Rotational and vibrational deactivation of excited HF molecules

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The transformation of rotational distributions of HF molecules formed in the $F+H_2$ reaction has been investigated for a successively increased number of collisions between these molecules and H_2, D_2 molecules and He, Xe atoms. It was found that, when the maximum number of collisions attained in these experiments was reached (~ 50), the rotational distribution had not approached the equilibrium state. The rate of rotational deactivation of HF molecules on He and Xe decreases with increasing J, so that more than 100 collisions are necessary for the deactivation of HF molecules ($J > 7$) by Xe atoms. It is shown that resonance transfer of rotational energy plays an important role in the rotational relaxation of HF molecules on H_2 and D_2. These processes enhance the rate of rotational deactivation of HF ($J > 7$) molecules by roughly an order of magnitude as compared with deactivation on helium and xenon. The most rapid rotational relaxation of HF occurs in deuterium. It is found that the rate of rotational deactivation depends on the vibrational number v and is greater for $v = 1$ than for $v = 2$ by a factor of about two.

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INTRODUCTION

It is well known [1] that vibrationally and rotationally excited HF molecules are formed in the $F + H_2 \rightarrow HF + H$ reaction with a nonequilibrium distribution, and that the rotational energy is greater by more than an order of magnitude than the mean energy in the equilibrium state with T = 300°K. Rotational relaxation of highly rotationally excited molecules has been investigated only qualitatively, so far. It may be considered that it is now established that the probability of rotational deactivation usually falls with increasing rotational quantum number J. [2] Polanyi et al. [3] have shown that, during the relaxation of HCl molecules on H_2, the probability $P^J_{J-\Delta J}$ of rotational deactivation, in which the quantum number J changes by ΔJ, satisfies the empirical formula $P^J_{J-\Delta J} \propto e^{-C\Delta E}$, where ΔE is the change in energy during the transition and C is a constant. Deactivation, whose rate decreases with increasing J, is connected most likely with the transformation of rotational into translational energy (R—T transfer) because an increase in J is associated with an increase in the distance between the rotational levels and, consequently, an increase in the Massey parameter $\Delta E/\hbar a v$, which is known to determine the probability of inelastic collision.

In addition to R—T transfer, collisions with resonance transfer of rotational energy may, in principle, play an appreciable role. In these collisions, the rotational energy given up by one molecule is equal to the rotational energy communicated to its partner in the collision. The importance of this type of collision has been demonstrated experimentally for H_2 and D_2 relaxing on H_2 and D_2. [5] The rotational relaxation of highly rotationally excited HF molecules has not, so far, been investigated. The aim of this work was to investigate the rate of deactivation of HF molecules formed in the $F + H_2$ reactions during collisions with H_2, D_2, He, and Xe. We have shown that the resonance transfer of rotational energy from HF molecules to H_2 and D_2 plays a determining role in the rotational deactivation of highly rotationally excited HF molecules with $J \geq 7$. In the case of rotational relaxation of HF on He and Xe, the rate of deactivation falls with increasing J, and more than 100 collisions are necessary for the complete deactivation of HF molecules formed in the $F + H_2$ reaction.

EXPERIMENTAL METHODS

We have observed a gradual change in the population n_{vJ} of individual vibrational-rotational levels of the HF molecule as the mean number of collisions between HF and H_2, D_2 and He, Xe was increased in the observational zone. The source of the vibrationally and rotationally excited HF molecules was the chemical reaction $F + H_2$. The populations of the individual vibrational-rotational levels was determined spectroscopically [6] by the method of infrared chemiluminescence.

The experimental arrangement is described in [6]. The flux of reagents was determined from the drop in pressure in the reagent reservoirs, and was set by systems which automatically maintained constant reagent flux to within about 1%. The fluorine atoms were produced from F_2 molecules in a radiofrequency discharge (1.6 MHz, 100 W). The flux of F_2 did not exceed 6 μmole/sec, and the flux of H_2, D_2, He, and Xe was varied between 0.5 and 23 μmole/sec.

