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Characterization of inverted populations in chemical lasers by temperaturelike distributions: Gain characteristics in the $F + H_2 \rightarrow HF + H$ system

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With the aid of the temperature parameters characterizing product state distributions in a number of chemical reactions, frequently used concepts in chemical laser studies can be expressed in a compact form. The assumption of a rotational–translational microcanonical equilibrium in the product atom—diatom system leads to simple expressions for population inversions and gain factors. (However, the equilibrium assumption is not necessary; the expressions will retain their simple form also when the vib–rotational distributions are more specific.) The main advantage is that of using only one or two parameters instead of different vibrational and rotational temperatures for every transition. Two special situations are considered in detail: (a) a nonrelaxed initial product population and (b) a vibrationally nonrelaxed but rotationally thermal population. As a specific example, the HF laser with $F + H_2 \rightarrow HF + H$ as the pumping reaction is studied. Rate equations governing the emission of different laser transitions are solved. In the solution, cascading and pumping effects are considered but not rotational or vibrational relaxation. The detailed rate constants of HF formation in different vib–rotational levels used in the calculation are those which lead to equipartition (microcanonical equilibrium) of rotational and translational energies. Comparison with experimental results indicates that the model calculations are in agreement with some chemical laser and trajectory studies which show initial population peaked at some high rotational states. The chemiluminescence measurements for low reagents energies show relatively lower peaks.

I. INTRODUCTION

It was recently noticed that vibrational state distributions of the products in a number of exothermic atom–diatom reactions may be characterized by a single temperaturelike parameter.[1] This parameter specifies the deviations of the observed vibrational energy distribution from a suitably defined microcanonical equilibrium distribution. Rotational distributions within vibrational manifolds can be characterized in a similar way. This is done either by the introduction of an additional temperature parameter[2] or by assuming that there is an equipartition of the nonvibrational energy between the rotational and translational degrees of freedom (R–T equilibrium).[3] The reactions which were found to follow this pattern are typical pumping reactions for chemical lasers, i.e., their products are formed with a large amount of vibrational population inversion. On the basis of this notion we will attempt in this paper to reformulate in a more compact form some of the expressions generally used in chemical laser studies. The comprehensive description given in the following should be particularly useful in numerical model studies of chemical lasers. It may also provide an easier starting point for rotational energy distribution and relaxation investigations in amplifying media. The formalism of the subsequent sections which will be explicitly applied to the R–T-equilibrium case can be easily extended to more general cases.

The reaction $F + H_2 \rightarrow HF + H$, besides being an efficient pumping reaction for a hydrogen fluoride chemical laser, provides a test case of particular importance since it was studied by different techniques. Product state distributions were investigated by chemical laser[4] and chemiluminescence methods[5,6] and were extensively analyzed by classical trajectory calculations.[7–9] The isotopic reaction $F + D_2 \rightarrow DF + D$ was studied also by the molecular beam method.[10] The description of the vibrational state distribution with the aid of the temperature parameter was shown to be in good agreement with the experimental data.[1] Concerning the rotational state distribution there is, however, some disagreement in the literature.[5–10] In the following, we will discuss this question by comparing the consequences of the use of the temperature parameters to the interpretation of recent experimental results for a pulsed HF laser.[11]

So far, the question of rotational energy distribution has not been dealt with in chemical lasers in any detail before. In fact the original rotational distribution has scarcely been resolved experimentally. In most cases it has even been chosen deliberately such as to assure complete rotational relaxation (and hence a Boltzmann equilibrium over the rotational states). This reflects the difficulties in dealing with a great multitude of vib-rotational states and corresponding radiational and nonradiational transitions if the populations of these states do not follow a simple pattern. In this kind of treatment, however, not only valuable kinetic information is lost but also potential laser energy is given away since the effective population inversion of a totally unrelaxed distribution can be larger than that of a partially relaxed one. In addition, it has to be assumed that rotational and vibrational relaxation occurs on a strictly separable time scale. This may be questionable in view of the very fast vibrational relaxation of molecules like HF as long as no detailed information on rotational relaxation particularly of higher rotational states is available.

For a better understanding of the problem we first give a brief summary of the conventional description of chemical lasers.[12,13] In order for laser emission to be possible in a suitable optical resonator the Schawlow–Townes condition has to be met:

$$V^2 R_1 R_2 T^2 \geq 1 . \tag{1}$$

Here V is the single-pass gain and V^2 is the round trip gain of the photons in the cavity with $R_{1,2}$ and T referring to reflection and transmission losses. The gain V in (1) is the maximum gain at the threshold of oscillations:

$$V = \exp \sigma \Delta N l . \tag{2}$$

The population inversion ΔN in this expression is (for chemical lasers where the lasing species are diatomic molecules)

$$\Delta N = N_{v'J'} - (g_{J'}/g_J) N_{vJ} , \tag{3}$$

where N_{vJ} is the population and $g_J = 2J+1$ is the degeneracy of a vib–rotational level. The primed indices refer to the upper states. The cross section $\sigma(\mathrm{cm}^2)$ is related to the Einstein coefficient of stimulated emission B by $\sigma = Bg(\nu)/\Delta\nu c$, where $g(\nu)$ is a line shape factor which depends on the type of line broadening and $\Delta\nu$ is the linewidth. The product $\alpha = \sigma \Delta N$ is often referred to as the gain factor.

