Effect of the rotational relaxation rate on the operation of a pulsed H_2+F_2 chemical laser

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The effect of the rotational relaxation rate on the characteristics of an H_2+F_2 chemical laser with HF as the active molecule is analyzed. Two limiting cases are considered: the case of rotational equilibrium, and the case of "frozen" rotational relaxation. The part played by vibrational relaxation processes is examined. It is shown that the maximum efficiency of the chemical laser is higher in the case of rotational equilibrium than in the case of frozen rotational relaxation.

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INTRODUCTION

A number of papers have recently been published on the theoretical analysis of pulsed chemical lasers in which HF is the active molecule.[1–5] In all these papers it was assumed that rotational-translational equilibrium obtains during the course of the reaction and the lasing action. A recent study of ours[6] showed, however, that the rate of rotational deactivation of the high rotational states on which lasing mainly takes place is low (deactivation in ~100 collisions). Moreover, there are a number of processes going on in a chemical laser that disturb the rotational equilibrium: the chemical reaction that produces HF molecules in high rotational states,[7–9] induced emission in the P branch, and vibrational $V-T$ relaxation of the HF molecules, which, it is assumed, takes place via the $V-R$ mechanism.[10–11] Hence a rigorous analysis of generation in a chemical laser should be carried through without assuming rotational equilibrium. In view of the lack of complete data on the rotational relaxation of HF molecules on various components of the mixture, however, an exact quantitative analysis of the lasing process is not possible at present.

In this paper we analyze the effect of the rotational relaxation rate on the characteristics of an H_2+F_2 chemical laser. We shall examine two limiting cases: the case of fast rotational relaxation, in which the relaxation rate is much higher than the rates of the processes that disturb the rotational equilibrium, and the case of "frozen" rotational relaxation, in which the relaxation rate is much lower than the rates of the processes that disturb the rotational equilibrium. In selecting the frozen rotational distributions we made use of our earlier results on the transformation of the rotational distribution in the $F+H_2$ reaction incident to an increase in the number of collisions.[6] In the conclusion we discuss some features of the operation of real chemical lasers.

1. FAST ROTATIONAL RELAXATION

The presence or absence of rotational equilibrium in a chemical laser is determined by the relation between the rotational relaxation rate and the rate of the processes that disturb the equilibrium rotational distribution. The higher the chemical-reaction rate (which depends mainly on the initiation), the greater the deviation from rotational equilibrium. The case of fast rotational relaxation corresponds to operation of the laser under conditions of weak initiation and high dilution of the working mixture by an inert gas.

In this case, as soon as the inversion of the vibrational–rotational transition $(v+1,J)\to(v,J+1)$ which has the highest gain of those in the given vibrational band reaches the threshold, lasing commences on that single transition (Fig. 1a). Fast rotational relaxation will convert HF molecules from the other rotational levels of the upper vibrational state $(v+1)$ to the $(v+1,J)$ level, and conversely, will convert molecules from the $(v,J+1)$ level to the other rotational levels of the lower vibrational state v on which lasing is not taking place. Since the absolute threshold inversion is usually much lower than the absolute population (see, e.g.,[2]), the lasing, which tends to equalize the populations $n_{v+1,J}$ and $n_{v,J+1}$, reduces the population of the upper vibrational level $v+1$ as compared with that of the lower level v (the well known "partial inversion" regime—see, e.g.,[12]). Then the maximum inversion shifts to the $(v+1,J+1)\to(v,J+2)$ transition, and the onset of lasing on this transition further reduces the population of the upper vibrational level as compared with that of the lower one. The shift of the lasing action toward transitions with higher values will continue until the inversion at some transition falls below the threshold value. The lower the threshold inversion, the higher the J values for the transitions on which lasing will eventually take place for a fixed rotational temperature. An increase

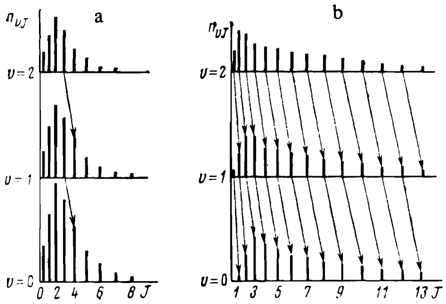

FIG. 1. Diagrams illustrating the lasing process in the cases of fast rotational relaxation (a) and of frozen rotational relaxation (b).

of the rotational temperature will cause the lasing to shift to even higher-J transitions.