The reagents were introduced into the reaction chamber through a coaxial quartz tube [1] in which the partially dissociated fluorine entered through the inner tube and the H_2 molecules through the outer tube. On leaving this injector, the atoms and molecules of fluorine formed an inner molecular beam which expanded in the outer H_2 beam. In some experiments, helium, deuterium, or xenon was introduced together with hydrogen through the outer tube. A fixed probe was introduced into the chamber for measurements of pressure in the region where the two molecular beams intersected. In these measurements, we used nitrogen instead of fluorine. We found that the nitrogen pressure at different points in the inner beam fell rapidly with distance from the axis, and was directly proportional to the nitrogen flux, but was practically independent (to within 10%) of the hydrogen flux in the outer beam. The hydrogen pressure in the outer beam was not very dependent on the position of the probe, but increased in proportion to the flux of hydrogen. It was practically independent of the flux of nitrogen. The pumping speed for hydrogen and nitrogen, determined from these measurements, was 1000 and 500 liters/sec, respectively.

When the vibrationally excited HF molecule strikes the cold wall (the walls of the reaction chamber were liquid nitrogen-cooled), it sticks to it for a time sufficient for total deactivation.[1,7] The maximum rate of loss of excited HF molecules due to this mechanism, calculated from the number of collisions with the walls and the attachment probability (actually equal to unity), amounted to 13 000 liters/sec. The rate of pumping of CO_2 molecules by the cold walls, determined in experiments in which carbon dioxide was introduced through the outer tube, was 10 000 liters/sec, which is close to the maximum.

It follows from the foregoing that the number of collisions between the resulting HF molecules and the molecules of any other gas in the zone of observation increases in proportion to the flux of this gas under these experimental conditions. To increase the number of collisions, we partially covered the pumping line, which reduced the rate of pumping of hydrogen, deuterium, helium, xenon, and fluorine by a factor between 1.5 and 3. Under these conditions, the rate of removal of excited HF molecules was practically constant. Rough estimates, based on measurements of pressure in the observation zone, showed that, for a hydrogen flux of 4 μmole/sec, the HF molecules underwent 1—3 collisions with H_2 molecules in the observation zone.

When the fluorine flux was 6 μmole/sec, the number of collisions between the HF molecules and the molecules and atoms of fluorine did not exceed 10. The number of collisions between HF and H_2 molecules was determined more reliably from the change in the intensity of HF emission when the mixture H_2 + He (1 : 1) in the outer tube was replaced by $H_2 + D_2$ (1 : 1). For the same flux and degree of dissociation of fluorine, and equal fluxes of H_2 + He and $H_2 + D_2$, the reduction in the intensity of HF emission was found to be proportional to the loss of F atoms through the $F + D_2$ reaction. These experiments showed that, when H_2 + He (8 μmole/sec) was replaced by an equal flux of $H_2 + D_2$, the emission intensity and hence the mean concentration of fluorine atoms in the reaction zone were reduced by 10 ± 3%.

Under steady-state conditions, the concentration of fluorine atoms is given by

$$[F]=W/(B+K_1[H_2]+K_2[D_2]),$$

where W is the rate at which the fluorine atoms enter the reaction zone, B is the probability of removal of a fluorine atom by pumping, K_1 is the rate of the $F + H_2$ reaction, and K_2 is the rate of the $F + D_2$ reaction. Consequently,

$$\frac{\Delta[F]}{[F]}=\frac{K_2[D_2]}{B+K_1[H_2]+K_2[D_2]}$$

Assuming that, on the average, $K_1/K_2 = 1.6 \pm 0.3$[8] for $[H_2] = [D_2]$, we obtain

$$B=(4.6^{+5}_{-2,5})K_1[H_2].$$

This means that, under these particular conditions, the fluorine atoms are pumped out more rapidly than they react with H_2 by a factor of two-ninths. Assuming that, on the average, $K_1 = 2 \pm 0.6 \times 10^{-11}$ cm³/molecule · sec,[9] which corresponds to one reactive collision of F with H_2 out of 15 ± 5, we find that the number of collisions between the F atoms and the H_2 molecules under these conditions is $3.3^{+6}_{-2.5}$.

