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LASER COLLISIONAL PUMPING OF HF MOLECULES

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The effect of IR laser radiation on molecules can result in the production of strongly nonequilibrium molecular gas states because of the selective "heating" of the vibrational degrees of freedom. Research to use vibrational-translational nonequilibrium occurring during the absorption of laser radiation for its effect on chemical processes has recently been performed. As a rule, the possibilities of stimulating and controlling reactions relate primarily to the high reactivity of vibrationally excited molecules, as well as to the formation of high-activity particle concentrations during nonequilibrium dissociation caused by "heating" the molecular vibrations. At this time a sufficiently large number of papers devoted to both the dissociation of molecular gases and to laser-induced chemical reactions (e.g., [1, 2], as well as the surveys [3, 4]), have been published. Let us note that the proof of the selective action of laser radiation on the progress of a process is not indisputable in many of the reported cases. Hence, further research in this area is expedient.

Various aspects of vibrational kinetics have been examined in a number of theoretical papers (cf. [5-10]), for systems of anharmonic oscillators under conditions of a strong deviation from equilibrium (finding the vibrational distribution function and the energy relaxation rate, determining of the energy dissipation of the vibrational degrees of freedom, estimating the nonequilibrium dissociation rates).

Because of the lack of quantitative data on the rate constants of all the possible relaxation processes for the majority of molecular systems, the theoretical comprehension necessarily remains at a qualitative level.

An analysis of the processes occurring during the insertion of significant quantities of energy during laser exposure, and the determination of the limit energy capacity of the vibrational degrees of freedom, the total energy capacity, as well as the comparison of theoretical and experimental results, are performed more conveniently on model systems. Small atoms and, especially, diatomic molecular gases, can be model systems since the relaxation processes (rotational-translational (R-T), vibrational-translational (V-T), vibrational-vibrational (V-V) exchanges) have been studied to greatest degree for small-atom molecules, and the structure of the energy levels of these molecules is simple.

At this time, an experimental investigation of the vibrational pumping of HF molecules because of resonance absorption of HF laser radiation by HF molecules in the low vibrational states and subsequent pumping in the high state in collisions of vibrationally excited molecules has been performed. For brevity, we will later denote such a process laser-induced collisional pumping (LCP). A pulsed HF laser with ~ 10 -J radiation energy and a pulse duration of $2 \mu\text{sec}$ at the foundation [11] was used in the experiments. The spectrum consisted of 20 lines of the first four vibrational-rotational HF bands. About 10% of the laser pulse energy was concentrated in the 1-0 band, about 80% in the 2-1 band, while the rest of the energy was distributed between the 3-2 and 4-3 bands. The 1-0 band started with an intense P_8 line, and the most intense lines in the the 2-1 band were P_7 and P_8 . Singularities associated with the spectral composition of the radiation result in the process of laser energy absorption being started by the HF molecules populating the rotational half-level $J = 8$ of the vibrational ground state. Consequently, a small fraction of the molecules being pumped are initially in resonance with the laser radiation (a fractional part of $\sim 10^{-3}$ of the total number of molecules is in the initial state at the $J = 8$ level). The total radiation intensity (the mean during a pulse) was $I \approx 0.5 \text{ MW/cm}^2$ ($6.5 \cdot 10^{24}$ photons/cm²·sec) and could be increased by focusing to $I \sim 10 \text{ MW/cm}^2$ ($1.3 \cdot 10^{26}$ photons/cm²·sec). Focusing was performed by a lens with a 50-cm focal length. A cylindrical zone of 6 mm diameter was exposed at

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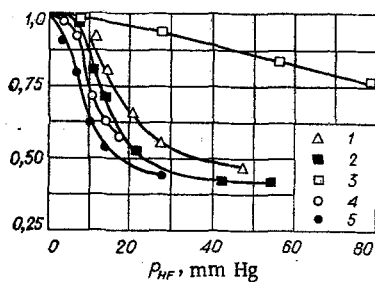