After oscillation has started the gain expression (2) changes since saturation effects become appreciable. For a sufficiently large field intensity σ becomes a function of intensity. In the saturated oscillator limit the laser output E (joules/cm^2 of laser aperture) is simply given as

$$E = \frac{(\Delta N - \Delta N_0) h\nu}{1 + g_{J'}/g_J} , \tag{4}$$

where ΔN_0 is the threshold value of the population inversion. For a reasonably large laser oscillator the threshold inversion which can be calculated from Eqs. (1) and (2) if the resonator losses are known is only a negligible fraction of the total inversion ΔN. It should be stressed that Eqs. (2) and (4) apply only to a situation of homogeneous broadening of the laser transition.[14]

For quasisteady state conditions of a laser oscillator, the intensity of stimulated emission directly reflects the pumping, and the output signal can be used to analyze growth and decay of the inversion $I(t) \propto \Delta N(t)$. Such conditions can be found not only in cw lasers but also in pulsed lasers with not too short a pulse duration. The populations N_{vJ} are then proportional to the detailed rate constants k_{vJ}. We shall use this fact later, deriving expressions for gain constants and population inversions.

As mentioned above, the population inversion is usually written for the special case of completely relaxed rotation (assuming an unrelaxed vibrational distribution at the same time) characterized by a rotational temperature equal to the kinetic gas temperature. An effective vibrational temperature T_v is introduced to relate the populations of just the two vibrational levels connected by the radiational transitions in question:

$$\Delta N_{vJ}^{v'J'} = \mathrm{const}\, g_{J'} \{\exp -[E_{v'}/kT_v + E_{J'}(v')/kT_R] - \exp -[E_v/kT_v + E_J(v)/kT_R]\} . \tag{5}$$

$E_{v'}$, $E_{J'}(v')$ and $E_{v'}$, $E_J(v)$ are the vibrational and rotational energies of the upper and lower level, respectively. The notation $E_J(v)$ accounts for the weak dependence of E_J on v. It has been shown first by Polanyi[12] that the sign and the extent of the population inversion ΔN is related to the ratio T_v/T_R.

The scheme outlined above suffers from several inconsistencies. First, apart from being defined as a quasithermodynamic temperature, T_v has only a loose physical meaning. Secondly, different T_v's must be assigned to different $v' \rightarrow v$ transitions. In principle, Eq. (5) can be extended to include the case of no rotational relaxation. In this case, however, T_R is not an ordinary temperature any more but, like T_v, its value will differ from one $J' \rightarrow J$ transition to the other. Such difficulties do not arise if the product state distributions can be characterized by one or two (temperature) parameters as will be shown in the following sections. Characterizing the distributions in ΔN (or in the rate constants k_{vJ} which are more conventionally used than populations N_{vJ}) by the same one or two parameters for all $v'J' \rightarrow vJ$ transitions we obtain much simpler descriptions of chemical lasers.

Closed-form expressions for N_{vJ} will be presented in the next section in two special cases:

(a) The reaction products have the vib–rotational distribution as found immediately after the reaction, i.e., no rotational or vibrational relaxation has occurred. (b) The products are in thermal equilibrium regarding rotation and translation, with temperature T_R, while the vibration still retains its original distribution. We will then try to compare this description with experimental results from a pulsed HF laser in which rotational relaxation is believed to be partially arrested.

II. CASE A: THE VIBRATIONAL AND ROTATIONAL DISTRIBUTIONS WITH NO ROTATIONAL RELAXATION

In several recent papers[1–3] it has been shown that vibrational distributions resulting from some exothermic reactions of the type $X+LY \rightarrow LX+Y$ (X and Y are halogen atoms and L is H or D) as well as from the reactions $F+H_2$ $(D_2) \rightarrow HF(DF)$ $+H(D)$ and $O+CS \rightarrow CO+S$ (exceptions are mentioned later) can be described by the formula

$$P(f_v)=Q_v^{-1}P^0(f_v)\exp[-\lambda_v f_v] , \tag{6}$$

with

$$P^0(f_v)=(1-f_v)^{3/2}/\sum_{v=0}^{v^*}(1-f_v)^{3/2} . \tag{7}$$

In these equations $f_v=E_v/E$ is the fraction of the total energy E available to the products (exothermicity plus reactants energy) in the vibrational state v. v^* corresponds to $E_{v^*}\le E\le E_{v^*+1}$ and Q_v is a normalization factor. λ_v is a constant, independent of v but E dependent, which was called the (reciprocal) vibrational temperature parameter. For the reactions mentioned above, λ_v is negative with values ranging from ~ −5 to ~ −10. $P^0(f_v)$ is proportional to the density of states of the atom–diatom system with total energy E in the vibrational state v.[1–3,15] When all vibrational states of the products are equally probable $P(f_v)$ $=P^0(f_v)$, or $\lambda_v=0$. Hence, λ_v provides a quantitative measure for the deviations from a microcanonical equilibrium. As λ_v becomes more negative vibrational population inversion increases. The connection between the probabilities $P(f_v)$, the rate constants $k(f_v)$ and the initial vibrational state populations $N(f_v)$ is simply $P(f_v)=k(f_v)/k$ $=N(f_v)/N$, where k is the overall rate constant and N is the total number of product molecules. The dependence on the reactants state is implicitly contained in λ_v.