Since the HF molecules are removed from the reaction zone more rapidly than the fluorine atoms, they should undergo fewer collisions with the H_2 molecules. Comparison of the pressure distributions for the N_2 and CO_2 molecules show that the latter were removed from the reaction zone three times more rapidly than the former. We note that the HF molecules are formed, in in general, at all points in the observation zone, whereas the CO_2 molecules are introduced practically exclusively in the central part. The distribution of the density of HF molecules must therefore lie somewhere between the CO_2 and N_2 distributions, but is unlikely to differ too much from the CO_2 distribution. In view of the foregoing, the mean number of collisions between the HF and H_2 molecules in the observation zone for a hydrogen flux of 4 μmole/sec was assumed to be $Z_{H_2} = 1.5$. (Strictly speaking, the true number of collisions lies somewhere between 0.3 and 9.)

The number Z_X of collisions experienced by the HF molecules under different conditions was determined from the formula

$$\frac{Z_x}{Z_{H_2}}=\frac{f_x}{f_{H_2}}\frac{S_{H_2}}{S_x}\frac{V_x}{V_{H_2}}=\frac{f_x}{4}\frac{1000}{S_x}\frac{V_x}{1800}$$

where f_X is the flux of the given gas in μmole/sec, f_{H_2} = 4 μmole/sec, S_X is the pumping speed for the given gas in liters/sec, S_{H_2} = 1000 liters/sec, V_X is the thermal velocity of the given molecules in m/sec, and V_{H_2} = 1800 m/sec.

The experimental conditions and the corresponding mean numbers of collisions between HF molecules and H_2, D_2, He, and Xe are given in the table.

EXPERIMENTAL RESULTS

A. Rotational relaxation. The rotational distributions obtained in experiments 1—25 (see Table I) are shown in Figs. 1—6. The resultant population of all the rotational levels for each curve is 100. The uncertainty in the determination of the population of an individual rotational level does not exceed 0.3 of one scale division in the figures.

Figure 1 shows the rotational distribution of the HF molecules in the second vibrational level (v = 2) after 1, 6, 10, and 32 collisions with H_2 molecules (curves 1, 2, 3, and 4, respectively), and after 7 collisions with H_2 and 20 collisions with He (curve 5). As can be seen, as the number of HF—H_2 collisions increases from 1 to 6 and 10 (curves 1 and 2, 3), the population of the levels

TABLE I

No.	Number of collisions with reagents				Vibrational distribution		
	H_2	He	D_2	Xe	n_1	n_2	n_3
1	0.6				0.40	1	0.43
2	~3			~50	0.63	1	0.35
3	1.2				0.35	1	0.48
4	6				0.36	1	0.50
5	6				0.37	1	0.48
6	0.8				0.40	1	0.45
7	10						
8	2.9	2.2					
9	2.7	2.1					
10	2.9		2.2				
11	2.7	2.1					
12	2.7		2.1				
13	2.5	2.0					
14	2.7		2.1				
15	2.2		5.6				
16	3		7.5				
17	3	7.5					
18	10				0.36	1	0.42
19	10				0.36	1	0.44
20	10				0.29	1	0.42
21	10				0.34	1	0.44
22	32				0.56	1	0.37
23	32				0.53	1	0.42
24	32				0.56	1	0.39
25	6.8	20			0.45	1	0.40

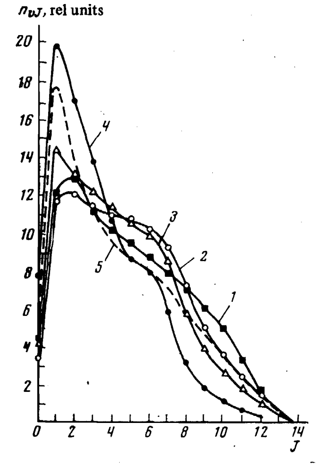

FIG. 1

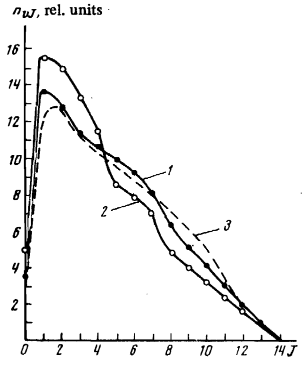

FIG. 2

FIG. 1. Transformation of the rotational distribution for v = 2 as the hydrogen flux is increased: curve 1—average distribution obtained from experiments 1, 3, 6; curve 2—average distribution for experiments 4, 5; curve 3—average distribution for experiments 7, 18, 19, 20, and 21; curve 4—average distribution for experiments 22, 23, 24; curve 5—distribution obtained in experiment 25.

