USE OF ELECTRON BEAM DIAGNOSTICS TO INVESTIGATE

FLOW OF HYDROGEN FLUORIDE GAS

G. G. Hartvich, A. E. Zarvin, V. V. Kalyada, UDC 533.6.011.8 + 537.533
and V. Zh. Madirbaev

This paper presents results of investigations of flow of hydrogen fluoride mixtures, based on the electron beam diagnostic technique (EBD), used successfully previously in molecular gas dynamics to measure density, velocity, velocity distribution functions, and populations of internal degrees of freedom of a number of molecular systems [1-3]. We have measured the radiative spectra of hydrogen fluoride in an electron beam, developed a model of the processes occurring in interaction of an electron with the HF molecule, and studied special features of the radiation under steady conditions in supersonic flow.

The need to investigate processes occurring in hydrogen fluoride mixtures is due primarily to the development of chemical lasers based on combustion reactions of fluorine in hydrogen. The visualization of complex flows, including flows that are not self-luminous, the measurement of density of mixture components at any point in the flow, and the monitoring of populations of individual energy levels of the hydrogen fluoride molecule can substantially enhance the effectiveness of both experiment and theory in this field.

The first radiative spectrum of the $A^2\Sigma^+ - X^2\Pi_i$ transition of the HF^+ ion was obtained in [4] in a low-voltage discharge at a potential of 60 V, a current of 4 A and an HF vapor pressure of 0.27 N/m^2. The authors were able to record the vibrational transitions (0–0), (1–0), (0–1), (1–1), (2–0), (2–2), (3–0), (3–2), lying in the wavelength range 350-460 nm, reduce the data, and evaluate the constants. They recorded no transitions from $v' > 3$ (v' is the vibrational quantum number in the radiative state of the $A^2\Sigma^+$ HF^+ ion). For the (3-0) and (3-2) bands they observed a sharp truncation of the branches for $N' > 3$ (N' is the rotational level in $A^2\Sigma^+$ HF^+), and for the (2-0) band for $N' > 9$, which is explained by dissociation to $A^2\Sigma^+$. Analogous results regarding the limit of dissociation were obtained in [5, 6] in photoelectronic and photoionization experiments. A more detailed spectroscopic study of the HF^+ ion in an electron beam was performed in [7]. The measurements were made in the HF vapor pressure range $0.04-0.4$ N/m^2, and the excitation was produced by a pulsed electron beam with energy up to 2 kV. The authors gave computed values of the Frank—Condon factor for the radiation, measured the lifetimes of the vibrational levels and the fluorescence quenching constants in $A^2\Sigma^+$. However, the authors of those papers were not able to obtain data on the mechanisms and the probabilities, partly because they used low-energy electrons, for which reason the model of the $X^1\Sigma^+$ HF $\rightarrow$ $A^2\Sigma^+$ HF^+ transition becomes extremely complex.

1. An experimental facility was developed (Fig. 1) for gasdynamic electron beam investigations with HF and other toxic and chemically active easily condensible gases. The facility consisted of a gasdynamic chamber in which was mounted the nozzle unit 1, carried on a 3-axis traverse mechanism, and acting as the source of the jet of test gas. The gasdynamic chamber was made of stainless steel plates 12 mm thick. Since the HF vapor pressure in the chamber during the experiment did not exceed 700 N/m^2, we used quartz windows without added heat shielding (i.e., blowing). A well-collimated electron beam 2 with electron energy of ~10 keV, falling on the collector 3, was formed with the aid of the electron-optical system 4.

Focusing of the radiation on the entrance slit of the spectrometer was accomplished by the large-diameter quartz lens 5. The twin type SPM-2 monochromator 6, positioned on the transverse table directly ahead of the chamber window, was used to record survey spectra and to draw the total intensity of the individual vibrational bands. The rotational structure of the band was resolved using the type DFS-12 spectrometer 7. A quartz multi-strand light pipe 8 was used to transmit the radiation to the spectrometer inlet slit. Spectral scans were accomplished by the recording system, including the type FÉU-118 photomultiplier in the body 9, cooled by liquid nitrogen, a type V5-24 high-voltage source 10, and a type IMT-05 dc
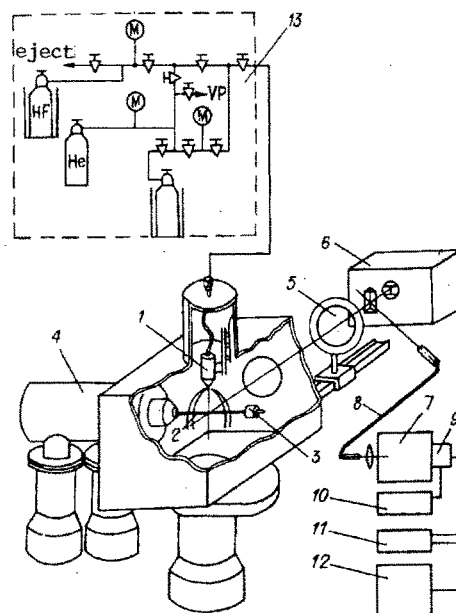
Fig. 1