By comparison to the very comprehensive chemiluminescence measurements of Polanyi and coworkers[16] and to several classical trajectory calculations[7–9] it was found[3] that for some reactions the joint vibrational–rotational distributions can be described by the formula

$$P(f_v,J)=Q_{vr}^{-1}(2J+1)[1-f_v-f_J(v)]^{1/2}\exp[-\lambda_v f_v] . \tag{8}$$

Here J is the rotational quantum number and f_J (v) is the fraction of energy in rotation. The factor in front of the exponential in the rhs of Eq. (8) is proportional to the density of states of the atom–diatom system with total energy E and in the state v, J.[1–3,15]

Equation (8) represents a situation where the nonvibrational energy is equipartitioned among the rotational and translational degrees of freedom.[3] (It should be emphasized again that the term equipartition here always refers to the atom–diatom system only.) In an independent approach Levine, Johnson, and Bernstein[2] applied the following equation,

$$p(f_v,J)=Q_{vr}^{-1}(2J+1)[1-f_v-f_J(v)]^{1/2} \times\exp[-\lambda_v f_v-\theta_r f_r/(1-f_v)] , \tag{9}$$

to the interpretation of vib–rotational energy distributions. The parameter θ_r used here was called the rotational temperature parameter and allows for more specific rotational energy release than that predicted by Eq. (8). Equations (8) and (9) [as well as any expression which includes in the exponent in Eq. (8) an additional function F $(f_r/1-f_v)$] are consistent with Eq. (6), i.e., by summing over all J values one gets Eq. (6) as the result. Thus any vib–rotational distribution can be tested only for reactions for which the vibrational energy distribution follows Eq. (6). [Some remarks concerning the theoretical background and aspects of Eqs. (6)–(9) will be given in Sec. V.)

Levine *et al.*[2] compared Eq. (9) to several chemiluminescence measurements.[16] For the $Cl+HI$, $Cl+DI$ reactions they found that θ_r is small. On the other hand they observed that for the reaction $F+H_2 \rightarrow HF+H$, θ_r is large. Here the peaks in the experimental (chemiluminescence[5]) rotational distributions occur at J values lower than those predicted by Eq. (8).

The predictions from Eq. (8) for $F+H_2$ are in agreement with trajectory calculations[7–9] and (as will be shown later) with chemical laser measurements. Thus this reaction provides an interesting test case for our $R-T$ equilibrium assumption. For this reason we shall write the expressions for the population inversion and gain factors only for distributions described by Eq. (8). It should be stressed, however, that writing the same expressions corresponding to Eq. (9) or more specific distributions is a straightforward procedure.

If we assume that in a situation of zero rotational relaxation the energy distribution of the HF molecules is given by Eq. (8), then for P-branch transitions $(v'=v+1\rightarrow v,\ J'=J-1\rightarrow J)$ we find the following expression for ΔN:

$$\Delta N_{vJ}^{v'J'} = c(2J-1)\exp[-\lambda_v f_v]\{q_v^{-1/2}[S_{v+1} - J(J-1)]^{1/2} - [S_v - J(J+1)]^{1/2}\} . \qquad (10)$$

c is a proportionality constant, and the dimensionless quantities q_v and S_v are defined by

$$q_v = (b_v/b_{v+1})^{1/2}\exp[2\lambda_v \Delta f_v] , \qquad (11)$$

$$S_v = (1 - f_v)/b_v , \qquad (12)$$

where $\Delta f_v = f_{v+1} - f_v$ and $b_v = B_v/E$. Here, and later in the calculation we use the anharmonic oscillator–vibrating rotor levels scheme[17]:

$$E_v = \omega_e v - \omega_e x_e v(v+1) ,$$

$$E_J(v) = B_v J(J+1),$$

with

$$B_v = B_e - \alpha_e(v + 1/2) .$$

The ground vibrational energy is not taken here into account, and the units are cm^{-1}.

III. CASE B: ROTATIONAL DISTRIBUTION CORRESPONDING TO THERMAL EQUILIBRIUM

In this case it is assumed that N_{vJ} is the product of the vibrational distribution of Eq. (6) with a thermal rotational distribution:

$$N_{vJ} \propto (1 - f_v)^{3/2}(2J+1)\exp[-\lambda_v f_v - \beta b_v J(J+1)] , \qquad (13)$$

with $\beta = E/kT_R$. When the rotational distributions within each v state are thermal they almost overlap, with only small deviations due to the differences in b_v. The maxima of these distributions occur at $\hat{J} \approx (2\beta b_v)^{-1/2} - 1/2$. For HF with $T_R = 300\ ^\circ\text{K}$ this corresponds to $\hat{J} = 2$. For these reasons intense $v'J' \rightarrow vJ$ transitions are expected in this case only if $P(f_{v'}) > P(f_v)$ ("total vibrational inversion"[12,13]). The necessary laser requirement $\Delta N > 0$ (for the P branch) is equivalent to the following inequality

$$-\lambda_v \Delta f_v + \beta J\{2b_v + \alpha(J-1) - 3/2\ln[1 - \Delta f_v/(1 - f_v)]\} > 0 \qquad (14)$$

