A NUMERICAL INVESTIGATION OF THE PULSED NF₃ + H₂ CHEMICAL LASER USING A MODEL WHICH INCLUDES ROTATIONAL RELAXATION AND SEMI-CLASSICAL LASER EQUATIONS

John R. Creighton
(Ph. D. Thesis)

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LAWRENCE LIVERMORE LABORATORY

University of California - Livermore, California - 94550

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John R. Creighton
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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 vibrational-rotational state separately, allowing rotational relaxation between adjacent states as well as vibrational relaxation and lasing according to P-branch selection rules. Simplified semi-classical laser equations, roughly equivalent to laser rate equations, are used; and waveforms for each P-branch transition are obtained. Simultaneous solution of a simplified set of chemical kinetic rate equations gives the pumping rate for each state.

Calculated waveforms agree with experiment and show several features not seen when rotational equilibrium is assumed: simultaneous lasing on many transitions, cascade behavior, spikes due to laser relaxation oscillations,

non-Boltzmann rotational distributions, and "hole burning" in the population distributions. The calculations give insight into the physical phenomena governing the shape and duration of the waveforms. The effect of varying certain parameters, relaxation rates, temperature, pressure, and diluents, is studied. Best fit to experimental waveforms is obtained when the rotational relaxation rate and collisional line broadening rate are approximately equal at about 10 times the hard sphere collision rate.

The IXION computer code, developed for these calculations, is described in detail. In addition, an analytic model is presented which accounts for major features of the total (all transitions) output waveform of the laser assuming rotational equilibrium, a steady state laser model, and constant temperature. A second computer code, MINOTAR, was developed as a general purpose chemical kinetics code. It verifies the analytic model and extends the results to adiabatic reactions where the temperature varies, and can yield waveforms using the assumptions of rotational equilibrium and a steady state laser. The MINOTAR code, being general, can also be used for chemical kinetics problems such as air pollution and combustion.

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1. INTRODUCTION

This report presents physical models which explain the major features of the pulsed $\text{NF}_3 + \text{H}_2$ hydrogen fluoride laser initiated by a short duration electric discharge. The work was performed over a period of several years in support of the experimental program of Pearson, Gregg, and co-workers (1973a, 1973b). The pulsed laser was chosen in an attempt to obtain short duration, high intensity pulses for laser fusion.

In the $\text{NF}_3 + \text{H}_2$ laser the electric discharge dissociates a fraction of the NF_3 to give F atoms and other species which are not important to laser action. The chemical reaction

creates vibrationally and rotationally excited HF which lases. It is also possible to build a pulsed HF laser using a mixture of F_2 and H_2 so that the chemical reaction

produces additional excited HF, and also creates a new F atom to replace the one consumed in reaction 1.1, constituting a chain reaction. This report is primarily concerned with the $\text{NF}_3 + \text{H}_2$ laser which depends only on reaction 1.1; but the analytic theory is extended to cover the chain reaction which includes 1.2. This report doesn't explicitly consider the "continuous wave" HF laser where the chemical reactions take place in flowing mixtures of reactant gases yielding HF, although the chemical kinetics is similar.

When this work was begun in 1970 a number of experiments had been reported in the literature and some modeling work was in progress. Bibliographies of published HF laser work up to mid-1971 are given in Chester and Hess (1972) and Dobratz (1972). My initial numerical calculations showed that with a couple of assumptions an analytic model could be constructed for the $\text{NF}_3 + \text{H}_2$ chemical laser. The reaction of H with NF_3 is orders of magnitude slower than reaction 1.1, so the laser is controlled by reaction 1.1. A fast electric discharge dissociates NF_3 to give an initial concentration of F atoms, which are consumed by reaction 1.1. It can be shown that laser output is generally proportional to the rate of formation of HF, which can be calculated from Eq. 1.1. This leads to a non-linear rate equation which would require a numerical solution except that we can make a further assumption. Because the initial concentration of F atoms is small we can assume that the concentration of H_2 is constant and get a solution for the laser pulse shape, which is an exponential decay at a rate governed by the consumption of F atoms. This is discussed in Section 4 and is extended to include reaction 1.2 as well as vibrational deactivation and recombination. This simple theory agreed with experiment when the measured rate constant for reaction 1.1 was used.

This analysis led to a new method of determining chemical kinetic rate constants (Creighton, 1972 and Pearson, et al., 1972b). A number of experiments had been done using NF_3 with a variety of hydrocarbons. Kinetic rate constants

were obtained by measuring the decay constants of the wave-forms (Creighton, 1972). Eight of these kinetic rates agreed with experimental rates tabulated by Trotman-Dickenson (1967). The rates for the other eight hydrocarbons were apparently the first reported. While this work was in progress Pummer and Kompa (1972) published a similar analysis and experimental rates for a few reactions. A year later Igoshin and co-workers (1973) described a measurement of the kinetic rate for the reaction

using a similar technique. Apparently unaware of the earlier work they developed their technique independently and erroneously claimed to have made the first direct measurement of this rate. However, they made a significant contribution by refining the technique to get quite accurate results.

Numerical solutions of the chemical kinetics equations are required if the temperature is allowed to vary because the equations become highly non-linear due to the temperature dependence of the rates. A computer is also required to treat the kinetics in more detail because of the large number of variables. For example if each vibrational state of HF is treated as a separate species and recombination and vibrational deactivation reactions are included the complete kinetics involves about 15 species and 50 to 100 reactions.

Numerical solutions of the kinetics is not straightforward, as it might appear. The equations are ordinary

differential equations but they are "stiff" in the sense that they involve time constants that differ by many orders of magnitude. Some of the time constants are in the sub-nano-second range and others in the microsecond range. Standard numerical techniques, such as Runge-Kutta require that the time step of the numerical method be less than the shortest time constant, to maintain numerically stable solutions. This uses excessive amounts of computer time, and leads to disastrous round-off and truncation errors.

Emanuel (1964) has gotten around this problem by taking advantage of the fact that steady state approximations can be invoked throughout most of the problem. This eliminates the short time constants at the cost of using sophisticated logic to test the validity of the steady state approximation. For the present work the MINOTAR* code was constructed using a numerical method devised by C. W. Gear (1971). This method gives stable solutions when the time step is orders of magnitude larger than the shortest time constant, provided all variables are changing slowly. (Gear's method is discussed in Appendix B.) The superiority of this method is illustrated by an example. The MINOTAR code was able to calculate and $H_2 + F_2$ explosion in 300 time steps, using less than 10 seconds of CDC 7600 computer time. The same calculation using Emanuel's (1971) NEST code was not complete after using 10 minutes on the CDC 7600 computer (Rapagnani, 1973).

*The proper spelling is MINOTAUR but the computer accepts only seven-letter names.

Kinetics calculations using the MINOTAR code are presented in Section 5 and compared with the analytic model.

The analytic and the kinetics codes can calculate the overall laser waveform. If rotational equilibrium within each vibrational level is assumed, the codes can also calculate population inversions and small signal gains. They cannot calculate laser saturation effects. Turner, Adams and Emanuel (1973) have added a steady-state laser model to the NEST code. This model treats laser saturation, but because it assumes rotational equilibrium it calculates lasing on only one P-branch transition at a time for any pair of adjacent vibrational levels. As the temperature and populations change other transitions lase, but only one at a time. This is known as J-shifting (Chester, 1970; Emanuel, 1971). Experiments with pulsed HF lasers show simultaneous lasing on several transitions between pairs of vibrational levels. To calculate this a model must include rotational non-equilibrium.

The IXION computer code was constructed to study the effects of rotational non-equilibrium in the HF chemical laser. The population of each vibrational-rotational state is treated separately. Each state receives an appropriate fraction of the HF which is formed by the chemical reaction. Rotational relaxation to adjacent states is allowed. Vibrational relaxation and lasing follow P-branch selection rules. Lasing is treated by means of semi-classical laser equations. These are derived in Section 6. By using a

steady-state approximation on a phase angle the semi-classical equations are simplified, but still give more accurate time constants than the usual laser rate equations. Both semi-classical and rate equations give a much more accurate waveform than a steady-state laser model. Section 6 also shows that the dipole selection rules prevent non-resonant interactions between two laser transitions in a cascade. The only coupling is due to sharing the population of a common state. Relaxation oscillations are a significant part of the experimental laser waveform, so there is an extensive study of the stability of laser equations in Section 6. Instability shows up as a sequence of spikes. Stable solutions are equivalent to steady-state solutions and have smooth waveforms which follow the pumping rate after an initial transient. Calculated waveforms show examples of both stable and unstable waveforms.

Section 7 gives a detailed description of the IXION code. Section 8 presents calculated waveforms which are in good agreement with experimental waveforms. The waveforms show simultaneous lasing on many transitions. The various spikes and humps are calculated and can be seen to be due to relaxation oscillations and changes in gain as the populations change (temperature was held constant). The agreement between calculated and experimental waveforms allows us to use the code to interpret the physical phenomena involved in the laser. All of the major features of the laser pulse are explained in terms of the results of the code. The code

shows details such as populations and inversions which are very difficult to measure experimentally. As a result the code is extremely useful in illuminating the underlying physical phenomena. The calculations show that many significant phenomena can only be explained by a model which includes rotational non-equilibrium and accurate laser equations.

To complete the study calculations were done varying a number of parameters. These are presented in Section 9. Variation of the rotational relaxation rate showed the best agreement between experimental and calculated waveforms when using a rotational relaxation rate based on estimates of the physical phenomena involved. After this work was completed Peterson, Lindquist and Arnold (1974) published the results of a direct measurement of the rotational relaxation rate. Their rate was a factor of 2 higher than the estimate used for this work (5 times gas kinetic collision frequency). Calculations using an extremely large rotational relaxation rate are consistent with models that assume rotational equilibrium. The code was unable to explain the experimentally observed decrease in energy at pressures above 100 Torr, but this is probably due to electric discharge phenomena which were not modeled in the code. Variation of other parameters gave results which were predicted by the analytic model.

One appendix is worthy of note. Appendix D gives a simple model for rotational relaxation based on dipole-dipole interactions. The model appears to be qualitatively, but not quantitatively, correct.

2. THE SPECTROSCOPY OF HYDROGEN FLUORIDE

2.1 Introduction

Before analyzing the dynamics of the HF laser, it is useful to devote a few paragraphs to a discussion of the spectroscopy of HF.

The HF laser operates on vibrational-rotational transitions all lying within the electronic ground state. This is distinctly different from atomic lasers which operate on electronic transitions. The output of an HF laser is dramatically different from that of a typical atomic laser. The atomic laser usually operates on one or a very few lines in the visible or near-infrared (~ 1 micron or shorter wavelength). Because vibrational-rotational levels are not equally spaced the HF laser may lase on several out of nearly 100 possible transitions; with wavelengths in the infrared, near three microns.

2.2 Vibrational-Rotational Spectrum

Hydrogen fluoride is a heteronuclear diatomic molecule and therefore has a fairly simple spectrum. There is a single vibrational degree of freedom. In the Born-Oppenheimer approximation the two nuclei move in a central force potential. If this potential is expanded in a Taylor series about the minimum point, r_0 , the leading term is proportional to $(r - r_0)^2$. This is an harmonic oscillator potential with quantum energy levels given by

$$E_v = (v + 1/2) \hbar \omega_v \quad (2.1)$$

Where v , an integer, is the vibrational quantum number; the frequency, ω_v , is a function of the masses and the force constant. The vibrational levels of a harmonic oscillator are evenly spaced. Since the internuclear potential is not exactly a parabola, cubic and higher terms in the Taylor series must be included. This leads to terms proportional to $(v + 1/2)^2$, $(v + 1/2)^3$, etc., in the energy levels. In the HF spectrum these anharmonic terms are significant.

A molecule can also rotate. The simplest model for the rotational motion is a rigid rotor. In this model the two nuclei rotate about their center of mass with constant internuclear distance. The quantum energy levels of a rigid rotator are

$$E_J = (\hbar^2/2I) J (J + 1)$$

where I is the moment of inertia, and J , an integer, is the rotational quantum number. There is an additional magnetic quantum number m . The rotating charge distribution has a magnetic moment, so if a magnetic field is applied the direction of the rotation is also quantized. If the rotational quantum number is J , there are $2J + 1$ allowed orientations of the angular momentum vector. In the absence of the magnetic field each rotational state can be considered $(2J + 1)$ -fold degenerate. This is analogous to angular momentum in electronic spectra except that there is no

1/2 integer spin. (We neglect nuclear hyperfine structure.) This $(2J + 1)$ -fold degeneracy is important in calculating partition functions and equilibrium population distributions.

The rigid rotor model is not accurate because at higher values of J the centripetal forces increase the internuclear distance. This leads to terms in $J^2(J + 1)^2$ and higher powers. There is also an interaction with the vibrational motion. At higher vibrational energies the nuclei spend more time at large separation and this affects the rotational motion through increased moment of inertia. When all of these effects are included, the energy of a state with quantum numbers v and J is given by

$$\begin{aligned}
 E_{v,J} = & \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 \\
 & + \omega_e y_e(v + 1/2)^3 + \dots + B_v J(J + 1) \quad (2.2) \\
 & - D_v J^2(J + 1)^2 + \dots
 \end{aligned}$$

The notation used in equation 2.2 is that used by Herzberg (1950).

In principle, the constants in equation 2.2 can be calculated quantum mechanically from first principles. In practice, accurate spectra are measured and fitted to equation 2.2 to give the constants. Once this is done equation 2.2 can be used to interpolate and extrapolate to new levels. These constants are also useful for tabulating the spectra of molecules, since the spectra can be calculated from the constants. Such a table is given in Herzberg (1950). The constants can also be used to calculate thermodynamic tables by means of a partition function.

2.3 Selection Rules

The spectral lines arise when the molecule makes a transition from one energy level to another. Certain selection rules limit the number of possible transitions. For a harmonic oscillator the vibrational transition selection rule is $\Delta v = \pm 1$, with + 1 representing absorption and - 1 representing emission. The rotational selection rule is

$$\Delta J = \pm 1, 0.$$

Both rules operate simultaneously so that in the case of emission $\Delta v = - 1$ and $\Delta J = - 1, 0$, or 1 . By convention these are denoted as R, Q, and P branch transitions. When the electronic ground state is a singlet the Q branch is forbidden. Thus HF has only P and R branch transitions in its vibrational-rotational spectrum.

If the potential is anharmonic, as in the case of HF, transitions with $|\Delta v| > 1$ are also allowed but are much less probable than those with $|\Delta v| = 1$. The rotational selection rule, $\Delta J = \pm 1$, is valid in any case. These are electric dipole transition selection rules; there are different selection rules for electric quadrupole and magnetic dipole transitions. These are unimportant in the HF laser because the transition probabilities are small.

In the HF laser we are then concerned only with P and R branch electric dipole transitions. The observed spectra from HF laser generally involves only P-branch transitions. It is difficult to maintain an R-branch population inversion because of the Boltzman factor in population distributions. Lasing on the P-branch transitions tends to deplete the R-branch inversion.

It is worth noting that the HF laser operates on allowed transitions with lifetimes on the order of 10^{-3} seconds. Most visible lasers operate on transitions which are forbidden because it is too hard to pump allowed transitions of 10^{-8} seconds. Small perturbations of the electronic states give the forbidden transitions a finite probability with lifetimes in the range of 10^{-3} to 10^{-5} seconds. The lifetime of HF is relatively long primarily because the lower frequency drastically reduces the density of modes into which the molecule can emit. However, since the transition is fully allowed the stimulated emission cross section in HF is large, leading to high gain lasers. The visible laser tends to have a smaller stimulated emission cross section because the transition is largely forbidden.

Tables of the spectra of HF are given in Appendix A. Because of anharmonic terms and the vibrational dependence of the rotational constants the lines are nearly all separated by more than the Doppler line width. The few lines which overlap do so by accident, not because of natural periods in the spectrum.

The standard notation for vibrational-rotational lines is to give the branch and rotational quantum number in the lower vibrational level, e.g. P3. We shall also use the notation V2-1 to indicate a transition from $v = 2$ to $v = 1$. Thus a V2-1 P3 transition connects the states $v = 2, J = 2$ and $v = 1, J = 3$.

3. EXPERIMENTAL BACKGROUND

The calculations presented here were part of a program involving both experiment and theory. The experiments were performed by Dr. Richard Pearson and co-workers, and many of the experimental results have been published (Pearson, et al. 1973a, 1973b). There was consistent communication between myself and Dr. Pearson, and he has kindly made his experimental notetooks available. This section will briefly review the experimental work, both the published material and some that has not been published.

3.1 Apparatus

A schematic diagram of the experimental apparatus is shown in Fig. 3.1. The electric-discharge laser tube consisted of a row of 51 aluminum electrodes spaced 1.0 cm apart in a thick-walled, 3/4-in-ID Teflon¹ tube 65 cm long. Each electrode is ballasted with a 1000- Ω resistor that discharged to a 1/4-in diam aluminum bar 50 cm long, across a 1.52-cm discharge gap. The tube had Brewster angle BaF₂ windows held in place by a stainless-steel window holder. Viton O-rings were used to seal windows and electrodes. The laser tube was filled with premixed gases from a stainless-steel and Teflon vacuum line.

The laser cavity had a high-reflectivity gold-coated rear mirror with a 10-m radius of curvature and a flat output mirror. Experiments using output mirrors with

¹Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U. S. Atomic Energy Commission to the exclusion of others that may be suitable.

90%, 50%, 8%, and 0% reflectivity showed that maximum lasing energy was obtained with a BaF_2 flat (8 percent measured). The energy delivered to the laser was calculated from measurements of the current and voltage across the discharge as a function of time. The energy out of the laser was determined by a cone ballistics laser calorimeter. A second detector and a PE Model E-1 monochromator were used to study the pulse shape of individual spectral lines. Both detector outputs were displayed in a dual-beam oscilloscope to give relative timing. Electrical-energy input could be varied by adjusting resistor R (Fig. 3.1). For most experiments a resistor was not used.

At low pressures (< 15 Torr), the discharge current pulse terminated before any lasing began; at higher pressures (> 25 Torr) lasing began before the discharge pulse had ended and persisted well beyond cessation of current flow. A 10-30 min. evacuation of the laser tube was found to be necessary between successive firings and was used to avoid a reduction of laser output from residual explosion products of the previous firing.

Occasionally, a permanent reduction of laser output was observed, and when it reached 10 percent the laser was dismantled and cleaned. Restoration of the output to a standard $\text{NF}_3\text{-H}_2$ mixture was achieved by washing the laser tube with aqueous detergent, then rinsing with water, methanol, and acetone. The tube was then evacuated overnight. The gases used were the highest grade commercially available.

3.2 Waveforms

A particular series of experiments was chosen for comparison with calculations. The series was performed by Major Gordon L. Hermann, USAF, during February, 1971. The series involved several hundred laser shots at a 5:1 ratio of $\text{NF}_3:\text{H}_2$. Most shots were at 15 Torr total pressure with about 20% at 60 Torr. This series was selected because each shot recorded the waveform for one single transition along with the total laser waveform. The total pulse energy was also measured by a calorimeter.

The waveforms for individual transitions obtained from experiment are shown in Fig. 3.2. These were obtained in experiments at 15 Torr total pressure with the $\text{NF}_3:\text{H}_2$ ratio about 5.2. The waveforms shown are the only ones observed, except that a very weak V3-2 P3 was seen in one case. The V1-0 P5 is apparently missing due to coincidence with a water vapor line. Since part of the laser cavity was open to the laboratory atmosphere, the absorption by water vapor probably prevented lasing on the P5 line. Searches were made for the V3-2 P5, V2-1 P 7 and V1-0 P8 lines, and they were not found within the limits of experimental sensitivity. The sensitivity was limited by electrical noise which created noise equal to 5 to 10% of the height of the V2-1 P5 transition. Thus it is not clear whether the missing transitions are completely missing or merely too weak to be detected.

The amplitude scale of the waveforms is arbitrary because they were obtained by splitting off an unknown fraction of the beam. In the case of the individual transitions the light was also passed through a monochromator which had uncalibrated losses. The heights are proportional to the signal recorded by the oscilloscope, but there may still be errors in the relative scale between individual transitions because they were often made several days apart, and light collection efficiencies could change due to changes in alignment or systematic changes in laser operation.

The waveforms shown in Fig. 3.2 were replotted by hand from oscilloscope photos. In that process the waveforms were considerably smoothed as shown by comparison with Fig. 3.3. Some of the wiggles in Fig. 3.3 represent small perturbations in the true waveform and some represent electrical noise due to ringing in the pulsed power supply. Both types of variation were smoothed out in the process of replotting. This must be kept in mind when comparing with calculated waveforms. The general outline of the experimental waveform, including multiple humps has been preserved.

There is also a problem of experimental reproducibility. The samples chosen were believed to be representative, but there were significant variations in experimental waveforms. There was little variation for P3 and P4 except occasional changes in amplitude. These were usually accompanied by other anomalies in the laser pulse. When the laser was restored to its normal operating condition, these waveforms returned to normal. Nearly half the experimental waveforms were V2-1 P5.

while the general shape was fairly consistent, the relative heights of the spikes varied from time to time. The P6 and P7 waveforms were more erratic. They sometimes looked like the P5, they were often as shown, and sometimes disappeared entirely. They seemed to be particularly sensitive to some variation in the laser, but the source is not clear.

Figure 3.4 shows a similar set of waveforms where the total pressure was 60 Torr. Waveforms for a number of transitions are missing. Those that appeared at 15 Torr were skipped in this experimental series. The P8 and P2 transitions were checked and were not lasing, or were not detectable.

Another phenomenon is significant. At 15 Torr the total laser energy, as measured by calorimeter, was about 1 millijoule. At 60 Torr we would expect the energy to be 4 millijoules. Instead, the total energy was only about 2 millijoules. This discrepancy will be discussed later.

In addition to recording the total laser energy, the partitioning of this energy among the various transitions has been calculated, and is shown in Table 3.1. The fractions were calculated by graphically integrating the waveforms of Fig. 3.2. The values given should be considered approximate, since the pulse heights depend on pulse to pulse reproducibility, which was not very good.

3.3 Dissociation of NF_3 by the Electric Discharge

There is good reason to expect the output of the $\text{NF}_3 + \text{H}_2$ laser to rise in a roughly linear fashion with

increasing pressure. It will be shown in Section 4 that the total laser output energy is proportional to the initial number of fluorine atoms created by dissociating NF_3 . If the fraction of NF_3 dissociated is independent of the pressure, the output energy should rise linearly with increasing pressure. Figure 3.5 shows that the output energy increases for pressures up to about 80 Torr and then drops off at higher pressures. This could be explained if the fraction of NF_3 which is dissociated decreases at higher pressures. We will examine the experimental data for the discharge to see if there is evidence for this hypothesis. The experimental data is from Pearson, et al. (1973a, 1973b); and from unpublished data of G. L. Hermann.

The source of F atoms is dissociation of NF_3 by the electric discharge. The physics of this process is quite complicated, but we can make some observations based on experimental data. We note from Fig. 3.6 that the current decreases slowly with increasing pressure, and we note from Fig. 3.7 that E/P is approximately constant at higher pressures. Actually, Fig. 3.7 shows V/Pd where V is the voltage, d is the spacing between electrodes, P is the pressure, and E the electric field. Figure 3.8 shows that the voltage remains finite in the limit of zero pressure. If we ascribe the finite voltage to a potential drop near the electrodes, then E/P is nearly constant over the entire experimental range. The simplest model for a discharge assumes that an electron gives up most of its kinetic energy in an inelastic collision (von Engel, 1956), and then obtains an average kinetic energy eE by the

time it has another inelastic collision. The mean-free path, λ , is proportional to $1/P$, so if E/P remains constant the average electron energy at the time of an inelastic collision remains the same as the pressure varies. The inelastic scattering can excite the molecule, dissociate it, ionize it or attach the electron. The physics of these processes is quite complicated, but if the energy of electron impact remains the same the probabilities for these processes should remain the same. The fact that E/P remains constant as pressure increases means that the probabilities will remain the same, but the number of inelastic collisions will be proportional to the pressure, P . Thus the number of F atoms produced by dissociation will also be proportional to P if the current remains the same. We have seen, however, that the current decreases with increasing pressure, so there may be a pressure where the number of F atoms is a maximum. This may explain the fall-off in energy and power at higher pressures.

The equivalent electrical circuit of the pulser and discharge is shown in Fig. 3.9. The pulser is equivalent to a voltage source, V_S , and a source impedance, R_S . (This is an accurate representation because the pulser is constructed from transmission line, rather than a conventional capacitor.) The output of the pulser is connected to a terminating resistor, R_T , to prevent reflections of the pulse which might damage the pulser. The laser discharge with a series resistor, R_D , is also connected across the output, in parallel with the terminating resistor. The

discharge is represented as a voltage source, V_D ; and the resistor R_D is in two parts, a current limiting resistor designated as R in Fig. 3.8 and an equivalent 20 ohms made up of 1000 ohms in series with each of the 51 pins in the discharge tube.

We can find the discharge current by analyzing the equivalent circuit. Clearly,

$$I = I_D + I_T \quad (3.1)$$

$$I_T R_T = I_D R_D + V_D \quad (3.2)$$

$$V_S - I_S R_S - I_T R_T = 0 \quad (3.3)$$

In the experiments R_T was designed to equal R_S . Solving Eqs. 3.1 to 3.3 with $R_S = R_T$ gives the discharge current

$$I_D = \frac{V_S - 2V_D}{R_S + 2R_D} \quad (3.4)$$

The factors of 2 arise because of the terminating resistor which carries substantial currents at larger values of V_D . The nominal value of V_S is 160 kV with $R_S = 80$ ohms. If we obtain V_D from Fig. 3.8 with $R_D = 20 + R$, the calculated discharge currents agree with Fig. 3.6.

We can now estimate the total number of F atoms created by the discharge. As shown above, the number of F atoms produced by one electron in the discharge is αV if E/P remains constant. The value of α can be determined empirically. The number of electrons is proportional to the current, so the number of fluorine atoms, F_0 , is proportional to $V_D I_D$. The values of V_D from Fig. 3.8 can be represented by

$$V_D = V_e(R) + \gamma P \quad (3.5)$$

with γ about 200 V/torr. The constant, $V_e(R)$, is independent of the pressure but is a function of the series resistance R . For a fixed value of R ,

$$F_0 = \eta I_D V_D = \eta \frac{V_S - 2V_e - 2\gamma P}{R_S + 2R} (V_e + \gamma P) \quad (3.6)$$

If we neglect V_e compared to V_S and γP

$$F_0 = \eta \gamma \frac{V_S - 2\gamma P}{R_S + R} \quad (3.7)$$

When F_0 is plotted against P the curve is a parabola with a maximum at $\gamma P = V_S$. If V_S is 160 kV and γ 200 V/torr, this maximum occurs at about 800 torr. The maximum of Eq. 3.6, which includes V_e , occurs at about 600 torr. This is an order of magnitude larger than the experimental maximum. Figure 3.10 shows laser output energy as a function of discharge energy. This shows that the fall-off in laser pulse energy is not solely due to passing the discharge energy peak. It appears that other phenomena are important in determining the pressure for maximum laser energy.

This is reinforced by experimental data for mixtures of $SF_6 + H_2$ where the maximum laser energy was obtained at about 120 torr and the energy was nearly four times the maximum obtained with $NF_3 + H_2$ (Fig. 3.11). The discharge energies were very nearly the same, as is shown in Fig. 3.12. Apparently the discharge creates more F atoms in SF_6 than it does in NF_3 .

Apparently the non-uniform fields due to the geometry also have an influence. The discharge goes from pins perpendicular to the laser axis to a cylindrical wire parallel to the laser axis. Electrodes with these shapes cause the electric field to be highly non-uniform and add additional complications to understanding the physics involved. The distribution of laser intensity relative to the electrodes is shown in Fig. 3.13. The distribution was measured two meters from the laser output mirror with an array of pyroelectric detectors. From this distribution the size of the laser beam waist was estimated. It is in agreement with the size determined by spots burned into film near the laser output mirror. There is some evidence that the spot narrows by 20 to 50% at pressures over 200 torr. This may result in reduced laser energy and power.

V1-0						V2-1			
Line	Expt.	Calc.	Renorm	Line	Expt.	Calc.	Renorm	Line	Expt.
P3	.027	.012	.016	P3	.064	.011	.015	P3	.064
P4	.121	.038	.051	P4	.114	.078	.104	P4	.114
P5	*	.108	-	P5	.225	.185	.247	P5	.225
P6	.093	.145	.193	P6	.144	.086	.115	P6	.144
P7	.114	.053	.081	P7	0	.026	-	P7	0
P8-P14	0	.046	-	P8-P14	0	.066	-	P8-P14	0

*Probably inhibited by coincidence with H₂O absorption line.

V3-2					
Line	Expt.	Calc.	Renorm	Line	Expt.
P3	0	.023	-	P3	0
P4	.098	.092	.123	P4	.098
P5	0	.026	-	P5	0
P6-P14	0	0	-	P6-P14	0

Table 3.1 Fraction of Laser Energy Emitted on Each Transition. Column labeled renorm is calculated energy renormalized by ignoring transitions not measured experimentally.

Fig. 3.1 Schematic of apparatus used for $\text{NF}_3\text{-H}_2$ chemical laser experiments.

Fig. 3.2 Experimental waveforms for individual laser transitions. Total pressure was 15 Torr with $\text{NF}_3:\text{H}_2$ ratio 5%. Peak total power is about 2kW.

Fig. 3.3 Oscilloscope trace showing total laser pulse and V¹-0 P7 waveform. Horizontal sweep is 0.2 microsec/cm. Vertical scale is uncalibrated.

Fig. 3.4 Experimental waveforms at 60 Torr total pressure with $\text{NF}_3:\text{H}_2$ ratio 5.2. Absence of several waveforms is due to an incomplete search.

Fig 3.5 Laser energy versus pressure for the $\text{NF}_3\text{-H}_2$ system at different reactant ratios: $R = \text{NF}_3/\text{H}_2$.

Fig. 3.6 Discharge current versus pressure for $\text{NF}_3/\text{H}_2 = 5.4$, using current-limiting resistors and a discharge time of 70 ns.

Reproduced by permission from Pearson, et. al. (1973a and 1973b)

Fig. 3.7 E/P (volts/centimeter torr) of the discharge versus pressure for $NF_3/H_2 = 5.4$, using current-limiting resistors and a discharge time of 70 ns.

Fig. 3.8 Voltage across laser tube (not including ballast resistors) versus pressure for $NF_3/H_2 = 5.4$, using current-limiting resistors and a discharge time of 70 ns.

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Fig. 3.9 Equivalent circuit of Pulser and Discharge in the Laser Tube.

FIG. 3.10 Laser energy versus energy deposited in the gas from the discharge at several different pressures for $\text{NF}_3/\text{H}_2 = 5.4$ and a discharge time of 70 ns.

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FIG. 3.11 Variation of laser pulse energy with pressure for mixtures of $\text{SF}_6 + \text{H}_2$ and $\text{NF}_3 + \text{H}_2$.

Fig. 3.12 Discharge current and voltage for several mixtures of SF_6 , NF_3 and H_2 .

Fig. 3.13 Approximate distribution of Laser intensity using 80 Torr SF_6 plus 20 Torr H_2 .

4. AN ANALYTIC MODEL OF THE CHEMICAL LASER

Many of the basic features of the HF chemical laser can be understood in terms of a simple analytical model. Numerical calculations are required to understand many details but the general pulse shape and pulse width can be obtained from the analytical model. The analytical model consists of a steady-state laser model and simplified treatments of the chemical kinetics.