TABLE 1

v'	v'			
	0	1	2	3
	$q_{vv'}$			
0	0,0275	0,0620	0,0825	0,0849
1	0,102	0,136	0,104	0,0581
2	0,190	0,114	0,0233	0,0002
3	0,233	0,0246	0,0113	0,0448
4	0,206	0,0086	0,0808	0,0544

amplifier 11, with type KSP-4 recorder 12. A parallel signal from the photomultiplier was routed to a type ISKRA-226 computer.

The gas panel 13 was mounted in a fume cupboard, with only the valve handle and the electric drive of the accumulator showing on the outside. The HF supply lines to the chamber were protected by a steel shell, connected to an exhaust fan system. To avoid accumulation of condensate the lines were heated by means of steady-state heaters.

Pump-down of the hydrogen fluoride was accomplished by oil-vapor pumps, protected by standard type Du 160 nitrogen traps. At the end of the experiment the chamber and the beam were closed off by gate-valves, and after cooling of the pumps the HF from the traps ahead of the gate-valves was drawn by chilling into nitrogen traps built in ahead of the mechanical pumps. Then after pumping out the fore-vacuum lines from the oil pumps these traps were flushed with inert gas. Before exiting to the atmosphere the gases to be ejected were passed through an alkali neutralizer mounted in the fume cupboard. The residual traces of HF were pumped out by a fore-pump.

To generate the diagnostic electron beam we used a standard type ÉOSS-2 electron-optical system. The electron source is a tablet of lanthanum hexaboride heated by a tungsten coil. The electron energy (up to 30 keV) was determined by the cathode potential relative to ground. The emission current was controlled by the modulator unit, the voltage from which, of amplitude up to 1500 V relative to the cathode, was applied to the blocking electrode. To maintain the operating vacuum in the cathode region while the chamber pressure varied we used a two-section structure of the beam unit and a differential pumping system, generally analogous to those used in the Siberian Branch of the Institute of Thermophysics, Russian Academy of Sciences [1].

To ensure safe operation with hydrogen fluoride we developed and set up an automated autonomous monitoring system to track the operating parameters of the facility and simultaneously to react to nonstandard situations. The system controlled the vacuum units,
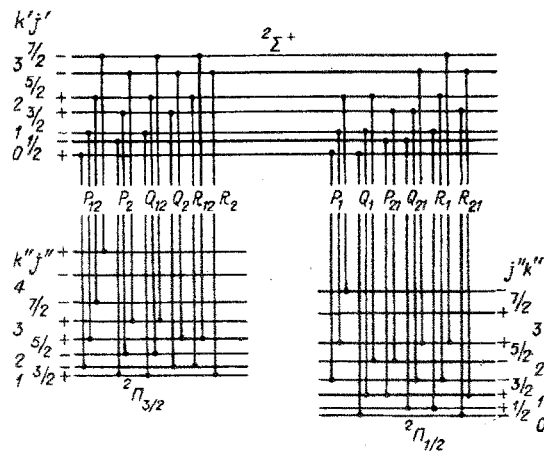
Fig. 2

switched on and off the electron beam and vacuum gauges, could stop the supply of HF from the gas panel, and eject HF to the nitrogen trap bank. The operator could assign the level of operation of protection from the electron beam and the other elements of the facility upon a pressure increase, a dangerous voltage drop in the electric circuit, etc. An operating test of the system showed it to be reliable and convenient in use, not only when operating with aggressive substances, but also generally when operating with vacuum pumps. As the supersonic jet source we used a sonic nozzle. We used technically pure HF, containing a small addition of N_2.