where $\alpha = \alpha_e/E$. The α-containing term can be ignored for molecules like HF where $\Delta f_v \approx 0.3$ ($\lambda_v = -6.5$) and typical J's are relatively small since $\alpha \ll b_v$. For heavier molecules like CO, where $\Delta f_v \approx 0.055$ ($E \approx 90$ kcal/mole and $\lambda_v = -7.7$ for the $O + CS \rightarrow CO + S$ reaction[3,18] and $\hat{J} \sim 25$, this term is not negligible any more. For typical chemical laser reactions, obviously $\lambda_v < 0$ and the only negative term in the lhs of expression (14) is the last one. For R-branch transitions $J' = J+1 \rightarrow J$ the second term is $-\beta(J+1)[2b_v - \alpha(J+2)]$, and thus except for very large J which are usually not populated it is negative. As an example we consider again the HF chemical laser pumped by $F + H_2 \rightarrow HF + H$. Here $-\lambda_v \Delta f_v \sim 2$ and $2\beta b_v \sim 0.2$. Thus even for transitions from $v' = 3 \rightarrow v = 2$ ($v = 3$ is less populated than $v = 2$[5]) ΔN is positive for all J since for $v' = 3$ the last term is ~ -1.8. However, remembering that (14) is only a necessary condition and the value of the lhs of this inequality is small, the above conclusion should be checked for any given set of laser parameters.

IV. COMPARISON WITH EXPERIMENT

Rotational relaxation of the HF molecule is reported to require an average number of nine HF–HF collisions at a temperature of ~ 400 °K.[19] At this temperature the maximum level populations are found at $J = 3, 4$. To account for the J dependence of this relaxation a simple model has been suggested by Polanyi and Woodall.[20] This model assumes an exponential dependence of the relaxation probability for $J \rightarrow J - \Delta J$ on the amount of rotational energy to be transferred in the collision. ΔJ is unrestricted except for the relation

$$P_{J-\Delta J}^{J} = N\exp[-C\Delta E] , \qquad (15)$$

where ΔE is the energy difference between the two rotational states and N and C are constants. It is seen from this expression that rotational relaxation times are drastically increased in going to the higher J levels. Accordingly complete thermal rotational equilibrium should not be considered to be self-evident in the normal operating range of HF lasers, i.e., pressures of 1–100 torr and μsec pulse durations. There is some indication for incomplete rotational equilibration prior to emission in a few chemical laser studies which employed flash photolysis initiation.[21–23] However, no detailed analysis has been given of these observations. Nonthermal rotational energy distributions are more obvious in pulsed discharge-initiated HF lasers. Table I shows some of the relevant spectral measurements. For these measurements mostly hydrogen-lean SF_6/H_2 reaction mixtures have been used. Thus the pumping reaction of a fluorine atom with a hydrogen molecule is preceded by the discharge-initiated dissociation of SF_6.

$$SF_6 \xrightarrow{e^-} SF_5 + F , \qquad (16)$$

$$F + H_2 \longrightarrow HF + H . \qquad (17)$$

The reaction of a H atom with SF_6, a possible secondary pumping step, is believed to be slow.[24] The reaction $H + SF_5 \rightarrow HF + SF_4$, however, cannot be excluded as a minor contribution to the laser pumping[25] and could perhaps influence the observed spectral distribution to a small extent.

The highest rotational state into which transitions from $v+1$ are compatible with energy conservation is

TABLE I. Emission spectra of HF lasers showing high rotational transitions.

Vibrational–rotational transitions			Reference
$v=1\rightarrow 0$	$v=2\rightarrow 1$	$v=3\rightarrow 2$	
$P(2)-P(17)$	$P(2)-P(9)$	$P(4)-P(5)$	Ultee[26]
$P(8)-P(13)$	$P(4)-P(12)$	$P(2)-P(8)$	Wood, Burkhardt, Pollack, and Bridges[27]
$P(6)-P(15)$	$P(2)-P(15)$	$P(2)-P(8)$[a]	Deutsch[28]
$P(4)-P(8)$	$P(3)-P(8)$	$P(4)-P(7)$[b,c]	Jacobson and Kimbell[29]
$P(3)-P(15)$	$P(2)-P(12)$	$P(2)-P(8)$[a]	Wood and Chang[30]
$P(1)-P(13)$	$P(1)-P(10)$	$P(3)-P(6)$[d]	Green and Lin[31]
$P(4)-P(17)$	$P(3)-P(16)$	$P(2)-P(8)$[c]	Pummer and Kompa[11]

[a] Also purely rotational laser emission observed in the same system.

[b] Some of the lines not seen with H_2 but only with hydrocarbon compounds.

[c] Some lines missing in the sequence.

[d] R-branch emission observable with grating in the cavity.

$$J^* \approx 1/2 + S_{v+1}^{1/2} \; . \tag{18}$$

The most probable J value [as determined from Eq. (8)] occurs at $J \approx (S_v/2)^{1/2}$. The highest J value for which ΔN (in the P branch) is still positive is determined by Eq. (10) to be

$$\begin{aligned} J_m &= (2r_v)^{-1}\{1 + [1 + 4r_v^2 (S_{v+1} - q_v S_v)/(1-q_v)]^{1/2}\} \\ &\approx (2r_v)^{-1} + [(S_{v+1} - q_v S_v)/(1-q_v)]^{1/2} \; , \end{aligned} \tag{19}$$

with $r_v = (1-q_v)/(1+q_v)$. If we assume that for the reaction considered here $E = 34.7$ kcal/mole and $\lambda_v = -6.5$ (see however the discussion below) then we find for P-branch transitions from the most populated level $v=2$, $\Delta f_v = 0.31$, $S_2 = 219$, $S_1 = 402$ and $q_1 = 1.85 \times 10^{-2}$ (spectroscopic data from Ref. 17). From Eqs. (18) and (19) one gets $J^* \simeq J_m = 15$ (note that the J's correspond here to $v=1$, thus transitions from $v=2$ are possible in principle from $J' = J - 1 = 14$). For $v = 3\rightarrow 2$ and $v = 1 \rightarrow 0$ we find $J^* = J_m = 7$ and 20, respectively. From Table I we see that the emission lines observed in HF lasers span almost entirely the range of transitions compatible with energy conservation.