4.1 The Steady-State Laser Model

We deal first with the laser model. It is well known that if light of the appropriate wavelength is passed through an inverted medium the intensity will be

$$I = I_0 e^{2\sigma\Delta N z}$$

where ΔN is the population inversion, σ is the stimulated emission cross section, z is the distance traveled, and I_0 is the intensity at $z = 0$. We wish to analyze a laser cavity containing an inverted medium of length L_g , one perfectly reflecting mirror and a second mirror with reflectivity ρ . Light which has just been reflected from the second mirror will be amplified as it passes through the inverted medium. It will then be reflected and amplified a second time. Finally, it is reflected by the second mirror. If I_1 is the intensity at that point, then $I_1 = I_0 \rho \exp(2L_g \sigma \Delta N)$. To maintain a steady state I_1 must very nearly equal I_0 , so we have $\rho \exp(2L_g \sigma \Delta N) = 1$. This can be rewritten

$$N = \log(1/\rho)/2\sigma Lg. \quad (4.1)$$

Physically, the population inversion adjusts itself until the gain equals the loss, including output, in one round trip through the cavity. This can occur because an increase in light intensity can deplete the inversion. The intensity then adjusts itself so that it depletes the population inversion which compensates for the increase due to pumping. This steady-state intensity, I_S , is easily calculated.

Consider a laser with N_1 molecules (atoms) in an upper state and N_0 in a lower state, so that $\Delta N = N_1 - N_0$. Assume that only the upper state is pumped at a rate S_1 by some mechanism such as a chemical reaction. The rate of creation of photons by stimulated emission is $\sigma I_S \Delta N / \hbar \omega$, and the rate equations for the populations are

$$dN_1/dt = S_1 - \sigma I_S \Delta N / \hbar \omega \quad (4.2a)$$

$$dN_0/dt = \sigma I_S \Delta N / \hbar \omega. \quad (4.2b)$$

Since ΔN is constant in the steady state,

$$dN_1/dt = dN_2/dt$$

and

$$I_S = S_1 \hbar \omega / 2\sigma \Delta N. \quad (4.3)$$

Equations 4.2 and 4.3 also imply that the output power plus other losses equal one half the pumping rate into the upper state, because in the steady state I_S remains constant and the number of newly created photons, $\sigma I_S \Delta N / \hbar \omega$, must equal the number lost. If the lower level were also pumped at a rate S_0 the output rate would be proportional to $1/2(S_1 - S_0)$. The principal conclusion reached in this discussion is the

fact that the output power is proportional to the pumping rates as long as the laser operates with gain equal to loss. Therefore, the problem of determining the steady-state power output reduces to the problem of determining the pumping rate.

We can generalize this to the case of the HF laser where several vibrational levels are pumped. The chemical reaction

pumps four vibrational levels from $v = 0$ to $v = 3$. Twenty-five percent of the molecules go into $v = 3$, 52% into $v = 1$, and 8% into $v = 0$ (Cohen, 1971). Representing these as S_3 to S_0 we can write rate equations

$$dN_3/dt = S_3 - B_3 \phi_2 (N_3 - N_2) \quad (4.5a)$$

$$dN_2/dt = S_2 + B_3 \phi_2 (N_3 - N_2) - B_2 \phi_1 (N_2 - N_1) \quad (4.5b)$$

$$dN_1/dt = S_1 + B_2 \phi_1 (N_2 - N_1) - B_1 \phi_0 (N_1 - N_0) \quad (4.5c)$$

$$dN_0/dt = S_0 + B_1 \phi_0 (N_1 - N_0) \quad (4.5d)$$

Steady state implies that $dN_3/dt = dN_2/dt = dN_1/dt = dN_0/dt$.

Let the output power on transitions between $v = 1$ and $v = 0$

be $P_0 = \sigma I_S N/\hbar\omega_0$, and let P_1 and P_2 be the corresponding powers on other transitions. At steady-state $\sigma_1 I_{S1} = B_1 \phi_0$

and we get

$$P_2 = 1/2 \hbar\omega_2 (S_3 - S_2) \quad (4.6a)$$

$$P_1 = 1/3 \hbar\omega_1 (S_3 + S_2 - S_1 - S_0) \quad (4.6b)$$

$$P_0 = 1/6 \hbar\omega_0 (S_3 + S_2 + 2S_1 - 4S_0) \quad (4.6c)$$

All of the pumping terms, S_0 through S_3 , are proportional to the rate of formation of HF. The total power is also proportional to the rate of formation, but it is no longer one half the pumping rate as it was in the two-level case. Instead, there will be some other numerical factor.

The steady-state solution will be valid over most of the pulse, but it neglects transients at the beginning of the pulse. Detailed discussion of the transient solution will be postponed to a later section because the rate equations are nonlinear and must be solved numerically. For the present we will merely note that there is a delay from the start of pumping to the time that a threshold inversion is reached. There is a further, and perhaps longer, delay until the laser intensity builds up to the steady-state value. The intensity will in fact, overshoot steady state and execute a damped oscillation about the steady state. For the moment we will neglect this and consider only the steady state.

In the steady state the sum of the output power plus losses equal a fraction of the pumping rate. The HF chemical laser operates well with a low reflectivity mirror so that we can neglect losses in comparison with the output power. Thus we can find the output power once we know the pumping rate.

4.2 Chemical Pumping of the HF Laser

4.2.1 Introduction

In the HF laser the pumping rate is determined by the rate at which HF is formed in vibrationally excited states. This study is primarily concerned with lasers where reaction 4.4 is the source of HF. The fluorine atoms are obtained by dissociating compounds such as NF_3 or SF_6 . (See Section 3.) This is readily done by an electric discharge which can be complete before much of the fluorine can react. This will allow us to assume an initial density, F_0 , of fluorine atoms and ignore the details of the discharge. The discharge undoubtedly creates ions and other chemical species but they seem to react on a much slower time scale than reaction 4.4 so that they can be ignored.

A second important case is when molecular fluorine, F_2 , is the source of the fluorine atoms. Then the reaction

is an additional source of HF. The reaction now proceeds as a chain where reaction 4.4 provides the H atom for reaction 4.7, which then provides a new F atom for reaction 4.4. This proceeds until one of the reactants is consumed or until the atoms are removed by a recombination reaction of the form

These will be discussed later. Chain reactions, 4.4 plus 4.7, give a different waveform than the single reaction, 4.4. The waveform for reaction 4.4 will be derived first, then the waveform for the chain reaction.

4.2.2 The F + H₂ Reaction

If the rate constant for reaction 4.4 is k_1 , the rate of disappearance of fluorine atoms is

$$-d[F]/dt = k_1 [F] [H_2], \quad (4.11)$$

where the brackets designate the density of the species and the minus sign represents disappearance of [F]. If there is a large excess of H₂ over F, the value of [H₂] will be roughly constant. If the initial density, [F], is F_0 the solution of Eq. 4.11 is

$$[F] = F_0 \exp(-k_1 [H_2] t). \quad (4.12)$$

We note also that

$$d[HF]/dt = -d[F]/dt = k_1 F_0 [H_2] \exp(-k_1 [H_2] t). \quad (4.13)$$

This is the rate of formation of HF so the pumping terms in Eq. 4.6 are proportional to this. In particular, $S_3 = .25 d[HF]/dt$. Equation 4.13 says that the pulse shape will be an exponential decay. Examination of experimental waveforms shows that the later part of the pulse is approximately an exponential decay. The early part of the pulse has some additional structure as shown in Fig. 3.2. There is a delay while the population inversion builds up to threshold and further delay while the intensity builds up. The $v = 2$ to $v = 1$ transitions lase first because $v = 2$ is the

most strongly pumped. The $v1-9$ and $v3-2$ transitions lase a bit later and form the second spike. From then on the pulse follows the exponential decay.

An HF laser can also be made to operate if a hydrocarbon or metal hydride is substituted for H_2 in reaction 4.4. The value of k_1 will then be different and the pulse width will be correspondingly different. A number of experiments have been performed with various hydrocarbons and metal hydrides. The pulse widths have been measured and rate constants obtained from Eq. 4.13. Where the rate constants were known from other sources the agreement was quite good. Details of this work are reported in Creighton (1972) and Pearson, et al. (1973b).

Equation 4.13 was obtained assuming no consumption of H_2 . This restriction is easily removed by noting that $[H_2(t)] = H_0 - F_0 + [F(t)]$, where H_0 is the value of $[H_2]$ at $t = 0$. This gives

$$d[F]/dt = -k_1 [F] \{H_0 - F_0 + [F]\}. \quad (4.14)$$

The solution of this is straightforward, yielding

$$d[HF]/dt = AH_0F_0 e^{-At}/(H_0 - F_0 e^{-At})$$

with

$$A = k_1 (H_0 - F_0) \quad (4.15)$$

This agrees with Eq. 4.13 when $F_0 \ll H_0$, and remains valid provided $F_2 < H_0$. A similar solution can be obtained for the case $F_0 > H_0$ by expressing $[F]$ in terms of $[H_2]$ and solving for $d[H_2]/dt$. The case where $F_0 = H_0$ can also be readily

solved. The solutions are shown in Fig. 4.1, where the ratio NF_3/H_2 was varied while keeping the total number density constant. Three dissociation fractions of F_0/NF_3 are shown along with the solution of Eq. 4.13.

4.2.3 The Chain Reaction of H_2 with F_2

The chain reaction case differs from the single reaction just discussed, in that it involves two reactions

The relevant kinetic rate equations are

$$d[F]/dt = -k_1 [F][H_2] + k_2 [H][F_2] \quad (4.16)$$

$$d[HF]/dt = k_1 [F][H_2] + k_2 [H][F_2] \quad (4.17)$$

$$\text{and } d[H_2]/dt = -k_1 [F][H_2]. \quad (4.18)$$

The reaction now is controlled by consumption of H_2 or F_2 , whichever is smaller. (In the case of the single reaction, (Eq. 4.4) consumption of F atoms was dominant.) The chain reaction rapidly reaches a steady state where the F consumed by reaction 4.4 is replaced by reaction 4.7, and both H_2 and F_2 are consumed at the same rate. We will first obtain the steady-state solution and then the transient.

For the sake of algebraic simplicity, we will treat the important special case where the initial values of $[H_2]$ and $[F_2]$ are equal. This case is important because it gives

the maximum total energy for a fixed total pressure. Peak power can be increased, at the cost of shorter duration and less energy, by making the mixture rich in F_2 to compensate for the fact that $k_2 < k_1$.

We can obtain the steady-state solution by setting Eq. 4.16 to zero, giving

$$k_1 [F][H_2] = k_2 [H][F_2]. \quad (4.19)$$

In this special case $[H_2] = [F_2]$, and in general $[H] = F_0 - [F]$, because we assumed no recombination to remove atoms, and there is no additional source of atoms once F_0 atoms have been dissociated. The steady-state value of $[F]$ is $F_0 k_2 / (k_1 + k_2)$.

Putting this in Eq. 4.18 gives

$$\frac{d[H_2]}{[H_2]} = \frac{-k_1 k_2}{k_1 + k_2} F_0 dt \quad (4.20)$$

which has the solution

$$[H_2] = H_0 \exp[-k_1 k_2 F_0 t / (k_1 + k_2)], \quad (4.21)$$

where H_0 is the initial density of H_2 . Inserting the expressions for $[F]$ and $[H_2]$ in Eq. 4.17 gives the rate of formation of HF,

$$d[HF]/dt = \frac{2k_1 k_2}{k_1 + k_2} F_0 H_0 \exp[-k_1 k_2 F_0 t / (k_1 + k_2)]. \quad (4.22)$$

This is an exponential decay as was the single-step reaction; the principal difference is the magnitude of the time constant. For the single-step reaction the time constant was $1/k_1 [H_2]$, for the chain reaction it is $(k_1 + k_2/k_1 k_2 F_0)$. At room temperature k_1 is about $4k_2$ and normally F_0 is a few percent

of H_0 . These values give the chain reaction a time constant which is an order of magnitude larger than the time constant of the single-step reaction.

Equation 4.22 ignores an initial transient resulting from the fact the $[F]$ initially equals F_0 and $[H]$ is zero. The transient value of $[F]$ can be obtained from Eq. 4.16 if consumption of H_2 is neglected.

$$[F] = \frac{F_0}{k_1 + k_2} (k_2 + k_1 e^{-t/\tau_1}) \quad (4.23)$$

$$1/\tau_1 = k_1[H_2] + k_2[F_2] \quad (4.24)$$

The first term of Eq. 4.23 is the steady-state solution and the second is the transient. The transient time constant is the same order of magnitude as the single-step time constant. When Eqs. 4.21 and 4.23 are substituted in 4.17, an approximate solution is obtained which gives both the transient and the steady state.

$$d[HF]/dt = \frac{k_1 k_2}{k_1 + k_2} F_0 H_0 e^{-t/\tau_2} [2 + (k_1/k_2 - 1)e^{-t/\tau_1}] \quad (4.25)$$

$$1/\tau_2 = \frac{k_1 k_2}{k_1 + k_2} F_0 \quad (4.26)$$

Figure 4.2 shows this solution for $[H_2] = [F_2]$ and $k_1 = 4k_2$. The figure also shows the single-step solution for comparison.

In summary, solutions for both the single-step reaction and the chain reaction have been obtained. The laser waveforms, proportional to $d[HF]/dt$, both have an exponential decay, but the time constant for the chain reaction will normally be an order of magnitude larger.

4.3 The Effects of Vibrational Deactivation

The discussion so far has neglected vibrational deactivation of the vibrationally excited states. This will now be treated by perturbation methods.

Vibrational energy can be converted to translational energy by reactions of the form

where M can be any molecule. The reverse reaction is highly improbable because very few molecules have enough translational energy to vibrationally excite HF. In reality, we should have a series of reactions like 4.27, one for each species with a different rate for each. However, the contribution of reaction 4.27 to the deactivation rate has the form

$$k_3 [\text{M}][\text{HF}(v)].$$

Mathematically the correct results are obtained if we let $k_3 [\text{M}] = \sum_i k_i [\text{M}_i]$. The largest k_i is obtained when $[\text{M}_i]$ is another HF. In that case, vibrational deactivation occurs once every 50 to 100 collisions. Most other molecules require 10^3 to 10^6 collisions to vibrationally deactivate HF.

Vibrational deactivation of HF can also occur by near-resonant transfer of a vibrational quantum to another molecule, as in the following reaction:

This differs from reaction 4.27 because the reverse rate is comparable to the forward rate. The vibrationally excited H_2

can store energy, removing it from early portions of the laser pulse and returning some of it later. Some of the energy transferred to H_2 will be lost due to vibrational deactivation of H_2 . The rate for vibration-vibration exchange, k_4 , is smaller than the vibrational-translational exchange rate, k_3 , for HF-HF collisions. Therefore, we introduce little error by neglecting the energy storage and simply add $k_4[H_2]$ to the term

$$\sum_i k_i [M_i].$$

We will treat vibrational deactivation by perturbation methods using Eq. 4.13 to obtain the value of HF. Integrating Eq. 4.13 gives

$$[HF] = F_0 [1 - \exp(-k_1 [H_2]t)]. \quad (4.29)$$

When we add vibrational deactivation to Eq. 4.13

we get

$$d[HF]/dt = k_1 F_0 [H_2]_0 \cdot e^{-t/\tau} - k_3 [HF(v)][M]. \quad (4.30)$$

For simplicity, consider only two levels, HF(1) and HF(0). In the steady state $[HF(1)] = [HF(0)] + \Delta N_c$, and since normally $\Delta N_c \ll [HF(0)]$, $[HF(1)]$ is approximately equal to $[HF(2)]$, and both are approximately equal to half of $[HF]$, as given by Eq. 4.29. (With more states equality would hold, but the fraction would be smaller.) Using this value, and inserting the photons as $P/h\nu$, we can write equations similar to 4.2.

$$\begin{aligned} d[HF(1)] &= k_1 F_0 f_1 H_0 e^{-t/\tau} - 1/2 k_3 [M] F_0 (1 - e^{-t/\tau}) - P/h\nu \\ d[HF(0)] &= k_1 F_0 f_0 H_0 e^{-t/\tau} + 1/2 k_3 [M] F_0 (1 - e^{-t/\tau}) + P/h\nu \end{aligned} \quad (4.31)$$

Where f_1 is the fraction of HF created in state 1, f_0 is the corresponding fraction in state 0, and $1/\tau = k_1 H_0$. The

condition $d[\text{HF}(1)]/dt = d[\text{HF}(0)]/dt$ gives

$$P/\omega = 1/2(f_1 - f_0) k_1 H_0 F_0 e^{-t/\tau} - 1/2 k_3 [M] F_0 (1 - e^{-t/\tau}) \quad (4.32)$$

This is shown in Fig. 4.3 with $2P/\omega$ labeled "Laser," the first term on the right labeled " $[\text{HF}]$ " and the second labeled "Vib. Deact." The figure clearly shows that vibrational deactivation reduces both the pulse width and the total energy. However, the effect is fairly small because $k_1 = 10 k_3$.

A similar result can be obtained for the chain reaction, neglecting the transient term in Eq. 4.24 and noting that in this case $[\text{HF}] = H_0 (1 - e^{-t/\tau_2})$. The result is

$$\begin{aligned} 2P/\omega = 1/2(f_1 - f_0) \frac{k_1 k_2}{k_1 + k_2} F_0 H_0 e^{-t/\tau_2} \\ - 1/2 k_3 [M] H_0 (1 - e^{-t/\tau_2}). \end{aligned} \quad (4.33)$$

This is similar to Eq. 4.32 except that $k_3 [M]$ may be comparable to $k_1 k_2 F_0 / (k_1 + k_2)$, because $F_0 \ll [M]$. In the case of the chain reaction the laser pulse may be terminated by vibrational deactivation, instead of consumption of H_2 . Thus vibrational deactivation may be a major factor in the total laser energy in the case of a chain reaction.

4.4 Variation of Laser Pulse Energy with Pressure

The experimental variation of total laser energy with pressure is shown in Fig. 3.5. There is clearly a maximum at 60 to 80 torr and a decrease in total pulse energy at higher pressures. Additional data shows that the peak power also reaches a maximum at about 80 torr and then drops off. (Pearson, et al., 1973a) The total energy drops off

faster because the pulse width is also decreasing with increasing pressure. We will compare our analytic model with these results and find that the model predicts a monotone increasing output energy as the pressure increases, provided the fraction of NF_3 dissociated to form F atoms is the same at all pressures. This is true when we include any other two-body collisional deactivation process. We will examine three-body process and find that they predict a decrease in output energy at higher pressures. However, when numerical values are inserted in the equations the peak energy occurs at pressures which are orders of magnitude larger than the experimental pressure. It therefore appears that at higher pressures a smaller fraction of NF_3 is dissociated.

4.4.1 Two-Body Reactions

The laser power when vibrational deactivation is neglected is proportional to $d[\text{HF}]/dt$ as given by Eq. 4.13 (or Eq. 4.15). This equation shows monotone increasing peak power with increasing pressure. Also equation 4.13 is easily integrated to show that the total pulse energy is proportional to F_0 .

When two-body vibrational deactivation is added, the output power is given by Eq. 4.32. Again the power increases with increasing pressure. To obtain the total pulse energy we must integrate Eq. 4.32. The integration must be cut off when the power decays to zero. This occurs at a time

$$T = \tau \ln \left(\frac{f_1 - f_0 + \mu_3}{\mu_3} \right)$$

$$\text{where } 1/\tau = k_1 H_0 \text{ and } \mu_3 = (k_3 [M])/(k_1 H_0) \quad (4.34)$$

When $t > T$ the steady state breaks down, Eq. 4.32 is no longer valid, and clearly there is no additional power output.

Integrating Eq. 4.32 from 0 to T gives the total pulse energy

$$W_{\text{Total}} = 1/2\kappa\omega F_0 \left\{ f_1 - f_0 - \ln[1 + (f_1 - f_0)/\mu_3] / \mu_3 \right\} \quad (4.35)$$

The quantity in brackets is dimensionless, and independent of pressure. Therefore vibrational deactivation does not cause lower output energy at high pressures. It can be shown that this is true for any process that depends on two-body collisions.

4.4.2 Three-Body Reactions Recombination

Some chemical reactions involve three bodies and these reactions contribute terms of the form $k[A][B][C]$ to the rate. Consider, for example, the reaction

Where M is some molecule. If the significant chemical reactions are 4.4 and 4.9, then

$$d[F]/dt = k_1[F][H_2] - k_5[F][F][M]. \quad (4.36)$$

This equation has the solution

$$[F] = F_0 e^{-t/\tau} \left[\frac{k_1 H_0}{k_1 H_0 + k_5 F_0 [M] (1 - e^{-t/\tau})} \right] \quad (4.37)$$

and the laser power is proportional to the rate of creation of HF,

$$d[HF]/dt = k_1[H_2][F]. \quad (4.38)$$

In the event the k_5 is zero, substituting (4.37) in (4.38) gives Eq. 4.13, as it should. In the event the k_5 is reasonably large, the power will drop off much faster, although the initial peak will be the same size. This will occur when

$k_1 H_0/k_5 [M][F_0]$ is on the order of unity. At 300 K, k_1 is about $10^{12} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ (Cohen, 1971) and k_5 is less than $10^{16} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$. With F_0 approximately $0.1 H_0$ the value of $[M]$ would have to be about $10^{-3} \text{ moles/cm}^3$ for the two terms to be equal in magnitude. This corresponds to a pressure of 20 atmospheres, but experimentally the peak occurs at about 0.1 atmosphere. There is some uncertainty in the exact value of k_5 (Cohen, 1971), but it could scarcely be that large. Also Eqs. 4.37 and 4.38 show that the three-body recombination reduces the pulse width at, say, 10% of peak. If this is plotted versus pressure, the line will curve at high pressure. This is not seen in experimental data.

It appears, therefore, that three-body recombination of F cannot account for the drop in laser power at higher pressures. The same argument applies to reaction 4.10, especially since it creates HF. Reaction 4.8 might actually enhance the power because it restores some of the H_2 which was considered to be consumed in the previous analysis. Thus we conclude that recombination reactions 4.8 to 4.10 cannot account for decrease in laser energy and power at pressures above 80 torr.

4.4.3 Three-Body Vibrational Deactivation

W. Klemperer (1972) has suggested that the anomalously high vibrational deactivation rate of HF may be due to dimer formation. It is well known that dimers, trimers and hexamers of HF exist in equilibrium with the monomer at room temperature (Kollman and Allen, 1970; Del Bene and Pople, 1971; Franck and Meyer, 1959; Dyke, Howard and Klemperer, 1972;

Smith, 1958 and 1959). The proposed mechanism for deactivation is that two HF molecules collide and that before they can separate again the complex is struck by a third molecule. This third molecule absorbs vibrational energy which causes the two HF molecules to be bound into a dimer but in a high vibrational state. The bonding is known to be a hydrogen bond with a bond energy of about 6 kcal/mole. Once the bond is formed the vibrational modes can exchange energy. This may lead to unimolecular decomposition, where after the dimer has suffered up to 10,000 collisions with other molecules it will break apart, but with a high probability that the resulting HF molecules have lost their vibrational energy. The net result is an apparent deactivation of the vibrationally excited HF or even a temporary apparent removal of HF molecules from the system. We wish to estimate the magnitude of this effect.

The three-body reaction can be written

where we assume that at least one of the HF molecules is vibrationally excited. Klemperer (1972) has suggested that the rate constant, k_6 , should be taken to be the three-body gas kinetic collision frequency. This was estimated by assuming that two HF molecules come together in a binary collision and form a complex with a lifetime of roughly one vibrational period. The density of these short-lived complexes

with other molecules can be computed. If the binary collision cross section is 10^{-15} cm^2 and the vibrational period is 10^{-13} seconds, then k_6 is approximately $5 \times 10^{17} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$.

To obtain the laser power we neglect recombination and consumption of H_2 so that the value of $[\text{F}]$ is given by Eq. 4.11. If we consider only two vibrational levels the laser power is

$$P/h\nu = 1/2 (f_1 - f_0) k_1 \text{H}_0 \text{F}_0 e^{-t/\tau} - 1/2 k_6 [\text{M}][\text{HF}]^2. \quad (4.40)$$

In the second term the $1/2$ comes from the fact that approximately one half of the HF is in the upper vibrational state. Substituting the value of $[\text{HF}]$ from Eq. 4.29 gives

$$P/h\nu = 1/2 (f_1 - f_0) k_1 \text{H}_0 \text{F}_0 e^{-t/\tau} - 1/2 k_6 [\text{M}] \text{F}_0^2 (1 - e^{-t/\tau})^2. \quad (4.41)$$

This is similar to Eq. 4.32 except that the second term now depends on the third power of the pressure, assuming F_0 proportional to the pressure. The total pulse energy is obtained by integrating Eq. 4.41 to the time, T , where P goes to zero. For this purpose we re-write Eq. 4.41

$$P = A p^2 e^{-t/\tau} - B p^3 (1 - e^{-t/\tau})^2$$

where p represents the pressure. We can find the time when the power goes to zero if we neglect $e^{-2T/\tau}$ compared to $e^{-T/\tau}$.

$$T = \tau \ln \left(\frac{A + 2Bp}{Bp} \right) \quad (4.42)$$

The total pulse energy is then given approximately by

$$W = A p^2 \tau \left[\frac{A + B p}{A + 2 B p} \right] - B p^3 \tau \left[T/\tau + 2 \left(\frac{A + B p}{A + 2 B p} \right) + 1/2 - 1/2 \left(\frac{B p}{A + 2 B p} \right)^2 \right] \quad (4.43)$$

The terms in square brackets vary slowly with pressure; and since τ_{ap}^{-1} , the first term is roughly linear in pressure and the second quadratic. As a result, Eq. 4.43 approximates a parabola with a maximum when $A p^2 = B p^3$, or when $(f_1 - f_0) k_1 H_0 F_0 = k_6 [M] F_0^2$. To evaluate this numerically, assume the $(f_1 - f_0) = 1/3$ and that $[M] = [H_2] + [NF_3] \approx 6 H_0$. The measured value of k_1 is $2 \times 10^{13} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ and k_6 is estimated above as $5 \times 10^{17} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$. The equality is then satisfied when $F_0 = 2.2 \times 10^{-6} \text{ moles/cc}$, equivalent to a pressure of about 40 torr. Since F_0 seems to be less than a tenth of the total initial pressure, this would require a total pressure around 400 torr, five times higher than the experimentally observed maximum. Thus HF dimer formation doesn't seem to account for the fall-off of laser pulse energy above 60 torr. Not only is the magnitude of the effect too small, but Eq. 4.41 shows that the peak laser power should continue to increase with pressure, in contrast to experimental results.

Three possible reasons for the fall-off in laser energy and power have been investigated: three-body recombination of fluorine atoms, vibrational deactivation of HF by three-body reaction which form dimers, and a peak in the discharge energy (See Section 3). All three mechanisms give approximately the correct shape for the laser energy

versus pressure curve, but the calculated pressure for maximum energy is one to two order of magnitude too high. It appears that the reason for the fall-off in energy is likely to be found in the physics of the discharge, but that is not well understood at present.

Fig. 4.1 Variation of laser pulsewidth as a function of the ratio NF_3/H_2 at constant total pressure. Curves are shown for three initial dissociation ratios and for the case with H_2 assumed constant. In the lower right hand corner the pulse is limited by consumption of H_2 .

Fig. 4.2 Comparison of rates of formation for chain reaction ($\text{H}_2 + \text{F}_2$) and $\text{F} + \text{H}_2$. Initial conditions: $[\text{H}_2] = [\text{F}_2] = 10 [\text{F}]$, and $k_1 = 4k_2$.

Fig. 4.3 Effect of two body vibrational deactivation on laser output. Laser output is HF minus Vib. deact.

5. THE MINOTAR CODE FOR CALCULATING CHEMICAL KINETICS

5.1 Introduction

The analytic model of the previous section is based on approximations. Equations 4.13 and 4.22 were derived neglecting vibrational de-activation, recombination, and consumption of some reactants. These effects were later included by means of approximations and perturbation techniques. Exact solutions require numerical techniques. There are two reasons for this. The more fundamental reason is that the equations are non-linear in the dependent variables. Specifically, a term such as $k_1 [F][H_2]$ involves the product of two dependent variables, the densities of fluorine atoms and hydrogen molecules. Differential equations containing such terms can only be solved analytically under rather special conditions. In order to solve more general cases numerical solutions are required. The second reason for using numerical solutions is that a large number of variables are involved and the computer is more or less required just to do the necessary bookkeeping. For example, in the chain reaction, $H_2 + F_2$, seven vibrational levels of HF are involved. If we include formation and vibrational deactivation of HF along with radical formation and recombination and chain branching mechanisms we get 60 to 100 chemical reaction steps, and perhaps fifteen species as dependent variables. Even if this could be solved analytically, the labor involved in keeping track of these variables would be enormous.

For these reasons the MINOTAR code was constructed. The analytic approximations are quite useful for obtaining physical insight, but the numerical solutions are useful for establishing the validity of the approximations. (In fact, the approximations leading to Eq. 4.13 were first seen in the process of setting up a test problem to verify the MINOTAR code.)

5.2 The Gear Method for Solving Differential Equations

The usual methods for solving ordinary differential equations numerically are Runge-Kutta, the Adams predictor-corrector and its variants, Nordsieck's method, and Hamming's method, a particularly useful form of predictor-corrector method. The Runge-Kutta method is frequently used because it is quite easy to change the step size of the independent variable.

The initial attempt to solve the chemical kinetics problem used a Runge-Kutta method, but it immediately became clear that it would take tens of minutes of computer time to solve a single problem. Further investigation revealed that the chemical kinetics equations contained several time constants differing by several orders of magnitude. Such equations are known as "stiff" equations, apparently because they were first recognized in structural analysis. All of the standard techniques for solving ordinary differential equations have a domain of stability which limits the time step to a small multiple of the shortest time constant (Seinfeld, et al., 1970). If a larger time step is chosen, errors due

to machine roundoff and truncation errors in the numerical procedure are amplified at each time step and the solution rapidly goes to infinity. The situation is analogous to using the first few terms of a slowly converging infinite series, for example a cosine. Unless the argument is kept small, the first few terms of the series give an erroneous result. The chemical reactions which cause problems are reactions such as radical formation or recombination, which are essentially at equilibrium over most of the reaction, but can change very rapidly. Minor errors in these reactions can be amplified if the time step becomes too large. When these reactions are actually creating or removing radicals we want to follow them. When they are in equilibrium we don't want them controlling the time step.

One way to achieve this is to add logic which checks to see if these equations are near equilibrium and to solve them algebraically in that case. This has been done in the Aerospace Corporation's NEST code (Emanuel, 1964; Turner, Adams and Emanuel, 1973), and works satisfactorily. The logic, however, is fairly complicated. One is also concerned that forcing the equations to steady state may introduce errors.

