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CALCULATION OF ROTATIONAL NONEQUILIBRIUM IN A PULSED HF LASER

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CALCULATION OF ROTATIONAL NONEQUILIBRIUM IN A PULSED HF LASER *

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ABSTRACT

Waveforms and population distributions have been calculated by a numerical model and compared with experiment for an electric-discharge-initiated, pulsed $\text{NF}_3 + \text{H}_2$ chemical laser. The model treats each rotational state separately and allows rotational relaxation between adjacent states. Lasing is treated by equations equivalent to laser rate equations. Good agreement is obtained between calculated and experimental waveforms. Initially, population distributions are far from equilibrium. At the end of the pulse, they approach, but do not reach, Boltzmann equilibrium.

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INTRODUCTION

Many investigators have used analytic models to describe the operation of HF chemical lasers. A bibliography of such work published before August, 1971, is contained in Ref. [1]. These models assume rotational equilibrium within each vibrational level and either calculate small signal gain or assume steady-state (gain equals loss) lasing. Many of the main features of the HF laser are described by such models, but the large number of states and interactions requires a computer model to obtain more detail. The RESALE code is an example of such a computer model. The assumptions and methods used in the RESALE code have been described by Emanuel [2]. He assumes rotational equilibrium within each vibrational level and a steady-state laser model. The chemical kinetics are treated in detail. This code has been widely used and accurately describes many details of the HF chemical laser. Although simultaneous lasing on several transitions has been seen experimentally, the assumptions in the RESALE code restrict lasing to one P-branch transition at any one time between two vibrational levels. The assumptions of the present model permit simultaneous lasing on several transitions.

Recently, several investigators have examined the assumption of rotational equilibrium by means of models that treat rotational relaxation [3,4,5]. We report results of a calculation that allows rotational relaxation and treats lasing action by means of equations equivalent to laser rate equations.

EXPERIMENTAL WAVEFORMS

The calculations will be compared with experiments where lasing was obtained from a mixture of NF_3 and H_2 in a ratio of 5:1. The experimental

apparatus is described in detail in Ref. [6]. The laser was initiated by a transverse discharge from 51 pins 1-cm apart in a 2-cm-diameter tube filled with the gas mixture. The tube had Brewster angle windows. The 65-cm long optical cavity used a 10-m radius gold-coated mirror and a BaF₂ flat with a measured reflectivity of 8%. The laser output beam was split into three parts for simultaneous measurement of the total pulse energy, the waveform of the total pulse, and the waveform of a single P-branch laser transition.

The electric discharge dissociated a small fraction of the NF₃ to give an initial concentration of F atoms. The discharge pulse duration (about 70 ns) was short compared to the total laser pulse (about 2 μs). It was shown earlier [6] that the principal chemical reaction pumping the laser is

Other reactions appear to be too slow to affect the lasing in a major way. Analysis of the laser beam intensity profile indicates that the discharge across a 13-mm gap at each pin is approximately cylindrical with a 2.7-mm-diameter (FWHM). Fifty-one such discharges make the effective gain length equal 13.5 cm. Experimental waveforms for a mixture of NF₃ (13 Torr) and H₂ (2.5 Torr) are shown in Fig. 1. The total waveform is shown along with all P-branch transitions that were observed to lase. The V1-0 P5 transition apparently is missing because it coincides with an H₂O line. No R-branch lasing was observed or expected. Weak lasing on additional P-branches might have been missed because of the large amount of electrical noise, which can be seen on the initial portion of each waveform.

THE NUMERICAL MODEL

The numerical model treats each rotational state separately up to $J = 20$. Four vibrational levels, $v = 0$ to $v = 3$, were used for a total of 80 states. The coupling of the states by various pumping and relaxation rates is shown in Fig. 2. The arrows represent chemical pumping rates for each state. The horizontal lines represent rotational relaxation between adjacent states. The diagonal lines represent V-T relaxation and population changes due to lasing.

