission bands of HF^+ ion are overlapped by the lines of atomic fluorine, hydrogen, and other impurities [10], the spectra were recorded with the maximum resolution provided by the recording system. The lines of HF^+ were isolated in the spectrum obtained and were used to carry out the summation of the strengths. Such processing did not involve recording the total band strength, and therefore, only relative measurements can be discussed. Figure 1 shows as a function of current the strengths of band regions (1−0) and (2−0) processed in this manner (points 1 and 2) and their ratio I_{2-0}/I_{1-0} (points 3). Within the measurement error, the observed dependences of the strengths I_{1-0}, I_{2-0} are linear (dashed and dot-dash approximating curves, respectively), and their ratio is independent of current (continuous curve).

The distribution of line strengths within a band was studied in the same current range. The portion of the (1−0) band in the 383.0-386.5 nm wavelength range is shown in Fig. 2. Shown for convenience under the spectrum are the numbers of the individual peaks (indicated by arrows), the positions of the individual rotational lines of the $A^2\Sigma^+ - X^2\Pi_i$ transition of HF^+, as well as the lines of impurities and dissociation products. The spectrum of HF^+ is considerably overlapped by lines of the Balmer series of hydrogen and lines of atomic fluorine, and as a result, only the lines R_1Q_{21} (3/2), R_1Q_{21} (5/2), Q_1P_{21} (5/2), and R_1Q_{21} (9/2) (peaks 1, 2, 5, and 6) are free from the superposition of impurities in this portion. Curves 1-4 represent the contours of the spectra at currents of 3.35, 9.5, 14.3, and 18.3 mA, respectively. Each spectrum is normalized to the sum of the strengths of several lines of HF^+ (peaks 1, 2, 5, 6). Peak 3 is completely overlapped by the thick line of atomic hydrogen (peak 4).

As current increases, the structure of the spectrum remains unchanged, but the line strength ratio changes; a marked increase in the normalized line strengths of the impurities (mainly, atomic fluorine) is observed, whereas the ratio of the lines of hydrogen fluoride ion remains practically constant. These trends are clearly seen in Fig. 3, which shows the dependence on current of the absolute values of the strengths of the individual peaks normalized to current and gas pressure and normalized to unity at the minimal value of current (3.35 mA). Thus, the values of current are correlated for each peak of the function $f = [I_j(i)/(ip)]/[I_j(i = 3.35\ \mathrm{mA})/(ip)]$. The normalization used makes it possible to establish the presence of nonlinear channels during excitation or deactivation of the radiant state. The labelling of the peaks is the same as in Fig. 2. On this scale, by definition, when i = 3.35 mA, f = 1 for all the peaks. It is clear from the graph that within the experimental error, the line strengths of HF^+ ion are linear with respect to current. Since hydrogen and fluorine appear as a result of dissociation of the hydrogen fluoride molecule, they were also expected to be present in a constant ratio in the spectrum. This was not observed, however. For hydrogen (peaks 4 and 12), the dependence on current is weak, whereas for atomic fluorine (peaks 8-10), a sharp increase in strength is observed as the electron current increases. The causes of this difference between the strengths of hydrogen and fluorine have not been established by the authors thus far, although there are reasons to assume that this is due to an appreciably higher rate of migration of hydrogen from the observation region.

Thus, the above results show that the influence of mechanisms 1.2 and 1.3 on the population of the $A^2\Sigma^+$ state of HF^+ is negligible in the range of current variations in question.

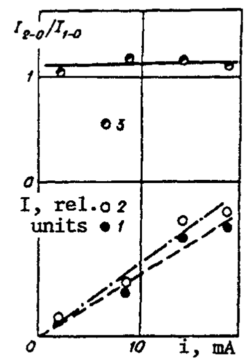
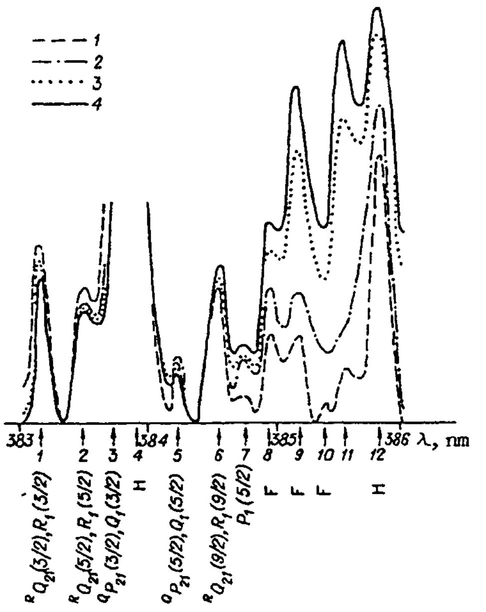