We undertook numerical calculations to determine the maximum efficiency of a chemical laser under conditions of fast rotational relaxation (by the maximum efficiency we mean the ratio of the lasing energy to the total chemical-reaction energy, neglecting vibrational relaxation). The calculations reduced to the computation of the final vibrational distribution and the final vibrational energy in accordance with the final rotational temperature, as fixed by the reagent-conversion depth η. The lasing energy is the difference between the initial store of vibrational energy in the HF molecules and the calculated energy, and in the adopted model it is independent of how the process develops in time.

The calculations were performed on a BÉSM-6 computer for a model chemical laser containing an H_2+F_2+X gaseous mixture (X represents a monotonic inert diluent) of composition $H_2:F_2:X=0.25:0.25:0.5$ at a total pressure of 1 atm and operating without vibrational relaxation. The length of the effective region of the laser was taken as 100 cm, and the losses due to escape of radiation, as 60% for two passes.

In a real laser, vibrational relaxation processes quench the lasing action when the reagents are relatively little depleted. It was accordingly assumed for the model laser that the chemical reaction stops at reagent-conversion depths $\eta \leqslant 30\%$; this corresponds to the final temperature $T_{\text{fin}}=\eta Q/C_V+T_0$, where Q is the heat of reaction and C_V is the heat capacity of the mixture (cooling due to the lasing action was neglected). The threshold inversion was determined on the basis of the losses and the cross section $\sigma=10^{-17}$ cm^2 for induced emission on the $v=1\to v=0$ transition.[13,14] The v dependence of σ[15] was taken into account in the calculations, but the J dependence of σ was neglected. The factor $(T_{\text{fin}}/300)^{1/2}$ was introduced to take the temperature dependence of the width of the HF line, and hence that of the threshold inversion, into account. The results of the calculations are presented in Table I. It will be seen that the maximum efficiency of the model chemical laser varies little over the selected range of η values, although it does exhibit a tendency to fall with increasing temperature. The calculations also showed that the distributions of the HF molecules over the vibrational levels resulting from the combined action of lasing and rotational relaxation are close to equilibrium distributions for definite vibrational temperatures $T=T_{\text{vib}}$ (see Fig. 2b); there is an appreciable excess of molecules above the equilibrium population only for vibrational levels with $v>4$, but transitions involving such levels contribute little to the lasing intensity.

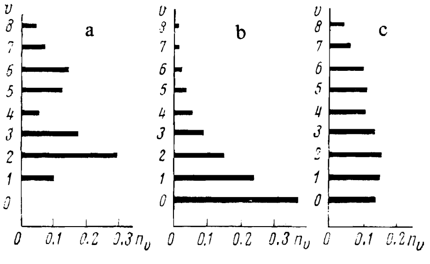

FIG. 2. Distribution of HF molecules over vibrational levels: a) initial distribution of HF molecules produced in $F+H_2$ and $H+F_2$ reactions; b) distribution reached as a result of lasing under conditions of fast rotational relaxation; c) distribution reached as a result of lasing under conditions of frozen rotational relaxation.

TABLE I.

η, %	T_{fin}, K	Efficiency, %
4	700	39
8	1000	35.4
12	1500	30.7
18	2000	27.5
29	3000	22

2. FROZEN ROTATIONAL RELAXATION

In the case of frozen rotational relaxation, there is no coupling during lasing between the rotational sublevels of a single vibrational level. The induced emission couples pairs of levels (v,J) and $(V-1,J+1)$ at which the threshold inversion has been reached. As a result, independent groups of cascade-coupled vibrational-rotational levels are formed (Fig. 1b). The lasing process equalizes the populations of all the levels within a group (except for differences measured by the threshold inversion) independently of the other level groups. To calculate the maximum efficiency of a chemical laser under conditions of frozen rotational relaxation we made numerical calculations for a model chemical laser, which is just like the one described in Section 1 except for the following two additional assumptions: 1) the rotational relaxation rate is much lower than either the rate of deactivation of the HF molecules by radiation or the reaction rate; and 2) the "initial" rotational distribution is the same for all vibrational levels with $v=1-8$.[7,9] The calculation of the lasing efficiency reduced to the determination of the number of molecules that changed their vibrational quantum number by unity during passage from the initial vibrational-rotational distribution of the HF molecules to the final distribution.