In more precise mathematical terms the model consists of a differential equation for the population of each state, a differential equation for the electric field on each P-branch transition, and an equation for each corresponding dielectric polarization. The population equation is

$$\begin{aligned} \frac{dN(v,J)}{dt} = & S(v,J)R_p \\ & + R_r \{ Q(J+1) N(v,J+1) + K(v,J) Q(J-1) N(v,J+1) \\ & - Q(J) [1 + K(v,J-1)] N(v,J) \} \\ & + R_v [b(J) N(v+1, J-1) - b(J+1) N(v,J)] \\ & + 2E(v,J) P(v,J) \sin \phi_s - 2E(v-1, J+1) P(v-1, J+1) \sin \phi_s \end{aligned} \quad (2)$$

where R_p is the rate of formation of HF, $S(v,J)$ is the probability that HF will be formed in the state (v,J) , R_r is the rotational relaxation rate for a state with $J = 4$, $Q(J)$ is a scaling factor to give the appropriate variation of rotational relaxation rate as a function of J , and $K(v,J)$ is the equilibrium constant between states $|v,J\rangle$ and $|v, J+1\rangle$. The product $R_v v b(J)$ gives the vibrational relaxation rate including appropriate variation with v and J .

The last two terms treat population changes as a result of lasing from a higher energy state and lasing into a lower energy state (Fig. 2).

The variable E is proportional to the amplitude of the electric field, and is calculated from the equation

$$dE(v,J)/dt = -E(v,J)/2\tau_c + f_c P(v,J) \sin \phi_s. \quad (3)$$

The quantum numbers, v and J , refer to the lower energy state, τ_c is the lifetime of a photon in the cavity, and f_c is the fraction of the cavity filled with active medium. $P(v,J)$ is proportional to the dielectric polarization and is given by

$$dP(v,J)/dt = -P(v,J)/T_2(v,J)$$

$$+ \mu^2 v \hbar \omega b(J) E(v,J) [N(v+1, J-1) - \left(\frac{2J-1}{2J+1}\right) N(v,J)] \sin \phi_s. \quad (4)$$

where T_2 is the phase relaxation time that determines the collision broadened linewidth. The string of factors $\mu^2 v \hbar \omega b(J)$ gives the dipole matrix element in appropriate units. The matrix element for $v_l=0$ P_7 is $\mu^2 \hbar \omega_{p7}$. The small rotational variation of the matrix element is included in $b(J)$ [7], and vibrational variation is proportional to v . The factor $\hbar \omega$ corrects for the different energies of the transitions. The angle ϕ_s is the steady-state value of a phase angle between the electric field and the polarization in radiation theory. If an appropriate differential equation were integrated to give $\sin \phi$, we would have a complete set of semi-classical laser equations which could treat coherence effects [8]. Tests with appropriate parameters showed that using ϕ_s , the steady-state value of ϕ , gave similar results with a large saving in computer time. The main effect of integrating the differential equation for ϕ was a slight damping of the relaxation oscillations. Typically the

magnitude of $\sin \phi_s$ was 0.7 to 1 and was positive during emission and negative during absorption. Equations (3) and (4) are equivalent to laser rate equations [9] except that they give a more accurate time constant when τ_s is comparable to τ_2 , as they were in the experiments being modeled. Lasing was assumed to occur on a single mode.

The chemical pumping rate, R_p , the vibrational relaxation rate, R_v , and the rotational relaxation rate, R_r , were calculated in a chemical kinetics subroutine which assumed a constant temperature of 300 K. The equations were

$$\begin{aligned} R_p &= 7.1 \times 10^{12} [F] [H_2] \\ R_v &= 7.1 \times 10^9 [H_2] + 1.6 \times 10^7 [NF_3] \\ &\quad + 7.2 \times 10^{11} [F] + 1.4 \times 10^{12} [HF] \\ R_L &= 8 \times 10^{15} ([H_2] + [NF_3] + [F] + [HF]) \\ R_r &= 1/2 R_L. \end{aligned} \tag{5}$$

The rate constant for R_p was taken from Ref. [10] and those for R_v from Ref. [11]. V-R and V-V relaxation were neglected. R_L is the collision frequency for line broadening. The rate constant was taken from HF self-broadening data [7]. In the absence of data, other molecules, principally NF_3 , were assumed to have the same cross section. Rotational relaxation was assumed to be proportional to the line broadening collision frequency because both phenomena depend on torques exerted by long-range dipole and multipole interactions [12]. It was assumed that half of all line broadening collisions involve rotational relaxation and the rest

merely change the phase. Experimental data [13] published after this work was completed give rotational relaxation cross sections for HF, which equal the line broadening cross section [7]. Rotational relaxation of HF by H_2 may be an order of magnitude smaller.