We will then examine the intensity relations both in the model and in the experiments. Only two of the papers cited in Table I give integrated output intensities of single vib–rotational transitions. Jacobson and Kimbell observed intensity maxima at P_{3-2} (5, 6), P_{2-1} (6, 7) and P_{1-0} (7, 8).[29] This behavior is suggestive of a cascading sequence of P-branch transitions. Pummer and Kompa[11] found the most intense lines at P_{3-2}(6, 7), P_{2-1}(8) and (12), and P_{1-0}(9), (12) and (15, 16). They reported in addition that the higher J lines disappeared when the pressure of the reaction mixture was raised above a few torr. Since these high J transitions can in no case be explained by a simple rise in the gas temperature it is concluded that the rotational state distribution is nonthermal and that rotational relaxation is at least partially arrested.

We will attempt here to interpret the intensity distribution, and in particular the multiple maxima in the $v = 2 \rightarrow 1$ and $v = 1 \rightarrow 0$ transitions as a combined result of both the original energy partitioning in the reaction and cascading emission (i.e., in this stage we do not take into account the relaxation processes, see Section V). To this end first the normalized gain factors α_{vJ} are calculated. These can be represented as

$$\alpha_{vJ} = \sigma_{vJ} \Delta N_{vJ} \propto \sigma_{vJ} \Delta k_{vJ} \tag{20}$$

because of the proportionality $N_{vJ} \propto k_{vJ}$. $\Delta k_{vJ} = [k_{v'J'} - (g_{J'}/g_J) k_{vJ}]$ where again $v' = v+1$ and $J' = J+1$ for R-branch and $J-1$ for P-branch transitions, respectively. The detailed rate constants k_{vJ} are calculated as $k_{vJ} = (k'_{vJ}/\sum k'_{vJ})k$ where $k = 3.8 \times 10^{-11}\,\mathrm{cm}^3$ molecule^{-1} $\cdot$ sec^{-1} (400 °K) is the overall rate constant for the $F + H_2$ reaction,[32] and where k'_{vJ} is given by Eq. (8) as

$$k'_{vJ} = (2J+1)[1 - f_v - f_J(v)]^{1/2} \exp(-\lambda_v f_v) \; . \tag{21}$$

The value of the total energy E is not precisely known in chemical lasers or chemiluminescence measurements, and the uncertainty is believed to be ~1 kcal/mole (350 cm^{-1}). An estimation of E in the laser experiment is possible on the basis of the spectral data. The highest vib–rotational level contributing to the laser emission is $v=3$, $J=7$,[11] with corresponding energy of 12 390 cm^{-1}. In the chemiluminescence experiment[5] E is estimated as $E = -\Delta H + E_A + (5/2)RT = 34.7$ kcal/mole or 12 150 cm^{-1}. Therefore, we have performed our calculations for two slightly different energy values. The first is the chemiluminescence value above, and the second is 12 550 cm^{-1} which is an average value between $v=3$, $J=7$ and $v=3$, $J=8$. The value of $\lambda_v = -6.5$ was determined from the chemiluminescence data.[1] On the basis of the notion that enhanced reagent energy leads to a smaller amount of population inversion ($\langle f_v \rangle$),[1,33] we assume that for the higher energy value λ_v would be less negative. Therefore, for the higher energy the value of $\lambda_v = -6.0$ was estimated. The uncertainties associated with this estimation may influence the predicted ratios of integrated outputs from different vibrational levels, but they have no effect on the rotational distributions within vibrational manifolds. The stimulated emission cross section to be used in the calculations is given as

$$\sigma_{vJ} = A_{vJ} g(\nu)/8\pi\omega^2 \Delta\nu \tag{22}$$

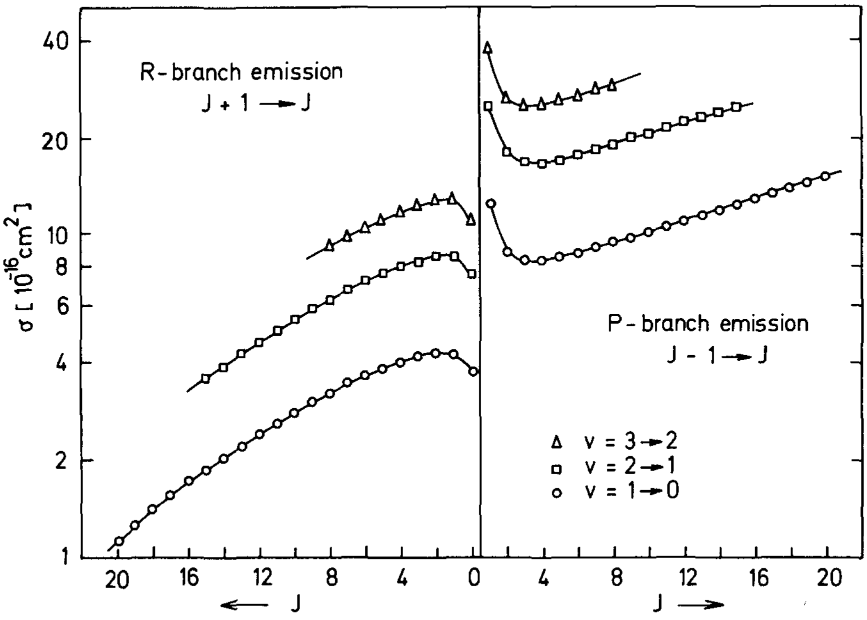

FIG. 1. Cross sections of *P*-branch and *R*-branch transitions for the HF molecule. The calculation is according to Eq. (22) with A_{vJ} from Ref. 34.