2. In the present work the measurements were made with the ordinary EBD scheme. By recording the radiative spectra of excited molecules and ions, with a known mechanism for excitation and quenching, one can determine the populations of the internal degrees of freedom of the molecules in a chosen local volume, and by moving the gas source relative to the measurement point one can draw the population distributions and the gas density profiles over the entire flow volume. For a number of molecules (N_2, CO, HCl, etc.) it has been shown [8-10] that the transition to the excited state of the ion is accomplished according to the Franck—Condon principle, and consequently the model of the excitation process is appreciably simplified.

The Frank—Condon factors for excitation of $A^2\Sigma^+$ HF^+ by fast electrons, computed in the optical model approximation [11], are shown in Table 1. The scheme of rotational transitions in the HF ion radiation is shown in Fig. 2, where it can be seen that the ground state of the $X^2\Pi_i$ ion is split into two states due to λ-twinning: $^2\Pi_1/_2$ and $^2\Pi_3/_2$, spaced 300 cm^{-1} apart. In addition, in $A^2\Sigma^+$ and $A^2\Pi_i$ there is substantial spin splitting. Therefore, allowing for the selection rules $\Delta j = 0$, ± 1 we have in the spectrum of each vibrational band two groups of 6 branches, superimposed. We computed the wavelengths of the rotational lines in the radiation from the formula [12]

$$\lambda_{jj''} = [\nu_{00} + G(v') - G(v'') + F_i'(N, j) - F_j''(j)]^{-1},$$

where $\lambda_{j'j''}$ is the wavelength of a rotational line; and $G(v')$ and $G(v'')$ are the rotational terms of the top and bottom states:

$$G(v) = \omega_e (v + 1/2) - \omega_e x_e (v + 1/2)^2 + \omega_e y_e (v + 1/2)^3.$$

The rotational terms of the top and bottom states were determined from the formulas [4]:

$$F_1'(N, j) = B_v' N(N + 1) - D_v' N^2 (N + 1)^2 + H_v' N^3 (N + 1)^3 + \gamma \frac{N}{2},$$

$$F_2'(N, j) = F_1'(N, j) - \gamma \left(N + \frac{1}{2}\right),$$

$$F_1''(j) = B_v'' [(j + 1/2)^2 - \Lambda^2 - (1/2) \sqrt{4(j + 1/2)^2 + Y(Y - 4)\Lambda^2}] - D_v'' j^4,$$

$$F_2''(j) = B_v'' [(j + 1/2)^2 - \Lambda^2 + (1/2) \sqrt{4(j + 1/2)^2 + Y(Y - 4)\Lambda^2}] - D_v'' (j + 1)^4,$$

$$B_v = B_e - \alpha_e (v + 1/2), \quad D_v = D_e + \beta_e (v + 1/2), \quad \Delta j = 0, \pm 1.$$
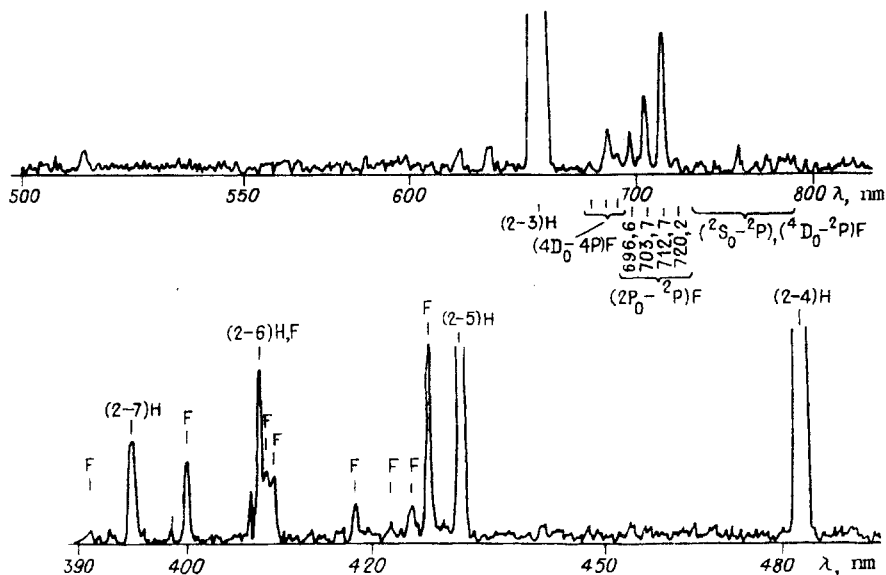
Fig. 3

The spectroscopic constants B_e, α_e, D_e, β_e, ω_e, $\omega_e x_e$, $\omega_e y_e$, and γ for the states $A^2\Sigma^+$ and $X^2\Pi_i$ HF^+ were taken from [13].