The rotational relaxation rate that goes from state $|v, J\rangle$ to state $|v, J - 1\rangle$ is $Q(J)R_L$. The values of $Q(J)$ are proportional to the collision broadened linewidth shown in Fig. 3. Figure 3 also shows the rotational relaxation models of Polanyi and Woodall [14] normalized to $Q(4)$. The model permitted relaxation only to adjacent states to conserve computer time. The dephasing time, T_2 , is a function of $Q(J)$. Figure 3 shows that the product $Q(J) R_L$ is less than the equivalent Doppler width, R_D at high J . To give the correct gain at line center the Doppler width and R_L are added in quadrature

$$T_2 = (Q^2(J) R_L^2 + 1.75 \times 10^9)^{-1/2}. \quad (6)$$

The pumping rate for each state of HF is given by $S(v, J) R_p$. The values of $S(v, J)$ are taken from Polanyi and Woodall's data [15], except that their method doesn't give the distribution into $v = 0$. From available data [11] it appeared reasonable to assume $S(0, J) = 1/2 S(1, J = 1)$. The values of $S(v, J)$ are given in Table 1.

The model used one differential equation of the form of (2) for each of the 80 states of HF included. In addition, there were two differential equations of the form of (3) and (4), making a total of 200 simultaneous ordinary differential equations. These were integrated using a variable timestep, variable order, Adams predictor-corrector option in C. W. Gear's integrating subroutine [16]. The computer code gave tabular and graphic output,

including snapshots of the population distributions, and the waveforms and inversions of each P-branch transition. The output of the code was also used to make a computer-generated color movie showing the interaction of the populations with the laser intensities.

RESULTS AND DISCUSSION

Calculated waveforms are shown in Fig. 4 for the case with 13 Torr of NF_3 and 2.5 Torr of H_2 . The initial density of F atoms was adjusted to give an output energy of 2.4 mJ/cm^2 , corresponding to the experimental 1 mJ with a beam area of 0.4 cm^2 . The initial density of F atoms corresponded to 0.16 Torr, a dissociation of 1.25% of the NF_3 . The agreement between calculated and experimental waveforms is good, although there are differences in some details. The number of humps in the waveforms generally agree and the durations are comparable in both calculated and experimental waveforms. Experimental waveforms are smoothed somewhat by the 10- to 30-ns response of the detector. Experimental waveforms have a longer delay to laser turn-on and have slightly different decay constants. The calculations show lasing on V3-2 P3 and P5, which were not seen experimentally. The calculated V3-2 transitions turn on before the V1-0. This, and the number of V3-2 transitions which lase, can be changed in the calculations by adjusting pumping and relaxation rates. Both experimental and calculated waveforms show simultaneous lasing on several transitions. Similar agreement between calculated and experimental waveforms was obtained for a total pressure of 60 Torr. The same parameters were used except that dissociation of NF_3 was only 0.62%.

Agreement between experiment and calculated waveforms is good enough that the results of the model can be used to understand details of the laser operation. Examination of population distributions shows that P3 and P4 transitions depend mainly on energy stored in the "total inversion" which exists before the laser turns on. As the laser approaches steady state a "partial inversion" develops and the gain on P3 and P4 drops below threshold. At later times there is clear evidence of J-shifting [2,17] as well as cascades where the transition is coupled to others by sharing a common population.

In some computer runs the rotational relaxation rate was varied. At low rates the output consisted of a series of spikes, while cascades dominated the laser action. At very high rates the waveforms were smoother and J-shifting dominated laser behavior. Cascade action was largely suppressed. The waveforms were not very sensitive to varying the rotational relaxation from half to twice the nominal rate.