Another method, perhaps more elegant, is to use Gear's method to solve the stiff system of equations (Gear, 1971a, 1971b; Hindmarsh, 1972a, 1972b, 1973). Gear's method is a predictor-corrector which is arranged to be stable against noise in the terms with fast time constants. The method

uses numerical approximations to high-order derivatives for the predictor and corrector steps. The values of the dependent variables are obtained from a truncated series of the form

$$y(t + \Delta t) = y(t) + a_1 h y^{(1)} + \dots + a_n h^n y^{(n)} \quad (5.1)$$

where h is the time step and $y^{(n)}$ is the n th derivative of y . The coefficients $a_1 \dots a_n$ are chosen to make the truncated series give bounded error for those terms which have fast time constants but are near equilibrium. The order of the truncated series is the number of derivatives. The order may vary from 1 to 6, with a different set of coefficients, a_n , for each order. The derivatives are stored in the form $h^n y^{(n)}$, so that the time step, h , is easily changed by simply rescaling the derivatives. Tests and controls for changing the time step and order are included in Gear's algorithm (Gear, 1971a, Hindmarsh, 1972a). The power of this method is best shown by an example. The chain reaction, $H_2 + Br_2$, was run to $t = 10^{13}$ seconds in less than three hundred time steps. The first step was only 10^{-10} seconds, but the last step was 10^{12} seconds. The normal Runge-Kutta method would have kept the time step at less than 10^{-6} seconds for this problem.

The Gear method has a disadvantage for some problems. In order to get large time steps the corrector used a generalized Newton-Raphson iteration technique. This requires inversion of the Jacobian matrix $|\partial \dot{y}_i / \partial y_k|$, where $\dot{y}_i$ is dy_i/dt . In problems with a large number of variables, evaluation and inversion of this matrix requires considerable computation. If the problem is not stiff, it may be more

efficient to use another method. It turns out that by proper choice of the coefficients, a_n , the Gear method is converted to an Adams predictor-corrector. Gear has included a flag in his algorithm which allows the user to select the Adams method up to order 12. This can be useful for some problems. The chemical kinetics problems considered so far have had only 10 or 15 variables, so the stiff method has been chosen.

5.3 Details of the Code

5.3.1 Computing the Derivatives

Regardless of the method of integration, the chemical reactions must be put in a form that can be used by the computer. If Y_i is the density of chemical species i , the reaction numbered j can be written

where A_{ij} and B_{ij} are stoichiometric numbers for species i in reaction j . When A and B are stored as matrices the rate equation for species Y_k can be written (Emanuel, 1971)

$$\begin{aligned} dY_k/dt = \sum_j \left\{ -A_{kj} k_j \prod_i Y_i^{A_{ij}} \right. \\ \left. + B_{kj} k_{-j} \prod_i Y_i^{B_{ij}} \right\} \quad (5.3) \end{aligned}$$

The forward reaction rate is k_j and the reverse rate is k_{-j} . The forward reaction depletes the density of Y_k (if $A_k \neq 0$); and the reverse reaction increases the density if $B_k \neq 0$. The forward and reverse rates are related by the equilibrium constant, $K_p = k_j/k_{-j}$. This in turn is obtained from

$$k_p = \exp (-\Delta G_f^*/RT), \quad (5.4)$$

where ΔG_f^* is the standard Gibbs free energy of formation at the temperature T . Since both the rates and ΔG_f^* are functions of temperature, the code must also be able to calculate the temperature.

In the MINOTAR code the densities of the species Y_j are stored as a vector and the stoichiometric numbers A_{ij} and B_{ij} as matrices. A subroutine named DIFFUN furnishes a vector dY_i/dt to the Gear subroutine. The algorithm is based on Eq. 5.3 and a listing of DIFFUN is given in Appendix E. The rates k_j and k_{-j} are stored as vectors and are computed by a thermodynamic subroutine named THERMO.

5.3.2 Computing the Thermodynamics

The function of subroutine THERMO is to calculate the temperature and then the forward and backward rates. It can do this for either an isothermal reaction or a constant volume adiabatic reaction, assuming ideal gases. (Corrections for heat transfer could easily be added by means of an additional subroutine.) In order to calculate the temperature for an adiabatic reaction THERMO must store the enthalpy of formation at 298K and coefficients to calculate the specific heat (or enthalpy) for each species as a function of temperature. The forward rates are assumed to be in the form

$$k_j = A_j T^{B_j} \exp (-E_{aj}/RT),$$

and are stored as A_j , B_j , E_{aj} , for each reaction. To obtain

reverse rates, coefficients to compute ΔG_f° for each species must also be stored. Subroutine THERMO first calculates the temperature and then for each reaction it calculates the forward rate, the equilibrium constant and the reverse rate.

The temperature calculation requires some comment. The state of the system can be described in terms of the temperature and the densities, since we assume constant volume and an ideal gas law. Let the densities be represented by a single variable, ρ . The input routines specify initial temperature T_0 and density ρ_0 . At time step k the Gear subroutine gives the density ρ_k . The schematic thermodynamic path for the temperature calculation is shown in Fig. 5.1. Point i represents the initial state (T_0, ρ_0) . Point 1 represents the state $(T = 298K, \rho_0)$ and point 2 represents $(298, \rho_k)$. The energy at point 2 is defined as the heat of formation at 298K for densities ρ_k , i.e.,

$$E_2 \equiv \Delta H_f^{298}(\rho_k) - \rho_k RT_2.$$

Similarly, at point 1

$$E_1 \equiv \Delta H_f^{298}(\rho_0) - \rho_0 RT_1$$

and at point i

$$E_i = E_1 + \int_{298}^{T_0} C_v(\rho_0) dT.$$

On the first pass through THERMO, E_i is calculated and stored. On succeeding steps the Gear subroutine gives ρ_k and we calculate $E = E_2 - E_i$. Since the system is assumed to be adiabatic the energy at state k is the same as that at state i , so that going from point 2 to point k at constant density

ρ_k we have

$$\int_{298}^{T_k} C_v(\rho_k) dT = \Delta E. \quad (5.5)$$

The integral has to be calculated iteratively because the final temperature, T_k , is unknown. For each species, Y_i , coefficients for the specific heat, a_{ki} , are stored so that

$$C_v(T) : \sum_i Y_i (a_{1i} - R) + \sum_i Y_i a_{2i} T + \sum_i Y_i a_{3i} T^{-1} \dots \sum_i Y_i a_{7i} T^{-3} \quad (5.6)$$

Each term in Eq. 5.6 can be integrated so that the integral of Eq. 5.5 becomes an algebraic expression in the temperature, T . Eq. 5.5 is then solved by Newton-Raphson iteration for T_k . The temperature at the previous time step, T_{k-1} , is used as the starting value and convergence to eight significant figures is achieved in one or two iterations.

There may be more elegant ways to compute the temperature but this one has worked well, provided the densities are used properly. The Gear method and the densities for the current predictor or corrector step must be used. An attempt to calculate an interpolated temperature at the midpoint between two steps led to disastrous instabilities. The present version works well, and since it always calculates the temperature starting at the same reference state it doesn't develop cumulative errors in the temperature.

The forward and reverse reaction rates are calculated in a straightforward manner. A listing of subroutine THERMO can be found in Appendix E.

5.3.3 Input/Output Routines

The remainder of the subroutines in the MINOTAR code handle input/output and control the Gear subroutine.

Output Format

The output consists of both tabular and graphical output. The graphical output shows pressure, total density and temperature as a function of time. In addition, the density of selected species can be displayed and the net rates of selected reactions. The input routines allow the user to select the molecular densities to be displayed and to select which ones appear on the same plot. Similar selection is provided for graphical display of rates. The net rate displayed involves densities of molecules as well as forward and reverse rate constants. For example, if reaction J is

the rate which is displayed is $R(J) = -k_f [A][B] + k_r [C][D]$.

Clearly

$$\begin{aligned} d[A]/dt &= d[B]/dt = R(J) \\ &= -d[C]/dt = -d[D]/dt. \end{aligned}$$

On the other hand, in the reaction

$$R(J) = -k_f [A]^2[M] + k_r [B][M],$$

and

$$d[A]/dt = 2 R(J), \quad d[B]/dt = -R(J) \quad \text{and} \quad d[M]/dt = 0.$$

The absolute value of $R(J)$ is displayed on a logarithmic scale with net forward rates ($R(J) < 0$) shown as dotted lines and net reverse rates are solid lines.

The tabular output gives the same data as the graphs, arranged in a column at each time/step. Each page contains eight columns and, in addition, all densities, net rates and equilibrium constants at the time the page is completed. A sample page is shown in Table 5.1. Examination of the table will show that the time for printout is nearly always a "nice" number in the sense that it corresponds to a multiple of some convenient interval. This is achieved by interpolation because a time step of the code generally doesn't correspond to a convenient interval. The interval is selected by the user as an input option. This feature is a great help in comparing two separate calculations because data can be compared at identical times.

Under some conditions the code will take many time steps between printout intervals. In this case the code will print a column every M time steps, independent of the printout interval. The time of these printouts is not a "nice" number, but the printout is included on the assumption that many time steps imply significant changes in some variable. The number of steps, M , can be set by the user.

Examples of the graphical output will be presented shortly.

Input Format

The input to the MINOTAR code is in the free-format, blank-delimited form; i.e., data may be punched in any column and symbols are separated by blanks. A sample input deck is shown in Table 5.2. The free-format is convenient and greatly reduces input errors. It also allows the chemical equations to be written in readable form. The input routine recognizes certain key words such as TITLE, EQUATIONS, and PLOT. The routine then takes the appropriate branch in order to handle the data which follows. The input deck has a certain syntax which makes it essentially a simple computer language. A user's manual for the code is available, but a brief description of the input deck will be given.

The input routine is based on free-format input subroutines written by Alex Cecil (1965). The subroutines recognize three types of symbols: numbers, alphanumeric symbols beginning with an alphabetic character, and special characters which include all punctuation marks except the period. (A symbol is a string of characters separated from other symbols by blanks.) Cecil's subroutines read the input cards and give the symbol (or its value in the case of a number) and identify the type of symbol. When an alphanumeric symbol is read, the first three letters are compared with a symbol table. The symbol table contains two levels of symbols: block headers and identifiers. When the symbol read in matches a block header, the input routine branches to an appropriate block of coding, where it remains until another

block header is found. Within a block the routine searches for appropriate identifiers and stores the data which follows. The data is assumed to be in the proper sequence. The input routine will catch many, but not all, errors in the sequence in which data is entered.

The proper sequence for the input deck is the TITLE block followed by the CONTROLS block to specify the temperature (a second CONTROLS block can be used to specify other control parameters). Next is the SPECIES block which identifies the molecular species and their initial densities. A table of molecular symbols is set up and the thermodynamic data for each species is looked up in a disc file named JANAFB. The next block, EQUATION, reads the chemical equations and sets up the reaction matrices, A_{ij} and B_{ij} of Eq. 5.3. The RATES block specifies the rates in Arrhenius form, and the PLOT block specifies the graphs to be plotted. The key work, GO, indicates the end of the input deck and tells the code to begin calculating.

Before calculation actually begins the code gives several pages of output which indicate how the routine interpreted the input data. Examination of these pages can be used to detect misinterpretation of the input data. An independently useful feature is the printout in symbolic form of the rate equations for each species, as shown in Table 5.3. This is useful because it is easy to make mistakes in obtaining these equations by hand if the set of reactions is large.

Surprisingly, it is quite easy to write the input routine in a free-format version. An earlier version of MINOTAR used a fixed format input deck, and it took more than a week to write and debug the input routine. The free-format version was written and debugged in less than a week. This effort has been repaid several times by the time saved in setting up input decks.

5.4 Calculations of HF Kinetics

5.4.1 Simplified Reaction Scheme

The sample input (Table 5.2) and output (Tables 5.1 and 5.3) were from a calculation of the $H_2 + F_2$ kinetics. The species labeled HF.0 represents the ground state of HF and HF.1 represents the $v = 1$ state of HF. This is a greatly simplified reaction scheme because it assumes only $v = 0$ and $v = 1$ vibrational levels. It also assumes in reactions 1 and 2 that all of the HF is formed in $v = 1$. Nevertheless, this simple scheme illustrates the essential features of the laser, as did a two-level analytic model.

The scheme used assumes a constant volume, adiabatic explosion beginning with 2.5 torr each of H_2 and F_2 in 10 torr of helium at 300 Kelvin. To start the reaction the initial partial pressure of F atoms was set at 0.1625 torr. This could be achieved by a fast electric discharge; a flashlamp pulse would probably last a microsecond or two, which is a significant fraction of the laser pulse. Reactions 1 and 2 constitute the chain reaction. Reactions 3 and 4 represent vibrational deactivation of HF. Reaction 3 represents the

anomalously fast deactivation by F and HF . The variation of the reaction rate with temperature doesn't follow the standard Arrhenius form (Cohen, 1971; Bott and Cohen, 1971; Shin, 1972). The negative activation energy represents a curve fitting and has no physical significance. Reaction 4 is the vibrational rate for the other species in the problem. This rate is much lower than reaction 3. Reaction 5 represents recombination of F. Because the back reaction is included it can also represent thermal dissociation of F_2 . A similar reaction for recombination of H could have been included, but recombination doesn't seem to have a major affect on the lasing.

5.4.2 Simulation of the Single-Step Reaction

A subset of this scheme can be used to simulate the $\text{NF}_3 + \text{H}_2$ or $\text{SF}_6 + \text{H}_2$ laser. In these lasers the electric discharge dissociates NF_3 in about 70 nsec to give a ratio of densities $[\text{F}]/[\text{NF}_3] = 0.0125$. A typical experiment used 12.5 torr of NF_3 mixed with 2.5 torr of H_2 . The reaction of H with NF_3 is orders of magnitude slower than reaction 2, so only reaction 1 is important in producing HF. Because helium was already in the thermodynamic table and NF_3 wasn't, the reaction was simulated by using the scheme of Table 5.2 with the rate constant of reaction 2 arbitrarily reduced four orders of magnitude. (The exact value wouldn't affect the results.) The 10 torr of the He plus 2.5 torr of F_2 simulate the vibrational deactivation due to NF_3 . The specific heat of He is less than that of NF_3 , but the temperature rise is not very large.

The results of the calculation are shown in Figs. 5.2 to 5.4. Figure 5.2 shows the density of the major species. H_2 is consumed by reacting with F atoms and the amount of HF formed equals the amount of H_2 consumed. The model assumes that all of the HF is formed as HF.1, most of it in the first two microseconds. Vibrational deactivation via reactions 3 and 4 then converts HF.1 to HF.0. The consumption of F atoms is clearly seen in Fig. 5.3. The density of H atoms is the mirror image of the F atoms, an obvious result of reaction 1. Figure 5.4 shows the rate of formation of HF from reaction 1 and the rate of vibrational deactivation from reaction 3. The other reactions are insignificant under the chosen conditions. The curvature in the rate for reaction 1 in the first 2 microseconds is due to the rise in temperature from 300 to 380K. The laser output, in the steady state, is proportional to the rate of reaction 1 minus the rate of reaction 3. Figure 5.4 is quite similar to the results of the analytic model shown in Fig. 4.5, except that Fig. 5.4 is a semilogarithmic plot and the vibrational relaxation is smaller because more HF was formed with the larger initial dissociation assumed for Fig. 4.5.

5.4.3 Simulation of the $F_2 + H_2$ Chain Reaction

We now return to the $F_2 + H_2$ reaction with the appropriate rate in reaction 2. The results of the calculation, shown in Figs 5.5 to 5.8, are quite different from those of Figs. 5.2 to 5.4. Figure 5.5 shows that nearly all of the H_2 and F_2 are consumed and create about 20 times as much HF

as the previous reaction. This is accompanied by a rise in temperature to nearly 5000K as shown in Fig. 5.6. The temperature would be lower if lasing occurred because a significant fraction of the heat of reaction would be lost as radiation. On the other hand, the calculation neglects the energy deposited by the electric discharge. It is typically comparable to that lost by radiation.

Figure 5.7 shows the densities of F and H atoms. Initially the F atoms disappear as in Fig. 5.3. By about 1 microsecond the density of H atoms has built up to where reaction 2 replaces F atoms as fast as they are consumed by reaction 1. At this point the reaction has reached steady state and F_2 and H_2 are consumed at an equal rate, as shown in Fig. 5.5 and especially in Fig. 5.8, where the net rates for reactions 1 and 2 are virtually identical from 1.5 to 3.5 microseconds. The small difference in rates between 4 and 5 microseconds is due to rapid dissociation of F_2 to give additional F atoms. The additional F atoms cause an increase in the rate of reaction 1 until it creates enough H atoms to bring up the rate of reaction 2. After 4.5 microseconds both rates fall off mostly because the temperature has risen to where reactions 1 and 2 are approaching equilibrium.

If this reaction were pumping a laser at steady state the pulse shape would be proportional to the sum of

the rates of reactions 1 and 2 in Fig. 5.8, up to the point that the vibrational deactivation rates of reactions 3 and 4 become comparable. This occurs at about 2 microseconds.

The laser pulse differs in shape, duration, and magnitude from the $\text{NF}_3 + \text{H}_2$ laser pulse. All three differences come from the fact that the $\text{F}_2 + \text{H}_2$ reaction is a chain and converts virtually all of the H_2 and F_2 to HF. In the $\text{NF}_3 + \text{H}_2$ reaction the amount of HF cannot exceed the initial density of F atoms. In these two calculations the initial density of F atoms was about 6% of the total H_2 density. In the chain reaction the total amount of HF formed is about 20 times larger, resulting in a larger magnitude pulse. The duration of the $\text{NF}_3 + \text{H}_2$ laser pulse is set by consumption of F atoms. In the chain, F atoms are replaced by reaction 2 and the pulse lasts longer. Finally, the peak of the laser pulse occurs later in the chain reaction because the increased rate due to increased temperature more than compensates for consumption. As a result, the pulse shape for the $\text{F}_2 + \text{H}_2$ laser differs from that of the $\text{NF}_3 + \text{H}_2$ laser.

Vibrational relaxation is much more important in the chain reaction. It is relatively unimportant in the $\text{NF}_3 + \text{H}_2$ laser because the F atoms are consumed before vibrational relaxation can occur and also because the density of HF remains relatively small. In the chain reaction the pulse duration is longer because reaction 2 replaces the F atoms consumed by reaction 1. As a result, the pulse

can be terminated by vibrational deactivation. In addition, the vibrational rate is larger because more HF is created and because of the large temperature rise. The net result is that in the chain reaction the laser pulse is terminated by vibrational deactivation before all of the reactants are consumed. Examination of Fig. 5.5 and 5.8 shows that the laser pulse terminates at about 2 microseconds. In Fig. 5.5, the density of HF.1 is seen to peak at about 3.1 microseconds and then fall off. This is due to vibrational deactivation. The laser pulse, assuming steady state, would terminate when the slope of the HF.0 curve matches that of HF.1 (at about 2.5 microseconds). Figure 5.8 shows that this corresponds to the time when the vibrational deactivation rate becomes comparable to the rate of generation of HF.

To summarize, the kinetics of the $\text{NF}_3 + \text{H}_2$ laser is dominated by consumption of F atoms, and vibrational deactivation plays a secondary role. The kinetics of the $\text{F}_2 + \text{H}_2$ laser is much different because reaction 2 replaces the F atom consumed in reaction 1. The amount of HF formed greatly exceeds the initial density of F atoms resulting in a much larger laser pulse. Vibrational deactivation terminates the laser pulse because HF is generated for a longer time and in larger quantities.

F2 + H2 LASER SIMULATION

2.5 TORR OF H2 AND F2, 0.1625 TORR INITIAL F, ADIABATIC AT 300K

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THERMODYNAMIC VARIABLES

TIME	.0E+00	.0E+00	2.623E-12	5.708E-10	8.464E-09	5.000E-08	1.000E-07	1.500E-07
TEMP.	3.000E+02	3.000E+02	3.000E+02	3.000E+02	3.005E+02	3.028E+02	3.057E+02	3.088E+02
PRESSURE	1.516E+01	1.516E+01	1.516E+01	1.516E+01	1.519E+01	1.530E+01	1.545E+01	1.581E+01
DENSITY	8.105E-07	8.105E-07	8.105E-07	8.105E-07	8.105E-07	8.105E-07	8.105E-07	8.105E-07
STEP NO.	0	1	11	21	31	36	41	43
TIME STEP	1.000E-16	1.000E-16	5.961E-12	1.529E-10	2.363E-09	1.146E-08	3.065E-08	3.065E-08

SELECTED CONCENTRATIONS IN MOLES/CC

H2	1.336E-07	1.336E-07	1.336E-07	1.336E-07	1.336E-07	1.332E-07	1.328E-07	1.325E-07
F2	1.336E-07	1.336E-07	1.336E-07	1.336E-07	1.336E-07	1.336E-07	1.336E-07	1.336E-07
HF, I	.0E+00	.0E+00	2.110E-14	4.591E-12	6.797E-11	3.984E-10	7.699E-10	1.176E-09
HF, O	.0E+00	.0E+00	7.309E-21	3.459E-16	7.582E-14	2.604E-12	1.022E-11	2.259E-11
F	8.686E-09	8.686E-09	8.686E-09	8.681E-09	8.618E-09	8.292E-09	7.914E-09	7.552E-09
H	.0E+00	.0E+00	2.110E-14	4.590E-12	6.785E-11	3.940E-10	7.719E-10	1.134E-09

RATES (MOL/SEC-CC) FROM SELECTED REACTIONS

TIME	.0E+00	.0E+00	2.623E-12	5.708E-10	8.464E-09	5.000E-08	1.000E-07	1.500E-07
REACTION 1	-8.044E-03	-8.044E-03	-8.044E-03	-8.042E-03	-8.012E-03	-7.859E-03	-7.685E-03	-7.520E-03
REACTION 2	.0E+00	.0E+00	-7.239E-09	-1.575E-06	-2.341E-05	-1.402E-04	-2.856E-04	-4.363E-04
REACTION 3	.0E+00	.0E+00	-5.572E-09	-1.212E-06	-1.789E-05	-1.031E-04	-2.004E-04	-2.933E-04
REACTION 4	.0E+00	.0E+00	-3.639E-13	-7.920E-11	-1.179E-09	-7.102E-09	-1.460E-08	-2.251E-08
REACTION 5	1.812E-13	1.812E-13	1.812E-13	1.810E-13	1.774E-13	1.597E-13	1.406E-13	1.234E-13

SNAPSHOT OF ALL CONCENTRATIONS AT 1.762E-07 SECONDS, TEMP IS 310.51

1.323E-07/H2	1.336E-07/F2	5.345E-07/HF	7.369E-09/F	1.318E-09/H
1.376E-09/HF, I	3.091E-11/HF, O	6.775E-09/M	8.017E-07/M2	8.105E-07/M2

SNAPSHOT OF RATES OF INDIVIDUAL EQUATIONS AT 1.762E-07 SECONDS

11-7.44E-03	21-5.18E-04	31-3.40E-04	41-2.69E-08	51 1.15E-13
MASS BALANCE ERROR RATIOS				
-2.54E-13/M	-3.32E-13/F	.0E+00/HF		

SNAPSHOT OF EQUILIBRIUM CONSTANTS

11 2.99E+14	21 1.32E+62	31 8.32E+07	41 8.32E+07	51 3.21E-21
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Table 5.1 Sample tabular output page from the MINOTAR code. These results were generated using the input shown in Table 5.2.

```

TITLE
F2 + H2 LASER SIMULATION
2.5 TORR OF H2 AND F2, 0.1625 TORR INITIAL F, ADIABATIC AT 300K
CONTROLS
TEMP 300. ADIABATIC
SPECIES
TORR H2 2.5 / F2 2.5 / HE 10. / F .1625 / H 0.
/ HF.1 0. / HF.0 0.
CATALYSTS
COMP M1 = F + HF.0 + HF.1
/ M2 = F2 + H2 + HE + H
/ M21 = M2 + M1
EQUATIONS
REACTION 1 F + H2 = HF.1 + H
REACTION 2 H + F2 = HF.1 + F
REACTION 3 HF.1 + M1 = HF.0 + M1
REACTION 4 HF.1 + M2 = HF.0 + M2
REACTION 5 F2 + M21 = M21 + 2.0 F
RATES
FORWARD 1 1.2E14 0. 1.7
FORWARD 2 1.438E14 0. 2.400
FORWARD 3 2.0E9 1.1 -2.0
FORWARD 4 2.6E-2 3.6 0.
FORWARD 5 5.0E13 0. 35.200
CONTROLS
K 1.E-16 KMIN 1.E-24 KMAX 1.E-7
TIMESTEP 5.E-8 QUIT 10.E-6 DEBUG 10 KEEP
PLOT CONCENTRATIONS MOLECULES H2 F2 HF.1 HF.0 / F H /
RATES REACTION 1 2 3 4 / 5
GO

```

Table 5.2 Sample input for the MINOTAR code.

F2 + H2 LASER SIMULATION
 2.5 TORR OF H2 AND F2 0.1625 TORR INITIAL F. ADIABATIC AT 300K
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COMPUTED RATE EQUATIONS

0 D[H2]	1/DT = -1.00*KF(1)*[H2]	[IF	[I	
	+ 1.00*KR(1)*[H	[HF.1	[I	
0 D[F2]	1/DT = -1.00*KF(2)*[F2]	[IH	[I	
	+ 1.00*KR(2)*[F	[HF.1	[I	
	-1.00*KF(5)*[F2]	[IM2]	[I	
	+ 1.00*KR(5)*[IF	[** 2.0)[IM2]	[** 1.0]	
0 D[IF]	1/DT = -1.00*KF(1)*[H2]	[IF	[I	
	+ 1.00*KR(1)*[H	[HF.1	[I	
	+ 1.00*KF(2)*[F2]	[IH	[I	
	-1.00*KR(2)*[F	[HF.1	[I	
	+ 2.00*KF(5)*[F2]	[IM2]	[I	
	-2.00*KR(5)*[IF	[** 2.0)[IM2]	[** 1.0]	
0 D[IH]	1/DT = 1.00*KF(1)*[H2]	[IF	[I	
	-1.00*KR(1)*[H	[HF.1	[I	
	+ 1.00*KF(2)*[F2]	[IH	[I	
	+ 1.00*KR(2)*[F	[HF.1	[I	
0 D[HF.1]	1/DT = 1.00*KF(1)*[H2]	[IF	[I	
	-1.00*KR(1)*[H	[HF.1	[I	
	+ 1.00*KF(2)*[F2]	[IH	[I	
	-1.00*KR(2)*[F	[HF.1	[I	
	+ 1.00*KF(3)*[HF.1]	[IM1]	[I	
	+ 1.00*KR(3)*[HF.0	[IM1]	[I	
	-1.00*KF(4)*[HF.1]	[IM2]	[I	
	+ 1.00*KR(4)*[HF.0	[IM2]	[I	
0 D[HF.0]	1/DT = 1.00*KF(3)*[HF.1]	[IM1]	[I	
	-1.00*KR(3)*[HF.0	[IM1]	[I	
	+ 1.00*KF(4)*[HF.1]	[IM2]	[I	
	-1.00*KR(4)*[HF.0	[IM2]	[I	

Table 5.3 Chemical kinetic rate equations derived by the
 MINOTAR computer code using the input of
 Table 5.2.

Fig. 5.1 The thermodynamic path for calculating the temperature in the MINOTAR code. The density vector is a function of the densities of all species. The initial state is "i", the state at time step k is "k".

Fig. 5.2 Densities of the major species in the $NF_3 + H_2$ simulation.

Fig. 5.3 Densities of the atomic radicals, H and F , in the $NF_3 + H_2$ simulation.

Fig. 5.4 Rates of reactions 1 and 3 in the $\text{NF}_3 + \text{H}_2$ simulation.

Fig. 5.5 Densities of the major chemical species in the $\text{H}_2 + \text{F}_2$ chain reaction.

Fig. 5.6 Temperature change in the $\text{H}_2 + \text{F}_2$ chain reaction.

Fig. 5.7 Densities of the radicals, H and F, in the $\text{H}_2 + \text{F}_2$ chain reaction.

Fig. 5.8 Rates of the reactions in the $\text{H}_2 + \text{F}_2$ chain reaction.

6. LASER EQUATIONS FOR A MORE DETAILED MODEL

6.1 Introduction

The laser model of previous sections has assumed that lasing occurs between two vibrational levels and ignored the rotational structure of these levels. It is possible, in a numerical model, to assume rotational equilibrium at the translational temperature within each vibrational level. Then the gain for each P-branch transition can be calculated, along with the threshold population inversion for each transition. Between any two vibrational levels one transition will have the smallest threshold inversion. If a steady-state laser model is used, the population difference will be clamped by that threshold inversion. Other P-branch transitions between the same vibrational levels will then be below threshold, and will be unable to lase. Therefore, a model which assumes rotational equilibrium and a steady-state laser will have only one P-branch transition lasing between two vibrational levels at any time. As populations and temperatures change the threshold inversions also change. From time to time a nonlasing transition will develop a threshold inversion smaller than that of the transition that is currently lasing. The lasing then will switch to the new transition. This is referred to in the literature as J-shifting (Emanuel, 1971; Chester, 1970).

Earlier studies used this model for the HF laser (Emanuel and Whitier, 1972; Turner, Adams, and Emanuel, 1973).

The next obvious improvement in an HF laser model was to separate the rotational states and allow them to relax towards equilibrium with realistic relaxation rates. (Assuming rotational equilibrium is equivalent to assuming an infinite rotational relaxation rate.) If the rotational states are separated, several P-branch transitions can lase between two vibrational levels at any time, in agreement with experiment.

The original plan was to treat rotational states separately using a steady-state laser model for each transition. Upon examination, it appeared to be just as simple to use laser rate equations in the computer code. Preliminary calculations showed that certain assumptions implicit in laser rate equations might be violated in the HF laser so semi-classical laser equations were used.

The semi-classical laser equations are also rate equations in the sense that they involve time derivatives. The term "laser rate equations" used here is a part of laser jargon. It refers specifically to treating the laser in terms of a one equation for the population inversion and another equation for the photon density. "Laser rate equations" can be derived from the Einstein treatment of stimulated emission (Pantell and Puthoff, 1969). "Semi-classical laser equations" are derived by treating the population inversion quantum mechanically and the radiation field classically by means of Maxwell's equations (Shirley, 1968; Davis, 1963). This results in differential equations

for the electric field, the dielectric polarization, the phase angle between them, and the population inversion. "Semi-classical laser equations" are equivalent to laser rate equations when the dielectric polarization is damped much more rapidly than the electric field.

Laser cascades occur in the HF laser because high vibrational numbers are pumped. The molecule then goes to the vibrational ground state by emitting several photons. The selection rules require that the laser transitions be P-branch transitions and that the molecule drop one vibrational level at a time. This is a cascade. Adjacent cascades are coupled by rotational relaxation, but not by radiation except in the unlikely case that there is also R-branch lasing.

Haken (1965) has treated cascades extensively using laser rate equations. When semi-classical equations are used there is a possibility that the electric fields or polarizations of two non-resonant transitions may interact. Haken's work does not treat this problem. Therefore it was necessary to derive semi-classical laser equations for a cascade. It is shown that in general there can be radiation from the highest level to the lowest in a cascade, but this is prevented in a diatomic molecule by the selection rules. Thus the cascade can be treated as two isolated transitions coupled only by a shared molecular level. In order to understand the relaxation oscillations in the laser pulse there is an extensive treatment of the stability of the various laser equations.

6.2 Derivation of Semi-Classical Laser Equations for a Three-Level Cascade

Semiclassical equations to describe a two-level laser are well known (Shirley, 1968; Davis, 1963). The two-level laser has a single transition at a frequency defined by the energy difference of the two levels, with some modification of the frequency if the cavity is tuned slightly off the atomic resonance. If, for simplicity, we restrict ourselves to consideration of a single mode of the cavity and assume that the gain medium is spatially uniform, we get equations of motion for four variables: the electric field, the electric polarization, the phase angle between the field and the polarization, and the inversion. There is also a fifth equation for the phase angle of the electric field relative to the time base. This is of little importance unless we are considering noise or coherence time.