Fig. 1

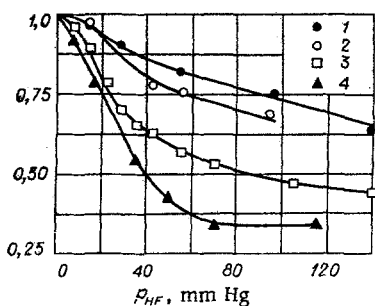


Fig. 2

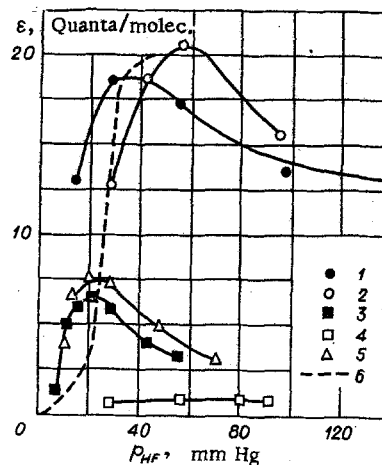


Fig. 3

the lens caustic, where the zone diameter was kept practically constant at a length of ~ 6 cm. The dependence of the integrated transmission of an HF-filled absorption cell on the cell length L and pressure p_{HF} was studied in a number of tests. Transmission of an absorption cell filled with a mixture of HF and a buffer gas (He) was studied in another series of tests. The spectra of the laser radiation passing through the cell were recorded simultaneously. The experimental results are represented in Figs. 1-3 (in Fig. 1, $L = 1$ cm, $I = 0.56$ MW/cm 2 ; $L = 1.7$ cm, $I = 0.62$ MW/cm 2 ; $L = 1.7$ cm, $I = 0.65$ MW/cm 2 ; for curves 1, 2, and 3, respectively. Also in Fig. 1 for an HF + He mixture at a constant total pressure of 430 mm Hg, $L = 5.5$ cm, $I = 0.64$ MW/cm 2 ; $L = 10$ cm, $I = 0.65$ MW/cm 2 for curves 4 and 5, respectively. In Fig. 2, $L = 1.7$ cm, $I = 11.2$ MW/cm 2 ; $L = 1.7$ cm, $I = 10$ MW/cm 2 , a mixture of HF + He at a constant total pressure of 430 mm Hg; $L = 5.5$ cm, $I = 9.6$ MW/cm 2 ; $L = 10$ cm, $I = 11.3$ MW/cm 2 for curves 1, 2, and 3, respectively, and in Fig. 3, $L = 1.7$ cm, $I = 11.2$ MW/cm 2 , $L = 1.7$ cm, $I = 10$ MW/cm 2 , mixture of HF + He at a constant total pressure of 430 mm Hg, $L = 1.7$ cm, $I = 0.62$ MW/cm 2 ; $L = 1.7$ cm, $I = 0.65$ MW/cm 2 , a mixture of HF + He at a constant total pressure of 430 mm Hg; $L = 1.0$ cm, $I = 0.56$ MW/cm 2 for the corresponding curves 1-5, respectively). Tests showed a noticeable difference in the nature of HF absorption at intensities 0.5 and 10 MW/cm 2 . The results reduce to the following:

1) For an unfocused laser beam the dependence of the transmissivity of the absorption cell on p_{HF} is of quasithreshold nature in the absence of a buffer gas: At low pressures ($p_{HF} \leq 7$ mm Hg) the radiation is absorbed weakly; furthermore, the cell transmissivity drops sharply for a small change in the pressure (curves 1 and 2 in Fig. 1);

2) upon dilution of the HF absorption of the unfocused beam attenuates sharply (by about an order) (curve 3 in Fig. 1);

3) for a focused beam, dilution of HF by a buffer gas affects the magnitude of the transmissivity weakly (curves 1 and 2 in Fig. 2);

4) for a focused beam, up to ~ 20 quanta of laser radiation are absorbed for each initial HF molecule (curves 1 and 2 in Fig. 3);

5) as the optical density grows, the level of the laser energy which has passed through the cell emerges at a plateau corresponding to $\sim 35\%$ of the transmissivity for the focused and $\sim 40\%$ of the transmissivity for the unfocused beams.