The population distribution early in the laser pulse is approximately the same as the pumping distribution. As time goes on, a double-humped structure develops. One hump approximates a Boltzmann distribution and a pumping distribution is superposed on it. This can be seen in Fig. 5, although the pumping hump is getting weak. The $V = 3$ distribution is approximately Boltzmann because only low J states are pumped. Figure 5 also shows some hole-burning in the distribution due to laser action. A little later, relaxation fills in the holes and the distributions remain smooth until the end of the pulse. Figure 6 shows the population distribution at 2 μ s, approximately the end of the pulse. The distribution approaches a Boltzmann distribution except for a small, high energy tail. When these populations are shown on a semi-logarithmic plot (Fig. 7) the tail is quite small in absolute magnitude, but is several orders of magnitude larger than a Boltzmann distribution. The tail is overpopulated

because the chemical reaction is still pumping those states and the distribution represents an equilibrium between pumping and relaxation. This helps explain the lasing seen by Pummer and Kompa [18] on P9 - P18.

The variation of several parameters and rates has been studied. Vibrational deactivation was not important in this case because it is slower than reaction 1. Other results will be reported later.

CONCLUSIONS

The results of the calculation show that including rotational relaxation and laser rate equations in a model of the pulsed HF laser gives good agreement with experiment. The calculations show that the population distributions are far from rotational equilibrium at early times; at the end of the laser pulse, they approach, but do not reach, Boltzmann equilibrium. These results augment but do not contradict the results of simpler models. These conclusions apply to a pulsed HF laser where the F atoms are created in a very short time and reaction 1 dominates the chemistry. Different conclusions might be reached for the $H_2 + F_2$ laser, for CW HF lasers, and for lasers where F atoms are created throughout the pulse.

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Table 1. Percentage of HF formed in the state $|v, J\rangle$ by the reaction

$F + H_2 \rightarrow HF + H$. Negligible quantities are formed with $J > 15$. The percentage formed in state $|0, J\rangle$ is estimated to be half of that in state $|1, j-1\rangle$.

$v \backslash J$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
0	0.	0.	0.	0.	0.	0.08	0.39	0.88	1.54	1.58	1.35	0.92	0.73	0.43	0.11	0.
1	0.	0.	0.	0.	0.16	0.77	1.77	3.08	3.16	2.70	1.85	1.46	0.85	0.23	0.	0.
2	0.	0.	0.67	2.54	4.82	6.58	7.82	7.98	7.09	5.28	3.78	2.54	1.61	0.73	0.26	0.
3	1.16	5.58	6.78	5.74	3.36	1.44	0.23	0.	0.	0.	0.	0.	0.	0.	0.	0.

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FIGURE CAPTIONS

- Fig. 1. Experimental waveforms for a pulsed laser. Lasing was obtained using 13 Torr of NF_3 and 2.5 Torr of H_2 at an initial temperature of 300 K.
- Fig. 2. Schematic diagram of the computer model.
- Fig. 3. Collision broadened linewidth used in code. The solid line for $J > 4$ is proportional to Polanyi's model [10], $\exp(-0.0085 \Delta E)$. The dashed line is proportional to $1/J$. The arrow indicates the Doppler linewidth at 300 K. Rotational relaxation was assumed proportional to collisional linewidth.
- Fig. 4. Calculated waveforms for a pulsed laser. Lasing was obtained using a mixture of NF_3 (13 Torr) and H_2 (2.5 Torr) at a constant temperature of 300 K.
- Fig. 5. Population distributions for each vibrational level at 429 ns. States with the same vibrational quantum number are joined by straight lines. Dashed line shows Boltzmann distribution at 300 K.
- Fig. 6. Population distributions for each vibrational level at 2.0 μs . The dashed line shows Boltzmann distribution at 300 K.
- Fig. 7. Semi-logarithmic plot of actual population distributions for $V = 2$ (dots) at 2 μs compared to Boltzmann distribution (solid line). N_0 is the population for the state where $J = 0$.

Creighton - Fig. 1

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Creighton - Fig. 3

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Creighton - Fig. 5

Creighton - Fig. 6

Creighton - Fig. 7