3. Examples of survey spectra in the wavelength range 390-800 nm are shown in Fig. 3, and in the range 340-390 nm in Fig. 4, taken in static conditions with the working chamber filled with hydrogen fluoride to a pressure of 8 N/m^2. The spectra were obtained on SPM-2 with an electron beam current of 1.1 mA. As follows from the results presented, in the entire spectral range studied it proved to be extremely complex to pick out from the fluctuating background the spectral structures belonging to the vibrational band of hydrogen fluoride. Most of the strongest lines in the present series of experiments, except in the region 350-390 nm, have the characteristic shape of atomic peaks.

In order to interpret the results obtained in Figs. 3 and 4 we have placed marks above or below the experimental spectra, corresponding to estimates of the location of the main lines of atomic hydrogen and fluorine, and also of some of the HF^+ transitions. As can be seen from the graphs, in this way we have managed to identify practically all the strongest atomic peaks with the Balmer series of hydrogen, and also some lines of fluorine, mainly corresponding to doublet—doublet and quartet—quartet transitions. In the region from 350 to 390 nm we observed quite intense bands corresponding to the vibrational transitions (1-0), (2-0), (3-0), $A^2\Sigma^+ - X^2\Pi_i$ HF^+. Unfortunately, these bands are also substantially overlapped by radiation of atomic fluorine and hydrogen, and at a resolution of 1.5 nm/mm available with the SPM-2 monochromator one cannot always identify the HF^+ lines reliably. The intensity of the atomic peaks proved unexpectedly high, although in the experiments we used technically pure hydrogen fluorine in which the impurities did not exceed 2%. Tests also have shown that in conducting measurements in static conditions, i.e., without careful prior filling of the evacuated chamber with hydrogen fluoride to the fixed pressure, the intensity of the atomic peaks of hydrogen and fluorine increased with time, while that of the HF^+ bands decreased.

In our view, such intense lines of atomic hydrogen and fluorine are found in the spectra because the potential curves of the $X^1\Sigma^+$ HF and $A^2\Sigma^+$ HF^+ states have been substantially displaced relative to one another, and when the Frank—Condon principle holds in the excitation a considerable fraction of the hydrogen fluoride molecules transfer into the dissociation region. This special feature makes it extremely difficult to perform electron beam spectroscopy of hydrogen fluoride, thereby singling out the latter from a series of diatomic gases investigated. The most complex measurements are EBD measurements in static conditions in which the number of secondary electrons increases appreciably [14] in the region of the observations. Therefore, the static conditions in the experiments whose results are shown in Figs. 3 and 4, were created by arranging a weak flow of hydrogen fluoride from a tank via a side valve, with continuous pumping of the chamber volume using vacuum pumps. The required static pressure was set up under equilibrium of the incoming and outgoing flows via throttling of the pumping system.
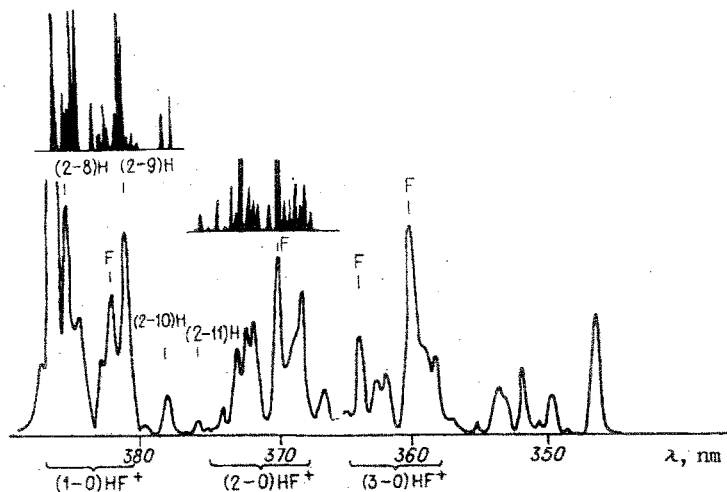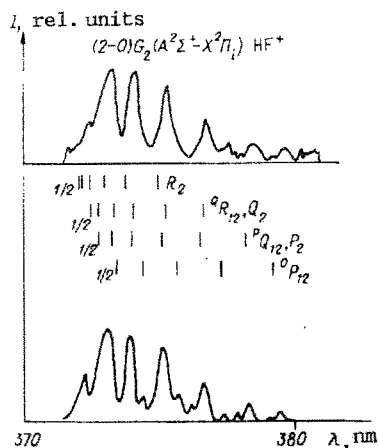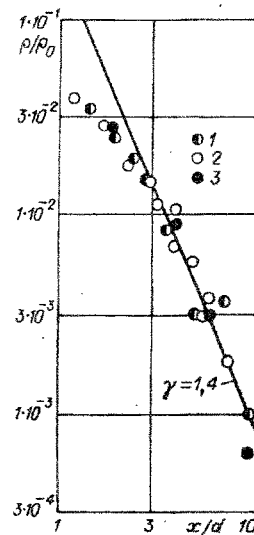
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Fig. 4