In a cascade there are a number of transitions coupled by common levels. The simplest case is a three-level cascade. (This is not to be confused with the three-level system used to describe the ruby laser. In that system the third level is part of the pumping scheme for a single laser transition between two levels.) The three-level cascade is shown in Fig. 6.1. The two-laser transitions, at different frequencies, are coupled by a common atomic or molecular level, level 2. It would be convenient to treat each transition as an independent transition coupled only by the population of the common level. (We will show later that the HF laser cannot have transitions directly from level 3 to level 1.) We can then use the well-known equations for a two-level laser. In order to determine the interaction

between the two transitions, it is necessary to derive equations for a three-level cascade.

Begin by assuming electric fields of the form $e_1(t) e^{-i(\omega_1 t + \phi_1)}$ and $e_2(t) e^{-i(\omega_2 t + \phi_2)}$, where e_1 and e_2 are the envelope of the electric field and vary slowly compared to the optical frequencies ω_1 and ω_2 . Since we wish to compare the calculation with experiments, we may consider only the envelope and neglect the rapidly oscillating terms, $e^{-i\omega t}$. Since the laser is nonlinear we must consider terms with frequencies $\omega_1 \pm \omega_2$. Terms at the sum frequency will average to zero when integrated over the detector response time. In the case of HF vibrational-rotational transitions the difference frequency will exceed 10^{11} sec^{-1} so we can also neglect it. We will also neglect mode-locking since the relevant frequencies are at least an order of magnitude above the detector response, and because it will be much simpler to consider a single mode on each transition. Javan (1957), Bloembergen and Shen (1964) and Feld and Javan (1969) have done very general derivations of the three-level laser. The derivation used here is an algebraically simpler one based on a generalization of the derivation of a two-level laser by Shirley (1968). The algebraic simplicity results from the use of raising and lowering operators.

Let the energies of the states be $H_{33} > H_{22} > H_{11}$, and define $\hbar\omega = H_{22} - H_{11}$, $\hbar\omega_2 = H_{33} - H_{22}$, and $\hbar\omega_3 = H_{33} - H_{11} = \hbar(\omega_1 + \omega_2)$. The molecular states can be represented as vectors

$$\psi_1 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}, \quad \psi_2 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \psi_3 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad (6.1)$$

The raising operators for the molecule are represented by

$$\sigma_1^+ = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix}, \quad \sigma_2^+ = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \text{and} \quad \sigma_3^+ = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (6.2)$$

where σ_1^+ raises the molecule from state 1 to state 2, and σ_2^+ raises from state 2 to state 3, etc. The corresponding lowering operators are

$$\sigma_1^- = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}, \quad \sigma_2^- = \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \text{and} \quad \sigma_3^- = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} \quad (6.3)$$

Number operators giving the number in each state can now be defined:

$$n_1 = \sigma_1^- \sigma_1^+ = \sigma_3^- \sigma_3^+, \quad n_2 = \sigma_1^+ \sigma_1^- = \sigma_2^- \sigma_2^+ \quad \text{and}$$

$$n_3 = \sigma_2^+ \sigma_2^- + \sigma_3^+ \sigma_3^-. \quad \text{These have the property that}$$

$$n_1 \psi_2 = n_1 \psi_3 = 0, \quad \text{etc.} \quad \text{They are represented by the matrices}$$

$$n_1 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad n_2 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \text{and} \quad n_3 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (6.4)$$

We also let a_1^+ and a_1 be the creation and annihilation operators for the radiation at the transition with frequency ω_1 . The cavity mode frequency for this transition will be ω_{c1} , which may differ slightly from ω_1 . The number of photons in the mode is given by the operator $a_1^+ a_1$. Corresponding operators are a_2^+ a_2 and a_3^+ a_3 for the modes at frequencies ω_{c2} and ω_{c3} .

We wish to write a Hamiltonian for a system of molecules, therefore we will have to sum over all molecules. Setting the ground state energy to zero we obtain the Hamiltonian

$$\begin{aligned}
 H = & \hbar\omega_{c1} a_1^+ a_1 + \hbar\omega_{c2} a_2^+ a_2 + \hbar\omega_{c3} a_3^+ a_3 \\
 & + \sum_j \hbar\omega_1 n_{2j} + \sum_j \hbar\omega_3 n_{3j} \\
 & + \hbar b_1 \sum_j (\sigma_{1j}^+ a_1 + \sigma_{1j}^- a_1^+) + \hbar b_2 \sum_j (\sigma_{2j}^+ a_2 + \sigma_{2j}^- a_2^+) \\
 & + \hbar b_3 \sum_j (\sigma_{3j}^+ a_3 + \sigma_{3j}^- a_3^+) \quad (6.5)
 \end{aligned}$$

where the first three terms are the Hamiltonian for the radiation, the second two are the Hamiltonian for the system of molecules, and the last three terms are the interaction Hamiltonian. The factors b_1 , b_2 and b_3 are proportional to the dipole matrix elements. We have dropped terms in the interaction Hamiltonian of the form $\sigma_1^+ a_1^+$ and $\sigma_1^- a_1$ because they represent creation (annihilation) of a photon along with increasing (decreasing) the energy of the molecule, and are thus highly improbable. Neglecting these terms is equivalent to the rotating wave approximation.

We obtain differential equations for each operator from the Heisenberg equation of motion

$$i\hbar \frac{dA}{dt} = [A, H] + i\hbar \frac{\partial A}{\partial t} \quad (6.6)$$

where the first term on the right is the commutator $[A, H] = (AH - HA)$, and the second term vanishes except when A has an explicit time dependence. When the Hamiltonian of Eq. 6.5 is inserted in Eq. 6.6 the commutators are readily evaluated and are tabulated in Appendix C. We obtain the following equations:

$$i\dot{a}_1 = \omega_{c1} a_1 + b_1 \sum_j \sigma_{1j}^- \quad (6.7a)$$

$$i\dot{a}_2 = \omega_{c2} a_2 + b_2 \sum_j \sigma_{2j}^- \quad (6.7b)$$

$$i\dot{a}_3 = \omega_{c3} a_3 + b_3 \sum_j \sigma_{3j}^- \quad (6.7c)$$

$$i\dot{\sigma}_{1j}^- = \omega_1 \sigma_{1j}^- + b_1(n_1 - n_2) a_1 + b_2 \sigma_{3j}^- a_2^+ - b_3 \sigma_{2j}^+ a_3 \quad (6.8a)$$

$$i\dot{\sigma}_{2j}^- = \omega_2 \sigma_{2j}^- + b_2(n_2 - n_3) a_2 - b_1 \sigma_{3j}^- a_1^+ + b_3 \sigma_{1j}^+ a_3 \quad (6.8b)$$

$$i\dot{\sigma}_{3j}^- = \omega_3 \sigma_{3j}^- - b_1 \sigma_{2j}^- a_1 + b_2 \sigma_{1j}^- a_2 + b_3(n_1 - n_3) a_3 \quad (6.8c)$$

$$i\dot{n}_{1j} = b_1(\sigma_{1j}^- a_1^+ - \sigma_{1j}^+ a_1) - b_3(\sigma_{3j}^+ a_3 - \sigma_{3j}^- a_3^+) \quad (6.9a)$$

$$i\dot{n}_{2j} = -b_1(\sigma_{1j}^- a_1^+ - \sigma_{1j}^+ a_1) + b_2(\sigma_{2j}^- a_2^+ - \sigma_{2j}^+ a_2) \quad (6.9b)$$

$$i\dot{n}_{3j} = -b_2(\sigma_{2j}^- a_2^+ - \sigma_{2j}^+ a_2) + b_3(\sigma_{3j}^+ a_3 - \sigma_{3j}^- a_3^+). \quad (6.9c)$$

The summations in equations 6.7 and 6.8 have dropped out because operators for one molecule commute with those for other molecules. Analogous equations can be obtained for a^+ and σ^+ operators.

In order to get macroscopic variables we must take expectation values of Eqs. 6.7 to 6.9. To save space we will drop some of the equations for transition 2, and obtain

$$\frac{d}{dt} \langle a_1 \rangle = -i\omega_{c1} \langle a_1 \rangle - ib_1 \sum_j \langle \sigma_{1j}^- \rangle \quad (6.10a)$$

$$\begin{aligned} \frac{d}{dt} \langle \sigma_{1j}^- \rangle &= -i\omega \langle \sigma_{1j}^- \rangle - ib_1 \langle (n_1 - n_2) a_1 \rangle - ib_2 \langle \sigma_{3j}^- a_2^+ \rangle \\ &+ ib_3 \langle \sigma_{2j}^+ a_3 \rangle \end{aligned} \quad (6.10b)$$

$$\begin{aligned} \frac{d}{dt} \langle n_{1j} \rangle &= -ib_1 \langle \sigma_{1j}^- a_1^+ \rangle + ib_1 \langle \sigma_{1j}^+ a_1 \rangle + ib_3 \langle \sigma_{3j}^+ a_3 \rangle \\ &- ib_3 \langle \sigma_{3j}^- a_3^+ \rangle \end{aligned} \quad (6.10c)$$

$$\begin{aligned} \frac{d}{dt} \langle n_{2j} \rangle &= ib_1 \langle \sigma_{1j}^- a_1^+ \rangle - ib_1 \langle \sigma_{1j}^+ a_1 \rangle \\ &- ib_2 \langle \sigma_{2j}^- a_2^+ \rangle + ib_2 \langle \sigma_{2j}^+ a_2 \rangle \end{aligned} \quad (6.10d)$$

$$\begin{aligned} \frac{d}{dt} \langle \sigma_{3j}^- \rangle &= -i\omega_3 \langle \sigma_{3j}^- \rangle - ib_3 \langle (n_1 - n_3) a_3 \rangle \\ &+ ib_1 \langle \sigma_{2j}^- a_1 \rangle - ib_2 \langle \sigma_{1j}^- a_2 \rangle \end{aligned} \quad (6.10e)$$

At this point we encounter a difficulty because

$\langle \sigma_1^- a_1^+ \rangle \neq \langle \sigma_1^- \rangle \langle a_1^+ \rangle$. However, if we have an intense radiation field the quantum number for the harmonic oscillator is large and by the correspondence principle should behave classically. Therefore we make a semi-classical approximation $\langle \sigma_1^- a_1^+ \rangle = \langle \sigma_1^- \rangle \langle a_1^+ \rangle$, and similar approximations for other products (Shirley, 1968).

We can now make the connection with macroscopic variables.

$$A_1 = \langle a_1 \rangle e^{i\Omega_1 t} \quad (6.11a)$$

where ω_1 is the frequency of the electric field and may be different from both ω_1 , the molecular resonance frequency, and ω_{c1} , the cavity resonance frequency. We also have

$$A_1^* = \langle \sigma_{1j}^+ \rangle e^{-i\omega_1 t} \quad (6.11b)$$

and the product $A_1^* A_1$ is the number of photons in the radiation field. The variable A_1 is connected to the electric field by

$$E_1(t) = \sqrt{\frac{\hbar \omega_{c1}}{2\epsilon V}} (A_1 e^{-i\omega_1 t} + \text{c.c.}). \quad (6.12)$$

The carrier frequency is handled so that $E_1(t)$ is the envelope of the electric field; V is the volume of the system and ϵ the permittivity. We also define macroscopic variables

$$P_1 = \sum_j \langle \sigma_{1j}^- \rangle e^{i\omega_1 t} \quad (6.13)$$

and

$$P_1^* = \sum_j \langle \sigma_{1j}^+ \rangle e^{-i\omega_1 t}$$

which are connected to the envelope of the polarization by

$$\mathcal{P}_1 = \frac{\mu_{12}}{V} (P_1 e^{-i\omega_1 t} + \text{c.c.}), \quad (6.14)$$

with μ_{12} the electric dipole matrix element.

Finally, we have the populations

$$N_1 = \sum_j n_{1j} \text{ and } N_2 = \sum_j n_{2j}. \quad (6.15)$$

With macroscopic variables defined, we take derivatives of Eqs. 6.11, 6.13 and 6.15 and substitute in Eqs. 6.10, giving

$$\begin{aligned}
\dot{A}_1 &= i(\Omega_1 - \omega_{c1}) A_1 - ib_1 P_1 \\
\dot{A}_2 &= i(\Omega_2 - \omega_{c2}) A_2 - ib_2 P_2 \\
\dot{A}_3 &= i(\Omega_3 - \omega_{c3}) A_3 - ib_3 P_3 \\
\dot{P}_1 &= i(\Omega_1 - \omega_1) P_1 + ib_1 A_1 (N_2 - N_1) - ib_2 A_2^* P_3 + ib_3 A_3 P_2^* \\
\dot{P}_2 &= i(\Omega_2 - \omega_2) P_2 + ib_2 A_2 (N_3 - N_2) + ib_1 A_1^* P_3 - ib_3 A_3 P_1^* \\
\dot{P}_3 &= i(\Omega_3 - \omega_3) P_3 + ib_3 A_3 (N_3 - N_1) + ib_1 A_1 P_2 - ib_2 A_2 P_1 \\
\dot{N}_1 &= ib_1 (P_1^* A_1 - A_1^* P_1) + ib_3 (P_3^* A_3 - A_3^* P_3) \\
\dot{N}_2 &= -ib_1 (P_1^* A_1 - A_1^* P_1) + ib_2 (P_2^* A_2 - A_2^* P_2) \\
\dot{N}_3 &= -ib_2 (P_2^* A_2 - A_2^* P_2) - ib_3 (P_3^* A_3 - A_3^* P_3)
\end{aligned} \tag{6.16}$$

(The equations for A_k and P_k contain factors $e^{i\omega_k t}$, but they are not shown because they can be factored out.)

Similar equations may be obtained for a two-level system:

$$\begin{aligned}
\dot{A} &= i(\Omega - \omega_c) A - ibP \\
\dot{P} &= i(\Omega - \omega) P + ibA (N_2 - N_1) \\
\dot{N}_1 &= ib (P^* A - A^* P) \\
\dot{N}_2 &= -ib (P^* A - A^* P)
\end{aligned} \tag{6.17}$$

The population equations for the three level case (Eq. 6.16) are an obvious generalization of the two-level equations (6.17), but the polarization equations have terms of the form $b_1 A_1 P_2$ which represent a new physical effect. This is a type of two-photon interaction. The electric field at frequency ω_1 interacts with the polarization at

frequency ω_2 to create a polarization at frequency ω_3 , the sum of ω_1 and ω_2 . The original polarization was created by absorption of a photon at ω_2 , so the polarization at ω_3 is the result of absorbing two photons, the sum of whose frequencies is resonant with ω_3 . The photons need not be absorbed simultaneously; however, if we added damping terms to Eqs. 6.16 both photons would have to be absorbed in an interval shorter than the damping time. Similarly, the polarization at ω_3 interacts with emission of a photon at ω_1 or ω_2 to give a polarization at ω_2 or ω_1 , respectively. The net result is that radiation on two of the frequencies pumps or depletes radiation on the third. This has been discussed extensively in the literature (Javan, 1957; Bloembergen and Shen, 1964; Feld and Javan, 1969; Haken, et al., 1965).

In the present case we have a simplification. Selection rules forbid dipole transitions at ω_3 in the vibrational-rotational spectrum (the rule is $\Delta J = \pm 1$ allowed and ω_3 has $\Delta J = \pm 2$, which is forbidden). As a result, b_3 is zero and many of the coupling terms drop out. Most important, the second term in the equation for $\dot{A}_3$ drops out, causing A_3 to oscillate at a constant amplitude. In reality, loss of photons will have the effect of adding a damping term so that A_3 will always be zero. If b_3 is finite but much smaller than b_1 and b_2 , then A_3 will still be infinitesimal because the other transitions will clamp $(N_3 - N_1)$ to

the same order of magnitude as $(N_2 - N_1)$ and $(N_3 - N_2)$ and the damping term will be much larger than $b_3 P_3$. This will be more clear after we have discussed the steady-state solutions.

The vanishing of A_3 is important because b_3 is in fact finite due to an allowed electric quadrupole transition, but b_3 will be several orders of magnitude weaker than b_1 or b_2 . This situation is not unique to the HF chemical laser. Electric dipole transitions are allowed only between states of opposite parity, and electric quadrupole transitions between states of the same parity. But quadrupole transitions are orders of magnitude weaker than dipole transitions. The factors b_1 , b_2 , and b_3 can all be of comparable magnitude in the special case where the states are mixtures of comparable fractions of even and odd parity.

Equations 6.16 give a complete description of the three-level system, but it is convenient to reduce the complex variables to real variables, and drop terms containing A_3 .

$$\begin{aligned}
 \text{Let } A_1 &= q_1 e^{i\theta_1} \\
 b_1 P_1 &= i p_1 e^{i(\theta_1 - \phi_1)} \\
 b_2 P_2 &= i p_2 e^{i(\theta_2 - \phi_2)} \\
 P_3 &= i p_3 e^{-i\theta_3}
 \end{aligned} \tag{6.18}$$

Note that p_1 and q_1 are defined so that absorption or emission of light is a maximum when ϕ_1 and ϕ_2 are zero. When these expressions are substituted in Eqs. 6.17 for the two-level system we get six real equations

$$\begin{aligned}
 \dot{q} &= p \cos \phi \\
 \dot{p} &= b^2 q (N_2 - N_1) \cos \phi \\
 \dot{N}_1 &= 2 p q \cos \phi \\
 \dot{N}_2 &= -2 p q \cos \phi \\
 \dot{\theta} &= \Omega - \omega_c - (p/q) \sin \phi \\
 \dot{\phi} &= \omega - \omega_c - [p/q + b^2(q/p)(N_2/N_1)] \sin \phi
 \end{aligned} \tag{6.19}$$

When these are substituted into Eqs. 6.16 for the three-level system we obtain a larger set of real equations.

$$\begin{aligned}
 \dot{q}_1 &= p_1 \cos \phi_1 \\
 \dot{q}_2 &= p_2 \cos \phi_2 \\
 \dot{p}_1 &= b_1^2 q_1 (N_2 - N_1) \cos \phi_1 + b_1 b_2 q_2 p_3 \sin (\xi + \phi_1) \\
 \dot{p}_2 &= b_2^2 q_2 (N_3 - N_2) \cos \phi_2 - b_1 b_2 q_1 p_3 \sin (\xi + \phi_2) \\
 \xi &= \theta_1 + \theta_2 + \theta_3 \\
 \dot{p}_3 &= -(b_1/b_2) q_1 p_2 \sin (\xi - \phi_2) \\
 &\quad + (b_2/b_1) q_2 p_1 \sin (\xi - \phi_1) \\
 \dot{N}_1 &= 2 p_1 q_1 \cos \phi_1 \\
 \dot{N}_2 &= 2 p_2 q_2 \cos \phi_2 - 2 p_1 q_1 \cos \phi_1 \\
 \dot{N}_3 &= -2 p_2 q_2 \cos \phi_2
 \end{aligned}$$

$$\dot{\theta}_1 = \dot{n}_1 - \omega_{c1} - (p_1/q_1) \sin \phi_1$$

$$\dot{\theta}_2 = \dot{n}_2 - \omega_{c2} - (p_2/q_2) \sin \phi_2$$

$$\begin{aligned} \dot{\theta}_3 = \dot{n}_3 - \omega_3 - \frac{b_1 q_1 p_2}{b_2 p_3} \cos (\xi - \phi_2) \\ + \frac{b_2 q_2 p_1}{b_1 p_3} \cos (\xi - \phi_2) \end{aligned}$$

$$\begin{aligned} \dot{\phi}_1 = \omega_1 - [p_1/q_1 + b_1^2 (q_1/p_1)(N_2 - N_1)] \sin \phi_1 \\ + b_1 b_2 q_2 (p_3/p_1) \cos (\xi + \phi_1) \end{aligned}$$

$$\begin{aligned} \dot{\phi}_2 = \omega_{c2} - \omega_2 - [p_2/q_2 + b_2^2 (q_2/p_2)(N_3 - N_2)] \sin \phi_2 \\ - b_1 b_2 q_1 (p_3/p_2) \cos (\xi + \phi_2) \end{aligned} \quad (6.20)$$

The differences between the two level and three level systems are confined to the polarization terms and to the phase angles coupling the polarization to the electric field.

The equations thus far have no losses and no pumping mechanism. We shall introduce these phenomenologically.

Photons, will be lost from the cavity, so we damp the electric field at a rate $\beta = 1/2 \tau_c$, where τ_c is the cavity lifetime.

The principal contributions to this rate are transmission and absorption at the mirrors, and scattering and diffraction losses. Each molecular level will be pumped at a rate W and will gain or lose population through collisional processes (and spontaneous emission) at a rate γ . We will write this relaxation in a form appropriate to vibrational relaxation in that all relaxation will be to lower energy states. This differs from the common practice of writing the relaxation so

that the populations relax toward zero inversion (Pantell and Puthoff, 1969). The rate γ equals $1/T_1$, customarily called the "energy relaxation time". There is also a relaxation rate γ' for the polarization. In a semi-classical view the polarization results when a photon is absorbed and excites an oscillator, in phase with the exciting field. When the oscillators collide with other particles (or phonons in a solid) their phase is changed in a stochastic manner. The macroscopic polarization involves an average over all oscillators, thus it is large when the oscillators are all in phase and vanishes when the oscillators have random phase. The rate, γ' , equals $1/T_2$, the "phase relaxation time", and can be obtained from collisional line broadening data. When we insert the phenomenological damping rates we get equations of the form

$$\dot{q}_1 = -\beta q_1 + p_1 \cos \phi_1$$

$$\dot{p}_1 = -\gamma_1' p_1 + b_1^2 q_1 (N_2 - N_1) \cos \phi_1 + b_1 b_2 q_2 p_3 \sin (\xi + \phi_1)$$

$$\dot{N}_1 = W_1 + \gamma_2 N_2 + 2p_1 q_1 \cos \phi_1$$

$$\dot{N}_2 = W_2 + \gamma_3 N_3 - \gamma_2 N_2 + 2p_2 q_2 \cos \phi_2 - 2p_1 q_1 \cos \phi_1$$

$$\begin{aligned} \dot{p}_3 = & -\gamma_3' p_3 - (b_1/b_2) q_1 p_2 \sin (\xi - \phi_2) \\ & + (b_2/b_1) q_2 p_1 \sin (\xi - \phi_1) \end{aligned}$$

$$\dot{q}_2 = -\beta q_2 + p_2 \cos \phi_2$$

$$\dot{p}_2 = -\gamma_2' p_2 + b_2^2 q_2 (N_3 - N_2) \cos \phi_2 - b_1 b_2 q_1 p_3 \sin (\xi + \phi_2)$$

$$\dot{N}_3 = W_3 - \gamma_3 N_3 - 2 p_2 q_2 \cos \phi_2 \quad (6.21)$$

These equations, along with the $\dot{\theta}_k$ and $\dot{\phi}_k$ equations of 6.20 form the complete set equations for the three-level laser. The next section examines their steady-state solution, as well as the conditions where p_3 can be neglected. Equations 6.21 reduce to a set of two-level laser equations coupled by a common level if p_3 vanishes.

6.3 Steady State Values

The equations for the two level system with relaxation terms are

$$\begin{aligned}\dot{q} &= -\beta q + p \cos \phi \\ \dot{p} &= -\gamma' p + b^2 q (N_2 - N_1) \cos \phi \\ \dot{N}_1 &= W_1 + \gamma N_2 + 2qp \cos \phi \\ \dot{N}_2 &= W_2 - \gamma N_2 - 2qp \cos \phi \\ \dot{\phi} &= \omega - \omega_c - [p/q + b^2(q/p)(N_2 - N_1)] \sin \phi \\ \dot{\theta} &= \Omega - \omega_c - (p/q) \sin \phi\end{aligned}\quad (6.22)$$

We can obtain a steady state solution for these equations by setting appropriate derivatives to zero. By setting $\dot{q}$ to zero we obtain

$$p = \beta q \sec \phi. \quad (6.23)$$

The populations, at least in a chemical laser, will continue to rise, but the quantity $\dot{N}_2 - \dot{N}_1$, will vanish at steady state. Substituting Eq. 6.23 into the difference

$$\dot{N}_2 - \dot{N}_1 = W_2 - W_1 - 2\gamma N_2 - 4pq \cos \phi = 0 \quad (6.24)$$

gives

$$4\beta q^2 = W_2 - W_1 - 2\gamma N_2. \quad (6.25)$$

Multiplying the polarization equation by q gives

$$\begin{aligned} q\dot{p} &= -\gamma'qp + b^2q^2(N_2 - N_1)\cos\phi \\ &= q^2[-\beta\gamma' + b^2(N_2 - N_1)\cos\phi], \end{aligned} \quad (6.26)$$

which vanishes at steady state. This can occur only if $q = 0$, implying no lasing, or if

$$N_2 - N_1 = (\beta\gamma'/b^2)\sec\phi. \quad (6.27)$$

Equations 6.25 and 6.27 describe steady state operation of a two-level laser. The inversion described by Eq. 6.27 is the threshold inversion and the laser maintains itself at that inversion. The threshold inversion gives the laser a gain which just equals the losses. Earlier computer models have assumed that the laser, if inverted, had an inversion which was constant at the threshold value. Equation 6.25 then represents energy conservation, because $2\beta q^2$ is the rate at which photons are removed from the cavity, and $W_2 - W_1 - 2\gamma N_2$ is the net rate of pumping the inversion. The additional factor of 2 multiplying βq^2 is because emission of one photon decreases the population difference by two molecules. There is also a transient period before the laser reaches steady state. We shall be concerned with that in the next section.

The steady state photon density, q^2 , is expressed in terms of the pumping rate, W_2 . This pumping rate will have a minimum value which will just achieve a threshold inversion. We shall now find this minimum value.

For simplicity assume that the pumping rates W_2 and W_1 are constant in time. Formally integrating the population equations of 6.22 we get

$$N_2 - N_1 = (W_2 - W_1) t - 2 \int_0^t \gamma N_2(t') dt'. \quad (6.28)$$

Since we are interested in the time before lasing begins, $q_1 = 0$ and we have

$$N_2 = W_2 t - 2\gamma \int_0^t N_2(t') dt'. \quad (6.29)$$

These equations can be solved approximately by iteration, and for the first iteration we neglect the integral in Eq. 6.29 and substitute $N_2(t') = W_2 t'$ in Eq. 6.28, giving

$$N_2 - N_1 = (W_2 - W_1)t - \gamma W_2 t^2. \quad (6.30)$$

This is quadratic in t , with the inversion negative for $t > (W_2 - W_1)/\gamma W_2$ and maximum at $t = (W_2 - W_1)/2\gamma W_2$. If we let the maximum inversion equal threshold, and neglect W_1 , we get

$$(N_2 - N_1)_{th} \approx \frac{\beta \gamma'}{b^2} \sec \phi = W_2/2\gamma - W_2/4\gamma$$

which gives

$$W_2(\text{threshold}) = 4 \frac{\beta \gamma \gamma'}{b^2} \sec \phi. \quad (6.31)$$

The approximations we have used would affect the numerical factor, 4, but not the other parameters. In any case pumping at exactly W_2 (threshold) would not result in lasing because even if threshold is exceeded it requires a finite time for lasing to build up. Therefore, the pump rate will have to exceed the threshold rate.

We can normalize all pumping rates in terms of the threshold pumping rate. The pumping rates W_1 and W_2 have fixed ratios which depend on the pumping scheme, not the radiation parameters. As a result, we can write $W_2 - W_1 = kW_2$, where k is a constant of the pumping scheme. The expression for q^2 also contains a term in the population, N_2 . We see by Eq. 6.29 that N_2 is also a function of W_2 , so we can write $N_2 = f_2(t) W_2 t$, where $f_2(t)$ will depend on other parameters and will be of order unity. Using this we write

$$\begin{aligned} \beta q^2 &= kW_2 \sec \phi - 1/2 \gamma f_2(t) t W_2 \\ &= (k \sec \phi - 1/2 \gamma t f_2(t)) \zeta \frac{4\beta \gamma \gamma'}{b^2} \end{aligned} \quad (6.32)$$

where $\zeta = W_2/W_2$ (threshold).

The angle variables ϕ and θ also have steady-state values.

$$\tan \phi = \frac{(\omega - \omega_c)}{(\delta + \gamma')}, \quad (6.33a)$$

and the actual laser frequency adjusts itself so that

$$\dot{\theta} = 0, \quad (6.33b)$$

leaving θ arbitrary. Any perturbation, such as noise, will make $\dot{\theta} \neq 0$ until the transient dies out. After the disturbance θ will have a new value, which is arbitrary since there is no restoring force about some preferred value. This completes the discussion of two-level steady state.

When we examine the steady state for the three level system we must use Eqs. 6.21. The first gives us

$\beta q_1 = p_1 \cos \phi_1$ in the steady state, and, similarly,

$\beta q_2 = p_2 \cos \phi_2$. Substituting these into the population

equations and setting $(\dot{N}_2 - \dot{N}_1)$ to zero, etc., after some algebra we get

$$\begin{aligned} 2p_1q_1 &= \frac{1}{3} (w_3 + w_2 - 2w_1) - \gamma_2 N_2 \\ 2p_2q_2 &= \frac{1}{3} (2w_3 - w_2 - w_1) - \gamma_3 N_3 \end{aligned} \quad (6.34)$$

If we set $p_3 = 0$ and substitute in the equation for $\dot{p}_1$, we find, as in the two level case that

$$(N_2 - N_1) = \frac{\beta \gamma_1^2}{b_1^2} \sec \phi_1 \quad (6.35)$$

The steady-state values of q_1 and q_2 are functions only of the pumping rates due to energy conservation as seen in Eq. 6.34.

The polarizations, p_1 and p_2 are proportional to q_1 and q_2 at steady state, therefore, the only effect of p_3 on the steady state is a possible change in the threshold inversion. Let δn be the perturbation in the inversion due to p_3 so that

$$N_2 - N_1 = \frac{\beta \gamma_1^2}{b_1^2} \sec \phi_1 + \delta n. \quad (6.36)$$

Substitute this in Eqs. 6.21, setting $\dot{p}_1 = 0$ and $\dot{p}_3 = 0$.

The result is

$$\delta n = \frac{\beta q_2^2}{\gamma_3^2} \left[(b_2/b_1)^2 \sin^2 (\xi - \phi_1) - \sin (\xi - \phi_1) \sin (\xi - \phi_2) \right] \sec \phi_1 \quad (6.37)$$

As in the two level case we can write βq_2^2 as a function of w_2 , which in turn is a function of other parameters. This gives

$$\delta n = \frac{4B\gamma_2\gamma_1}{\gamma_3^4 b_1} \frac{1}{2} \left[k_2 \sec \phi_2 - \frac{1}{2} \gamma_3 + f_3(t) \right] \times \left[+ \frac{b_2^2}{b_1^2} \sin(\xi - \phi_1) - \sin(\xi - \phi_2) \right] \sin(\xi - \phi_1) \quad (6.38)$$

where $k_2 = (1/W_2)(2W_3 - W_2 - W_1)$ and $f_3(t)$ describes the dependence of N_3 on W_2 . Both k_2 and f_3 are of order unity. If we divide by the two level threshold value of $(N_2 - N_1)$ we get

$$\frac{\delta n}{(N_2 - N_1)_{th}} = \frac{4\gamma_2}{\gamma_3^4} \left[k_2 \sec \phi_2 - \frac{1}{2} \gamma_3 + f_3(t) \right] \times \left[(b_2/b_1)^2 \sin(\xi - \phi_1) - \sin(\xi - \phi_2) \right] \sin(\xi - \phi_1) \quad (6.39)$$

Thus the net effect of the coupling, p_3 , is to increase the inversion between levels 2 and 1, since $(b_2/b_1) > 1$ for a harmonic oscillator. A similar treatment for the inversion between N_3 and N_2 would show a decrease.

