Measurement of the rate of rotational relaxation of HF molecules

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The rate constants of the rotational relaxation of the level $v = 0$, $J = 8$ of HF molecules on HF, H_2, D_2, He, Ar, Xe, O_2, F_2, CO, CO_2, CS_2, and CCl_4 were determined by measuring the relaxation losses occurring when light is made to pass through a resonantly absorbing medium.

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Recently published calculations for a chemical laser using HF[1] show that the influence of the processes of rotational relaxation $(R-R)$ on its operating characteristics can be appreciable. The importance of investigating rotational-relaxation processes is due also to the fact, as shown in[2], that the $R-R$ relaxation is introduced into the vibrational degrees of freedom of molecular systems acted upon by monochromatic radiation. Recent experiments[3] have made it possible to establish that the rate of the $R-R$ relaxation of HF decreases with increasing rotational quantum number J and that even after ~ 100 molecular collisions no rotational equilibrium is established on levels with $J \gtrsim 7$. It was also shown that in $R-R$ relaxation, an important role is played by processes of resonant exchange in collisions with H_2 and D_2.

We present here the results of investigations of $R-R$ relaxation of HF by measuring the relaxation losses of the radiation energy when light is passed through a resonantly-absorbing medium. The possibility of using this procedure for investigation of radiation processes is well known,[4] but has not found extensive practical application.

We used in the experiments pulsed HF chemical laser. A monochromator was used to separate the line $R_8(1 \to 0)$ which has a duration $T = 1$ μsec and an average intensity $I_0 = 4.0 \times 10^{22}$ quanta/cm^2 sec. The radiation of the $P_8(1 \to 0)$ line was passed through an optical cell of stainless steel with CaF_2 windows, containing the HF molecules and a relaxant gas. With the aid of two calorimeters on both ends of the cell, we measured the absolute value of the radiation energy absorbed in the optical cell at different relaxant-gas pressures.

Preliminary investigations with pure HF have shown that bleaching of the medium takes place at the employed radiation intensities and pressures. Fig. 1 shows plots of $\ln(I_0/I)$ against Nl for a number of radiation intensities I_0 on the $P_8(1 \to 0)$ line prior to entering the optical cell (I is the radiation intensity after passing through the cell, l is the length of the cell, N is the population of the state $v = 0$, $J = 8$ of the HF molecules). It is seen from the figure that the plots are essentially nonlinear and diffraction of the absorbed intensity at fixed Nl increases with increasing I_0. This behavior is possible only if the medium becomes bleached, when the condition $I > I_{sat} = 1/2\sigma\tau_{rel}$ is satisfied (I_{sat} is the saturation intensity, σ is the absorption cross section, τ_{rel} is the characteristic
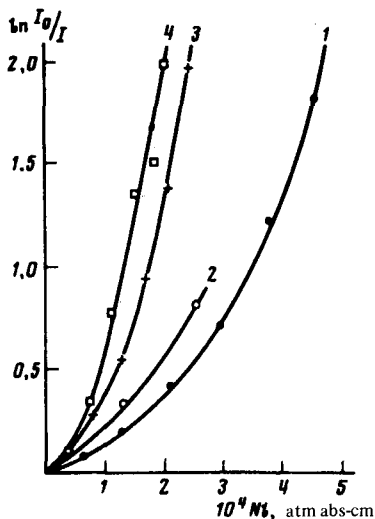
FIG. 1. Plot of $\ln(I_0/I)$ against N/l at $I_0 = 8 \times 10^{22}$ (1), 4×10^{22} (2), 2×10^{22} (3), and 0.8×10^{22} (4) quanta/cm^2 sec.

time of the relaxation processes). A reduction of the plots shown in Fig. 1 has made it possible to estimate the "unsaturated" absorption cross section of HF, which turned out to be $(4 \pm 1) \times 10^{-16}$ cm^2, and also the R—R relaxation constant of HF, namely, $\sim 10^3$ atm$^{-1}\mu$sec^{-1}.

In investigations with relaxant gases, we chose and maintained a constant pressure for the HF, namely 2 Torr. By way of example, Fig. 2 shows the
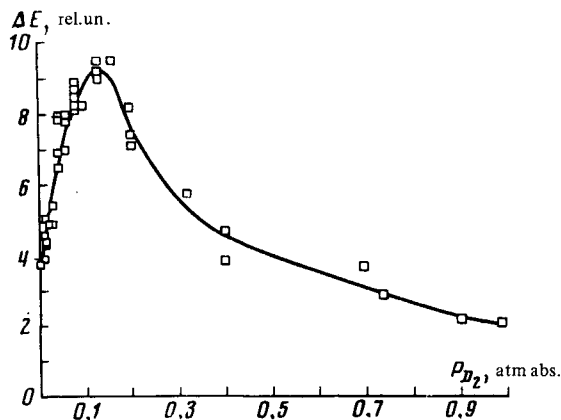

FIG. 2.

dependence of the absorption of the radiation energy on the pressure of D_2. It can be shown that if the following conditions are satisfied: 1) the decrease of the pulse intensity as a result of absorption is small; 2) $\tau_i \ll T$, where τ_i

$\approx 1/\sigma I$ is the characteristic time of induced absorption, then the energy absorbed per unit volume of the absorbing medium is given by the formula

$$\Delta E \approx a \mathcal{E} N T k_R p + \Delta E_o. \tag{1}$$

$\mathcal{E}$ is the energy of the radiation quantum, N is the initial population of the state $v = 0$, $J = 8$ of HF prior to the bleaching, k_R is the $R-R$ relaxation constant, p is the pressure of the relaxant gas, ΔE_0 is a constant term not connected with the $R-R$ relaxation on the relaxant gas, and α is a coefficient equal to unity of the rate of depletion of the level $v = 1$, $J = 7$ due to the vibrational-vibrational exchange of the HF molecules with one another or with the relaxant gas is equal to infinity, or equal to $\frac{1}{2}$ if there are no vibrational exchange processes. As shown by estimates based on the known data on the rates of the vibrational exchange,[5] our case corresponds best to the value $\alpha = 1$. Conditions 1) and 2) were satisfied in our experiments. Then, in accordance with Eq. (1), k_R can be determined from the initial slope of the plot of ΔE against the pressure p.[1] The table lists the obtained values of k_R for a number of gases (α was assumed equal to unity):

Relaxant gas	HF	H_2	D_2	He	Ar	Xe	O_2	F_2	CO	CO_2	CS_2	CCl_4
k_R, atm^{-1} μsec^{-1}	10^3	30	30	$\leqslant 5$	$\leqslant 5$	$\leqslant 5$	$\leqslant 10$	$\leqslant 20$	$\leqslant 20$	60	100	120

The obtained values of k_R correspond to collision-induced relaxation probabilities $\sim 10^{-1}$ (HF), $\sim 10^{-2}$ (CS_2, CCl_4), $\sim 3 \times 10^{-3}$ (H_2, D_2), and lower for the other gases. Such low probability values call for a more thorough analysis of the vibrational-rotational relaxation of the HF molecules in comparisons with the usually employed assumption that the $R-R$ relaxation is "instantaneous."[6]

[1]We note that the decrease of the absorption at high pressures (see Fig. 2) is connected with the decrease of the absorption cross section as a result of the collision broadening, and makes it possible in principle to investigate the broadening ability of different gases.

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