The initial distribution of the HF molecules over the vibrational levels was the following: $n_0=0$, $n_1=0.103$, $n_2=0.300$, $n_3=0.177$, $n_4=0.053$, $n_5=0.120$, $n_6=0.152$, $n_7=0.06$, and $n_8=0.04$[7-9] (Fig. 2a). The shape of the initial rotational distribution was varied to determine the effect of such variations on the energy of the laser. The experimental distributions obtained in[6] were taken as the initial rotational distributions. The calculated rotational distributions are shown in Fig. 3.

The threshold inversion was taken the same as in the calculations for the case of fast rotational relaxation. The results of the calculation are presented in Table II. It is evident from the table that 1) the efficiency depends weakly on the shape of the rotational distributions; 2) increasing η results in a slight increase in efficiency; and 3) the efficiency is lower than in the case of fast rotational relaxation.

The distribution of the HF molecules over the vibra-

TABLE II.

η, %	Rotational distribution (see Fig. 3)	Efficiency, %
4	curve 1	13.5
4	curve 2	14.0
12	curve 1	15.5
12	curve 2	16.0
29	curve 1	16.5
29	curve 2	16.7

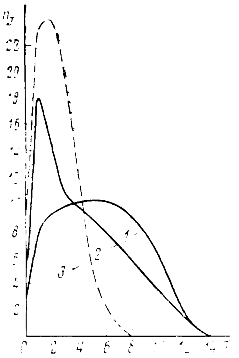

FIG. 3. Rotational distributions assumed as initial distributions in the calculations: 1—distribution of HF molecules produced in $F + H_2$ and $H + F_2$ reactions; 2—distribution reached after rotational relaxation corresponding to 9 collisions with H_2 molecules, 9 collisions with F_2 molecules, and 30 collisions with HE atoms; 3—equilibrium distribution at $T_{\text{rot}} = 300$ K.

tional levels resulting from lasing under conditions of frozen rotational relaxation differs from the equilibrium distributions (Fig. 2c).

3. REAL LASERS

Vibrational relaxation processes have a substantial effect on the energy characteristics of real lasers. It is known that quenching of an HF laser is due mainly to relaxation of HF molecules in collisions with one another.[1–3] At first, while the concentration of HF molecules in the active medium is low, lasing takes place virtually under conditions of no vibrational relaxation, i.e., at the onset of lasing, the real laser can be treated as a model laser.

As the HF accumulates, the part played by $V-V$ exchange processes, and after them by $V-T$ and R relaxation processes, becomes more and more important (the $V-V$ exchange rate is about an order of magnitude higher than the $V-T$ and R relaxation rates[16,17]). To estimate the part played by $V-V$ exchange under conditions of fast and frozen rotational relaxation, respectively, we made efficiency calculations for a model laser in which $V-V$ exchange was complete up to the onset of lasing. These calculations differed from those described in Secs. 1 and 2 in that the initial vibrational distribution was assumed to be an equilibrium distribution. It turned out that in the case of fast rotational relaxation, $V-V$ exchange reduces the efficiency from 22% to 13% at 3000 K and from 39% to 35% at 700 K; for frozen rotational relaxation, after $V-V$ exchange the efficiency decreased from 16% to 2–3%. From this we may conclude that $V-V$ exchange does not play a large part in a laser with fast rotational relaxation (this conclusion is in accordance with the results of[2]), while in a laser with frozen rotational relaxation, $V-V$ exchange practically quenches the lasing. We note that what was said above is valid provided the $V-V$ exchange processes do not alter the rotational distributions. In the opposite case, $V-V$ exchange could, in principle, facilitate the development of inversion on individual vibrational-rotational transitions. At present it is not known how the rotational state of HF molecules is changed in $V-V$ exchange processes. On the basis of general considerations, however, it seems that $V-V$ exchange does not make any substantial change in the rotational distributions.