Because γ_3^4 is usually several orders of magnitude larger than γ_2 the effect will be very small unless the pumping, represented by ζ is very large. In the case of the chemically pumped laser ζ may be large enough to make δn an appreciable quantity.

It appears then that in the steady state case the coupling will not be important. The principal effect is to cause the laser to operate at an inversion somewhat different than the threshold inversion for a pair of two level lasers using a common level. The perturbation, δn , on the inversion

is small when the pumping is just above threshold, so has a minor effect in that case. When the laser is strongly pumped n becomes appreciable but is still orders of magnitude smaller than actual populations, so it will have little effect on the laser output. Therefore, we conclude that we can neglect p_3 in the steady state.

The fact that we have a steady state solution with p_3 included doesn't guarantee that the laser will operate at the steady state; the steady state may represent an unstable solution. Stability will be examined in a qualitative fashion. Assume that q_2 rises a bit above its steady state value. Examination of Eqs. 6.21 shows that this will cause p_3 to increase, which in turn causes p_1 and q_1 to increase. However, the sum $q_1^2 + q_2^2$ is basically determined by energy conservation, so both cannot remain above steady state for long. A similar argument holds if q_1 is increased. This shows that p_3 cannot rob power from one lasing transition and feed it to the other. The argument is not sufficient to show that p_3 will not cause an oscillation centered about the steady state.

Thus far we have neglected the effect of $\sin(\zeta - \phi_1)$ on p_3 . The angle ζ is the sum of three arbitrary phase angles θ_1 , θ_2 , and θ_3 . They may assume any value at steady state and will change value upon any fluctuation of the other variables. As a result, the value of $\sin(\zeta - \phi_1)$ will be stochastic and will have an average value of zero when averaged over some time, unless something locks θ_1 , θ_2 , and θ_3

to some fixed value. This can occur under conditions such as those that cause mode locking, so that we can assume that the transient effects of p_3 will be associated with rapid variations like mode locking. Since we have already decided to neglect mode locking, we will also neglect p_3 and treat the cascade as a set of two-level transitions coupled only by sharing a common level. From here on we will consider only cascades with the radiation in each transition treated by equations for a two-level laser.

6.4 Stability of Two Level Laser Equations

The semi-classical equations of motion for a two level laser, including phenomenological damping terms, are

$$\dot{q} = -\beta q + p \cos \phi \quad (6.40a)$$

$$\dot{p} = -\gamma' p + b^2 q (N_2 - N_1) \cos \phi \quad (6.40b)$$

$$\dot{N}_1 = W_1 + \gamma_2 N_2 + 2pq \cos \phi \quad (6.40c)$$

$$\dot{N}_2 = W_2 - \gamma_2 N_2 - 2pq \cos \phi \quad (6.40d)$$

$$\dot{\theta} = \Omega - \omega_c - (p/q) \sin \phi \quad (6.40e)$$

$$\dot{\phi} = \omega - \omega_c - [p/q + b^2(q/p)(N_2 - N_1)] \sin \phi \quad (6.40f)$$

where q^2 is the density of photons in the cavity, and p is proportional to the polarization. The angle ϕ is the phase angle between q and $\dot{p}$, and θ is an arbitrary phase angle. The constant b is proportional to the dipole matrix element. There are three frequencies in these equations: Ω , the molecular resonance frequency; ω_c , the cavity resonance frequency; and ω , the laser frequency, which lies between

Ω and ω_c . If the cavity resonance, ω_c , is tuned exactly to the molecular resonance Ω , then $\Omega = \omega_c = \omega$. Because the cavity is many wavelengths long, the cavity will have many resonance frequencies, ω_c , spaced $c/2L$ apart. For any value of Ω there will be a cavity resonance, ω_c , such that $|\Omega - \omega_c| \leq c/4L$. If $\Omega = \omega_c$, Eq. 6.40f shows that ϕ will be driven to its steady-state value of zero. The laser is then said to be on tune. When $\phi = 0$ the cosine terms are unity and we can neglect Eqs. 6.40e and 6.40f. The angle θ will be constant and we will neglect it because we are not studying temporal coherence.

6.4.1 Laser Rate Equations

Before considering the general case we will consider a special case which gives considerable insight. Solid state lasers are generally operated under conditions where γ' is the orders of magnitude faster than other rates. Gas lasers operated at pressures of several Torr are generally collision broadened and also have γ' the fastest rate. In that case, if there is a perturbation from steady-state $\overset{\circ}{p}$ will return to zero before the other variables. Setting $\overset{\circ}{p} = 0$ we get

$$p = (b^2 q / \gamma') (N_2 - N_1). \quad (6.41)$$

Let $\psi = q^2$, the photon density, and substitute in Eqs. 6.40. The result is the well known laser rate equations,

$$\dot{\psi} = -2\beta\psi + \alpha\psi (N_2 - N_1)$$

$$(\dot{N}_2 - \dot{N}_1) = W_2 - W_1 - 2\gamma N_2 - 2\alpha\psi (N_2 - N_1). \quad (6.42)$$

These equations give a reasonably good description of the major features of laser behavior, especially in the regime $\gamma \gg \beta, \gamma$. The parameter α equals $2b^2/\gamma'$. If we write $(N_2 - N_1) = \Delta N$ we get steady state solutions

$$\begin{aligned}\Delta N &= 2\beta/\alpha = \beta\gamma'/b^2 \\ 4\beta\psi_0 &= W_2 - W_1 - 2\gamma N_2\end{aligned}\quad (6.43)$$

For algebraic simplicity we will assume $W_1 = 0$. If W_1 were not zero, the answer would differ by numerical factors of order unity. The value of N_2 is obtained from

$$\begin{aligned}N_2 + N_1 &= W_2 t \\ N_2 - N_1 &= \beta\gamma'/b^2\end{aligned}$$

which gives

$$N_2 = 1/2 W_2 t + \beta\gamma'/2b^2, \quad (6.44)$$

The maximum inversion, in the absence of lasing occurs at $t = 1/2\gamma$, so we will analyze stability at that point in time, giving

$$N_2 = W_2/4\gamma + \beta\gamma'/2b^2.$$

The pump rate, W_2 , was defined in Eq. 6.31

$$W_2 = 4\zeta \frac{\beta\gamma\gamma'}{b^2}$$

where $\zeta = W_2/W_2$ threshold. This gives

$$N_2 = (\zeta + 1/2) \frac{\beta\gamma'}{b^2} \quad (6.45)$$

Substituting in Eqs. 6.43 we get the steady-state solutions

$$\begin{aligned}\Delta N_0 &= \beta \gamma' / b^2 \\ \psi_0 &= (\zeta - 1/2) \gamma \gamma' / 2b^2\end{aligned}\quad (6.46)$$

To investigate the stability we linearize Eqs. 6.42 about the steady-state value by writing

$$\begin{aligned}\Delta N &= \beta \gamma' / b^2 + \delta N \\ \psi &= \psi_0 + \delta \psi,\end{aligned}\quad (6.47)$$

and substituting. We neglect terms in the product $\delta \psi \delta N$, and find that the steady state terms cancel. The resulting linearized equations are

$$\begin{aligned}\delta \ddot{\psi} &= (\zeta - \frac{1}{2}) \gamma \delta N \\ \delta \dot{N} &= -4\beta \delta \psi - 2\gamma \zeta \delta N.\end{aligned}\quad (6.48)$$

These can be converted to a single second order differential equation by differentiating the first equation and eliminating $\delta \dot{N}$ and δN . The result is

$$\delta \ddot{\psi} + 2\zeta \gamma \delta \dot{\psi} + 4(\zeta - \frac{1}{2}) \beta \gamma \delta \psi = 0 \quad (6.49)$$

Letting $\delta \psi = e^{\lambda t}$ gives the characteristic equation

$$\lambda^2 + 2\zeta \gamma \lambda + 4(\zeta - \frac{1}{2}) \beta \gamma = 0$$

which has roots

$$\lambda = \mu + i\nu = -\zeta \gamma \pm i \sqrt{4\beta \gamma (\zeta - 1/2) - \zeta^2 \gamma^2} \quad (6.50)$$

Thus the perturbation will be a damped oscillation at a frequency ν (radians/sec) about the steady-state value in the region where $\zeta > 1/2$ and $4\beta \gamma (\zeta - 1/2) > \gamma^2 \zeta^2$.

Contour plots of the frequency, ν , and damping, constant, γ , are shown in Fig. 6.2 as a function of γ' and β . In these plots the ratio $\gamma'/\gamma = 10^4$. It is reasonable to keep this ratio constant since both relaxation rates are proportional to the molecular collision probability provided γ is fast compared to spontaneous emission. The ratio, 10^4 , is the right order of magnitude for HF. For most other molecules the ratio would probably be much larger since vibrational relaxation of HF is anomalously fast. In the contour plot the pump rate is held constant for all values of β and γ' so that the pump parameter, ζ , varies on the graph. Contours of constant ζ are shown on the graphs as straight lines with a slope of $-1/2$ on the logarithmic plot. For values of $\zeta < 1$ the laser is below threshold, and for $\zeta < 1/2$ one of the two real roots is positive, and the frequency is zero. For moderate values of $\zeta\gamma$ the solution oscillates and for large values of $\zeta\gamma$ the solution is overdamped and again has two real roots. The more positive of these roots is shown on the contour plot since this represents the slowest recovery from the transient. As a result, the fastest time constants occur on the boundary between oscillating and overdamped solutions. This boundary is a straight line with a slope of -2 . Values of β and γ' to the left of the boundary yield overdamped solutions.

The variables γ' and β represent parameters which are readily adjustable experimentally. The photon decay rate, 2β , can be adjusted by changing mirror reflectivities or the

cavity length. The collision broadening rate, γ' , is adjustable by changing the pressure of the gas, or by adding other species. The ratio γ'/γ depends on molecular parameters and can be changed only a small amount by adding other species. The pump rate is also experimentally adjustable; the contour plot for other pump rates looks the same except for translation roughly perpendicular to lines of constant ζ . The translation is obvious from an examination of Eq. 6.50.

Laser rate equations (6.42) have no undamped oscillating solution because the real part of λ is always negative. This result has previously been noted by Makhov (1962) and Sinnet (1962). Even in the case that $4k^2\zeta^2\gamma^2 > 8\beta k\zeta\gamma$ the real part of λ is negative. As we shall see below, this is not always true if we do not force $\bar{p}$ in Eq. 6.42b to vanish. When ζ is reasonably small, e.g., 2 to 10, the solution will be an oscillation with frequency on the order of $\sqrt{\beta\gamma\zeta}$ damped at a rate γ . Since $\beta \gg \gamma$ under common laser operating conditions, the oscillation will continue for possibly tens or hundreds of cycles before it is damped to negligible proportions. As the pumping parameter, ζ , is increased both the frequency and the damping rate increase, but the damping rate increases much faster. As a result, if the laser is pumped harder it is damped rapidly, but a weakly pumped laser will oscillate for a long time. If the laser is pumped hard enough the damping will eventually be so fast that no oscillation at all will occur.

6.4.2 Semi-classical Equations with Cavity Tuned to Atomic Resonance

We will consider next the case where the laser is on tune, i.e. $\Omega = \omega = \omega_c$. In that case it is easily seen from Eq. 6.40f that the steady state value of ϕ is 0 or π and $\cos \phi = \pm 1$. Further examination shows that the solution $\phi = 0$ is stable when the inversion, $N_2 - N_1$, is positive, and that $\phi = \pi$ is stable when the inversion is negative. Steady state lasing occurs only for a positive inversion, so when the laser is on tune we get the following equations.

$$\begin{aligned}\dot{q} &= -\beta q + p \\ \dot{p} &= -\gamma' p + b^2 q (N_2 - N_1) \\ \Delta N &= N_2 - N_1 = W_2 - W_1 - 2\gamma N_2 - 4pq\end{aligned}\quad (6.51)$$

The steady state solution for these equations is

$$\begin{aligned}q_0^2 &= 1/4 (W_2 - W_1) - 1/2 \gamma N_2 = (2\zeta - 1) \gamma \gamma' / 4b^2 \\ p_0 &= \beta q \\ \Delta N_0 &= \beta \gamma' / b^2.\end{aligned}\quad (6.52)$$

As before we linearize by setting

$$\begin{aligned}q &= q_0 + \delta q \\ p &= p_0 + \delta p \\ \Delta N &= N_0 + \delta N, \\ N_2 &= \beta \gamma' / b^2 + 1/2 \delta N\end{aligned}\quad (6.53)$$

and neglecting products of the form $\delta q \delta N$, etc., we obtain the linearized equations

$$\begin{aligned}\delta \dot{q} &= -\beta \delta q + \delta p \\ \delta \dot{p} &= -\gamma' \delta p + \beta \gamma' \delta q + b^2 q_0 \delta N \\ \delta \dot{N} &= -\gamma \delta N - 4q_0 (\beta \delta q + \delta p)\end{aligned}\quad (6.54)$$

Substituting $q = e^{\lambda t}$ and differentiating, we obtain the characteristic equation

$$\lambda^3 + (\beta + \gamma + \gamma')\lambda^2 + (\gamma\beta + 2\zeta\gamma\gamma')\lambda + 2(2\zeta - 1)\beta\gamma\gamma' = 0 \quad (6.55)$$

This characteristic equation is the same as Shirley (1968), even though we treated the relaxation of population somewhat differently. Analytic expressions for the roots of this equation exist, (Birkhoff and MacLane, 1965), but the algebraic expressions are too complicated to be of much use.

Because the equation is cubic it must have either one or three real roots. Because all the coefficients are positive, all of the real roots must be negative (Turnbull, 1957). If there is only one real root there will be two complex conjugate roots and the perturbation will be

$$\delta q = c_0 e^{(\mu \pm i\nu)t} = c_0 e^{\mu t} \cos(\nu t + \eta) \quad (6.56)$$

where c_0 and η are constant of integration. The steady state solution will be a stable solution if and only if μ is negative. If μ is positive the output will oscillate about the steady with an exponentially increasing magnitude. (The exponentially growing solution is a small perturbation approximation; in reality the nonlinear terms will cause the

amplitude to assume a finite upper limit. This corresponds to energy conservation.) We wish to find the domains in which the steady-state solution is stable or unstable.

The roots of Eq. 6.55, the characteristic stability equation for the semi-classical laser on tune, are shown in Fig. 6.3. The damping constant is the most positive real portion of the three roots. The upper left-hand corner is almost identical to the plot for the rate equations, which is expected since this is the region where $\gamma' \gg \beta$, the assumption used to obtain the rate equations. In the lower right hand corner the oscillation is unstable, in contrast to the solution for the rate equations. Also, the solution is oscillatory for all values of γ' and β if $\delta > 10^3$. In the case of rate equations the contours for damping constant were straight lines with slopes of about -1. In the case of the semi-classical equations these contours are folded back in the lower right hand corner. As the pumping rate is changed the plot translates in the same manner as Fig. 6.2. The behavior of the laser in the various regions of Fig. 6.3 is illustrated by numerically integrating equations 6.51. The resulting photon densities in the cavity are plotted as a function of time in Fig. 6.4. In the unstable region, curve A in Fig. 6.4 and point (A) in Fig. 6.3, the solution is in a series of spikes. In the small signal approximation of Eq. 6.55 the envelope of the spikes should grow exponentially in time. In the numerical solution the nonlinear nature of the equations causes saturation effects which

limit the amplitude of the spikes. Physically, this is a result of energy conservation. In fact, in the numerical solution the first spike is the largest and it is rapidly damped. The first spike is large because there is a large delay to turn-on and a great deal of energy is stored in the inversion. After the first few spikes the laser settles down to a steady oscillation with an average power output equal to the steady state output. The peak power of each spike is many times the average power, but the duration of the spike is short compared to the time between spikes. A plot of the corresponding inversion shows the sawtooth shape characteristic of relaxation oscillations.

There are about 17 spikes per microsecond corresponding to an angular frequency of 1.2×10^8 radian/sec. Equation 6.55 gives a frequency of 1.4×10^8 at point (A).

Figure 6.4b shows the time history of the photon density in the overdamped region at point B. There is no oscillation, in agreement with Fig. 6.3; and the damping constant appears to be close to the 40 nsec. calculated from Eq. 6.55. As expected, a similar result was obtained when ϕ was allowed to vary.

Point (C) represents the condition where the photon density is a damped oscillation. The frequency, 3.2×10^7 rad/sec, agrees with the value from Eq. 6.55; and the damping constant appears to equal the predicted value of 100 nsec.

6.4.3 Semi-classical Equations Detuned

The stability of Eqs. 6.40 can also be determined for the case where the laser is detuned. In that case the steady state solution is

$$q_0^2 = (2\zeta - 1) \gamma \gamma' / 4b^2$$

$$p_0 = q_0 / \cos \phi_0$$

$$\Delta N_0 = \frac{\beta \gamma'}{b^2 \cos^2 \phi_0}$$

$$\tan \phi_0 = \frac{\Delta \omega}{\beta + \gamma'} = T \quad (6.57)$$

Again we linearize using Eq. 6.53 and

$$\phi = \phi_0 + \delta \phi;$$

and use the approximations: $\cos \delta \phi \approx 1$, $\sin \delta \phi \approx \delta \phi$.

When this is substituted in Eqs. 6.40 we obtain the following equation, written in matrix form.

$$\begin{pmatrix} \delta \dot{q} \\ \delta \dot{p} \\ \delta \dot{N} \\ \delta \dot{\phi} \end{pmatrix} = - \begin{pmatrix} +\beta & -\cos \phi_0 & 0 & \beta q_0 T \\ -\frac{\gamma' \beta}{\cos \phi_0} & \gamma' & -b^2 q_0 \cos \phi_0 & \beta q_0 \gamma' T / \cos \phi_0 \\ +4\beta q_0 & 4q_0 \cos \phi_0 & \gamma & -(2-1)\beta \gamma \gamma' T / b^2 \\ \gamma' T q_0 & \frac{\sin \phi_0}{q_0} & \frac{b^2}{\beta} \sin \phi_0 \cos \phi_0 & \beta + \gamma' \end{pmatrix} \begin{pmatrix} \delta q \\ \delta p \\ \delta N \\ \delta \phi \end{pmatrix} \quad (6.58)$$

Designating the matrix as A and the vector y this can be written as

$$\dot{y} = -A y$$

with the formal solution

$$y = y_0 e^{-\lambda t},$$

which is well defined, but difficult to evaluate. Since the equation is linear we can try a solution of the form $y = c e^{\lambda t}$, where c is a vector of constant co-efficients, and λ is a constant. Differentiating and substituting in Eq. 6.58 gives

$$\lambda c e^{\lambda t} = -A c e^{\lambda t} \quad (6.59)$$

dividing by $c e^{\lambda t}$ gives

$$\lambda - \lambda I = 0 \quad (6.60)$$

where I is the unit diagonal matrix. Evaluating the determinant of Eq. 6.60 gives the characteristic equation which we used previously to find the stability conditions.

Equation 6.60 also defines the eigenvalues of the matrix A . Therefore, rather than evaluate the determinant, the eigenvalues of A were obtained numerically. The eigenvalues can be either real or complex conjugate pairs. The laser parameters for Figs. 6.2 and 6.3 were used with a $\Delta\omega$ of 7×10^8 radians/sec (approximately the maximum detuning for a cavity with a round trip time of 5 ns.); there were at most one complex conjugate pair of eigenvalues and either two or four real eigenvalues. A contour plot of the most positive real part of any of the eigenvalues is shown in Fig. 6.5a, and a contour plot of the frequency is shown in Fig. 6.5b. Comparison with Figs. 6.2 and 6.3 shows that the principal effect of including detuning is to enlarge the domain of instability. There is a region within the unstable domain

which is also non-oscillatory. This represents a growing exponential output. As noted before, this growth is eventually limited by nonlinear terms in the original equations (6.40). The largest positive eigenvalue ($\sim 4 \times 10^8$) occurs near point (A).

The effect of allowing ϕ to vary with parameters for point (A) is seen by comparing Fig. 6.6a with Fig. 6.4a. The variation of the phase angle tends to damp the oscillations. This is in approximate agreement with the eigenvalues plotted in Fig. 6.5. The frequency is zero, and the calculated waveforms have little oscillation.

In general, allowing ϕ to vary did not result in vastly different waveforms. However it required several times as much computer time.

6.5 Summary

We have found that we can accurately estimate the stability of the laser about its steady state value by studying the linearized response to a small perturbation about the steady state value. In contrast to the stability criterion obtained from laser rate equations, there is an unstable region when $\beta \geq \gamma'$, provided the pumping parameter δ is large. In the region $\beta \leq .1\gamma'$ the stability is accurately predicted from laser rate equations, provided ζ is not too large, e.g. $\zeta < 10^3$. Most lasers are operated with high reflectivity mirrors which make β relatively small. Since it is usually difficult to pump a laser, most lasers are operated with a relatively low ζ . We will see later

that an HF chemical laser is very strongly pumped, and because of its high gain can be operated with low reflectivity mirrors, resulting in a large β . This is likely to cause unstable operation of the laser, or a damping constant which is large compared to the pulsewidth.

Fig. 6.1 Levels and transitions for a three level cascade.

a) Damping co-efficient - τ b) Frequency of oscillation - ω

Fig. 6.3 Contour plots of damping co-efficient and frequency of oscillation for Eq. 6.55. Parameters are the same as Fig. 6.2.

Fig. 6.4 Laser waveforms calculated from semi-classical equations (6.51) with cavity tuned exactly to atomic resonance.

a) Most positive of 2 damping co-efficients - τ

b) Frequency of oscillation

Fig. 6.5 Contour plots of damping co-efficient and frequency of oscillation for Eq. 6.58. There were either 2 or 4 real roots. Figure 6.5a shows the value of the least stable root. Parameters are the same as Fig. 6.2.

Fig. 6.6 Laser waveforms calculated using semi-classical equations (5.40) with laser detuned 7×10^8 rad/sec and phase angle, ϕ , allowed to vary. Other parameters are the same as Fig. 6.4A.

7. THE IXION[†] COMPUTER CODE

7.1 Introduction

The laser equations discussed in the previous section form the basis for a model of the HF chemical laser which treats each rotational level separately. Changes are required in the population equation: the relaxation term must be modified to include relaxation to adjacent rotational states, and most states are coupled to a higher vibrational state as well as a lower one. There are no formal mathematical problems involved in doing this because the damping term was introduced phenomenologically and can be altered on the same basis. We have already shown that a cascade can be treated as a series of two-level transitions coupled only by a common population.

A simplified set of semi-classical laser equations was chosen. The simplification consists of calculating the steady-state value of the phase angle, ϕ , (Eq. 6.40), and holding ϕ constant throughout the calculation. Tests showed that integrating the differential equation for ϕ increased the computing time an order of magnitude. The only major difference in the results was reduced spiking amplitude when ϕ was allowed to vary. It was decided to hold ϕ fixed in order to stay within the allocated computer budget. Laser rate equations would require about the same computer time as

[†]Ixion was a demi-god from Greek mythology. He murdered his father-in-law and became insane. Finally Zeus purified him so that he could live on Mt. Olympus. He repaid this kindness by attempting to seduce Hera, Zeus's wife. Ixion was tricked into a union with a cloud, rather than Hera, and thus begat the Centaurs. For his treachery Zeus sentenced him to be bound to a wheel and rotate forever in the air. This clearly is classical rotational motion without relaxation.

the simplified semi-classical equations. Rate equations assume that $\dot{p}$ is always small, but under some conditions in the HF laser this may not be true. The simplified semi-classical laser equations give more accurate results so they were used in the IXION code with modified relaxation terms.

The IXION code consists of a main program and a number of subroutines. The main code sets the initial conditions, and then calls the GEAR package of subroutines at each time step. After every few time steps it writes the current values of the populations and laser intensities into a disc file named SCRATCH. When the calculation has reached a preset time the main program terminates the problem.

The GEAR package consists of subroutine STIFFB to integrate the differential equations and associated subroutines for doing the associated matrix algebra. The GEAR package contains a method for integrating stiff differential equations or an alternate Adams predictor-corrector scheme. A sentinel can be set to select either method. Initial calculations showed that the equations were not stiff, but required short time steps because of the oscillatory nature of the solutions. Tests showed that the time step with the stiff method was twice as large as the time step with the predictor-corrector method. However, the stiff method required about five times as much computer time due to inverting the Jacobian matrix. The predictor-corrector method was chosen for most calculations because it was much faster due to not having to invert the

Jacobian matrix. The GEAR package obtained the appropriate differential equations from subroutine DIFFUNB.

Subroutine DIFFUNB furnishes the current numerical value of each time derivative to the GEAR package on each predictor or corrector step. There is a time derivative for each population level and two derivatives for each laser transition, one each for the electric field and the polarization. The code was dimensioned to treat six vibrational levels and up to 20 rotational states in each level. When the laser equations are added there are nearly 300 variables requiring time derivatives. Fortunately, there are only three types of variables so the subroutine has only three differential equations with indices corresponding to the appropriate quantum numbers. These equations will be described in detail. DIFFUNB requires certain rate constants which it obtains by calling subroutine CHEMIST. DIFFUNB also calculates equilibrium constant from spectroscopic data.

Subroutine CHEMIST calculates the rate of formation of HF, the basic rate constants for vibrational and rotational relaxation and line broadening. All of these are proportional to collision frequencies, and therefore are proportional to the densities of various chemical species. Subroutine CHEMIST contains the appropriate chemical kinetics equations. FORTRAN listings of subroutines DIFFUNB, CHEMIST can be found in Appendix F.

The output of the IXION code is contained in a disc file named SCRATCH. This is organized in blocks of about 200 variables (populations and intensities) at each time.

The file is written in BCD format rather than binary so that it can be read by humans as well as computers. In order to obtain time histories and plots, a separate computer code, EDITB, was written. This code, described below, reads SCRATCH, sorts the data into time histories and gives both graphic and tabular output. The results of the calculations will mainly be presented in the form of these graphs.

7.2 Ordering of the Molecular States

Computer solution of the equations requires that the states be ordered in some fashion. A spectroscopist would be inclined to order the states by quantum numbers, since this would order states in terms of energy. However, in considering a laser it is natural to order the states in cascades. A cascade is the set of levels which are connected by a series of radiative transitions (states coupled by diagonal lines in Figure 7.1).

When the computer output is organized in cascades the physical significance of the cascades is seen immediately because it is easy to see inversions. If the radiation is also ordered by cascades it is easy to see how the transitions interact via the common levels.

The cascade also turns out to be the natural ordering for numerical purposes. If the Gear method is used to integrate the differential equations the variables must be organized into a vector y with a derivative vector $\dot{y}$. The corrector step requires iteration by the Newton-Raphson

technique and this requires inversion of the Jacobian matrix $(\partial \dot{y}_i / \partial y_i)$. The inversion is greatly simplified if the non-zero matrix elements are concentrated in a narrow band about the diagonal. The narrowest bandwidth is achieved when the molecular levels are organized as a cascade, and the differential equations for radiative transitions are placed between those for the two levels connected by the transition. The equations have been ordered in this way in the IXION code. For example, if $Y(M)$ is a population, $Y(M+1)$ is a polarization, $Y(M+2)$ is an electric field and $Y(M+3)$ is the population of the level coupled to $Y(M)$ by the transition $Y(M+2)*Y(M+1)$.

7.3 The Population Equation

The basic population equation is

$$\dot{N}_1 = w_1 + \gamma_2 N_2 + 2pq \cos \phi. \quad (6.40c)$$

The first two terms were introduced phenomenologically, so it is equally proper to rewrite them to correspond to the scheme of Fig. 7.1. The IXION code uses the following population equation (in FORTRAN notation).

$$\begin{aligned} \text{YDOT}(M) = & 2.*CPH*(AV6*Y(M+1)*Y(M+2) - AV1*Y(M-2)*Y(M-1)) \\ A & +DETAIL(IV,J)*HFDOT \\ B & +VDOT*(VP*BN(J)*Y(M+3) - V*BN(J+1)*Y(M)) \\ C & +RDOT*(Y(M+16)*AJ*DJ(J+1)) \\ D & -(EQK(IV,J)*DJ(J+1) + DJ(J))*Y(M) \\ E & +EQK(IV,J-1)*Y(M-16)*DJ(J) \end{aligned} \quad (7.1)$$

The first line represents the interaction with the radiation. Line A is the chemical source term, Line B is the vibrational relaxation term and the remaining lines are rotational relaxation terms. These will be discussed in detail.

7.3.1 The Chemical Source Term

Each molecular level is pumped by a term of the form $\text{DETAIL}(\text{IV},\text{J}) * \text{HFDOT}$, where HFDOT is the total rate of formation of HF molecules and $\text{DETAIL}(\text{IV},\text{J})$ is the fraction of the total which is formed in the state with quantum numbers IV and J.

The values stored in the array, $\text{DETAIL}(\text{IV},\text{J})$ are given in Table 7.1 and Fig. 7.2. The values for $V = 1, 2$ and 3 are taken from chemiluminescence data of Pulanyi and Woodall (1972b). Chemiluminescence data doesn't give the population for the vibrational ground state, $V = 0$; so that had to be estimated. Following Cohen (1971) it was assumed that the total population with $V = 0$ was one-half that with $V = 1$. The remainder of the data suggested that the distribution shifted to higher J with lower V. Therefore the fraction of HF formed in the state $(0,\text{J})$ was set equal to half that in the state $(1,\text{J}-1)$.

The value of HFDOT can either be determined by a chemical kinetics code such as MINOTAR or by a subroutine which calculates HFDOT, perhaps by means of an approximation. The second approach was taken in the IXION code, mainly for simplicity. A subroutine named CHEMIST calculated HFDOT and the relaxation constants, VDOT, RDOT and GAMMA2. (The FORTRAN listing of CHEMIST is given in Appendix F.) The

algorithm for calculating HFDOT is:

$$\text{ERT} = 855./\text{TEMP}$$

$$\text{R1} = 1.2\text{E}14 * \text{EXP}(-\text{ERT})$$

$$\text{HFDOT} = \text{R1} * \text{H2} * \text{F}$$

where R1 is the rate constant (Trotman-Dickenson, 1967) and H2 and F are the densities of H₂ and F in moles/cc. The value, 855., is the activation energy divided by the gas constant. The value of F varies because of consumption by the chemical reaction and because of production by the discharge. After examination of experimental current waveforms, the production of F was approximated by $\sin(\text{Bt} + \pi/4)$ for values of t up to $\text{Bt} = 3\pi/4$, and zero thereafter. A normalization constant, B/1.707, set the value of the time integral to unity. The algorithm for F atom density is

$$\text{B} = 1.25\text{E}7$$

$$\text{ALPHA} = \text{B} * \text{TIME} + 0.25 * \text{PI}$$

$$\text{IF } (\text{ALPHA} > \text{PI}) \text{ ALPHA} = 0$$

$$\text{FDOT} = \text{F0} * (\text{B}/1.707) * \text{SIN}(\text{ALPHA}) - \text{HFDOT}$$

$$\text{F} = \text{FOLD} + (\text{TIME} - \text{TOLD}) * \text{FDOT}$$

with FOLD set equal to F whenever TIME was updated. This algorithm assumes that the density of H₂ remains constant. For most of the calculations, F0 was 1.25% of the density of NF₃, or 6% of the density of H₂. This amount of depletion is small compared to the uncertainty in the reaction rate. The value of B is chosen to match the experimental width of the current pulse.