For $p_{\text{HF}} \lesssim 7$ mm Hg, the unfocused laser beam is not attenuated during passage through the absorption cell (curves 1 and 2 in Fig. 1). We relate this to the fact that at low HF pressures, a saturation mode is reached which is due to the presence of a "narrow throat" for the insertion of energy into the system. The "narrow throat" of LCP occurs because the delivery of molecules at the low level of the absorbing transition is limited by the rate of the R-T processes. As the HF pressure increases, the delivery rate, and therefore, the laser-energy absorption rate as well, will grow. In the long run, the molecules lose the vibrational energy in V-T processes for a pumping constrained by R-T relaxation. A partial transition of the absorbed energy occurs in the translational-rotational degrees of freedom also because of the nonresonance of the V-V exchange. This causes heating of the system and an increase in population of the rotational sublevel responsible for the absorption. The nonlinear temperature dependence of the population results in a progressive acceleration of the energy insertion into the system and the passage to an unsaturated absorption mode. We characterize the absorption by the specific quantity ϵ , the mean number of quanta (with respect to the cell length) absorbed from the laser beam in a computation per each initial HF molecule: $\epsilon = \Delta E / q n^0 S L$, where ΔE is the absorbed energy, q is the energy of a HF laser quantum ($q = 10$ kcal/mole), n^0 is the initial HF concentration in the cell, S is the laser beam cross section, and L is the cell length. The above is illustrated graphically in Fig. 3 (curves 3 and 5) in which the dependence of ϵ on p_{HF} is shown: A sharp increase in the specific absorption occurs for a change in pressure in a small band. Upon dilution of the HF by a buffer gas, system heating because of laser energy absorption turns out to be insufficient to cause the necessary growth in population of the absorbing rotational sublevel. Consequently, the magnitude of the absorbed energy (curve 4) diminishes by approximately an order.

Each HF molecule absorbs 7.5 quanta, i.e., approximately half the store of quanta in the beam capable of being absorbed that arrives at each HF molecule, at the maximum of curve 5 in Fig. 3 ($p_{\text{HF}} \approx 20$ mm Hg) (according to the data in Fig. 1, this store is $\sim 60\%$ of the total store of quanta in the laser beam). It is seen from a comparison of the data (curves 3 and 5) for the cells differing noticeably (1.7 times) in size that the values of ϵ near the maximums of the curves differ moderately. It can be concluded that under these conditions absorption is realized in an optically thin layer in practice, and therefore, the mean specific absorption measured relative to the length of the cell is close to the true maximum for a given specific absorption intensity. The size of the absorbing layer becomes less than the cell size as the HF concentration increases. This results in an apparent reduction in the quantity ϵ .

For a 20-fold increase in the radiation intensity because of laser beam focusing, the specific absorption doubles approximately (curve 1) under conditions corresponding to the maximums of curves 3 and 5 in Fig. 3. The tendency to a further growth in the quantity ϵ as p_{HF} increases indicates that a saturation mode is hence again achieved which is due, as in the case considered earlier, to a constraint on the velocity of energy insertion in the system by the rate of the R-T processes. An increase in the rate of the R-T processes by raising the HF concentration yields the magnitudes $\epsilon \approx 20$ quanta/molecule for both undiluted HF and HF diluted with helium (curves 1 and 2 in Fig. 3). The HF should here be subject to significant dissociation. Indeed, practically complete adiabatic dissociation of HF in the equilibrium mode requires, on the one hand, the expenditure of ~ 16 quanta/molecule. The energy of the HF molecules reaching the $v = 19$ vibrational level during upward motion, because of V-V exchange, differs from the dissociation energy by just the quantity kT ; on the other hand, in practice, such molecules should dissociate in each collision. Hence, expenditures on HF dissociation should not exceed 19 quanta/molecule. The question is therefore what dissociation mode is realized in tests. If the equilibrium dissociation mode were realized, then upon diluting HF by the buffer gas the absorbed energy should increase noticeably since the energy capacity of the system is magnified substantially. This is valid if there is a sufficient store of quanta in the laser radiation flux. Let us estimate the magnitude of the store. Under test conditions the ultimate absorbed energy is $\sim 65\%$ of the total energy of the incident radiation. A simple computation shows that 100 quanta per HF molecule arrive near the maximums of curves 1 and 2 in Fig. 3 (on the average $p_{\text{HF}} \approx 50$ mm Hg), which are potentially absorbable, i.e., a five-fold store. The insignificant dilution by helium indicates that the HF dissociation occurs in the nonequilibrium mode, under conditions of "separation" of the vibrational from the translational temperature.