with the Einstein coefficient A_{vJ}[34] and transition wavenumbers ω. For a Doppler-broadened transition the line shape factor $g(\nu) = 0.94$ and the linewidth $\Delta\nu$ $(\text{sec}^{-1}) = \omega\ (8 \ln 2RT/M)^{1/2}$. Figures 1 and 2 give plots of $\sigma_{vJ}(\text{cm}^2)$ for the transitions in question and of the detailed rate coefficients k_{vJ} $(\text{cm}^3\ \text{molecule}^{-1} \cdot \text{sec}^{-1})$. Figure 3 then shows the gain products α_{vJ} (on a relative scale) both for the *R* branch and the *P* branch. Since the gain is always higher in the *P* branch, *R*-branch emission is never observed experimentally unless a wavelength-selective element is introduced in the laser cavity. Figure 3 shows that if the higher total energy is used the gain peaks shift to somewhat higher *J*. Thus the maximum gain should be expected at $P_{3\to2}(5-7)$, $P_{2\to1}(11-14)$, and $P_{1\to0}(15-18)$ which is in good agreement with the experimental findings.

To predict more details of the chemical laser output by this model a numerical simulation study was done. Since coherent effects are negligible under the experimental conditions used, the problem can be treated in terms of rate equations. Balance equations for the populations N_{vJ} and the photon densities Q_{vJ} as function of time can be written as follows:

$$dN_{vJ}/dt = k_{vJ}N_1N_2 + \sigma_{vJ}Q_{vJ}c\Delta N_{vJ} - \sigma_{v-1\,J+1} \times Q_{v-1\,J+1}c\Delta N_{v-1\,J+1} - A_{v-1\,J+1}N_{vJ} + A_{vJ}N_{v+1\,J-1}\,, \tag{23}$$

$$dQ_{vJ}/dt = A_{vJ}N_{v+1\,J-1} + \sigma_{vJ}Q_{vJ}c\Delta N_{vJ} - Q_{vJ}/\tau_p\,. \tag{24}$$

N_1 and N_2 are the time dependent concentrations of fluorine atoms and hydrogen molecules. Since the discharge is much shorter than the laser emis-

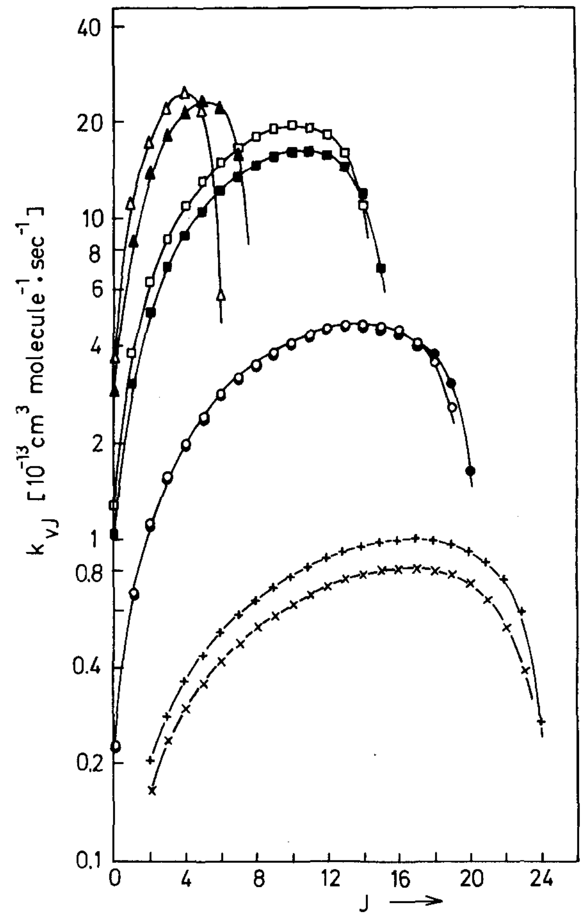

FIG. 2. Detailed rate constants into different vib–rotational levels of HF in the reaction F + H$_2$ → HF + F, calculated according to Eq. (21). Open symbols correspond to rate constants into different *v*, *J* levels for $E = 12\,150$ cm^{-1} and $\lambda_v = -6.5$. Filled symbols correspond to $E = 12\,550$ cm^{-1} and $\lambda_v = -6.0$ (see text).