To check the error introduced by assuming the density of H_2 constant, a constant temperature calculation was made with the MINOLAR code assuming $F_0 = 25\%$ of the H_2 density. The results are shown in Fig. 7.3. The solid line assumes constant H_2 and the dotted line includes corrections for depletion of H_2 . The difference between the two is relatively small for the first 2 microseconds. In experiments the oscilloscopes were generally set for 2 microseconds full scale. Therefore, depletion of H_2 was not included in the IXION code.

Earlier chemical laser codes have treated the production of HF and vibrational relaxation together. However, the two can be decoupled so long as the rate of formation of HF is not dependent on the population distribution of HF. The only known case where this is true is the postulated chain branching by the reaction

This reaction will increase the concentration of F atoms, thus accelerating the formation of HF. This has been studied in detail by Rapagnani (1972). The rate of this reaction has been estimated to be on the order of 10^{10} moles/cc-sec (Jensen, 1973). Rapagnani found that when using this rate the effect of Eq. 7.2 on the production of HF was negligible. Even at rates near gas kinetic (10^{14} mole/cc-sec) the rate of formation of HF was increased by less than an order of magnitude. Since experimental evidence shows the rate to be much smaller than 10^{14} , reactions similar to Eq. 7.2 have

been neglected in the IXION code. This permits formation of HF and vibrational deactivation of HF to be treated independently. Vibrational deactivation due to Eq. 7.2 can still be treated, but not the additional quantity of F atoms.

7.3.2 Vibrational Relaxation Terms

The contribution of vibrational relaxation to Eq. 7.1 is given by

$$VDOT*(VP*BN(J)*Y(M+3)-V*BN(J+1)*Y(M)).$$

The first term represents the increase in population of state Y(M) from the next higher state in the cascade, Y(M+3). The factor BN(J) gives the variation of the rate with rotational quantum number, and VP (equals V+1) the variation with vibrational quantum number. The second term represents the loss in population of state Y(M) due to vibrational relaxation. The factor VDOT depends on the density of collision partners and their relative efficiency in vibrational relaxation.

The form used for vibrational relaxation assumes that it is due to dipole interactions (Herzfeld and Litovitz, 1959). Vibrational relaxation then follows the same selection rules as radiation emission. The intensity dependence on vibrational and rotational quantum numbers is the same as for radiation and is discussed in more detail in the section on radiation.

The algorithm for calculating VDOT is

$$VDOT = (7.1E9*H2 + 1.6E7*F3N + 2.E6*HE \\ + .72E12*F + 1.42E12*HF)$$

where the numerical values are the reaction rates at 300K and the alphameric terms are the densities of the species which they represent. The rates are taken from Cohen (1971). The temperature variation was not included because it is more complex than that for other rates. The vibrational relaxation rate, at least for some species, appears to be minimum around 1000K and higher for temperatures which are higher or lower than this. If the IXION code is to be run at temperatures other than 300K these rates should be changed.

In the case of vibrational relaxation the equilibrium constant was neglected because the vibrational energy gap is large compared to kT . Even at 2000K the upward rate is only a few percent of the downward rate, and for temperatures likely to be found in the laser the upward rate is negligible.

Cohen's rates were based on experiment (Bott and Cohen, 1971; Airey and Fried, 1971; Cohen, 1971; Chen and Moore, 1971; Hancock and Green, 1972; Hancock and Smith, 1971; Solomon et al., 1971) with consideration given to theory. Experiment indicates that the relaxation rate for HF is orders of magnitude faster than that predicted by the older theories (Herzfeld and Litovitz, 1959; Landau and Teller, 1936; Rapp, 1960; Rapp and Kassal, 1969), which are satisfactory for many molecules. Newer theories which consider more complex interactions attempt to explain the anomalously fast rotational relaxation of HF (Shin, 1970, 1971 and 1972; Thompson, 1972).

The vibrational relaxation rate for H_2 used in calculating VDOT is for vibrational-translational transfer only. The vibrational states of H_2 are near enough to resonance with HF that the transfer to H_2 vibration is about twice the V-T rate. The algorithm required to calculate V-V transfer from HF to H_2 is more complex than the V-T transfer because vibrational energy stored as vibration in H_2 can be returned to the HF at a later time. In some runs a worst case was calculated by assuming the V-V rate but neglecting the return of the stored energy. Because the vibrational relaxation rate is slow, the higher rate had no visible effect for the chosen parameters. Vibrational-rotational relaxation was neglected. As will be shown later, in most of the cases calculated the lasing was terminated by depletion of F atom concentration before vibrational relaxation was significant. The situation would be dramatically different in the case of the chain reaction in an $H_2 + F_2$ mixture.

7.3.3 Rotational Relaxation Terms

Rotational relaxation terms couple the state $Y(M)$ to the two adjacent states $Y(M+16)$ and $Y(M-16)$ having the same vibrational quantum number, but with rotational quantum numbers $J + 1$ and $J - 1$. (See Fig. 7.1) The basic rate is the rate to go from J to $J-1$; the reverse rate, from $J - 1$ to J is related to this by an equilibrium constant. Thus there are four rotational relaxation terms, gain and loss

terms to each of two adjacent states. Rotational relaxation was limited to adjacent states for computational simplicity. Multi-quantum jumps at decreased probability would be a more accurate physical representation, but would greatly increase computation time.

The rotational relaxation terms are:

$$\begin{aligned} & \text{RDOT} * (\text{Y}(\text{M}+16) * \text{AJ} * \text{DJ}(\text{J}+1) - (\text{EQK}(\text{IV}, \text{J}) * \text{DJ}(\text{J}+1) \\ & + \text{DJ}(\text{J})) * \text{Y}(\text{M}) + \text{EQK}(\text{IV}, \text{J}-1) * \text{Y}(\text{M}-16) * \text{DJ}(\text{J})). \end{aligned}$$

The factors, DJ, give the rotational quantum number dependence of the rate. The factor AJ is for computational purposes; it is set to 1.0 except at the highest J values where it is set to 0.0 to cutoff extraneous values. The variables, EQK are the equilibrium constants.

The factor RDOT is the basic rate factor. The algorithm for RDOT is

$$\begin{aligned} \text{WIDTH} &= 4.6\text{E}13 * \text{SQRT}(\text{TEMP}) \\ \text{RROT} &= 0.5 * \text{WIDTH} \\ \text{RDOT} &= \text{RROT} * (\text{H2} + \text{F3N} + \text{F0} + \text{HE}) \end{aligned}$$

where the quantities in parenthesis are the densities of the collision partners. All collision partners are assumed equally efficient at rotational relaxation because relative efficiencies are unknown. The coefficient, WIDTH, is obtained from experimental line-width data (Meredith, 1972). It represents a rate constant about 10 times gas kinetic collision frequency (assuming a gas kinetic cross section of 10^{-15} cm^2 for HF). For most runs the value of WIDTH was left constant, but RROT was treated as an adjustable parameter,

because there was no experimental value available for RROT. The best fit of calculated results with experiment was found with $RROT = 0.5 * WIDTH$, or 5 times gas kinetic. Physically $RROT \leq WIDTH$ because $WIDTH$ represents those collisions where the molecule is knocked out of phase with the electric field, and $RROT$ represents a collision which changes the rotational quantum number, and that clearly destroys the phase.

It need not be disturbing that the cross section is greater than so-called gas kinetic. Gas kinetic cross sections are usually determined from collisions which alter the momentum of the molecule. Here we are dealing with torques resulting from long range dipole forces, and it is reasonable that they should have a larger cross section.

The ratio between the upward and downward rates is derived by considering the equilibrium distribution. At equilibrium the population distribution remains unchanged with

$$N_J = N_{J-1} \cdot \left(\frac{2J+1}{2J-1} \right) e^{-\Delta E/kT}$$

where N_J is the number of molecules in state J , $2J+1$ is the degeneracy of state J , and ΔE is the energy difference between states J and $J-1$. To maintain equilibrium we must have

$$k_+ N_{J-1} = k_- N_J$$

where k_- is the downward rate and k_+ the upward rate. Substituting we get

$$k_+ = k_- \cdot \left(\frac{2J+1}{2J-1} \right) e^{-\Delta E/kT} \quad (7.4)$$

The factor on the right hand side is the equilibrium constant. Although Eq. 7.4 is derived at equilibrium it is valid under most conditions even when the populations are not in equilibrium.

Within the IXION code the equilibrium constant is calculated by

$$\text{ARG} = (\text{TERM}(\text{IV}, \text{J}) - \text{TERM}(\text{IV}, \text{J}+1)) / (\text{R} * \text{TEMP})$$

$$\text{EQK}(\text{IV}, \text{J}) = \text{EXP}(\text{ARG}) / \text{GR}(\text{J}+1)$$

Where $\text{TERM}(\text{IV}, \text{J})$ is the energy (cm^{-1}) of the vibrational-rotational state with quantum numbers IV and J (see Table A2, Appendix A), and R is the gas constant, ($0.695/\text{cm-K}$). The factor, $\text{GR}(\text{J}+1)$, is the degeneracy ratio, $(2\text{J}+1)/(2\text{J}+1)$.

The dependence of the rotational relaxation rate on rotational quantum number is given by the array, $\text{DJ}(\text{J})$. Establishing the proper values for DJ was one of the more difficult tasks in setting up the model. No experimental data on the J dependence of the rotational relaxation rate in HF could be found. There was also no directly applicable theory. Polanyi and Woodall (1972a) had fit a simple model to experimental HCl rotational relaxation data. An attempt was made to estimate the rate with a classical model assuming that the dipole-dipole interaction was dominant. Incomplete results verified that the rotational relaxation rate decreased at higher J as did the HCl experimental data. In the process of obtaining line-broadening coefficients it was noted that experimental line widths for HF (Meredith, 1972) varied with J in the same manner as Polanyi and Woodall's best

model. This is not surprising, because line broadening is caused by two kinds of collisions: those resulting in a change of quantum number and those which merely change the phase of the oscillation. Clearly the line broadening collision rate is an upper limit on the rotational relaxation rate. For transitions in the visible region of the spectrum phase changing collisions dominate because the transition energy is much larger than kT . In the microwave spectrum line broadening is almost entirely due to changes in quantum number because the transition energy is much less than kT . The transition energies for HF are comparable to kT and both types of collision are important.

The choice of the rotational relaxation rate is discussed in more detail in Appendix D. The model obtains the J dependence of the rotational relaxation rate from experimental line-broadening data for (Meredith, 1972). The magnitude of the rotational relaxation rate, R_{ROT} , was taken as some fraction of the collision rate for line broadening. The fraction was taken as an adjustable fraction, with $1/2$ being a likely fraction. The variation of the rate, $DJ(J)$ with J is given in Fig. 7.4 and Table 7.2.

7.3.4 The Radiation Coupling Terms

The first line of Eq. 7.1,

$$YDOT(M) = 2.*CPH*(AV6*Y(M+1)*Y(M+2) - AV1*Y(M-2)*Y(M-1)),$$
 consists of two terms of the form $2pq \cos \phi$ of Eq. 6.40c. The first term represents the increase in population due to laser radiation from the next higher state in the cascade.

The second term represents loss of population to the next lower state via laser radiation. The coefficients AV1 and AV6 are set equal to 1.0, except at the top and bottom of the cascade where they are used to cut off extraneous values. The variables Y(M+1) and Y(M-2) represent polarizations while Y(M+2) and Y(M-1) represent electric fields.

The factor, CPH, represents the steady state value of $\cos \phi$, where the steady state value is given by Eq. 6.33a. The algorithm used to calculate CPH is

$$TPH = (4.7124E10/CAVLN)/(CAV1 + GAMMA2)$$

$$CSQ = 1./(1. + TPH**2)$$

$$CPH = \text{SQRT}(CSQ).$$

The first line corresponds to Eq. 6.33a with $\omega - \omega_c$ set to half the intermode spacing (maximum detuning). The factor, CAV1, corresponds to β in Eq. 6.33a, GAMMA2 corresponds to γ' , and TPH to $\tan \phi$. CAVLN is the cavity length. The remainder of the algorithm is a trigonometric identity.

As written, $\cos \phi$ is actually double valued since $\tan \phi$ is positive in the first and third quadrants. In the first quadrant $\cos \phi$ is positive and represents the case with positive inversion. When the inversion is negative ϕ is in the third quadrant so that $\cos \phi$ is negative and the inversion tends to restore itself by absorbing light from the fields. The variables p and q are lengths of a polar vector and may not be negative. Within the code the equivalent results are calculated in a different manner: $\cos \phi$ remains positive and the terms representing the

magnitude of the fields change sign. The equivalent of positive $\cos \phi$ is for the signs of the electric field and polarization to be the same. When the signs differ it is equivalent to $\cos \phi$ being negative.

Before using the steady state value in the code, tests were made using the complete time variation of ϕ . It turned out that ϕ spent most of its time near one of the steady state values and jumped rapidly to the other at appropriate times. The full variation of ϕ tended to smooth out the spiking somewhat and had little other effect on the waveforms, but it did require an order of magnitude more computer time. As a result the steady state value was used in the code.

7.4 The Polarization Equation

The differential equation for the polarization is

$$\dot{p} = \gamma' p + b^2 q (N_2 - N_1) \cos \phi \quad (6.40b)$$

The equivalent equation in the IXION code is

$$YDOT(M+1) = -DOMEGA*Y(M+1) + VP*BN(J)*BSQ*WAVNUM*CPH \\ *(Y(M+2)*(Y(M+3) - GR(J)*Y(M)) + Y(M+3)). \quad (7.3)$$

This form assumes that there is only one laser mode for each possible laser transition. This will be discussed in detail below.

7.4.1 Damping Term

The first term, $DOMEGA*Y(M+1)$, is the polarization damping term. The variable $Y(M+1)$ represents the polarization and the coefficient $DOMEGA$ is the linewidth for a Voigt profile combining the Doppler and collisional linewidths. The algorithm for $DOMEGA$ is

$$DPK = 2400. * \text{SQRT}(TEMP)$$

$$WAVNUM = \text{TERM}(IV+1,J-1) - \text{TERM}(IV,J)$$

$$WIDTH = 4.6E13 * \text{SQRT}(TEMP)$$

$$GAMMA2 = WIDTH * (H2+F3N+FO+HE)$$

$$DSQ = (GAMMA2 * DJ(J+1))^{**2} + (DPK * WAVNUM)^{**2}$$

$$DOMEGA = \text{SQRT}(DSQ)$$

The first term in DSQ is the square of the collisional linewidth and the second is the square of the Doppler linewidth. The coefficient DPK is the Doppler coefficient and WAVNUM is the reciprocal of the wavelength, with TERM(IV,J) being the energy in cm^{-1} of the state with quantum numbers IV and J. The linewidth coefficient, WIDTH, is set to the experimental value for HF self-broadening (Mereith, 1972). The collisional linewidth, GAMMA2, is obtained by multiplying WIDTH by the densities of the collision partners. Due to lack of other data, all collision partners are assumed to have the same efficiency. The variation of collisional broadening with rotational state is contained in the factor DJ(J+1). This factor was described in detail in Section 7.3.3.

The natural linewidth was neglected because it is several orders of magnitude smaller than either the collisional or Doppler linewidths. The collisional and Doppler linewidths are added in quadrature for reasons to be described below.

The laser cavity has many modes, separated by $C/2L$, near the frequency of the molecular resonance. A collisionally broadened line and a Doppler broadened line interact differently with these modes. If the line is collisionally

broadened to overlap several modes then a given molecule undergoes several phase changing collisions during a round-trip time, $2L/C$, of the light. The resonance of the molecule is therefore coupled to several modes, and often lasing will occur only on the mode with the highest gain, or on a few modes. On the other hand, if a line is Doppler broadened to overlap several modes the molecules can be divided into velocity groups each of which interact with one mode, but not with each other. In this case all of the modes with gains greater than unity can lase. When collisional and Doppler linewidths are comparable the collisions couple adjacent velocity groups so that the modes are coupled. A rigorous treatment of linewidths would involve several modes for each laser transition and would greatly increase the complexity of the calculation. For computational simplicity it was decided to consider only a single mode on each transition. Also, the calculations were being compared with experiments using an 8% reflectivity mirror which makes the modes rather wide and allows coupling between modes, complicating the interaction but making mode structure less important.

If we assume that only a single cavity mode is lasing for each transition we only need to calculate the gain at line-center, which is inversely proportional to the linewidth. The lineshape is a Voigt profile, which is basically a convolution of the Gaussian profile of the Doppler broadened line with the Lorentz profile of the collision broadened line. Because variances add under convolution the total

linewidth can be estimated from the sum of the squares of the two linewidths. Total linewidths were determined in this way for the IXION code. The resulting linewidth was then used to calculate an effective damping coefficient, DOMEGA, for the polarization.

7.4.2 Coupling to the Population Inversion

The string of factors $VP*BN*BSQ*WAVNUM$ in Eq. 7.3 is equivalent to b^2 in Eq. 6.40b. The variable $Y(M+2)$ is equivalent to q , and $Y(M+3) - GR(J)Y(M)$ is equivalent to $N_2 - N_1$, where $GR(J)$ is the degeneracy ratio, $(2J-1/2J+1)$. The last term requires some comment.

Equations 6.40a and 6.40b are written in a form which neglects the noise introduced by spontaneous emission. The equations have two steady state solutions with one of them being $p = q = 0$. If the equations are started at these values they will remain there. This is not a physically realistic situation, and to match physical reality we must add a term to represent the noise generated by spontaneous emission. The spontaneous noise term was lost in the derivation of Eq. 6.40 at the point where we made the semi-classical approximation on expectation values, $\langle \sigma_1^- a_1^+ \rangle = \langle \sigma_1^- \rangle \langle a_1^+ \rangle$. We now reintroduce it phenomenologically. In the usual treatment with the radiation field treated as a harmonic oscillator with quantum number n is proportional to the square of the electric field, i.e. q^2 , but we have q in Eq. 6.40b. There is no simple way to get $q^2 + 1$ so we use $q + 1$ and rewrite Eq. 6.40b as

$$\dot{p} = -\gamma'p + (q+1)N_2 - qN_1.$$

Physically this represents a spontaneous polarization of a molecule which results in an electric field for one photon.

If this treatment doesn't give exact quantitative results for the noise it will have little effect on the model. The noise is some 20 orders of magnitude below the steady state lasing level. Once threshold inversion is reached, the power increases exponentially with time until it overshoots the steady state value. The only effect of a change in noise level is a change in the time to reach steady state, since steady state power depends on the pump rate, not the initial conditions. This is a result of the non-linear nature of Eqs. 6.40. An order of magnitude change in the noise level will simply change the time to reach steady state by about 5%. Therefore, we need not be concerned about small errors, if any, in the treatment of the noise term.

The factor $GR(J+1)$ accounts for the fact that there are $2J+1$ values of the magnetic quantum number, m . The selection rule is $\Delta m = 0$ so that we have an inversion when $N_2/(2J-1) - N_1/(2J+1)$ is positive. In the absence of a strong magnetic field there are $2J-1$ transitions at a single frequency so the appropriate form for the inversion is $N_2 - GR \cdot N_1$ where GR is $(2J-1)/(2J+1)$. Any additional rotational dependence of the gain is included in the factor $BN(J)$.

The values of $BN(J)$ are taken from calculated matrix elements of Meredith (1972). The calculations are for a Morse oscillator and have a different rotational distribution

than a harmonic oscillator. The vibrational dependence is the same; namely, proportional to the vibration quantum number, v , of the upper state. In the code the vibrational dependence is treated by the factor VP. The values of BN(J) and GR(J) are shown in Fig. 7.5.

The product of factors VP*BN(J)*BSQ*WAVNUM is equivalent to the b^2 of Eq. 6.40b. The dimensions of the variables in Eq. 6.40b are chosen so that

$$b^2 = (\mu^2/6h^2\epsilon) \cdot \hbar\omega \quad (7.4)$$

where μ^2 is the dipole moment and ϵ the permittivity of the medium in S.I. units. The variable WAVNUM equals $1/\lambda$ so is proportional to $\hbar\omega$. The coefficients VP and BN were normalized to equal 1.0 for the V2-1, P(6) transition, so that

$$BSQ = (\mu^2/6h^2\epsilon)$$

for the V2-1 P(6) transition with WAVNUM in units of cm^{-1} . The numerical value of BSQ obtained from Meredith (1972) is 4.7×10^{-6} . This corresponds to a dipole moment of 0.125 Debye.

The factor CPH corresponds to $\cos \phi$ in Eq. 6.40b. This was discussed in detail in Section 7.3.4.

7.5 The Electric Field Equation

The electric field equation is

$$\dot{q} = -\beta q + p. \quad (6.40a)$$

The FORTRAN version in the IXION code is

$$YDOT(M+2) = -CAV1*Y(M+2) + FILL*Y(M+1) \quad (7.5)$$

where Y(M+1) is the polarization and Y(M+2) the electric field.

The coefficient $FILL$ occurs in Eq. 7.5 because the active medium doesn't fill the entire volume of the cavity, as was assumed in Eq. 6.40a. In the present case $FILL$ is just the gain length divided by the cavity length. There is some uncertainty in determining the gain length because of the non-uniform spatial distribution of the discharge. Experimental observations of the beam shape indicated that the discharge region consisted of 50 cylindrical discharges of about 2.5 mm diameter at half intensity. Thus the gain length was estimated at 13.5 cm. Further uncertainty arises because the low reflectivity output mirror causes the intensity to vary along the axis, causing a spatial variation in the threshold inversion. With an 8% output mirror the inversion will vary a factor of 2. Fortunately these uncertainties are not critical. The total power output depends linearly on the estimated active volume multiplied by the initial estimated F atom density. Time delays in the waveform have only a logarithmic dependence on the value of $FILL$.

Clearly the coefficient $CAVI$ is equivalent to β which equals $1/2\tau_c$, where τ_c is the lifetime of a photon in the cavity. Photons are lost from the cavity by transmission through the output mirrors, absorption loss at mirrors and windows, scattering losses in the gas and diffraction due to finite apertures in the system. Scattering and diffraction losses are a few percent or less in most experimental setups. Window losses, especially from reflection out of the cavity,

could be as large as 10 or 20 percent for unfavorable polarizations. However, we are comparing calculations with experiments which used low reflectivity mirrors, making other losses insignificant. If we consider only mirror losses we get

$$\delta = \frac{1}{2\tau_c} = - \frac{c \ln(\rho_1 \rho_2)}{4L_c} \quad (7.6)$$

where ρ_1 and ρ_2 are mirror reflectivities, L_c is the cavity length, and c is the velocity of light. To the extent that other losses can be lumped, rather than spatially distributed, they can be lumped into one of the mirror reflectivities.

The output intensity will be given by

$$I_{\text{out}} = (1 - \rho_2) I_{\text{cavity}}$$

and the other losses can be lumped under ρ_1 .

The algorithm for calculating CAV1 and FILL is

C = 3.E10

RHO1 = 0.08

RHO2 = 1.0

CAVLN = 65.

GAINLN = 13.5

CAV1 = -.25*C*ALOG(RHO1*RHO2)/CAVLN

FILL = GAINLN/CAVLN

The variable names correspond to those in Eq. 7.6. Reflectivity RHO1 was set equal to unity and RHO2 to 0.08.

Because of the low value of RH02 the output power is 92% of the power in the cavity at the output mirror. As a result the output from the code gave the power in the cavity rather than the actual output power. This should be corrected if different output mirrors are to be compared.

The code calculates power output per cm^2 of beam area. Examination of the experimental beam intensity pattern indicated that it was oval, about 2.5 mm wide and 15 mm high at half intensity. The effective area of the experimental beam was estimated to be 0.4 cm^2 . A calculated beam output of 2.5 mJ/cm^2 thus corresponds to an experimental output of 1mJ, a typical value.

7.6 Simulation of Detector Response

The experimental waveforms were obtained using a detector with a rise time of about 30 ns.; this was simulated in some computer runs to give a more accurate comparison.

The simplest form for detector response to a unit impulse function is $D(t) = e^{-t/\tau}$ where τ is the detector rise time and the function is normalized by the factor $1/\tau$. If the detector response function is $D(t)$ and the raw waveform is $f(t)$, the observed waveform $g(t)$ is obtained by convolution of $D(t)$ with $f(t)$, i.e.,

$$g(t) = \int_0^t D(t-u)f(u)du$$

where u is a dummy variable with dimensions of time.

This is easily implemented numerically if the raw waveform is given as a sequence of values at discrete times. The time step need not be uniform, but it is preferable that it be less than τ . The factor $D(t-u)$ can be written as a product

$$D(t-u) = 1/\tau e^{-(t-u_n)/\tau} e^{-(u_n-u_{n-1})/\tau} \dots e^{-(u_2-u_1)/\tau} e^{-(u_1-u)/\tau}.$$

For the most recent value of $f(t)$ the integral can be approximated by

$$(1 - e^{-\Delta t/\tau}) f(t_0).$$

(This form is chosen rather than $\Delta t f(t)/\tau$ because it gives a more accurate result when $f(t)$ remains constant.) On the next time step the same element has a contribution

$$e^{-\Delta t_1/\tau} (1 - e^{-\Delta t/\tau}) f(t_0),$$

so that $D(t-t_0)$ has become a product. With each time step another term is included in the product, yet the function $D(t-t_0)$ remains exact and the only approximation is in the initial step. Any error introduced in the initial step is damped out because $D(t-t_0)$ decreases monotonically.

The algorithm is simpler than the derivation, and was initially obtained heuristically. The algorithm, repeated each time step, is

$$DET = 1./30.E-9$$

$$AH = DET*(TIME-TOLD)$$

$$TOLD = TIME$$

$$SMULT = EXP(-AH)$$

$$DO\ 230\ LS = 1,320$$

$$230\ SMOOTH(LS) = Y(LS) + SMOOTH(SMOOTH(LS)-Y(LS))$$

where ΔH equals $\Delta t/\tau$ since on each time step $TIME = TOL + \Delta t$. This simple algorithm was used to simulate a detector response of 30 nanoseconds.

7.7 Temperature Rise

The temperature has been held constant in most runs with the IXION code, largely out of ignorance of the appropriate temperature dependence. These are two sources of temperature variation, the heat of reaction and the heating by the electrical discharge.

Heating due to the exothermic reaction is easy to estimate. The reaction $F + H_2 \rightarrow HF + H$ is exothermic by 32 kcal/mole. For the experiments where waveforms were compared to calculations it appears that the partial pressure of HF was about 1% of the total pressure. Thus the heat of reaction yields about 320 cal/mole of the total mixture. About half of this is radiated as laser energy. The specific heat of the mixture is about 13 Gibbs/mole so the temperature rise should be about 12 K, a rather small rise.

On the other hand, experiment (Pearson, et al., 1973a) shows that the laser output was about 1% of the electrical discharge energy. If the majority of the discharge energy, about 30 kcal/mole, went into heating the gases the temperature rise would be at least 1200K. Analysis of experimental time constants shows that the rate-constants are appropriate

to a temperature change of less than 200K (Pearson, et al., 1972b). The majority of this discharge energy is not accounted for.

The discharge energy can be partitioned into a number of modes: ionization, dissociation, radiation, electronic, vibrational and rotational excitation and translational energy. The chemical reaction rate depends mainly on the translational temperature because the reactants need translational energy to overcome the potential barrier. A simple calculation shows that little of the discharge energy goes initially into translational energy.

In the usual model of an electric discharge the electron gains a few tens of electron volts from the electric field between collisions. When it collides with an atom or molecule it gives up this energy. It also gives up some momentum, and, since momentum must be conserved, the molecule gains momentum. The momentum of the electron before collision has the magnitude

$$P_e = \sqrt{2m_e E_e},$$

where E_e is the kinetic energy of the electron, m_e its mass and P_e its momentum. If the molecule increases its momentum the translational energy change is

$$\Delta E_t = (p_M'^2 - p_M^2)/2M = \Delta p_M (p_M' + p_M)/2M$$

where p_M' is the momentum of the molecule after the collision, p_M the momentum before collision, and M the molecular mass.

$$\text{If } \Delta p_M = P_e \ll p_M$$

$$\Delta E_t = \sqrt{E_e E_t m/M}.$$

Typically $E_e \sim 1500$ kT and $E_t = 3/2$ kT. If the electron collides with an H_2 molecule, $\Delta E_t \sim$ kT. If the molecule is NF_3 the energy change is about $1/6$ kT. In either case, the increase in molecular kinetic energy is less than 10^{-3} of the electron energy. The remainder of the electron's kinetic energy must go into electronic or vibrational excitation of the molecule. Conservation of angular momentum requires the change in rotational energy to be comparably small.

Eventually, the electronic and vibrational energy must be transferred to translational energy, be radiated away, or be dissipated hydrodynamically. Typically vibrational-to-translational energy transfer requires thousands of collisions, but the laser pulse is complete by the time a few hundred collisions have occurred, so the translational temperature remains small. It is probably fortuitous that the increase in kinetic energy of H_2 gives an effective temperature of about 500 K, the temperature which estimates the pulse width correctly (Pearson, et al., 1972b).

Calculating the correct translational temperature is quite difficult, so calculations with the IXION code assumed a constant temperature, 300 K in most cases.

7.8 Codes to Rearrange Output

The output of the IXION code is a disc file, SCRATCH. The file is arranged in blocks, with each block containing the values of all powers and populations at one time, along

with a few auxiliary variables such as temperature and the step number. The interval for printouts is chosen so that the file contains between 100 and 1000 such blocks. An auxiliary file, GUIDE, gives statistics on SCRATCH so that editing coes can read it easily.

An obvious way of displaying data from a computer code is to have time histories of the variables. Two codes were written to produce graphical and tabular time histories from the data contained in the disc file, SCRATCH. One of these codes, COLLAGE, plotted the waveforms which will be shown in Fig. 8.1. A second code, EDITB, gave a more complete output. This output was arranged by cascades and showed the inversions and total populations for each inversion. If any of the transitions in the cascade lased, the lasing waveforms are also plotted. In addition, twenty snapshots of the population distributions are plotted. Because of the length of the SCRATCH file, (500K decimal words), the EDITB code had to do extensive sorting to efficiently transform from data blocked in time steps to time sequences for each of several hundred variables. In addition to the graphs EDITB provided tables of the time history of each variable.

The snapshots of population distributions suggested that a movie might be a useful way to display the data in order to increase our understanding of the physical processes. A code was written to make such a movie (Creighton, 1974). Single frames from the movie will be used in Section 8 to illustrate the operation of the laser.

TABLE 7.1. Fraction of HF going into
each vibrational-rotational state as
a result of the reaction

J	V=0	V=1	V=2	V=3
0	.0	.0	.0	.01158
1	.0	.0	.0	.05580
2	.0	.0	.00673	.06784
3	.0	.0	.02537	.05742
4	.0	.00161	.04816	.03357
5	.00080	.00771	.06576	.01436
6	.00385	.01766	.07819	.00232
7	.00883	.03082	.07975	.0
8	.01541	.03162	.07094	.0
9	.01581	.02697	.05282	.0
10	.01348	.01846	.03780	.0
11	.00923	.01461	.02537	.0
12	.00730	.00851	.01605	.0
13	.00425	.00225	.00725	.0
14	.00112	.0	.00259	.0
15	.0	.0	.0	.0

TABLE 7.2. Values of the vector, $DJ(J)$, which gives variation of collisional linewidth and rotational relaxation rate with rotational quantum number, J .