Let us take the following model, which results from the considerations elucidated above, to describe non-equilibrium dissociation:

- 1) The limiting stage of pumping in the saturation mode is R-T;
- 2) only the cascade-bound transitions $P_J(0-1)$ and $P_{J-1}(1-2)$ ($J = 8$) yield a fundamental contribution to laser energy absorption;

3) vibrational energy dissipation is determined mainly by the dissociation process;

4) molecular dissociation occurs from the boundary level $v_d = 19$.

Upon compliance with case 1) $n_v \ll n_{v=0} \approx n = n^0(1-\alpha)$ is valid, where α is the degree of dissociation. Neglecting the store of quanta at the vibrational degrees of freedom of the HF molecules, we have $\alpha \approx \varepsilon/v_d$. Taking case 2) in a quasistationary approximation for the pumping velocity into account, we obtain

$$\frac{d\varepsilon}{dt} = x_J \frac{(1-\alpha)}{\tau_{RT}^J}, \quad (1)$$

where $x_J = \frac{(2J+1)}{Q_{rot}} \exp\left[-\frac{Bhc}{kT} J(J+1)\right]$ is the normalized Boltzmann factor of the J-th rotational sublevel of the vibrational ground state, $Q_{rot} \approx kT/Bhc$ is the rotational statistical sum, B is the rotational constant, τ_{RT}^J is the characteristic time of R-T relaxation of the J-th sublevel. To describe the adiabatic dissociation process, we add the translational-rotational energy balance equation

$$C\Delta T = \alpha\Delta Q, \quad (2)$$

to (1), where $\Delta Q = qv_d - Q_d$ is the part of the energy of the vibrational quanta that makes the transition into heat during upward motion in energy space because of anharmonicity of the vibrations, Q_d is the HF dissociation energy ($Q_d = 135$ kcal/mole), ΔT is the gas temperature rise, $C = \sum_i c_i a_i$ is the effective specific heat of the

mixture, c_i is the specific heat of the i-th mixture component, and a_i is the ratio of the i-th component concentration to the initial HF concentration. Only two atoms are formed from the HF molecule during dissociation, and their total specific heat only exceeds the specific heat of the HF molecule by 20%; therefore,

$C \approx c_{HF} + c_{He} \frac{n_{He}}{n^0}$. From (1) and (2), we obtain

$$\int_1^y \frac{dy}{x_J \left(\frac{\Delta Q}{CT^0} - (y-1) \right)} = \frac{\tau_{imp}}{v_d} \left\langle \frac{1}{\tau_{RT}^J} \right\rangle, \quad (3)$$

where T^0 is the initial temperature, $y = T/T^0$, τ_{imp} is the duration of a laser pulse, $\left\langle \frac{1}{\tau_{RT}^J} \right\rangle = \frac{1}{\tau_{imp}} \int_0^{\tau_{imp}} \frac{dt}{\tau_{RT}^J}$. The

quantity ε is related to y by the relationship $\varepsilon = v_d C T^0 (y-1) / \Delta Q$. (4)