Fig. 5

Fig. 6

The large growth in the number of secondary electrons leads to an increased pressure in the region of observations, to values exceeding 10 N/m^2 (upper limit of application of EBD in the continuous regime). Therefore, responding to the great interest in conditions with pressures from 10 to 1000 N/m^2 in flow of hydrogen fluoride and their mixtures, the problem of using pulsed EBD becomes important [15].

We were able to obtain a more detailed distribution of line intensities in the vibrational transitions (1–0), (2–0), (3–0) $A^2\Sigma^+ - X^2\Pi_i$ HF^+ when using the type DFS-12 high-resolution spectrometer. The upper part of Fig. 4 shows an example of such a measurement for the spectral section 366-388 nm. For the (2-0) band the measurements give a number of peaks, representing superposition of HF^+ lines belonging to various branches, and also isolated lines of atomic hydrogen and fluorine. For the (1–0) band it is considerably more compled to single out the pure HF^+ spectrum, since besides atomic lines this region has superimposed bands of the background of molecular nitrogen. Nevertheless the individual HF^+ lines were singled out and interpreted. An example of this interpretation for the $G_2(A^2\Sigma^+ - X^2\Pi_i)$ HF^+ transition is shown in Fig. 5 where the upper part shows a spectral section in the region 370-380 nm obtained on the DFS-12 spectrometer in static conditions analogous to those described above, while the lower part of Fig. 5 shows computed results using a model proposed by the authors under the hypothesis of an equilibrium distribution of populations of rotational levels in $X^1\Sigma^+$ HF, with a temperature equal to that of the chamber wall; the good agreement between experiment and theory can be seen.

In evaluating the use of EBD in investigating flow of hydrogen fluoride mixtures one should also take account of the possibility of obtaining detailed gasdynamic information on

the flow, including the density distribution in the volume of the jet. An example of measurement of density of gaseous components on the axis of a supersonic jet formed in discharge of hydrogen fluoride through a sonic nozzle into a low pressure region is given in Fig. 6, where the points 1 are experimental values of density determined from radiation of the (2–0) HF^+ band. The data were obtained at a stagnation pressure of 4000 N/m^2, and a stagnation temperature of 470 K. The distribution of gas density in the jet was measured from the luminous intensity excited by the electron beam in the local volume in which the optics were focused, during displacement of the object studied relative to this point with the aid of the traverse mechanism. Since the monochromator was used it was possible, by setting up the corresponding wavelength, to conduct measurements of the distribution of density in the jet as a function of the varying parameter. Thus, besides HF we were able to determine the density from a radiative line of atomic fluorine (λ = 370.1 nm) and from the (0–0) N_2^+ band present in HF as a small additive (points 2 and 3, respectively). The line in Fig. 6 shows the isotropic density distribution for the diatomic phase (γ = 1.4); it can be seen that all three experimental density profiles in the jet, as one would expect, correspond to an expansion with γ = 1.4 (x/d is the distance from the nozzle rim, in calibers).

Thus, with the equipment and technique developed, in spite of the special feature of the excitation process discovered for the radiation in HF, we can measure the radiative spectrum of hydrogen fluoride using traditional electron beam diagnostics and we can apply it in gasdynamic investigations of hydrogen fluoride mixtures.

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