Fig. 1



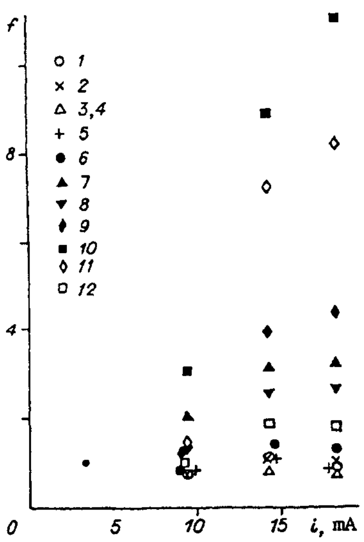


Fig. 2

Fig. 3

3. An analogous study was made to determine the dependence of the band strengths on the pressure p of the mixture. The measurements were carried out in the range p = 3-133 Pa at constant electron beam current i = 10 mA. The strengths were measured in the same way as in the preceding cases. Figure 4 shows the strengths of the (1−0) and (2−0) bands (points 1 and 2, respectively) as a function of pressure. The changes in the strengths of these bands are different. The strength of the (2−0) band increases linearly to a pressure of the order of 13 Pa, then reaches saturation. The strength of the (1−0) band in the initial portion is also linear, but the transition to a plateau is smoother and begins only at a pressure of about 40 Pa.

The dependence of the strength ratio of these bands I_{2-0}/I_{1-0} on density has a different form. Such a dependence on the reciprocal pressure (1/p) is shown in Fig. 5 in the case of normalization to unity at minimal pressure p = 3 Pa. It can readily be seen that in the new coordinates, this ratio exhibits a linear dependence (continuous straight line).

Thus, the linear dependence of the strengths on pressure (and hence, on density at constant gas temperature) takes place only at low pressures. Deviation from linearity occurs at different pressure values for different bands. Since analogous results were obtained earlier for other diatomic gases [12], one can speak of the extension to HF of the fundamental density limitation on the applicability of the optical model of excitation when a high-voltage electron beam is used. This limitation is due to the formation of an appreciable quantity of secondary electrons in the observation zone at pressures ~10 Pa. In [13], this phenomenon was not observed because the measurements were conducted only at low pressures of the gaseous medium.

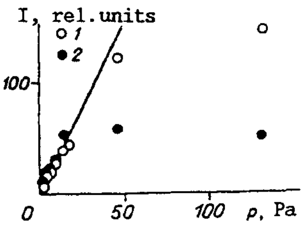


Fig. 4

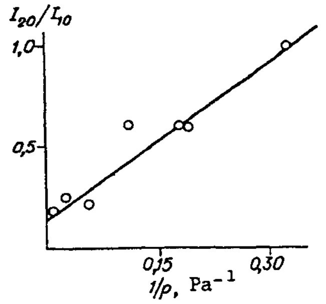


Fig. 5

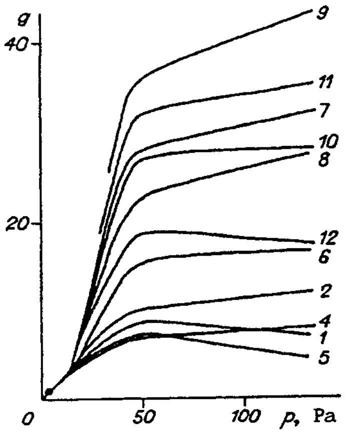


Fig. 6

Apparently, the development of a system of pulsed electron-beam diagnostics [14] will make it possible to move to a region of higher densities.

The linear dependence here observed of the band strength ratio of HF on the reciprocal pressure, not recorded in other gases, is either due, contrary to the conclusions of [15], to fluorescence quenching in HF, selective with respect to the vibrational levels, or to vibrational-rotational relaxation in the excited state of HF^+ ion.