FIG. 2. Transformation of rotational distribution of HF molecules when He is replaced by D_2. Curve 1—rotational distribution obtained from experiments 8, 9, and 11 (He); curve 2—experiments 10, 12, and 14 (D_2); curve 3—distribution obtained from experiments 1, 3, and 6.

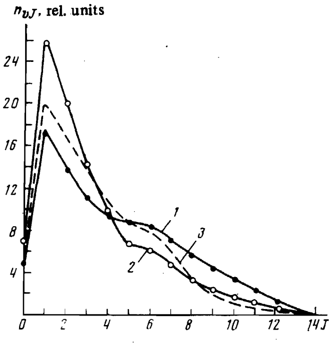

FIG. 3

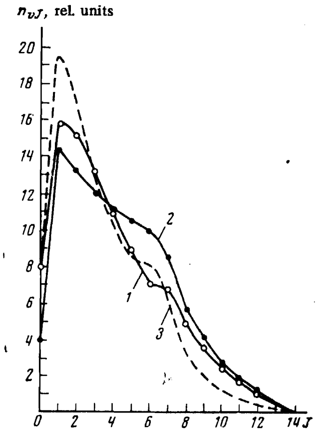

FIG. 4

FIG. 3. Rotational distribution obtained from experiments 17 (curve 1), 16 (curve 2), and 22, 23, and 24 (curve 3).

FIG. 4. Rotational distributions for v = 1 and v = 2 vibrational levels: curve 1—mean distribution for the v = 1 level obtained from experiments 18, 19, 20, and 21; curve 2—distribution for v = 2, experiments 18, 19, 20, and 21; curve 3—distribution for v = 2, experiments 22, 23, and 24.

with J = 9 and 10 decreases, whereas that of levels with J = 4, 5, 6, and 7 increases. The relative change in the populations is largest for levels with J = 9, 10. Further increase in the number of HF—H_2 collisions up to 32 (curve 4) makes the reduction in the population of J > 8 levels still more appreciable. Comparison of curves 2 and 5 shows that, if the HF molecules experience in addition to the six collisions with H_2 a further 20 collisions with He, then the population of J ≥ 9 levels remains practically unaltered. At the same time, there is appreciable relaxation on He for J < 9.

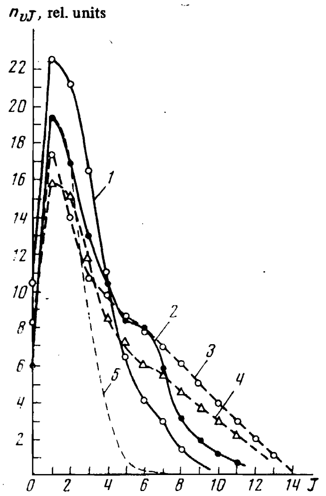

FIG. 5

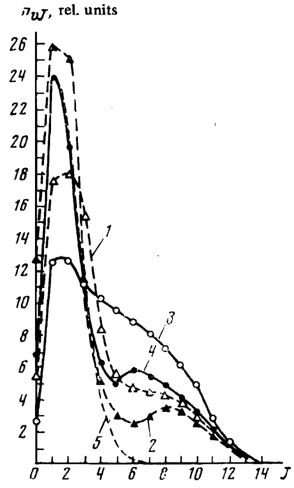

FIG. 6

FIG. 5. Rotational distributions for the v = 2 and v = 1 levels in the case of collisions with H_2 or He: curve 1—average rotational distribution for v = 1, experiments 22, 23, 24 (H_2); curve 2—distribution for v = 2, experiments 22, 23, and 24 (H_2); curve 3— rotational distribution for v = 2, experiment 25 (He); curve 4—distribution for v = 1, experiment 25 (He); curve 5—equilibrium rotational distribution for 200°K.