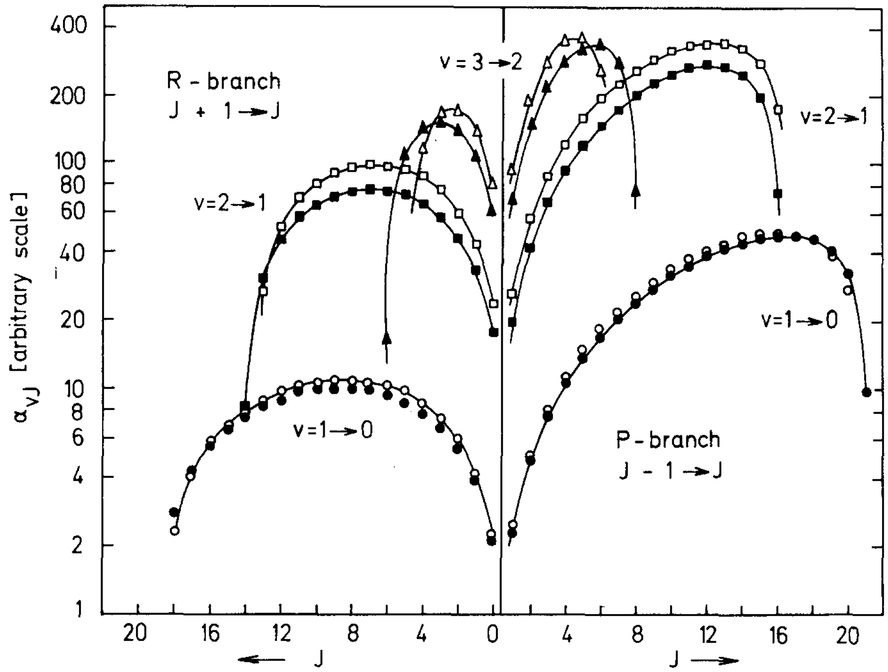

FIG. 3. Gain factors of P-branch and R-branch transitions calculated from Eqs. (20), (10), and (22). Symbols like in Fig. 2.

sion time the F atom production is considered as a step function at the beginning of the pumping process. Thus the time dependences of N_1 and N_2 are like in a bimolecular reaction with given rate constant and initial concentrations. The first term in Eq. (23) describes the formation of HF molecules in the state vJ. The next two terms correspond to the stimulated processes. The first one of these is applicable only in the case of cascading from the next higher state while the second one describes the depletion of N_{vJ} by stimulated emission. The stimulated emission rate is given as the product of the cross section σ_{vJ}, speed of light c, quantum density Q_{vJ}, and population inversion ΔN_{vJ}. As before, the indexing of σ, A, and Q refers to the lower state of the transition. The last terms in (23) account for the start of the lasing process by spontaneous emission. These terms become negligible once the emission has started. The second balance equation (24) describes the rate of change of the photon density Q_{vJ}. While the first two terms in this equation refer to the spontaneous and stimulated emission rates the last term describes the output coupling with τ_p being the average photon lifetime in the laser cavity. Accounting for the various v's and J's the expressions (23) and (24) result in some 80 coupled differential equations which were solved numerically. The relative output intensities calculated in this way are shown in Fig. 4. It is seen that the various experimentally observed maxima are perfectly reproduced if the higher total energy is used.

The intensity ratios for the three series of vibrational transitions as predicted by these model calculations are (a) for the higher energy value (with $\lambda_v = -6.5$) $Q_{1\to0}:Q_{2\to1}:Q_{3\to2} = 0.69:1:0.41$; (b) for the lower energy ($\lambda_v = -6.0$) $Q_{1\to0}:Q_{2\to1}:Q_{3\to2} = 0.69:1:0.54$. These results are not confirmed by the experimental results of Pummer and Kompa.[11] Instead, a lower relative intensity of the $v=3\to2$ transitions and a higher intensity of the $v=1\to0$ transitions is found. The calculations could possibly be adjusted by using an even less negative value of λ_v. However, we feel that at present the precision of the experimental results does not warrant such a modification. It should be noted that the intensity data of Jacobson and Kimbell $Q_{1\to0}:Q_{2\to1} = 0.69:1$[29] agree with the predictions above. However, no $Q_{3\to2}$ intensity is given there for the HF laser with H_2 as the hydrogen compound. Thus in order to test this aspect of the model more conclusively one will have to wait first for more refined laser experiments and second for the inclusion of relaxation phenomena in the model. Such measurements and calculations are in preparation.

V. DISCUSSION

In the previous sections we attempted to reformulate some commonly used expressions in chemical laser investigations in a more compact form. This was done on the basis of the notion[1-3] that the product energy distributions in a number of typical pumping reactions of chemical lasers can be characterized by means of simple functions. The small number of parameters, so called "temperature