J	$DJ(J)$	J	$DJ(J)$	J	$DJ(J)$
0	0.0	7	0.1169	14	0.009673
1	0.525	8	0.08187	15	0.006776
2	0.515	9	0.05735	16	0.004714
3	0.430	10	0.04017	17	0.003325
4	0.340	11	0.02814	18	0.002329
5	0.2382	12	0.01971	19	0.0011632
6	0.1668	13	0.01381	20	--

Fig. 7.1 Schematic diagram of the IXION model showing the individual states and the rates which couple them.

Fig. 7.2 Fraction of HF molecules formed in each vibrational-rotational state by the reaction $\text{F} + \text{H}_2$. The dashed curve is a Boltzmann distribution at 300K.

Fig. 7.3 Rate of formation of HF in the pulsed $\text{NF}_3 + \text{H}_2$ laser. The solid line represents the approximation of neglecting consumption of H_2 . The dotted line is an exact numerical result where about 2% of the H_2 is consumed.

Fig. 7.4 Dependence of HF self-broadened linewidth on rotational quantum number: Several curve fits are shown normalized to the linewidth at $J=4$. At 15 Torr and 300 K the Doppler width is approximately equal to the collisional linewidth at $J=7$.

Fig. 7.5 degeneracy ratio and relative gain for P-branch transitions.

8. CALCULATED WAVEFORMS AND DETAILS OF LASER OPERATION

8.1 Introduction

The IXION code, described in the previous section, has been used to calculate laser waveforms which could be compared with experiment. The relevant experiments are described in Section 3. The agreement between experiment and calculated waveforms is quite good. As a result we can consider that the code uses a fairly accurate model of the physics involved. Assuming that the model is correct we can increase our understanding of the operation of the pulsed HF laser. We will also examine the assumption of rotational equilibrium used in earlier codes, and show how the waveforms calculated by the IXION code are superior to those calculated with simpler models.

8.2 The Nominal Calculated Waveforms

The "nominal" calculated waveforms are shown in Fig. 8.1. The values of the parameters used attempt to match experimental values. The most important parameters are the total pressure of 15 torr with the ratio of NF_3 to H_2 equal to 5.2, the density of F atoms which was 1.25% of the initial density of NF_3 , and the peak rotational relaxation rate which was about five times gas kinetic. These values of the parameters were chosen as the nominal case because they seemed to be the best fit after running a number of cases. The judgment of best fit was made after visual compar-

ison, so is partially subjective. A quantitative fit, in this case, would only hide subjective judgments as to the relative importance of the features to be fit.

The calculated data will generally be displayed in the form of Fig. 8.1. The total power waveform will be enclosed in a box in the lower right hand corner. The full scale magnitudes of the time and power axis are given. The time scale is the same for the individual waveforms, but full scale power for the individual waveforms is $1/4$ that for the total power. If a spike is more than 110% of full scale, it is truncated at 110%. The power scale is adjusted for each run so that the total power spikes will be at least half of full scale, but not greater than full scale. In addition to the waveforms, a table was calculated showing the fraction of the total energy emitted on each transition. This will be shown in tabular form where it is appropriate. As a further aid in comparing calculated results with experiment, Fig. 8.2 shows the calculated results smoothed by a 30 nanosecond detector response time. The full scale power is half that of Fig. 8.1 because the smoothing reduced the height of the spikes

Comparison of calculated and experimental total power plots shows many similarities. The first spike in both cases is the V2-1 transitions beginning to lase. These are the first because they have the largest inversion as well as twice the dipole matrix element of the V1-0 transitions.

The second spike in the calculated results is the lasing on V3-2. The major spike occurs when V1-0 transitions begin to lase. At that point cascading begins and all four vibrational levels interact. Experimentally, the V3-2 and V1-0 transitions appear to start about the same time. Calculations at different vibrational rates have shown that this relative timing is fortuitous. Depending on the magnitude of the V3-2 inversions, they may begin to lase before, after or simultaneously with the V1-0 transitions.

The bumps and wiggles after the main spike in the calculated waveform are due to damped relaxation oscillation and a phenomenon similar to "J-shifting," where one transition suddenly drops a lot of power and another picks it up. This will be discussed later.

The calculated total energy is 2.40 mJ/cm^2 . The dissociation was adjusted to agree with the experimental .9 to 1.0 mJ over a 0.4 cm^2 beam area.

The pulsewidths of the individual calculated and experimental waveforms show the same trend: the pulsewidths increase from P3 to P6, and agree well in magnitude. The P7 transition is somewhat anomalous.

All of the P3 waveforms are rather narrow spikes. The calculated V2-1 P3 is a double spike, but the experimental trace shows only one (Fig. 3.2). An examination of the experimenters notebook showed three V2-1 P3 waveforms. Two had a single spike and one a double spike. The difference

depended on the time between the first spike and the major spike. The P3 transitions stop lasing because the inversion disappears. If it disappears before the major spike there will be only one P3 spike. The calculation shows a large V3-2 P3 spike, not shown with the experimental waveforms. An examination of the notebooks shows a probable weak lasing at just about the sensitivity limit of the detector. Some calculations with high vibrational relaxation rates have greatly reduced the V=3 population and reduced the P3 lasing. Even higher relaxation rates completely suppress all V3-2 lasing. The calculated relative heights of the V2-1 P3 and V1-0 P3 are not in agreement with experiment. The height of the V1-0 P3 pulse depends on the detailed chemical pumping rates which were estimated for V=0, due to lack of data, and the experimental heights may not be too accurate. The laser has some problems in reproducibility and the attenuators used with the detector were changed from time to time. As a result, pulse heights have to be compared to other transitions measured under similar conditions. The height of the P3 line may be as low as that of the P6 or it may be as high as shown.

The calculated P4 waveforms agree well with the experimental, except that the calculated V3-2 P4 waveform has a longer duration than the experimental. Both calculated and experimental waveforms show an initial spike and a later, weaker spike, or at least a hump. The laboratory notebook shows some variation on the V2-1 P4. In some cases the first

spike is higher than the second, in other cases they are equal, and sometimes the second spike is higher. The calculated waveform is within the limits of experimental variation. The calculated V3-2 P4 pulse is too wide to match experiment. Calculations indicate that this duration is due to a relatively large V3-2 inversion. Mechanisms which would deplete this inversion would probably reduce the pulsewidth. The V3-2 P4 pulse is terminated when the P5 reaches higher gain and the V=3 populations then feed the P5 rather than the P4 transitions. This is similar to "J-shifting." True "J-shifting" occurs only if there is rotational equilibrium in each vibrational level (Chester, 1970; Emanuel, 1971). We will also call the phenomenon seen here "J-shifting" in the absence of a better term.

The calculated and experimental V2-1 P5 waveforms agree in height, the number of spikes and duration. The experimental V1-0 P5 is missing due to water vapor absorption. Experimentally the V3-2 P5 was missing, although there is some indication of weak lasing at about the same time the P4 turns on. If the V3 population were depleted early the P5 would not appear at late times as shown in the calculated waveform.

The P6 and P7 transitions are the least reproducible experimentally, and are most sensitive to parameter changes in the calculated results. This will be seen later when more calculations are presented. The calculated V1-0 P6 and P7 waveforms are another example of "J-shifting." The

P7 output goes up at the point that P6 goes down. A closer examination shows that not only these two levels are "J-shifting" but two complete cascades. The first cascade is V3-2 P4, V2-1 P5, and VI-0 P6. The second cascade is V3-2 P5, V2-1 P6 and VI-0 P7. At about 1.4 microseconds, the entire first cascade gets weaker and the second gets stronger. This shows that cascades are relevant to the operation of the laser, but that their effect is diluted by the rotational relaxation. This will be discussed in more detail later.

The experimental waveforms show mixed evidence of the importance of cascades. The "J-shifting" is evident as we look down the V2-1 column of Fig. 3.2. As each transition goes out, the one below it has a hump or a spike. The evidence for cascades, however, is weak or contradictory. All of the transitions in the first cascade described above are present, but the waveforms appear to be rather independent. The second cascade lacks a V3-2 transition. If the cascade were strong we would see a late hump in the VI-0 P7 corresponding to that in the V2-1 P6. This hump is definitely missing. The hump in the P6 transitions is not very reproducible, so the experimental waveforms may be misleading. It is also possible that certain approximations in the calculations distort the results. In particular, the calculations assumed a constant temperature of 300K, and that rotational relaxation occurred by single quantum jumps. Neither of these is completely justifiable physically.

Neither the calculations nor experiments showed lasing on P2 transitions. Calculations showed weak lasing on V2-1 P7 to P14, and also on V1-0 P8 to P14. The amplitudes, however, were 30% of V2-1 P6, or less, and decreased to a few weak, isolated spikes at P14. If these transitions did in fact lase as calculated, the intensity was too low to distinguish them experimentally from the noise. Transitions up to P17 have been seen experimentally in a similar laser operating with lower threshold inversions (Pommer and Kompa, 1972).

The calculated fraction of the total laser energy emitted on each transition is compared with experiment in Table 3.1. Since experimental values were obtained by graphical integration of waveforms, the third column gives a better comparison. To obtain the third column the calculated values were summed over the experimentally measured transitions. The calculated values were then renormalized by dividing by this sum. Exact numerical agreement is not obtained, but general trends are the same. Comparing these energies gives less information than comparing waveforms.

In summary, very good general agreement between calculation and experiment has been obtained with only one fully adjustable parameter, the fraction of NF_3 dissociated. The fraction dissociated was adjusted to give about 2.5 millijoule/cm² output to correspond to an experimental output of about 1 millijoule in 0.4 cm². The fractional dissociation, 1.25%, was in agreement with Saha equilibrium calculations of Curry (1972). The rotational relaxation rate was adjusted

over two orders of magnitude, but best agreement was obtained when the rotational relaxation rate was a half of the line broadening collision rate, or equal to it. This is comparable to the experimentally estimated rotational relaxation rate for HCl (Polanyi and Woodall, 1972a). This is also the most reasonable physical estimate because line broadening is caused by collisions which either change the rotational state or perturb the phase of the rotating molecule by an angle on the order of π radians. A large fraction of line broadening collisions should involve a change of rotational state. Other parameters were set at the most likely value, based on known data or physical reasoning. The differences between the experimental and calculated results have been pointed out, but the overall agreement is surprisingly good.

Because of the good agreement between theory and experiment, we can have some confidence that the model is a reasonable representation of reality. The next section will describe in some detail the operation of the laser. The model describes the dynamics of variables which were not accessible experimentally. Therefore, we can use the model to increase our understanding of the relevant physical processes. When the description is finished, various parameters in the model will be varied and the results examined.

8.3 Sequence of Events During the Laser Pulse

8.3.1 Introduction

We can use the results of calculations with our model to understand what happens inside the laser. We can get information which is difficult to obtain experimentally such as the value of the populations and inversions. It might be possible to measure these variables experimentally, but it would be very difficult. On the other hand, these data come almost automatically from the code. The present model also gives considerably more detail than earlier models because rotational states are treated separately and the laser dynamics is treated by semi-classical equations. Thus the information used here to depict the operation of the laser is not available elsewhere.

To illustrate the sequence of events we will use single frames from a computer generated movie (Creighton, 1974). The movie was generated from output data of the IXION code using the set of parameters designated as the nominal case at 15 Torr. Each frame of the movie shows the population of each vibrational-rotational state, and the intensity of any laser transitions connecting it to other states. The total power waveform, up to the time which the frame represents, is shown in the upper right-hand corner. (See Fig. 8.3.) The populations of all states with the same vibrational quantum numbers are connected by straight lines. The horizontal axis is the rotational quantum number, J . The populations

in the movie are distorted, except for $V=0$, in order to preserve inversions. This is necessary because the inversion is given by

$$N(v+1, J-1) = N(v, J) \times (2J-1)/(2J+1).$$

If we plot the variables $N(v+1, J-1)$ and $N(v, J)$ we may have an inversion even when $N(v+1, J-1)$ is less than $N(v, J)$. This creates confusion in trying to interpret the results. The inversion can be preserved if we display $N(v, J)/(2J+1)$ rather than $N(v, J)$, but this creates other distortions. The populations at high J are already fairly small and if we divide them by 20 or 30 it is impossible to see their magnitude. Also the gain is roughly proportional to the total number of molecules in a given state so dividing the population by $2J+1$ gives a false impression of the relative gains. A different compromise was finally chosen. The bottom state in each cascade is $N(0, J_0)$. If we display $N(v, J) \cdot (2J_0+1)/(2J+1)$ we preserve inversions but with less distortion. The $V=0$ state has no distortion, and can be compared with the Boltzmann distribution (shown as a dotted line in Fig. 8.3). The low J populations and gains are overestimated for other vibrational levels. The worst distortion is for $V=3, J=0$ where the population is a factor of 7 too high. It is much less for all other states. This distortion seems to be more tolerable than the other types.

When lasing occurs the transition is marked by a line connecting the states involved. To show the intensity of the lasing an octagonal spiral is drawn at the center of the line

(see Figs. 8.4 and 8.5). The number of straight line segments in the spiral is proportional to the logarithm of the intensity (over about 2 decades). The visual appearance is more nearly linear because the area of the spiral is proportional to the square of the number of segments.

8.3.2 Initial Lasing on V2-1 Transitions

We now proceed to discuss the sequence of events. For the first 200 nanoseconds or so the populations build up, and rotational relaxation creates the double humped distributions seen in Fig. 8.3. All of the V2-1 and V1-0 transitions are inverted, as are the low J V3-2 transitions. Lasing first begins at V2-1 P9, rapidly followed by V2-1 P8. Figure 8.4 shows the population distributions at this point. The V2-1 transitions lase first because they are the most strongly inverted. All V2-1 transitions up to P15 have reached threshold inversion some time before Fig. 8.4, as have all V1-0 transitions up to P12. The radiation on all of these transitions has been increasing exponentially since they reached threshold inversion. The time constant for this increase depends on the magnitude of the inversion and the stimulated emission cross section. The cross sections for a given vibrational level are all within a factor of two, and are linearly proportional to the vibrational quantum number of the lower state.

The inversions reach threshold at different times for different values of J, partly because the magnitude of the threshold inversion is a function of J and partly because the

states are pumped at different rates. The threshold inversion is a function of linewidth and dipole matrix element (Eq. 6.27). The linewidth decreases with J for J greater than 2 and asymptotically approaches the Doppler linewidth for J greater than 8 (Fig. 7.4). The threshold inversion is inversely proportional to the dipole matrix element, which increases at high J (Fig. 7.5). As a result the threshold inversion decreases monotonically with J , when J is greater than 3.

The first laser transition to turn on in the present case is V2-1 P9. (In the movie "turn-on" is defined as reaching a level of 1% of the peak power of the highest spike.) Examination of the tabular output of the IXION code shows that most of the V2-1 transitions are increasing rapidly as P9 turns on. The P9 transition turns on first because it reached threshold before transitions of lower J , but it has a faster time constant than transitions of higher J because of its larger population. However, other transitions turn on almost immediately as shown in Fig. 8.5. The sequence of appearance of V2-1 transitions is P9, P8, P10, P7, and P6, all shown in Fig. 8.5. These are followed by P5, P4, P11, P3, P12, and P13 as seen in Fig. 8.6.

The fact that P9 turns on first is a function of the parameters chosen and some other transitions might turn on first if different parameters were chosen, particularly different values for linewidth and rotational relaxation rate. Experimentally, also, a different transition might turn on first, but the qualitative picture of what occurs is still correct.

Figure 8.5 shows an example of hole burning in the rotational distribution. On the $V=2$ level the J7 and J8 populations are depressed relative to others in that level. This loss of population has populated the J8 and J9 states in the $V=1$ level. The hole burning occurs because the lasing changes the molecular states much faster than rotational relaxation can smooth the distribution. Additional hole burning can be seen in Fig. 8.6, but a short time later rotational relaxation has smoothed this out as shown in Fig. 8.7.

The relaxation oscillations discussed in Section 6 are also visible in this sequence of frames. In Fig. 8.4 all V_2-1 transitions are inverted and the P8 and P9 transitions are starting to lase. In Fig. 8.5 the inversion has been lost on the P9 transition and is below threshold on P8. The intensity of radiation on these transitions is near its peak. Adjacent transitions are still increasing in intensity. Shortly after the peak of the first spike, Fig. 8.6, most of the V_2-1 inversions are reversed and the P7, P8, and P9 transitions have extinguished. The P4, P5, and P6 transitions are near their peak in intensity and are responsible for the spike in the total power. The P3 transition is just now turning on, as is the P12, which will shortly be followed by P13. The little jog on the leading edge of the total power curve occurred when the P8 and P9 transitions were getting weaker due to loss of inversion and the other transitions had not yet reached a high intensity.

It is interesting to note what has happened to populations of the vibrational levels in the period between Figs. 8.4 and 8.7. The population of the $V=3$ level has increased about 50% due to chemical pumping with a small loss due to vibrational relaxation. The population of the $V=2$ level has remained about the same because it has lost population to the $V=1$ level which now has about the same population as $V=2$. We will see later that at steady-state the population of all vibrational levels is about the same. The $V=0$ level, like the $V=3$ level, has increased about 50% in population.

The population distributions of Fig. 8.7 are still a long ways from a Boltzmann distribution, but rotational relaxation has increased the population at low J . The $V=1$ level has a larger population at high J than $V=2$. This is caused by the selection rules for lasing which cause an increase of one in the rotational quantum number. This difference will remain until lasing occurs on the 1-0 transitions.

Further insight into the processes we have been considering can be obtained by looking at the time history of the laser powers, inversions, and populations of one cascade. Figure 8.8 shows these variables for the cascade consisting of the states $V3J3$, $V2J4$, $V1J5$, $V0J6$, and the transitions that couple them. (In this figure the populations are not distorted.) In Fig. 8.8b we see the $V2-1$ inversion rising initially (curve labeled 1). At about 100 nanoseconds, it reaches threshold inversion. (In Fig. 8.8 the inversions at 1 microsecond equal threshold inversion.) At about 250 nano-

seconds the inversion begins to drop rapidly. Comparison with Fig. 8.8a and 8.8c shows that the drop occurs because of lasing, and that the population of V2J4 is decreasing and V1J5 is increasing. The changes in population are nearly mirror images at this point. Dropping the population of V2 J4 increases the V3-2 inversion and increasing the V1 J5 population increases the V1-0 inversion. (The time where the V2-1 inversion starts to drop corresponds to a time just after that of Fig. 8.5; and the minimum V2-1 inversion corresponds roughly to Fig. 3.6.) After the population of V2 J4 reaches minimum it is rapidly restored to equilibrium with adjacent states by rotational relaxation. As it approaches equilibrium, its population continues to increase due to chemical pumping but at a slower rate. A similar thing happens to the V1P5 population except that lasing leaves it overpopulated and rotational relaxation decreases the population. At about 300 nanoseconds V1P5 is near equilibrium and its population has begun to increase due to chemical pumping. At about that time additional processes become important because V3-2 P4 begins to lase.

8.3.3 Initial Lasing on V3-2 Transitions

Some V3-2 transitions were inverted from the beginning, but as shown in Fig. 8.4 the inversions were much smaller than the V2-1 inversions. Figure 8.8b shows that the V3-2 P4 inversion did not reach threshold until just before the V2-1 transitions lased. After that, the V3-2 transitions are highly inverted and the laser intensity builds up rapidly

from the noise level. The $V1-0$ inversions are about the same order of magnitude at 300 nanoseconds and the corresponding laser intensities are also building up, but the dipole matrix elements for $V3-2$ are 3 times those for $V1-0$, so the buildup on $V1-0$ is slower than $V3-2$. At about 320 nanoseconds $V3-2$ P3 and P4 begin to lase as shown in Fig. 8.7. The $V=3$ populations now drop and the $V=2$ populations rise. The $V=1$ level is still coupled to $V=2$ by $V2-1$ lasing transition so the $V=1$ populations also rise until $V=3$, $V=2$, and $V=1$ populations are all nearly equal as shown in Figs. 8.9 and 8.10. This significantly increases the $V1-0$ inversions as shown in Fig. 8.8b.

Another feature is that lasing on the $V3-2$ transitions now pumps the $V2-1$ transitions. This is seen in Fig. 8.8a where the $V2-1$ P5 power tends to follow the $V3-2$ P4 power with a slight lag in time. This can also be seen by comparing Fig. 8.7 with 8.9 and 8.10. The $V2-1$ P5 power increases a great deal from the level of Fig. 8.7. The effect is less pronounced with $V2-1$ P4. Figure 8.9 also shows that the $V3-2$ P3 inversion is nearly zero at the peak of the pulse. Figure 8.8b shows that, unlike the $V2-1$ transitions, the inversion doesn't reverse but rapidly settles down to steady state.

The timing of the $V3-2$ lasing relative to the $V2-1$ is dependent on the parameters used in the model. It should always occur after the $V2-1$ lasing because $V=2$ is more

strongly pumped than $V=3$. However, the $V3-2$ inversion may be weaker than the $V1-0$ inversion, depending on the populations of the $V=3$ level. In particular, a weaker pumping or faster vibrational relaxation could reduce the population at $V=3$. Experimentally it appears that the $V3-2$ lasing begins about the same time as $V1-0$.

8.3.4 Initial Lasing on $V1-0$ Transitions and Steady State

As noted above, lasing on $V3-2$ transitions increases the $V1-0$ inversions by increasing the populations of the $V=2$ and $V=1$ levels. At about 370 nanoseconds, the $V1-0$ transitions turn on. The sequence is similar to the $V2-1$ sequence, with some differences. The $V1-0$ sequence is $P10$, $P9$, $P11$, $P5$, $P4$, $P6$, $P3$, $P8$, $P7$, and $P12$. Figure 8.10 shows the populations and intensities at the instant that $P4$ turns on. It is interesting to note that $V2-1$ $P3$ through $P7$ are lasing, though $P7$ is weak and higher transitions are not lasing. Figure 8.11 shows the situation at the peak of the total power curve. All of the $V1-0$ transitions have turned on and the inversions have already reversed on $P4$ and $P5$. Also the $V2-1$ $P7$ transition is lasing strongly as are the $P8$ and $P9$ transitions. This occurs because depleting the population of $V=1$ pumps the $V2-1$ transitions just as augmenting the $V=2$ populations would. The $V2-1$ $P14$ transition has also turned on, but appears to be less directly connected with pumping due to depletion of the $V=1$ level. The close coupling between levels can also be seen in Fig. 8.8a where all three transitions contribute to the

largest spike. After the spike there are some small relaxation oscillations in the populations (Fig. 8.8c) after which the laser settles down to a steady state behavior as shown in Fig. 8.12. One of the notable features is the presence of lasing on all three transitions of two cascades. Simultaneously, however, there are cascades with only a single transition lasing. This shows that the operation of the laser cannot be characterized entirely in terms of the behavior of vibrational levels in equilibrium, but neither can it be characterized entirely in terms of cascades. The rotational relaxation and lasing are interacting in a more complex manner.

Steady state is characterized by the inversions for the relevant cascade being constant. Figure 8.8b shows that this begins shortly after the largest spike and continues for some time. Figure 8.12 shows all except a couple of high J inversions at steady state. However, the total population with $V=0$ exceeds that of $V=1$, which exceeds $V=2$, which exceeds $V=3$. This is the situation called "partial inversion" in the literature. The actual transitions are inverted but the total populations in the vibrational levels are not inverted. In contrast, the situation in Fig. 8.4 represents a "total inversion." The concept of "partial inversion" is useful when considering the entire vibrational level, but has less meaning with the present model. So long as the lasing continues at steady state, the population curves will remain close to each other, and will increase together in population.

The P1 and P2 transitions do not lase at any time. The reason for this can be seen by examining Fig. 8.13, which shows the populations and inversions for V2-1 P1 and V1-0 P2. Initially the V2-1 inversion is increasing but about the time it reaches threshold it is reduced because of a rapid buildup in the V=1 population. This buildup is quite different than the V1J5 buildup in Fig. 8.8c. There, the buildup was nearly instantaneous due to lasing. In the case of the P1 transition the buildup is due to rotational relaxation from states which were lasing.

The P5 transition turns on some 30 nanoseconds before the P1 inversion begins to disappear. When we examine the inversion for V2-1 P3 (Fig. 8.14b) we see that the P1 inversion begins to change a few nanoseconds after P3 turns on; and that the P3 inversion is also strongly affected by rotational relaxation, as shown by the flattened top on the inversion curve and the change of slope after lasing begins.

The increase in the V=1 population creates an inversion on V1-0 P2 that is well above threshold. This would readily lase if given time, but lasing on other V1-0 transitions depletes the P2 transition by building up V=0 and depleting V=1. This is further confirmed by examining the movie frames from Fig. 8.5 to 8.12.

8.3.5 J-Shifting

Figure 8.12 shows both V3-2 P3 and P4 lasing. Later than P3 transition ceases to lase because the inversion is lost as shown in Fig. 8.15. At about 1.35 microseconds the

V3-2 P5 transition turns on as shown in Figs. 8.16 and 8.17. About 100 nanoseconds later the V3-2 P4 transition turns off as shown in Figs. 8.18 and 8.8. There is little change in the lasing after this point except for a gradual reduction in laser power as shown in Fig. 8.19. This is similar to J-shifting as described by Chester (1970) and Emanuel (1971).

The mechanism by which this occurs can be seen by examining Fig. 8.17. The V3-2 P5 transition is inverted when the V2-1 transitions lase but is depleted before turn-on when the adjacent V3-2 P4 lases. For some time after that, the P5 inversion is positive but below threshold. The inversion continues to increase, reaching threshold at 0.9 microseconds, due to buildup in the V3J4 population. At that point, a slow buildup of the laser radiation begins, with turn-on occurring about 1.35 microseconds. The inversion then drops to threshold and rotational relaxation pulls the V3-2 P4 inversion below threshold, causing that transition to turn off (see Fig. 8.8).

This J-shifting has occurred at constant temperature. The possibility of this has been noted before (Emanuel, 1971). The J-shifting would be enhanced by a rising temperature which would cause the peak of the rotational distribution to shift to higher J as time increased. The phenomenon of J-shifting under the assumption of rotational equilibrium has been discussed extensively by Emanuel (1971). We will do a brief calculation to see if present results are in agreement with equilibrium theory.

At equilibrium, the populations of two adjacent rotational states are given by

$$\frac{N_J}{2J+1} = e^{-2\theta J} \frac{N_{J-1}}{2J-1}$$

where $\theta = B_0/RT$ and B_0 is the rigid-rotor spectroscopic constant. For HF, B_0 is 21 cm^{-1} so $\theta = 0.1$ at 300K. Let the V3-2 P4 inversion be constant at a value G_1 , then

$N_{3,3} - \frac{7}{9} N_{2,4} = G_1$, where $N_{2,4}$ is the population of the state $v = 2, J = 4$.

There is an additional constraint due to pumping that $N_{3,3} + N_{2,4} = f(t)$, where $f(t)$ is a pumping function. Normally $f(t)$ is monotonically increasing, although this is not necessary. At Boltzmann equilibrium, the populations for the V3-2 P5 transition are

$$N_{3,4} = \frac{9}{7} N_{3,3} e^{-8\theta}$$

$$N_{2,5} = \frac{11}{9} N_{2,4} e^{-10\theta} \quad \text{and the inversion is}$$

$$G_2 = N_{3,4} - \frac{9}{11} N_{2,5}.$$

When we solve these equations for G_2 , we get

$$G_2 = 0.625 G_1 + .046 f(t)$$

From Fig. 8.8 we find $G_1 = 1.3 \times 10^{-11}$ and $N_{2,4} = 9.3 \times 10^{-11}$ at 1.0 microsecond, resulting in a value of $6.4 G_1$ for $f(t)$. This gives

$$G_2 = .917 G_1 \text{ at 1 microsecond,}$$

which is an inversion of 1.1×10^{-11} . This agrees with the

inversion shown in Fig. 8.17 at 1 microsecond. This is somewhat higher than the threshold inversion for the V3-2 P5 transition ($.7 \times 10^{-11}$). Therefore, when P5 lases it pulls the P4 inversion below threshold.

If we had treated the laser in a steady state approximation, the results would have been slightly different. As soon as the P5 inversion reached threshold lasing would have switched to that transition and P4 would have been extinguished (Emanuel, 1971; Airey, 1970). With the present model, there was considerable delay after threshold was reached before the laser intensity built up, and both lased simultaneously for a while.

The mixture of cascade and equilibrium behavior is again illustrated in Figs. 8.8 and 8.17. When the V3-2 P4 turns off, the power is reduced in the lower steps of the cascade. The power represented by pumping into the V=3 level is transferred to the next cascade. Thus, we see that the cascades are important, yet power could not be transferred from one to the other unless the V=3 level behaves as a level which is nearly in equilibrium.

The non-equilibrium nature of the present model is shown in Fig. 8.17, where the populations are nearly constant, rather than monotone increasing. At higher J-values the populations actually peak and then fall off as shown in Fig. 8.20. This occurs because the chemical pumping is initially very strong and well out of equilibrium. As the chemical pumping rates fall, the populations at high J are reduced through rotational relaxation.

8.4 How Valid is the Assumption of Rotational Equilibrium?

Earlier models of the HF chemical laser have assumed rotational equilibrium within each vibrational level, and this equilibrium is usually taken to be at the translational temperature. The present model contains sufficient physical detail to see if the rotational equilibrium assumption is justified. We already know that the chemical pumping rate distribution is nowhere near the Boltzmann distribution at reasonable temperatures; we will want to see how rapidly this relaxes towards a Boltzmann distribution. We will also want to look at possible hole burning in the population distributions and to see if we can better understand J-shifting.

The population distribution at 41 nanoseconds is shown in Fig. 8.21. Comparison of Fig. 8.21 with the pumping rates (Fig. 7.2) shows that this distribution is mainly due to the pumping rates.

Somewhat later, at 156 nanoseconds, the population distributions develop a double hump as shown in Fig. 8.22. The high energy peak is nearly the same as Fig. 8.21, but an additional nearly-Boltzmann distribution is superposed on the pumping distribution. The $V=3$ distribution is very near to a Boltzmann distribution largely because the distribution of pumping rates for $V=3$ nearly coincides with the 300K Boltzmann distribution.

Around 200 nanoseconds lasing begins and greatly distorts the distributions. However, near the end of the pulse the distribution should be smoothed out, and might have a Boltzmann form.

The population distributions at 2.0 microseconds are shown in Fig. 8.23. At first glance they appear to approximate a Boltzmann distribution, but closer examination shows that all but $V=3$ have a population larger than Boltzmann at the higher energies. The nature of this high energy tail is better seen on a semi-logarithmic plot (Fig. 8.24). We then see that although there are very few molecules in the tail, the population ratio between adjacent states is not given by a Boltzmann distribution. However, for rotational quantum number less than 5 or 6 the population distribution is given to good accuracy by the Boltzmann distribution.

It seems clear that the major cause for the high energy tail is the fact that these states are still being pumped, though weakly, by the chemical reaction. Although some of the populations are six orders of magnitude too large, the absolute populations are small at high J . The time between collisions is 10 to 50 nanoseconds, so if the pumping were turned off the populations would reach the correct order of magnitude in a microsecond or less.

It is possible to fit a line through the tail of the distribution and obtain an effective temperature for states with rotational energies greater than 1000 cm^{-1} . This temperature would be in excess of 1000K, depending on the fit chosen. It is not clear that defining such a temperature for part of a distribution is meaningful.

