Vibrational relaxation of HF and DF in a shock wave

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Vibrational relaxation of HF and DF molecules is studied by recording the infrared radiation behind an incident shock front in mixtures of HF (DF) and Ar at temperatures of 1500–5000° K. The relaxation times in this temperature range can be represented by a temperature dependence of the type $A \exp(B/T^{1/3})$.

A number of researches have been reported recently on vibrational relaxation of hydrogen halides both at high temperatures, under conditions of shock heating,[1-4] and at temperatures close to room temperature.[5-8] It has been shown that the experimentally measured relaxation rates of these molecules are substantially greater than those calculated by means of the Landau-Teller theory. Moreover, the comparison of the results of experiments in shock tubes with measurements at room temperature reveals an additional sharp increase in the relaxation rate at temperatures less than 1000° K as compared with their values obtained by extrapolation of the data of measurements in shock tubes. In the case of HF, such a comparison indicates the presence of a maximum in the temperature dependence of the vibrational relaxation times for ~1000° K.[1,2,7] This is confirmed by the recent data of Bott,[2,8] obtained in the range of temperatures 300–4000° K by means of a combined technique using a shock tube and laser-excited infrared luminescence.

In the published theoretical papers these features are attributed to the significant participation of rotational motion in the vibrational relaxation of the hydrogen halides,[9-11] and also to the effect of the intermolecular forces of attraction, which increase with decrease in temperature.[12]

The absence, until recently, of data on the vibrational relaxation of HF was to a large degree due to difficulties in working with it. The results of the first experimental researches[1,2] on the study of relaxation of HF molecules in the temperature range 1400–40000° K diverge appreciably, although, as the authors point out, careful measures were taken in both experiments with regard to the purity of the HF. In this connection, the necessity arises of additional investigations, taking of all possible measures to eliminate the non-reproducibility of the results.

The vibrational relaxation of HF and DF molecules have been measured in the present research in the temperature range 1500–50000° K by means of a shock tube.

EXPERIMENTAL METHOD

The experiments were carried out on a shock tube of stainless steel with an internal diameter 3.7 cm and length of the low pressure section 205 cm in the observation window. The velocity of the shock wave was determined by means of ionization detectors located at distances of 10 cm from one another. Improvement of the time resolution of the detectors was obtained by amplification of the high-frequency components of the signal. The detector signals were recorded on a C1-29 oscilloscope screen. The error in the determination of the velocity here was $\lesssim 1.5\%$. The shock tube was evacuated by a diffusion pump to a pressure of 5×10^{-6}

mm Hg. The flow rate into the tube did not exceed 3×10^{-4} mm Hg/min.

Ar (99.99%) and He (99.99%) without additional purification were used in the experiments. The HF and DF were prepared before the experiments in a stainless steel vessel immersed in liquid nitrogen by admitting $H_2(D_2)$ into the F_2. The purification procedure included the pumping-out of gases not condensed in the cooled container by the diffusion pump, and subsequent slow heating of the vessel to the temperature at which the pressure of the HF(DF) in it amounted to 20–25 mm Hg. The pressure of the water vapor which could form during preparation of the HF(DF) because of the presence of traces of O_2 in the F_2, did not exceed 2×10^{-2} mm Hg at this temperature.

The mixing tank was then filled with the resultant gaseous HF(DF) to a pressure of 20 mm, after which the necessary quantity of Ar was added. The shock tube and also the entire vacuum system and the pressure measurement system were first passivized with F_2 for a long time. The pressure was measured by a specially constructed sylphon manometer in the range of 0–100 mm Hg and a standard vacuum gauge in the range 0–760 mm Hg.