The distribution of line strengths within a band was studied in the pressure range $p = 1.8$ to 130 Pa. It was found that as the pressure increased, the structure of the spectrum remained constant, but the line strength ratio decreased, and the rearrangement of the spectrum proceeded differently than in experiments where the beam current was varied. In particular, while a marked increase in the normalized line strengths of the impurities was observed in the spectrum as the current increased, the line ratio of HF^+ ion remained constant, and as the pressure increased, the spectrum of the ion changed. Figure 6 shows the pressure dependences of the parameter $g = (I/i)/[I/i(p = 5.2 \text{ Pa})]$ for the peaks of the spectrum (numbers 1-12; for the notation of the peaks, see Fig. 2; peak 11 was not identified). The nature of the changes was practically the same for the majority of the peaks. At pressures below 15 Pa, the increase in strength is linear as the pressure increases, indicating a predominant influence of excitation by fast primary electrons in compliance with the optical selection rules, and corresponds to the classical concepts [1]. As the pressure increased in the range $15 \leq p \leq 45$ Pa, a steeper increase in strength is noted for the majority of the peaks, each peak having its own slope of the curve. The first inflection of the dependence is localized in a narrow pressure range near 15 Pa. It is obvious that the smallest increase in strength is observed for HF^+ peaks 1, 2, 6 and atomic hydrogen 4, whereas for atomic fluorine 8, 9, 10 the slope of the curves increases more sharply. At pressure $p \sim 45$ Pa, a second inflection of the curve is clearly seen, after which the slope of the curves decreases (peaks 2, 6-11) or even becomes negative (peaks 1, 5, 12). On the whole, one can see that although the pressure dependence of the line strengths is individual for each peak, the HF^+ lines run in a compact group and increase more slowly than do the impurity lines. Such a change in the strengths of the HF^+ peaks may be due either to the influence of secondary electrons or to relaxation from upper populated levels. On the other hand, for atomic hydrogen and fluorine, which are the dissociation products of HF exposed to electron impact, the characteristics observed apparently are also due to the influence of secondary electrons. At pressures above 45 Pa, the principal role should be played by fluorescence quenching processes.

However, certain characteristics of the changes of the spectra with pressure remain unexplained, and therefore, the authors do not exclude the possibility of influence of other mechanisms not discussed here or of a complex superposition of several mechanisms. One should also point out an insufficient resolution of the spectrum, in the presence of which the superposition of individual lines may produce unexpected effects.

4. Thus, as follows from the experimental data, the ratio of the strengths in the spectrum of HF^+ is independent of the electron beam current but changes substantially as the pressure increases. That is to say, there are channels, secondary in pressure, in the excitation and deactivation of $A^2\Sigma^+$ of HF^+ (R_{14}, R_{15}, R_{22}, and R_{23}), and mechanisms R_{12} and R_{13} are improbable. Then the pumping rate of the j'-th level may be represented in the form

$$\frac{dn_{j'}}{dt} = \frac{1}{V}\left\{\sum_{v,j}\int_V n_j n_p v_p \sigma_{jj'}^{lnvv'} dV + \sum_{v,j}\int_V \int_{\sqrt{E_t}}^{\sqrt{E_p}} n_j n_s v_s \sigma_{jj'}^{lnvv'} f(v_s)\, dv_s dV\right\},$$

where the first sum is the rate of excitation of the molecules by primary electrons, and the second sum — by secondary electrons; n_j and $n_{j'}$ are the populations of the rotational levels in the $X^1\Sigma^+$ and $A^2\Sigma^+$ HF^+ states; n_p and n_s are the concentrations; v_p and v_s are the velocities of primary and secondary electrons; $f(v_s)$ is the function of distribution over the velocities of secondary electrons. Integration over energy is from the excitation threshold of $A^2\Sigma^+$ to the energy of primary electrons.

The emptying rate is described by the equation

$$\frac{dn_{j'}}{dt} = -\left\{n_{j'} \sum_{v''j''} A_{j'j''}^{v'v''} + n_{j'} n_0 K_{j'}^q\right\}.$$

Here the first term on the right is the emptying rate of the j'-th level due to spontaneous emission, and the second term — to nonradiative transitions (fluorescence quenching and vibrational-rotational relaxation in $A^2\Sigma^+$); K_j^q is the fluorescence quenching constant (which contains the integrated rate of vibrational-rotational relaxation in $A^2\Sigma^+$).