Computer calculations for lasers under both the assumptions discussed above (fast and frozen rotational relaxation) were published in[5], but the results turned out to be opposite to ours. Since the results obtained are not discussed in[5] and the initial rotational distributions for the case of frozen rotational relaxation are not given, it is difficult for us to suggest a reason for the discrepancy.

By now both limiting conditions of operation have been realized in actual chemical lasers. In the fast rotational relaxation regime, realized under conditions of high dilution of the reagents by SF_6 and C_2F_6 molecules, lasing is observed on just one line at a time: the onset of lasing on a second line immediately quenches the lasing on the first one.[18] The second regime has been achieved by very fast initiation[19,20]; in this case lasing takes place simultaneously on a large number of transitions (P_3–P_{15}) of a single vibrational band. Most chemical lasers operate under conditions in which the rotational relaxation rate is comparable with the rates of processes that disturb the rotational equilibrium. Then features of the rotational deactivation of the HF molecules in collisions with molecules of various components of the mixture have an appreciable effect on the spectral characteristics of the laser emission. We discovered an appreciable contribution from resonance $R-R$ transfer of rotational energy from $J = 0$ and $J = 10$ levels of HF molecules to H_2 molecules, as a result of which the population of rotational levels with $6 < J < 9$ increases.[6] This manifests itself in the emission spectrum of the lasers: the greatest fraction of the energy of the vibrational transitions is emitted in the P_7 and P_8 lines,[21–23] while lasing does not occur on the P_{10} transitions.[24] It has also been shown[6] that the probability for transfer of rotational energy from levels with $J > 7$ into translational energy is about an order of magnitude lower than the probability for resonance $R-R$ transfer; no less than 300 collisions with He atoms are required for complete rotational deactivation of HF molecules produced in the $F + H_2$ reaction. It may thus be assumed that in most cases lasing on HF takes place under conditions of appreciable deviation from rotational equilibrium.

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Coherent population of quasimolecular states by atomic scattering

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An analysis is given of the conditions for coherent population of the states of a quasimolecule produced during atomic scattering. It is shown that, within the framework of the model with isolated nonadiabatic interaction regions, the conditions for coherent population of the quasimolecular states improve with decreasing Landau–Stückelberg phases which arise in the region of the population of the quasimolecular terms. Existing experimental data are used to establish conditions for coherent population on the assumption of an effective interaction between these quasimolecular terms throughout the population region due to the rotation of the internuclear axis. Expressions are obtained for the depth of modulation of the total cross sections for different mechanisms of mixing of the interfering terms at large distances. The results are compared with measured total excitation cross sections for collisions between sodium ions and neon atoms.

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A simple model of a collision between two atomic particles, which produces oscillations on the total inelastic cross sections, was discussed previously in[1]. These oscillations are a consequence of interference between two vacant excited states of a quasimolecule which are coherently populated during the collision and interact at large internuclear distances.

According to this model, the ground-state term (term 0) of the system of colliding particles successively crosses the two excited terms 1 and 2 of the quasimolecule for internuclear distances $R=R_1$ and $R=R_2$ (Fig. 1), where the interaction between the ground and excited terms occurs in accordance with the Landau–Zener scheme. As the particles separate, an interaction occurs between the excited terms either due to pseudocrossing or as a result of the close approach at large internuclear distances (for $R=R_3\gg R_{1,2}$), which leads to the appearance of the interference term ΔW in the probabilities of population of inelastic scattering channels 1 and 2[1]:

$$\Delta W=2p_1[p_2p_3(1-p_1)(1-p_2)(1-p_3)]^{1/2}\{\cos(\chi+\chi_1-\chi_2)-\cos(\chi+\chi_1)+(1-p_2)\cos(\chi+\chi_2)-p_2\cos(\chi-\chi_2)-(1-2p_2)\cos\chi\}. \quad (1)$$

In this expression, $p_{1,2}$ are the probabilities of conserving the initial electronic state 0 after single crossing of the nonadiabatic regions at $R=R_{1,2}$, p_3 is the probability that the system will remain in the same electronic state after nonadiabatic interaction in the region $R=R_3$, and

$$\chi_k=2\varphi_k+\frac{1}{\hbar}\int_{-t_k}^{t_k}(E_k-E_0)\,dt, \quad (2)$$

where