The relaxation of the vibrational energy was traced by measuring the infrared radiation of the HF(DF) molecules heated by the shock wave. The radiation in the necessary wavelength range was separated by an IKM-1 infrared monochromator with an NaCl prism. The spectral half-width of the slit of the monochromator amounted to ~0.5 μ. The entrance slit of the monochromator was focused on the center of the shock tube by a system consisting of plane and spherical mirrors, so that the width of the image of the slit was equal to 1 mm. The radiation from the shock tube was introduced through a CaF_2 window and collimated, in order to separate the narrow band of observation. The distorting effect of the width of the observation band on the recorded exponential signal did not exceed 5%.[13] To record the infrared signal, a radiation detector of Ge with Au was used, as well as a broadband amplifier USh-2 and a C1-29 oscilloscope. The time constant of the system did not exceed 0.5 μsec.

The experiments were performed with mixtures containing 1, 2.5, 5 and 10% HF(DF) in Ar. The initial pressure in the low pressure section was chosen in the range 0.5–10 mm Hg, so that the infrared signal of the radiation had a sufficient value and, at the same time, the measured relaxation times exceeded the time constant of the system by several fold. Before each experiment, the tube was washed out for several minutes by the working mixture with subsequent pumping. To avoid the entry of atmospheric air in the tube during the

change of the diaphragm, He was first blown through the tube. The experiment was performed immediately after filling the low-pressure section with the working mixture (the time delay was not more than 1 min). In reduction of the experimental data, the temperature and the pressure in the mixture behind the shock front were calculated from the measured velocity and the known initial pressures (see, for example, [13]).

EXPERIMENTAL RESULTS AND DISCUSSION

The intensity of the recorded infrared radiation of the heated shock wave of the mixture increased according to the law

$$I = I_{\infty}[1 - \exp(-t/\tau)], \tag{1}$$

where I is the intensity of the radiation at the time t; I_{∞} is the equilibrium intensity of radiation of a given mixture at the temperature of the experiment, τ is the laboratory vibrational relaxation time.

The value of τ was determined for each experiment from the slope of the line plotted in the coordinates $[\ln(I_{\infty} - I), t]$, and was then recalculated in the proper time of the vibrational relaxation. The quantities $P\tau$, calculated from experimental data for mixtures with different amounts of HF and DF, are given in Figs. 1 and 2, respectively. P is the pressure of the mixture behind the shock front.

Different degrees of dilution of Ar made it possible to separate the contribution of the HF(DF) molecules themselves in Ar in the relaxation of HF(DF), according to the relation

$$(P\tau)^{-1} = X(P\tau)_{HF-HF}^{-1} + (1-X)(P\tau)_{HF-Ar}^{-1}, \tag{2}$$

where X is the fraction of HF(DF) in the mixture, $P\tau_{HF-HF}$ is the relaxation time of HF on HF, and $P\tau_{HF-Ar}$ is the relaxation time of HF on Ar. To obtain these times and their temperature dependence, the data shown in Figs. 1 and 2 were treated by the method of least squares in accord with (2) for several values of the temperature. The results are shown in Fig. 3 in the form of the usual dependence
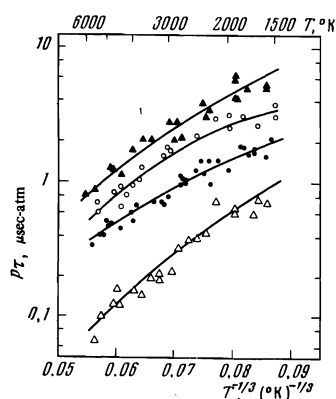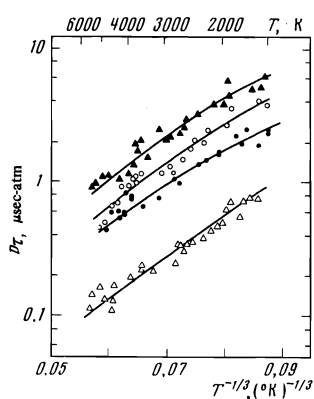
$$P\tau = A \exp(B/T^{1/3}). \tag{3}$$

The values of A and B are given in the table.