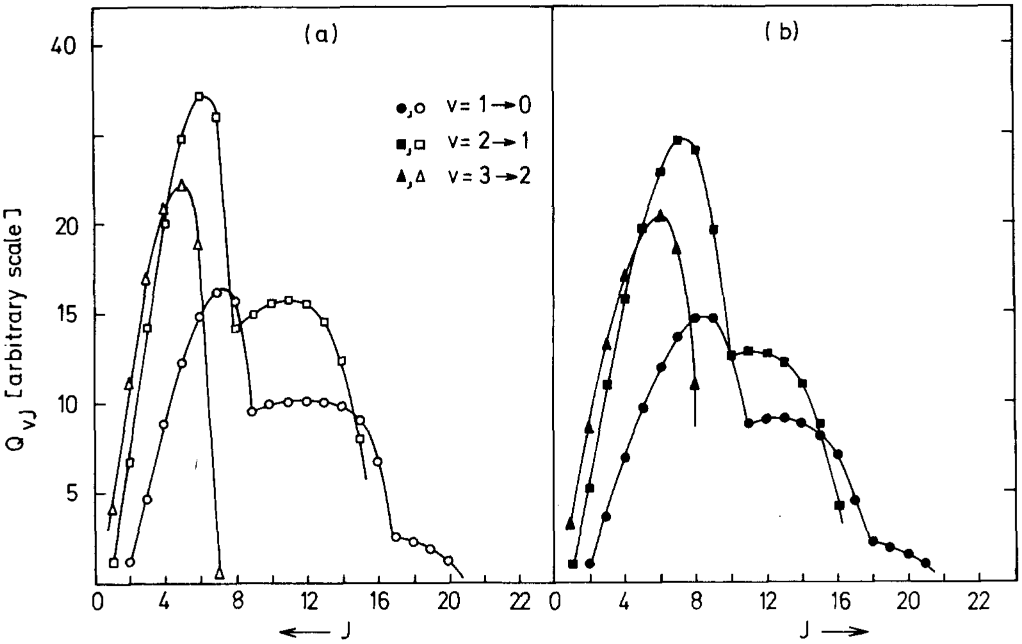

FIG. 4. Integrated output intensities calculated from Eqs. (23) and (24). Upper limit for integration $t = 200$ μsec. (The major contributions occur before $t = 50$ μsec. The relative intensities are already established at 20 μsec.) Other notation is as in Figs. 2 and 3.

parameters" characterizing the distributions, simplify to a major extent the form of the expressions for population inversions and gain factors which are used later to solve the rate equations for the output of the laser.

The discussion of the results has to serve two purposes, namely to critically review some conclusions with respect to the experimental data and besides that, to give some more of the theoretical background of the model proposed here.

It has been demonstrated above that the spectral distribution of the chemical laser output can be predicted on the basis of a simple model using just one parameter. More generally, a set of balance equations has been set up to describe time dependently the vib-rotational population inversion and the photon densities in the laser cavity. Quantitative intensity relations for single transitions derived from the model could not be fitted to the experimental data so far. This may be due in part to limitations in the rate equations because in this first approach collisional relaxation processes were ignored. Such processes, however, can now be studied experimentally with the aid of this or similar models. Thus, experiments have to be done to investigate rotational coupling phenomena and relaxation as function of various collision partners in the HF laser and in chemical lasers in general. Such measurements will also have to avoid some of the experimental shortcomings which were encountered in the previous investigations. These are the changes in the relative intensities due to absorption of some of the HF laser lines by atmospheric water, a more reliable evaluation of the total energy (and consequently of λ_v), and a more explicit consideration of the time dependence of the F atom production by the discharge.

One might question the general validity of such simple expressions for product state distributions. At present the best argument in favor of these expressions is the good fit they provide with experimental results.

Some exoergic reaction like $H + Cl_2 \rightarrow HCl + Cl$ do not "obey" Eqs. (6) or (8).[1,2] One probable reason for this may be that conservation of angular momentum was not considered in the derivation of $P^0(f_v)$ and $P^0(f_v, J)$. This was shown[2] to have only a minor effect in reactions like $Cl + HI \rightarrow HCl + I$, but for reactions with large reduced mass differences between reactants and products the effect may be appreciable. The appearance of temperature parameters can be justified to some extent from a theoretical point of view. These parameters provide a measure for the deviation of the observed product distributions from expected microcanonical distributions in the microscopic system of two (or more) product molecules. A quantity which was called the "surprisal" is simply related to the temperature parameters.[1-3] The average of the surprisal over the distribution is called the "entropy deficiency" and this provides a useful integral measure for the deviations mentioned above. A microcanonical distribution in the present sense should be in fact the one predicted by the well known statistical theory of chemical reactions.[35] The statistical theory amounts for equal probabilities of equal regions in the phase space of the product states. This means that phenomena like vibrational population inversion cannot be explained on the basis of simple statistical theory. In other words, a drastic modification of this approach is requested in order to account for example for such inverted distributions.

Temperature parameters like λ_v or θ_r appear naturally in the predicted distribution functions if different regions of the phase space (such as those corresponding to different vibrational states) are weighted according to some simple criteria. Such criteria are provided by a statistical mechanical approach or more accurately an information theory approach.[36,3] In terms of statistical mechanics the temperature parameters are essentially the "Lagrangian multipliers" characterizing the distributions obtained from the maximum entropy principle.[37] In the absence of constraints the resulting distribution is the microcanonical distribution while in the presence of constraints the distributions are of the canonical type.

The temperature parameters in Eqs. (6)–(9) can also be explained as a result of the maximization of a suitably defined entropy subject to some constraints.[36,3] Since we are concerned with a reactive system the constraints are of dynamical origin, and the entropy which has to be maximized is the entropy deficiency mentioned above.[1–3] To account for λ_v the constraint must be that the value of $\langle f_v \rangle$ is predetermined by the mechanism of the reaction.[36,3] To obtain θ like in Eq. (9) a similar constraint is imposed on $\langle f_r/(1-f_v)\rangle$.

The main power of the approach outlined above is that a small number of constraints may account, at least for the main features of the product distributions (small number of parameters). The problem remains how to determine the most relevant constraints. At present it is easier to go the opposite way and deduce the constraints from the analysis of the experiments. The "predetermining requirements" imposed on the reactive system are, obviously, related to the nature of the atoms taking part in the reaction and to the features of the potential hypersurface. An attempt to identify the value of $\langle f_v \rangle$ which turns out to be the most important constraint in a number of exoergic reactions[1–3] was done by Hofacker and Levine.[38] On the basis of their nonadiabatic strong coupling model for population inverting reactions[38] they expressed λ_v and $\langle f_v \rangle$ in terms of the curvature of the reaction path and the initial kinetic energy.

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