It is assumed $\left\langle \frac{1}{\tau_{RT}^J} \right\rangle = \frac{1}{(\tau_{RT}^J)_0}$, $(\tau_{RT}^J)_0$ is the characteristic time of R-T relaxation in the initial mixture, in the numerical solution of (3). According to data [12, 13], the R-T relaxation in He in the initial mixtures can be neglected for all the HF dilutions existing in tests. As the gas temperature rises, the helium contribution to the R-T exchange should grow and together with the contribution of the H and F atoms being formed during dissociation, should compensate to some degree the diminution in the rotational relaxation rate because of the drop in HF concentration. The quantity $(\tau_{RT}^J)_0$ is evaluated by using the formula $(\tau_{RT}^J)_0^{-1} = p_{HF} (p\tau_{RT}^J)^{-1} = p_{HF} \sum_i (p\tau_{RT}^{iJ})^{-1} x_i$, and the data of [3], where $p\tau_{RT}^{iJ}$ is the characteristic time of rotational energy transfer for

from the level i to the level J for $p_{HF} = 1$ mm Hg. According to the data in [13], $p\tau_{RT}^{J=8} \approx 7.0 \cdot 10^{-8}$ sec · mm Hg. The results of a computation using (3) and (4) for a HF + He mixture at a total pressure of 430 mm Hg are presented in Fig. 3 (curve 6). It is seen that quantitative agreement between experiment and computation is completely satisfactory; there is quantitative agreement between experiment and computation, the model describes abrupt growth of the specific absorption in a small range of HF pressure variation because of the increase in the rate of the R-T processes.

It follows from the experiments and the model analysis that dissociative instability occurs in the system with the acceleration of rotational relaxation because of the rise in HF pressure for a sufficient radiation intensity. We relate the "bleaching" of the medium observable in tests during the passage from an intensity of ~ 0.5 to the intensity 10 MW/cm² to this phenomenon (compare curves 2 in Fig. 1 and 1 in Fig. 2). The drop in curves 1 and 2 in Fig. 3 is a result of laser beam attenuation because of losses.

The "extra-limitation" of the transmissivity by the absorption cell by approximately an identical level for beam intensities differing by more than an order as the optical density rises can be explained by assuming that generation occurs earlier during the 2-1 transition than in the 1-0 transition. Then, the part of the laser energy which has passed through the cell prior to the time generation occurs at the 1-0 transition cannot be absorbed. Independently of whether the laser beam is focused or not, this part indeed determines the minimum level of cell transmissivity. The justification for the assumption results from the fact that the population of the $v = 2$ level is noticeably greater than the population of the $v = 1$ level because of the singularities in the primary vibrational distribution of the HF molecules obtained in the reaction $H_2 + F_2$, and hence the threshold is reached earlier for generation at the 2-1 transition. The assumption that generation does not occur simultaneously is indeed confirmed experimentally: It is seen from spectrograms obtained that the $P_6(2-1)$ line is not absorbed, therefore, generation ceases earlier there than it occurs at the 1-0 transition.

In conclusion, let us note that the high efficiency of LCP at comparatively low levels ($\sim 10^7$ W/cm²) of the incident radiation power and the small initial fraction ($\sim 10^3$) of the absorbing molecules has been demonstrated by the example of HF. Let us note that the power thresholds for collision-free pumping are in the limits 10^8 - 10^9 W/cm². It can be assumed that the HF pumping scheme and its fundamental regularities are sufficiently general. These regularities are the following: a) Rotational relaxation is the "narrow throat" of the pumping process in the saturation mode; b) dissociative instability of the system occurs for a sufficient laser radiation intensity when the rotational relaxation accelerates; c) the degree of nonequilibrium dissociation can reach a significant value (up to $\sim 100\%$). This corresponds to the formation of high-activity atom concentrations under sufficiently low-temperature conditions, which discloses prospects for investigation of their subsequent reactions.

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