FIG. 6. Transformation of rotational distributions for the v = 1 and v = 2 levels when xenon is added: curve 1—distribution for v = 1, experiment 1; 2—v = 1, experiment 2 (Xe); 3—v = 2, experiment 1; 4—v = 2, experiment 2 (Xe); 5—equilibrium rotational distribution for 200°K.

Figure 2 shows the rotational distributions of HF molecules in the v = 2 levels after three collisions with H_2 and two collisions with He (curve 1), and after three collisions with H_2 and two collisions with D_2 (curve 2). Curve 3 shows, for comparison, the rotational distribution of H molecules after one collision with H_2. It is clear that curves 1 and 3 are similar up to J = 7. The somewhat lower population of levels with J > 8 (curve 1), and the associated characteristic "knee" in region 7 < J < 10, are due to the increase in the number of collisions between HF and H_2, as indicated above. The replacement of He by D_2 (curve 2) modifies the shape of the rotational distribution curve by the appearance of the second knee in the region J = 5—4.

Figure 3 shows the rotational distributions of HF molecules after 7.5 collisions with He or D_2, and three collisions with H_2 (curves 1 and 2, respectively). The same figure shows the rotational distribution of HF molecules after 32 collisions with H_2 (curve 3). It is clear that the rotational levels with J > 7 relax on He more slowly than on H_2 and D_2, whereas the J = 5, 6, 7 levels are most rapidly depleted in collisions with D_2. On the whole, the rotational relaxation of HF molecules occurs most rapidly in collisions with D_2.

Figure 4 shows the rotational distributions for v = 1 (curve 1) and v = 2 (curve 2) in the case of HF molecules after 10 collisions with H_2. These distributions are substantially different. For v = 1, the population of J ≤ 4 levels is greater, and for J > 4 it is lower, than for v = 2. As the number of collisions with H_2 increases up to 32, the distribution for v = 2 (curve 3) becomes similar to the distribution for v = 1 after 10 collisions (curve 1). It may be concluded that the rotational distribution for v = 1 after 10 collisions is closer to the equilibrium state than in the case of v = 2.

Figure 5 shows the rotational distribution of HF molecules for v = 1 and v = 2 after 32 collisions with H_2 (curves 1 and 2, respectively), and after 20 collisions with He and 7 collisions with H_2 (curves 3 and 4). This figure also shows the rotational distribution for T = 200°K. As in the case of collisions with H_2, the HF—He collisions occur in such a way that the distribution for v = 1 (curve 4) is closer to the equilibrium state than for v = 2 (curve 3). Moreover, it is clear that, in both the first and second vibrational states, the rate of deactivation of high rotational levels is greater in the case of H_2 than in the case of He. It is noticeable that, both for H_2 and He, the rotational distributions corresponding to v = 1 and v = 2 show the maximum difference for intermediate values of J ($4 < J < 7$).

Figure 6 shows the rotational distributions of HF molecules for v = 1 and 2 after 50 collisions with Xe and 3 collisions with H_2 (curves 2 and 4, respectively). The figure also shows the rotational distributions obtained under the same conditions, but without a stream of xenon (curves 1 and 3), and the equilibrium distribution for T = 200°K (curve 5). It is clear that, after more than 50 collisions (largely with Xe), the rotational distribution has still not reached the equilibrium state. It is also noticeable that the difference between the v = 1 and v = 2 distributions for intermediate values of J ($4 < J < 7$) is again present. Curves 2 and 4 exhibit minima for intermediate values of J, which suggests that high levels ($J \geq 8$) are depleted more slowly than intermediate levels ($4 < J < 7$) during collisions with Xe.

Generalizing the foregoing results, we may conclude as follows:

1. Rotational relaxation of HF molecules on H_2, D_2 is different from relaxation on He, Xe. In the case of collisions with He and Xe, high rotational levels ($J \geq 8$) are depleted more slowly than in collisions with H_2 and D_2. Levels with J = 5, 6, and 7 are most rapidly depleted in collisions with D_2.

2. For a given number of collisions, the rotational distributions of HF molecules for v = 1 and v = 2 are different, and the difference reaches a maximum for intermediate values of J. The rotational distribution for v = 1 is always the closer to the equilibrium state.

3. In the case of collisions with Xe, rotational levels with $J > 8$ are depleted more slowly than the J = 4, 5, 6, and 7 levels.