At equilibrium, the emptying and pumping rates are equal, and therefore

$$n_{j'} = \frac{\left\{\sum_{v,j}\int_V n_j n_p v_p \sigma_{jj'}^{lnvv'} dV + \sum_{v,j}\int_V \int_{\sqrt{E_t}}^{\sqrt{E_p}} n_j n_s v_s \sigma_{jj'}^{lnvv'} f(v_s)\, dv_s dV\right\}}{V\left\{\sum_{v''j''} A_{j'j''}^{v'v''} + n_{j'} n_0 K_{j'}^q\right\}}.$$

Substituting Einstein's coefficient in radiation [9] and considering that in terms of the optical model of excitation $\sigma_{jj'}^{lnvv'} = \sigma_e^{ln} q_{vv'} P_{jj'}$ (σ_e^{ln} being the cross section for excitation of the $A^2\Sigma^+$ state by electrons, $q_{vv'}$, the Franck–Condon factor in excitation, and $P_{jj'}$, the Hönl–London factor in excitation), we have the strength of a rotational line

$$I_{v'v''}^{j'j''} = C\,\frac{hci_p \sigma_e^{ln} S_e^{nm}}{1 + \tau_{j'} n_0 K_{j'}^q}\,\frac{\nu_{j'j''}^4 q_{v'v''} P_{j'j''}}{\sum_{v''j''} (q_{v'v''} P_{j'j''} \nu_{j'j''}^3)} \sum_v \left[q_{vv'} \sum_j n_j P_{jj'}\right] [1 + f(n_0, f(v_s), E_p)],$$

where S_e^{nm} is the electronic-transition moment; $q_{v'v''}$ is the Franck–Condon factor in radiation; $P_{j'j''}$ is the Hönl–London factor in radiation; $i_p = n_p v_p$ is the current of the secondary-electron beam; $\tau_{j'}$ is the emission lifetime of the j' level; $f(n_0, f(v_s), E_p)$ is the contribution of secondary electrons to the excitation of the $A^2\Sigma^+$ state, described by the equation

$$f(n_0, f(v_s), E_p) = \frac{\sum_{v,j}\int_V \int_{\sqrt{E}}^{\sqrt{E}} n_j n_s v_s \sigma_{jj'}^{lnvv'} f(v_s)\, dv_s dV}{\sum_{v,j}\int_V n_j n_p v_p \sigma_{j'j''}^{lnv'v''} dV}.$$

TABLE 1. (2–0) G_2 Band of the $A^2\Sigma^+-X^2\Pi_i$ Transition of HF^+

Number of peak	Lines	Normalized strength of peaks	
		calc.	expt.
1	$R_2(1/2, 3/2, 5/2)$; ${}^QR_{12}$, $Q_2(1/2)$	0,105	0,094
2	$R_2(7/2)$; ${}^QR_{12}$, $Q_2(3/2, 5/2)$; ${}^PQ_{12}$, $P_2(1/2, 3/2)$; ${}^OP_{12}(1/2)$	0,292	0,277
3	$R_2(9/2)$; ${}^QR_{12}$, $Q_2(7/2)$; ${}^PQ_{12}$, $P_2(5/2)$; ${}^OP_{12}(3/2)$	0,190	0,210
4	$R_2(11/2)$; ${}^QR_{12}$, $Q_2(9/2)$; ${}^PQ_{12}$, $P_2(7/2)$; ${}^OP_{12}(5/2)$	0,230	0,193
5	${}^QR_{12}$, $Q_2(11/2)$; ${}^PQ_{12}$, $P_2(9/2)$	0,096	0,097
6	${}^OP_{12}(7/2)$	0,024	0,043
7	${}^PQ_{12}$, $P_2(11/2)$	0,038	0,046
8	${}^OP_{12}(9/2)$	0,026	0,040

Substituting into the formula for strength the corresponding values of Hönl–London factors [16], we obtain the line strengths for each branch of the $A^2\Sigma^+-X^2\Pi_i$ transition of HF^+.

To calculate the band structure and the line strength distribution of the indicated transition, we set up a program (allowing for the instrument function of the measuring system) that made it possible to perform calculations of the band profile and line strengths and to compare them with the spectra measured experimentally. Thus, to check the equilibrium of the spectra in measurements under static conditions, we compared the calculated spectra, based on the assumption of equilibrium distribution of the populations of the rotational levels in $X^1\Sigma^+$ of HF at a temperature equal to the temperature of the chamber walls, with the experimentally recorded spectra obtained in a vapor of pure HF in low-pressure statics, when the influence of secondary processes quadratic in density is negligible (see Table 1). It follows from the comparison of the spectra that at low pressures, the calculation satisfactorily describes the experiment. Estimates of the contribution of secondary electrons to the excitation of HF^+ lines make it possible to neglect them in the pressure range up to ~25 Pa. An estimate of the quenching constants of the rotational levels yields values comparable to data reported in the literature on the quenching of vibrational states [15].

The results obtained demonstrate the possibility of applying the EBD technique to studies in flows of hydrogen fluoride mixtures. However, the appreciable overlap of the recorded bands by the dissociation products of HF imposes serious limitations on both the wavelength range and the choice of the flow parameters being measured.

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