Figure 3 also shows for comparison the results of similar measurements of other authors. Solomon, Blauer and co-workers[1] and Bott and Cohen[2] give respectively the values 6.3×10^{-4} and 64, 1.02×10^{-2} and 34, 386 (in the same units as in the table) for A_{HF-HF} and B_{HF-HF}. The vibration relaxation times of HF on HF obtained by us are in excellent agreement (with accuracy within $\lesssim 10\%$) with the data of Bott and Cohen.[2] From the data of [1], the times for high temperatures are smaller by a factor of 2–2.5. Like the data of [2], our results indicate a significant contribution of Ar to the vibrational relaxation of HF in the mixture, especially at high temperatures. The values of the corresponding parameters from [2] are: $A_{HF-Ar} = 1.62 \times 10^{-3}$, $B_{HF-Ar} = 111.97$. The relaxation times of HF on Ar, obtained by us and by Bott and Cohen[2] differ in the range 1400–40000° K by not more than a factor of 1.5. The effect of Ar was not observed in [1].

During the preparation of the present paper, Blauer, Solomon and co-workers published their results for the vibrational relaxation of DF molecules.[3] According to their data, $A_{DF-DF} = 2.5 \times 10^{-3}$ μsec-atm and B = 56 ± 3 $(°K)^{1/2}$, which is in good agreement with our results. As in the case of HF, the effect of Ar was not revealed, whereas, according to our data, it is significant and its contribution increases with increase in temperature. The reason for this divergence is not clear.

Comparison of our results (as well as the results of [1,2]) for the vibrational relaxation times of HF and DF agrees with the representations of the important contribution of the mechanism of rotational-vibrational energy transfer, according to which the deuterated hydrogen halides relax more slowly. But, in contrast with the data of [1,3], our results also agree with the theoretical representations[11,12] on the important role of translational-vibrational energy transfer for deuterated hydrogen halides, which becomes especially significant with
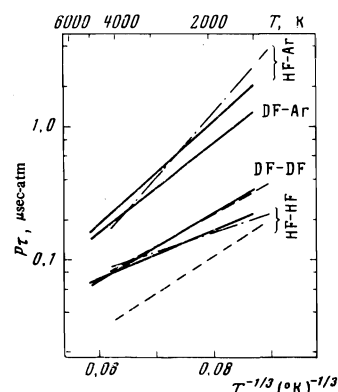
FIG. 3. Temperature dependence of the vibrational relaxation times of HF, DF; the continuous lines are from the present research, the dashed lines from Solomon and Cohen.[2] The relaxation times in Ar are reduced by a factor of 10.

FIG. 1.   FIG. 2.

FIG. 1. Vibrational relaxation times of HF in mixtures with Ar at a pressure of 1 atm. The HF content in the mixtures: $\triangle$ — 1, $\blacktriangle$ — 2.5, O — 5, $\bullet$ — 10%. The data for the one-percent mixture are reduced by a factor of 10.

FIG. 2. Vibrational relaxation times of HF in mixtures with Ar at a pressure of 1 atm. The DF content in the mixtures: $\triangle$ — 1, $\blacktriangle$ — 2.5, O — 5, $\bullet$ — 10%. The data for the one-percent mixture are reduced by a factor of 10.

Collision	A, μsec-atm	B, $(°K)^{1/3}$
HF — HF	$5.74 \cdot 10^{-3}$	42.00
HF — Ar	$8.49 \cdot 10^{-3}$	89.47
DF — DF	$2.26 \cdot 10^{-3}$	57.25
DF — Ar	$1.46 \cdot 10^{-2}$	78.04

increase in the temperature. According to our data, DF begins to relax more quickly than HF—in correspondence with the mechanism of translational-vibrational transfer, beginning with ~4500° K.

The much weaker temperature dependence for relaxation of HF(DF) on HF(DF) in comparison with the relaxations of HF(DF) on Ar can be explained most reasonably in accord with the theory of [12], by the presence of attraction forces between the HF(DF) molecules, the effect of which naturally increases with decrease in temperature.

The result obtained for the times $P\tau_{HF-Ar}$ and $P\tau_{DF-Ar}$ is opposite to that which might have been expected for predominance of the rotational-vibrational energy transfer. Evidently, in collisions with Ar, the role of this mechanism is smaller than in collisions of the same molecules, HF, DF.

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