B. Vibrational relaxation. Table I shows the relative populations of vibrational levels, n_v, obtained by summing the relative populations of the rotational sublevels. The vibrational distributions are not corrected for radiative deactivation. It is clear from the table that the vibrational distributions in experiments 1—6 and 18—21 are not very different and approach the mean distribution $n_1 : n_2 : n_3 = 0.35 : 1 : 0.45$.[6] The distributions in experiments 2, 22—25 are characterized by an appreciably higher relative population of the first vibrational level, and the distributions in experiments 22—24 are practically identical. The vibrational distributions in experiment 25 differ from those in experiments 22—24, and the difference lies outside the limits of experimental error.

DISCUSSION OF RESULTS

A. Rotational relaxation. According to the data of Polanyi and Woodall,[1] the initial rotational distributions of the HF molecules formed in the $F + H_2 \rightarrow HF + H$ reaction exhibit maxima for $J \approx 7$. Our "initial" distribution (Fig. 1, curve 1; Fig. 2, curve 3; Fig. 6, curve 3), obtained in experiments 1, 3, and 6 for the smallest number of collisions with H_2, D_2, He, and Xe, is appreciably different from that reported in[1]. This is connected with the rotational relaxation of HF molecules on atoms and molecules of fluorine, which was not controlled in our experiments. We have investigated the transformation of the "initial" rotational distribution through the increase in the number of collisions between HF molecules and H_2, D_2, He, and Xe.

Polanyi et al.[3] have shown that the probability of R—T transfer is described by the empirical formula $P^J_{J-\Delta J} = Ae^{-C\Delta E}$. It follows from this formula that, under our conditions, the rate of population of intermediate rotational levels of the HF molecule ($4 < J < 7$) during rotational relaxation should be substantially lower than the rate of depletion. As a result, the population of intermediate levels should fall with increasing number of collisions, and this fall should be more rapid than the reduction in the population of the higher rotational levels ($J > 8$). This is precisely the transformation of the rotational distribution of HF molecules obtained after 20 collisions with He (Fig. 3, curves 2 and 5): the population of the J = 4—7 levels falls and the result of this is an increase in the population of the $J < 3$ levels, whereas levels with $J > 8$ undergo practically no change. Further increase in the number of collisions is shown by the experiment with xenon (Fig. 6) to lead to the formation of minima in the region of J = 6 (v = 1) and J = 5 (v = 2).

The rotational distribution of HF molecules is transformed in a different way during collisions with H_2. As already noted, the population of the upper levels ($J > 8$) is more rapidly reduced during collisions with H_2 molecules, whilst the population of the J = 4—7 levels at first increases (curves 1 and 2 in Fig. 1). Since in experiments 4 and 5 (6 collisions with H_2) and experiments 18, 19, 21, and 22 (10 collisions with H_2) there was no detectable vibrational relaxation, it may be included that the reduction in the population of the $J > 8$ levels is connected with the transition of the HF molecules from levels with $J > 8$ to levels with J = 4—7. Consequently, in the case of rotational relaxation of HF on H_2, there is, in addition to R—T energy transfer, a further process which takes the HF molecules from the J = 9, 10 to the J = 8, 7, 6 levels.

The rate of this process is estimated to exceed the rate of R—T deactivation of levels with $J > 8$ by an order of magnitude. This may be the resonance transfer of rotational energy from HF to H_2. The frequencies ν of several rotational transitions of HF, H_2, and D_2 are listed in Table II. It is clear that the frequency of rotational transitions such as $J = 10 \rightarrow J = 9$ and $J = 9 \rightarrow J = 8$ in HF is close to the frequency of the rotational transition $J = 0 \rightarrow J = 2$ in H_2 and, therefore, the following processes should participate in the deactivation of the HF molecules:

$$HF(J=10)+H_2(J=0)\rightarrow HF(J=9)+H_2(J=2),$$
$$HF(J=9)+H_2(J=0)\rightarrow HF(J=8)+H_2(J=2).$$

The presence of resonance rotational-energy transfer is also confirmed by experiments in which deuterium was supplied together with hydrogen to the reaction zone. To eliminate the influence of R—T transfers, we compared the results of these experiments with the results obtained when deuterium was replaced by the same amount of helium. As can be seen from Table II, rotational transfer between HF and D_2 molecules is possible in the following processes:

$$HF(J=8)+D_2(J=1)\rightarrow HF(J=7)+D_2(J=3),$$
$$HF(J=5)+D_2(J=0)\rightarrow HF(J=4)+D_2(J=2).$$

TABLE II

HF molecule				H_2		D_2	
$v=2$		$v=1$					
$J'\to J$	ν, cm^{-1}	$J'\to J$	ν, cm^{-1}	$J'\to J$	ν, cm^{-1}	$J'\to J$	ν, cm^{-1}
3→2	114			0→2	363	0→2	180
4→3	152	4→3	158	1→3	618	1→3	305
5→4	189	5→4	197	2→4	910	2→4	450
6→5	227	6→5	236				
7→6	264	7→6	274				
8→7	300	8→7	312				
9→8	337	9→8	350				
10→9	373	10→9	388				

In fact, curve 2 in Fig. 2 shows the characteristic breaks corresponding to the relative increase in the population of the J = 4 and J = 7 levels as compared with the J = 5 and J = 8 levels. This suggests the presence of resonant collisions. Since, in the case of deuterium, we can have both resonance transfer for J ~ 7—10 and resonance transfer during the J = 5 → J = 4 transition, relaxation on D_2 molecules occurs more rapidly than on H_2 (Fig. 3).

As already noted, under identical conditions, the rotational distribution for v = 1 is always closer to the equilibrium state than for v = 2 (Figs. 4—6), i.e., the rotational relaxation of HF (v = 1) molecules occurs more rapidly than the relaxation of HF (v = 2) molecules (the initial distributions for v = 1 and v = 2 are similar [1]). The reason for this difference is not clear. The features noted above, namely, the relatively rapid deactivation from high rotational levels of HF in collisions with H_2, and the high rate of rotational relaxation of HF (v = 1) molecules as compared with HF (v = 2) molecules, can also be seen in the results published in [1]. It is clear from the rotational distributions in [1] (Fig. 5, experiments AV and AVI) that, as the flux of H_2 is increased, and separate sources are replaced by the coaxial design, i.e., for a larger number of collisions with H_2, there is a reduction in the populations of the J > 7 (v = 2) levels and an increase in the population of the J = 4, 5, 6 (v = 2) levels (experiments AV). Moreover, this increase in the number of collisions has a greater effect on the rotational distribution in the first vibrational state.

B. Vibrational relaxation. The departure of the observed vibrational distribution from the initial situation is due to radiative deactivation and to deactivation during collisions with the molecules and atoms in the observation zone. Estimates show that the increase in the population of the v = 1 level in experiments 2 and 25, as compared with experiments 1, 4, 18, 19, 20, and 21 (Table I) can be explained by the radiative deactivation of HF molecules due to the increase in the time spent in the observational zone in the case of a large number of collisions. The agreement between the vibrational distributions in experiments 24 and 22, 23 may be used to conclude that vibrational relaxation resulting in these distributions is not connected with relaxation on atoms and molecules of fluorine (in experiment 24 the flux of F_2 molecules was increased by a factor of three and the flux of F atoms by a factor of four as compared with experiments 22 and 23).

Comparison of the experimental conditions in the case of experiments 22—24 and 25 shows that the relatively high population of the v = 1 level in experiments 22—24 was due to the vibrational deactivation of HF molecules on H_2. This change in the population of the vibrational levels agrees with calculations if it is assumed that the number of collisions between HF and H_2 is 50, and the rate of deactivation of HF molecules is, on the average,

$$K_1=3.4\cdot10^{11}\ \mathrm{cm^3/mole\cdot sec},\qquad K_2=5.4\cdot10^{11}\ \mathrm{cm^3/mole\cdot sec}.$$

$$K_3=6.8\cdot10^{11}\ \mathrm{cm^3/mole\cdot sec},$$

for levels with v = 1, 2, and 3, respectively. [10] The number of collisions obtained in this way (~50) is in good agreement with the figure of 32, which is given in the table. This confirms the validity of the estimated value of Z_{H_2}.

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