It is clear that the assumption of rotational equilibrium within each vibrational level is incorrect up to the

time that lasing begins. At the end of the pulse, it is a reasonable approximation for states with low J . States with high J have very small populations, but still orders of magnitude larger than a Boltzmann distribution. Thus, we must conclude that the assumption of rotational equilibrium is valid only near the end of the laser pulse and then only with qualifications.

In addition to the non-Boltzmann character of the population distributions there is some "hole burning" in the populations as seen in Fig. 8.11. This occurs because lasing depletes the upper state (and augments the lower state) faster than rotational relaxation can smooth out the distribution.

8.5 Comparison of the IXION Code Results with Earlier Codes

Having seen how the results of the IXION code compared with experiment, it is interesting to compare the results with earlier codes. Figure 8.25 shows the total output power of the HF laser as calculated by the Aerospace Corporation's RESALE code (Rapagnani, 1973). This calculation was meant to simulate a laser with 20 torr total pressure, close to the conditions of Figs. 8.3 and 8.1. The RESALE code assumes rotational equilibrium and treats the lasing in a steady-state approximation. The general waveform is correct; i.e., an exponential decay. The waveform contains less structure than the experimental waveform (Fig. 3.3) and that calculated by the IXION code (Fig. 8.1). The RESALE code doesn't

calculate individual waveforms except for calculating the J value of the transition with maximum gain. This J value shifts from time to time, and the little glitches on the waveform of Fig. 8.25 represent the times when J -shifting occur. If waveforms were plotted by the RESALE code they would be approximately trapezoidal in shape because one transition turns off as the new one turns on. Figure 8.25 also shows the laser turning on very early. The RESALE model assumes turn-on occurs as soon as the first transition reaches threshold inversion. It neglects the delay due to the finite time required to build up the laser intensity.

The IXION model differs from RESALE by treating rotational relaxation explicitly and by using semi-classical laser equations in a simplified form. The calculated results are similar except that the IXION code gives more detail and better agreement with experiment. The addition of rotational relaxation to the IXION code permits it to calculate simultaneous lasing on several P-branch transitions. It also shows that cascade effects are important along with J -shifting. Treating the lasing by semi-classical equations gives appropriate delays to turn-on and allows large inversions to build up on certain transitions. It also shows certain structure in the pulse.

This has been achieved with a single adjustable parameter, the fraction of NF_3 dissociated. Other parameters, such as rotational relaxation rate have been adjusted but best results are obtained when they are set to the most likely value based on physical insight.

The calculated results of the IXION model agree well with experiment. Because of this agreement we can place some confidence in the details of the code. The code calculates variables, such as inversions which are difficult to measure experimentally. By examining the code output we can gain greater insight into the operation of the laser. The IXION code gives many more such details than the earlier codes.

Fig. 8.1 Calculated waveforms at 15 Torr total pressure;
 $\text{NF}_3/\text{H}_2 = 5.2$, 1.25% of NF_3 dissociated, rotational
 rate about SX gas kinetic. Total energy ≈ 2.40 mJ.

Fig. 8.2 Same waveforms as Fig. 8.1 except smoothed by a 30 ns. detector response.

Fig. 8.3 Single frame from a movie showing population distribution shortly before lasing begins.

Fig. 8.4 Lasing begins on V2-1 transitions.

Fig. 8.5 Additional V2-1 transitions turn on. Inversions for P8 and P9 are depleted, resulting in hole burning.

Fig. 8.6 Peak of the first spike. V2-1 P3 is just turning on, most other V2-1 inversions are depleted and some transitions have extinguished.

Fig. 8.7 Lasing begins on V3-2 transitions.

Fig. 8.8 Time history of the cascade consisting of V3-2 P4, V2-1 P5, and V1-0 P6.

Fig. 8.9 Peak of the second spike.

Fig. 8.10 Lasing begins on V1-0 transitions.

Fig. 8.11 Peak of the main spike.

Fig. 8.12 The beginning of steady state operation.

Fig. 8.13 Time history of the V2-1 P1, V1-0 P2 cascade.

Fig. 8.14 Time history for the V3-2 P2, V2-1 P3, V1-0 P4 cascade.

Fig. 8.15 Distributions at the instant V3-2 P3 extinguishes.

Fig. 8.16 Begin lasing on V3-2 P5.

Fig. 8.17 Time history of the V3-2 P5, V2-1 P6, V1-0 P7 cascade.

Fig. 8.18 Distributions when V3-2 P4 extinguishes.

Fig. 8.19 Distributions near the end of the pulse.

Fig. 8,20 Time history of the V3-2 P10, V2-1 P11, V1-0 P12 cascade,

Fig. 8.21 Population distribution before relaxation becomes dominant.

Fig. 8.22 Population distribution at 155 nanoseconds showing a double hump.

Fig. 8.23 Population distribution at 2.0 microseconds.

Fig. 8.24 Semi-logarithmic plot of population distributions after 2.0 microseconds. The solid curve is a Boltzmann distribution at 300 K.

Fig. 8.25 Total laser power as simulated by the RESALE computer code (courtesy of L. Rapagnani, 1973).

9. VARIATION OF PARAMETERS

We have now established the validity of the numerical model by comparison with experiment. We have also used the model to obtain insight into details of the operation of the laser. We will now use the model to study the effects of varying a number of parameters.

The first parameter to be studied is the rotational relaxation rate. Related to this is the addition of diluent, the variation of the rotational dependence of the rotational relaxation rate, and simulating earlier codes by using a very high rotational rate. The effect of varying the vibrational rate and the fraction of NF_3 which is dissociated will be studied. Finally we will examine the effects of varying the temperature and the total pressure of the $\text{NF}_3 + \text{H}_2$ mixture.

9.1 Variation of Rotational Relaxation Rate

Because there was very little experimental data available on the rotational relaxation rate, the first parameter to be varied was the rotational relaxation rate. An upper limit on the rotational relaxation rate is furnished by the experimental values of HF self-broadening. This is a soft upper limit in the sense that other collision partners may be more or less efficient than HF in causing line broadening. The code assumed that all molecules were equally effective at line broadening and used the experimental rate

for HF self-broadening, which is roughly ten times gas kinetic collision frequency. For the nominal case (Fig. 8.1) the rotational relaxation rate was set at $1/2$ the linewidth, i.e. 5 times gas kinetic.

Figures 9.1 to 9.4 show waveforms for a sequence of increasing rotational relaxation rates with other variables held constant. In Fig. 9.1 the rotational relaxation rate is only one-half of gas kinetic and the output is largely a number of spikes. This is similar to the output of the unstable laser (Fig. 6.4a). In Fig. 9.1 the line broadening rate is half the nominal value, namely, $5\times$ gas kinetic. The spiking is due to the low relaxation and line broadening rates.

Figure 9.2 shows the waveforms with the rotational relaxation rate set at $2\times$ gas kinetic. In this figure, and the following ones, the linewidth is set at the nominal value, $10\times$ gas kinetic. Although there are still many spikes, the waveforms of Fig. 9.2 are much smoother than those of Fig. 9.1, indicating greater damping of the relaxation oscillations. The damping is partly due to the increased linewidth and partly due to an increased effective pumping rate. The chemical pumping rate into a single state does not appear to be large enough to insure stability, but the higher effective pumping rate due to rotational relaxation from adjacent states leads to stability. Comparing these waveforms to the experimental (Fig. 3.2) we see that the duration of the calculated waveforms is too long. If we examine the cascades in Fig. 9.2

we see that all of the waveforms are similar, and we do not see the discontinuities caused by J-shifting as in the nominal case. Cascades appear to dominate over rotational relaxation at this relatively low rotational relaxation rate. The total energy has increased from 1.4 mJ/cm^2 in Fig. 9.1 to 1.7 mJ/cm^2 in Fig. 9.2. Figure 9.3 shows the waveforms for a rotational relaxation rate of 5x gas kinetic. This is identical to the nominal case except that the dissociation is 1% rather than 1.25%. Except for a reduced height the waveforms are nearly identical to the nominal case. (A calculation was done with the rotational rate 4x gas kinetic. The only significant difference from the 5x case was about 100 nsec. delay in J-shifting.) The nominal case has already been discussed in considerable detail, so no further comment is necessary here, except to note that the total energy has increased to 1.9 mJ/cm^2 .

Figure 9.4 shows waveforms when the rotational relaxation is set equal to the linewidth, i.e. 10x gas kinetic. The duration of most of the pulses is shorter and the energy is slightly greater. In some respects the 10x gas kinetic rotational case agrees better with experiment than the nominal case. The V3-2 and V2-1 transitions turn on at about the same time, the V2-1 P5 is more nearly the right width and the V2-1 P3 is a single spike. In other respects the agreement is worse. The P3 and P4 pulsewidths are too narrow and the interval between turn-on of the V2-1 and V1-0 transitions is too short. In most other respects the 5x and 10x waveforms are similar.

The case with rotational rate $5\times$ gas kinetic was chosen as nominal partly because it was felt that there should be significantly more phase-changing collisions than collisions which actually changed the quantum number. This may not be a correct assumption.

The total energy is seen to increase with increasing rotational relaxation rate. This is plotted in Fig. 9.5. This effect is exaggerated partly due to terminating the calculation at 2 microseconds, cutting off 20 to 30% of the total energy. When the calculation was extended to 5 microseconds (at 1.25% dissociation) the energies were 2.92 and 3.04 mJ/cm² at 2 and 5 times gas kinetic. Two mechanisms can contribute to the increased energy. First, the populations on the stronger transitions are five to ten times the threshold inversion, and are nearer threshold on the weaker transitions. As a result, a small but significant fraction of the population is used in maintaining threshold inversions (in addition to the fraction of the populations in the ground state). With higher rotational relaxation rates fewer transitions lase so fewer threshold inversions must be maintained. Second, and perhaps more important, at lower rotational relaxation rates the higher J states have larger populations. These transitions may lase for a short time then be unable to sustain threshold inversion and turn off. In that case a large fraction of the population is found in states which don't contribute to the lasing. As the rotational relaxation rate is increased this fraction of the

population finds its way to the lasing transitions and adds to the power output.

9.2 Addition of Diluent

Experimentally it was found that adding diluent to the $\text{NF}_3\text{-H}_2$ mixture decreased the energy by a few percent when the diluent was about 50% of the total mix. However, when the diluent was helium or NO the laser energy increased under certain conditions (Pearson, et al., 1973a). The experimental results with helium as a diluent are shown in Fig. 9.6. The increase may occur because the diluent affects the efficiency of the discharge in yielding F atoms; or it may occur because the diluent keeps the temperature lower. The fact that increasing rotational relaxation rates gave larger energy suggested that the increased energy with added diluent might be due to an increased rotational relaxation rate.

To test this, calculations were performed simulating the addition of helium. Adding helium increased the rotational and vibrational relaxation rates plus the linewidth. The results are shown as solid circles and triangles in Fig. 9.5 for helium partial pressures of 5, 15 and 45 Torr, with the $\text{NF}_3 + \text{H}_2$ total pressure held constant at 15 Torr. No rise in output energy with increased helium was found; instead the energy was found to drop a few percent. The drop is due to the increased threshold inversion resulting from the increased

linewidth. The increased vibrational rate was not sufficient to cause the energy drop since helium is many orders of magnitude less efficient than HF in producing vibrational relaxation.

The calculated results are in agreement with experiments using Ar, N₂, and Kr, but not with experiments using helium or NO. It appears that the addition of helium increases the efficiency of the discharge in producing F atoms. The temperature change should not produce the increase because the temperature change should be about the same for all of these diluents.

The calculated waveforms with added helium are shown in Figs. 9.7 and 9.8. There were no experimental waveforms to compare with the calculated waveforms.

Two trends are clear in the calculated waveforms. The waveforms are smoother, and with higher diluent the spikes are higher and the pulses narrower. (Note that the power scale is twice as large in Fig. 9.8.) The higher spikes are due mainly to the increased rotational rate. The narrower pulse-widths correlate with higher powers to keep the total energy about the same. Laser powers are limited by the pumping rate and increased rotational relaxation rates mean faster pumping from the entire vibrational level into a single state. The smoother pulses are a result of the increased linewidth and increased pumping rate, because both damp the relaxation oscillations.

The diluent also weakens or prevents oscillation on P3 and P7. The increased linewidth raises the threshold inversion, and the increased rotational relaxation depletes these populations. The combined result concentrates the lasing in P4 through P6. In general, higher rotational relaxation rates tend to concentrate the lasing in a few transitions.

9.3 Calculation to Approximate Rotational Equilibrium

Earlier models of the HF chemical laser have assumed rotational equilibrium within each vibrational level. This is equivalent to an infinite rotational relaxation rate, except that experimental linewidths are used to calculate the gain. (Physically, the collision broadened linewidth is proportional to the rotational relaxation rate because any collision causing rotational relaxation will destroy the phase coherence of that molecule.) To approximate the infinite rotational relaxation rate a calculation was done with the rotational relaxation rate 200 times gas kinetic, or 40 times the nominal value. The linewidth was left at its nominal value to simulate earlier models. A larger rotational rate would have been desirable, but computation time is roughly proportional to the rotational relaxation rate, so the factor, 200 times gas kinetic, was chosen to keep the computation time reasonable.

Models which assume rotational equilibrium allow only one transition at a time to lase between any two vibrational levels. The transition with the highest gain lases and others lack sufficient gain to lase. As populations

change the lasing can switch instantaneously to another transition. The calculated waveforms, Fig. 9.9, show approximately this behavior. There is some overlap in waveforms but there is a distinct tendency for only one transition at a time to lase between each pair of vibrational levels. In addition, cascade behavior seems to be totally missing, and lasing at high J was suppressed. The total energy is greater than earlier case because of the increased rotational relaxation rate. The total energy is 2.67 mJ/cm^2 in 2 microseconds as compared to the nominal value of 2.40 mJ/cm^2 at 5 times the gas kinetic collision frequency.

This calculation shows that the IXION code, in the limit of infinite rotational relaxation rate, will give the same results as earlier models, except for differences due to using semi-classical laser equations rather than a steady-state approximation.

9.4 Modification of the Rotational Relaxation Rate as a Function of Rotational State

The variation of the rotational rate, as used in the IXION code, was obtained by extrapolating from related experimental data, enlightened by a simple theory. The experimental data consisted of Polanyi and Woodall's work (1972a) on rotational relaxation of HCl, and HF self-broadening data (Meredith, 1972) which gives an upper limit on the rotational relaxation rate. A calculation was performed to test the sensitivity of the model to the assumptions.

To test the assumptions the rotational relaxation rate was set equal to 5 times gas kinetic for all rotational states. The collision broadened linewidths were also set equal at a value corresponding to 10 times the gas kinetic collision rate. This is not in agreement with the experimental self-broadening data, but does test the sensitivity of the model.

The calculated waveforms, shown in Fig. 9.10, differ significantly from the nominal case of Fig. 8.1. The P6 and higher waveforms are entirely missing in fig. 9.10, as is the V3-2 P5 waveform. This is partly due to the higher rotational relaxation rate at high J, and partly due to the higher threshold inversion at high J caused by the increased linewidth. Examination of the time history of the inversions shows that those transitions which did not lase did not reach threshold. Some of them would have reached threshold if the populations had not been clamped by lasing on the P3 through P5 transitions. Also they might have reached threshold if the threshold inversion had decreased with increasing J as in the nominal case.

If some respects Fig. 9.10 compares well with the waveforms at very high rotational rate (Fig. 9.9). This is not surprising because setting all rotational rates equal to the maximum greatly increases the effective rotational relaxation rate. The differences between the two sets of waveforms arise mainly from the different threshold inversions. The similarities arise out of the increased rotational relaxation rate.

The total energy with equal rotational relaxation rates is 2.56 mJ/cm^2 , a few percent higher than in the nominal case (Fig. 8.1) which had a total energy of 2.40 mJ at 2 microseconds. This is consistent with the increased effective rotational relaxation rate.

The waveforms based on the nominal model agree better with experiment than do those of Fig. 9.10. This indicates that the nominal case is a better description of experimental reality. Unfortunately, the high J waveforms were not measured experimentally. The sensitivity wasn't high enough to show that high-J transitions didn't lase weakly, as calculated. Other experiments (Pummer and Kompa, 1972) show that high J transitions do lase under some conditions. Experiments could be performed under conditions which were more sensitive to the assumptions in the model regarding the J-dependence of the rotational relaxation rate.

9.5 Vibrational Relaxation Rate

The anomalously high vibrational relaxation rate of HF has frequently been blamed for the low output of HF chemically pumped lasers. For the pulsed laser considered here, vibrational relaxation was expected to be unimportant compared to depletion of the fluorine atoms. This would not be true of a laser based on a chain reaction, and might not be true of a laser where the dissociation was fairly slow.

To verify that the vibrational relaxation rate was unimportant in the present case a number of runs were made at multiples of the nominal vibrational relaxation rate. The effect on the energy is shown in Fig. 9.11. A rate 20 times the nominal rate resulted in only a 20% drop in energy. One calculation was performed with all rates nominal except that the vibrational relaxation rate for H_2 was 100 times nominal. This results in approximately the same overall relaxation rate as multiplying the nominal rate by 9. This calculation is represented by an x in Fig. 9.11, and falls very close to the line connecting other values. In addition, some calculations were performed with the vibrational relaxation rates for H_2 and NF_3 erroneously set equal to the rate for HF. This is roughly equivalent to a multiplier of 110. A dissociation of 5% was required to obtain a total pulse energy of about 2 mJ/cm^2 . This is a reasonable extrapolation from Fig. 9.11.

The waveforms for the case with vibrational relaxation 20 times the nominal rate are shown in Fig. 9.12. The only major difference between those and the waveforms for the nominal case (Fig. 8.1) is a slightly reduced amplitude and a slightly faster decay in intensity.

The calculations presented here show that vibrational relaxation is not an important factor for the conditions studied. It seems unreasonable to think that the vibrational relaxation rate is more than 20 times the nominal value,

since the nominal value corresponds to vibrational relaxation every 50 collisions with HF. The nominal rate for H_2 may be low, but probably not more than the factor of 100 used in the calculation. The output is even less sensitive to the NF_3 rate, because it is so small.

In summary, the calculations were not very sensitive to vibrational relaxation rates within a physically reasonable range. Under other conditions, e.g. chain reaction, the laser could be quite sensitive to the vibrational relaxation rate.

9.6 Fraction of NF_3 Dissociated

At various times calculations were performed with the number of F atoms ranging from 1% to 10% of the NF_3 present. The total output energy was a linear function of the F atom concentration over this range. This is to be expected from the simple analytical models. The calculation used simplified model of the chemistry which neglected consumption of hydrogen and recombination of F atoms. Analysis of the rates shows that F atom recombination should not be significant under the conditions which were considered. Consumption of H_2 would introduce some non-linearity for higher percentages of F atom, but should not be significant at the nominal value, 1.25% dissociation.

9.7 Variation of Laser Output with Temperature

Calculations were done at constant temperatures from 200 to 700 K, with the pressure held constant at 15 Torr.

The total laser energy is shown as a function of temperature in Fig. 9.13. The energies at 200 and 300 K were based on calculations for a 5 microsecond scale, in order to include the entire pulse energy. At higher temperature the pulse is essentially complete by 2 microseconds, which was the scale for the calculations. The two time scales should introduce little error. The decrease in energy with increasing temperature is mainly due to the decreasing density (molecules/cm³) as we increase the temperature at constant pressure. If the density is held constant as the temperature is increased to 700 K the pressure is about 36 Torr. A calculation was done at 36 Torr and 700 K; the total laser energy for this case is shown as a triangle in Fig. 9.13. The energy at 36 Torr and 700 K is about 15% smaller than that at 300 K due to the HF being distributed over more rotational states.

The waveforms calculated for 15 Torr at 700 K are shown in Fig. 9.14. The amplitudes are much smaller than at 300 K because of the reduced density. The pulse widths are comparable because the reduced density is compensated by the increased rate constants. It is fortuitous that the two effects tend to cancel, because the rate constant could have a different temperature dependence.

The waveforms calculated for 36 Torr at 700 K are shown in Fig. 9.15. This case has the same number density as 15 Torr at 300 K. The amplitudes at 700 K are about double those at 300 K and the pulsewidths are about a half, so that

the total energies are nearly the same. This is due to the increased reaction rates. The lasing is shifted towards higher J at 700 K. This is expected because the population distributions are similarly shifted towards higher J at 700 K.

The principal effect of raising the temperature is to decrease the pulsewidth and increase the amplitude, provided the density is unchanged. The energy is decreased slightly because the molecules are distributed over more states. In addition there is the weakening or disappearance of P3 and P4 transitions and the strengthening of P7 and P8 transitions.

9.8 Total Output Energy as a Function of Total Pressure

In Section 3 we noted that experimentally the total laser energy did not increase linearly with increasing total pressure. In Section 4.4 we discussed possible mechanisms for this, based on an approximate analytic model. We were able to postulate phenomena that would cause non-linear output with pressure, but only at much higher pressures than were used in the experiments.

These mechanisms were not included in the IXION code, so total calculated laser output energy was expected to increase linearly with pressure. Never-the-less, calculations were done at total pressures from 1 to 310 Torr to see if there were any unexpected effects. In addition, there were experimental waveforms at 60 Torr (Fig. 3.4) to be compared with calculated waveforms.

The calculations showed, as expected, that total output energy was roughly proportional to pressure. The results are plotted in Fig. 9.16. At low pressures the total energy is less than the linear prediction because a larger fraction of the molecules is used to maintain a threshold inversion.

The experimental point at 60 Torr is less than half the calculated energy at 62 Torr. This indicates that the non-linear variation of energy with pressure is not due to laser dynamics. To simulate reduced dissociation efficiency the calculation was repeated assuming a dissociation of 0.6%. This gave better agreement with experiment as shown in Fig. 9.17. There is reasonably good agreement with experiment, but not as good as at 15 Torr. In particular, pulsewidths seem too long and the calculated intensities on P7 are too low.

In an attempt to get better agreement with experiment the calculation was repeated with the temperature increased to 400 K. (For constant density the pressure was 77.5 Torr.) The pulsewidth was shortened significantly and the P7 transitions compare better as seen in Fig. 9.18. The calculated P3 transitions were deleted from Fig. 9.18 because they were too weak to be seen at this scale. In spite of the better agreement with experiment the calculated J-shifting seems to occur later than the experimental.

The fact that the P3 transitions were observed experimentally tends to indicate low temperature but the

short pulse and early J-shifting seem to indicate a high temperature. A reasonable explanation for this would be a rapidly rising temperature, increasing a few hundred degrees by the end of the pulse. Estimating the appropriate temperature rise requires a detailed knowledge of the discharge physics which is beyond the scope of this work. It also appears that it would be very difficult to measure experimentally.

The differences between low and high pressure waveforms are surprisingly small, as seen by comparing Fig. 9.19 (1 Torr) with Fig. 9.20 (310 Torr). The apparently narrower pulsewidth at 300 Torr is deceptive, since the scale at 300 Torr is 1/100 of that at 1 Torr. The 300 Torr pulse is actually wider, relative to chemical reaction rates. This is largely due to the fact that the discharge is still creating new F atoms near the end of the pulse. In fact, the sinusoidal shape of the discharge current waveform can be seen near the end of the 310 Torr pulse. Experimental waveforms at these pressures were not available to compare with calculations.

Fig. 9.1 Waveforms at 15 Torr when the rotational relaxation rate is $1/2$ gas kinetic and linebroadening cross section is $5 \times$ gas kinetic. One-percent of the NF_3 is dissociated, total laser energy is 1.42 mJ/cm^2 .

Fig. 9.2 Waveforms at 15 Torr when rotational relaxation rate is 2X gas kinetic and linebroadening is 10X gas kinetic. Dissociation is 1%, total laser energy is 1.71 mJ/cm^2 .

Fig. 9.3 Waveforms at 15 Torr when rotational relaxation rate is 5X gas kinetic and linebroadening 10X gas kinetic. Dissociation is 1%, total energy is 1.89 mJ/cm^2 .

Fig. 9.4 Waveforms at 15 Torr when rotational relaxation rate and linebroadening are 10X gas kinetic. Dissociation is 1%, total energy is 1.98 mJ/cm^2 .

Fig. 9.5 Variation of calculated output energy vs. rotational relaxation rate normalized to gas kinetic. Numbered points indicate partial pressure (Torr) of helium.

Fig. 9.6 Laser energy versus percent He for $\text{NF}_3/\text{H}_2 \approx 5$, discharge time equals 8 ns, and reactant pressure ($P_{\text{NF}_3} + P_{\text{H}_2}$) equals (a) 30 torr; (b) 60 torr; and (c) 80 torr.

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Fig. 9.7 Waveforms at 15 Torr when 15 Torr of helium is added. Rotational relaxation rate is 5X gas kinetic, dissociation is 1.25%, total energy is 2.40 mJ/cm^2 , the same as the case without helium.

Fig. 9.8 Waveforms at 15 Torr with 45 Torr of helium added. Total output energy, 2.23 mJ/cm^2 , is somewhat less than the nominal case.

Fig. 9.9 Waveforms at 15 Torr when rotational relaxation rate is 200X gas kinetic to approximate the assumption of rotational equilibrium. Dissociation is 1.25%, total energy is 2.67 mJ/cm^2 .

Fig. 9.10 Waveforms at 15 Torr assuming rotational relaxation rate is 5X gas kinetic for all rotational states, independent of J. Dissociation is 1.25%, total energy is 2.56 mJ/cm^2 .

Fig. 9.11. Variation of laser output energy as a function of the vibrational relaxation rate. The point (x) represents the case where the vibrational rate for H_2 was 100 times nominal, but other rates were nominal. The equivalent multiplier is about 9.

Fig. 9.12 Waveforms at 15 Torr when vibrational relaxation rate is 20X the nominal value. Other parameters have nominal values as in Fig. 8.1. Total energy is 2.0 mJ/cm^2 .

Fig. 9.13 Total laser output energy at 15 Torr as a function of temperature. The dashed line is the proportional to the density of an ideal gas at 15 Torr pressure. The point marked 36 Torr at 700 K has the same density as the point with 15 Torr at 300 K.

Fig. 9.14 Waveforms at 15 Torr when temperature is 700 K. Other parameters have nominal values. Total energy is reduced to 0.84 mJ/cm^2 , mainly because of reduced density.

Fig. 9.15 Waveforms at 36 Torr and 700 K,¹ which has the same density as 15 Torr at 300 K. Energy is 2.33 mJ/cm². Time scale is shortened by increased rate constants.

Fig. 9.16 Calculated total laser output energy as a function of total pressure for a ratio $\text{NF}_3/\text{H}_2 = 5.2$. Dissociation is 1.25% at 300 K. The straight line is a linear fit at high pressure.

Fig. 9.17 Calculated waveforms at 62 Torr when dissociation is 0.6% at 300 K. Total energy is 4.5 mJ/cm^2 .

Fig. 9.18 Calculated waveforms at 400 K and 77.5 Torr (same density as 300 K, 58 Torr), with 0.6% dissociation. Total energy was 5.0 mJ/cm^2 . Laser intensity on P3 transitions was infinitesimal.

Fig. 9.19 Calculated waveforms at 1 Torr and 300 K.
Dissociation is 1.25%, total energy is 0.15 mJ/cm^2 .

Fig. 9.20 Calculated waveforms at 310 Torr and 300 K.
Dissociation is 1.25%, total energy is 64.3 mJ/cm^2 .

10. CONCLUSION

The discussion of the pulsed HF chemical laser has included two broad topics: modeling of the chemical kinetics and modeling of the laser action with rotational relaxation effects included.

The chemical kinetics accompanied by a steady state laser model was sufficient to determine the total laser waveform. With a steady state laser model the output power is proportional to the rate of formation of HF, so calculation of the laser waveform is reduced to a kinetics calculation. With simplifying assumptions, including constant temperature, a simple analytic model can calculate the rate of formation of HF. This can be done for the reaction $F + H_2 \rightarrow HF + H$ and for the chain reaction of $H_2 + F_2$. To obtain exact solutions of the kinetics, including temperature variation, the MINOTAR computer code was developed. A severe computational problem, the solution of "stiff" differential equations, was overcome by using a numerical technique developed by C. W. Gear (1971a). The exact numerical calculations verify the results of the analytic model under conditions where the temperature change is small. The MINOTAR code is also a useful tool for investigating more complicated kinetics problems such as those involved in combustion and air pollution.

In order to calculate the waveforms of individual P-branch transitions a better laser model was needed. The model treated each vibrational-rotational state separately

with adjacent rotational states coupled by rotational relaxation. In addition the model used semi-classical laser equations so that transient effects in the laser waveforms could be correctly calculated. Earlier models (Chester, 1970; Emanuel, 1971) assumed rotational equilibrium within each vibrational level and used a steady state laser model. The assumption of rotational equilibrium causes these models to calculate a single P-branch transition lasing between two vibrational levels at any instant. The rotational levels must be partially de-coupled in order to calculate simultaneous lasing on several transitions, in agreement with experiment. The steady-state laser model ignores spiking behavior in the laser waveforms and grossly underestimates the time delay to the beginning of the laser pulse. The new model, incorporated in the IXION code, gives good agreement with experiment. Simultaneous lasing on several P-branch transitions is seen and individual calculated P-branch waveforms are quite similar to experimental waveforms. The calculated waveforms show spiking which explains the jagged nature of the experimental waveforms. The calculated time delays and pulse durations are approximately the same as those seen experimentally. Because the calculations agree with experiment they can be used to help interpret experiment. In particular, the time histories of the populations and inversions are readily available from the calculations but would be difficult to obtain experimentally.

The new model showed that our knowledge of the rotational relaxation rates is inadequate. Recent experimental data (Peterson, 1974) indicates that collisional line broadening in HF may be entirely due to rotational relaxation, so that it may be possible to determine rotational relaxation rates from line broadening experiments. These rates are an order of magnitude faster than rotational relaxation rates inferred from ultrasonic measurements. No serious attempt has yet been made to resolve this discrepancy.

Because of the limited experimental data available for rotational relaxation rates an attempt was made to calculate the rates. This is presented in Appendix D. The physical model appears to be qualitatively correct but the quantitative results are not adequate. This deserves further examination and comparison with line broadening theories which give quantitatively correct results.

The new model has not been applied to the $H_2 + F_2$ chain reaction laser. One would expect the model to show simultaneous lasing on several transitions, and spiking behavior in laser waveforms similar to that seen in the $F + H_2$ laser. However, one would expect differences because the longer pulse would make vibrational relaxation important and would cause the rotational distributions to be nearer to a Boltzmann equilibrium.

It would be desirable to compare these calculations with an experiment which didn't involve the uncertainties of electric discharge physics. The ideal experiment would be

one where F atoms were produced by photodissociation with a short laser pulse. Photodissociation by a flashlamp would be slower than the chemical reaction except at very low pressures; and the laser waveform would be nearly the same as the flashlamp waveform. In a properly designed experiment the initial density of F atoms could be determined and the active volume accurately known. There would probably be some discrepancies between the results of such experiments and calculations. Attempts to eliminate the discrepancies should lead to further insight into the physics of the laser.

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Appendix A — Vibrational-Rotational Spectrum of Hydrogen Fluoride

The following tables give the calculated spectrum of HF. The calculation is based on a Dunham expansion using co-efficients from Mann, et al. (1961). These accurate co-efficients are obtained by a curve fit to extensive experimental data. The values of the co-efficients are given in Table A1, along with the equivalent symbol in Herzberg's notation (1950). (There is a minor correction to get from Dunham co-efficients to Herzberg's.) Table A2 gives HF vibrational rotational term values up to $v = 9$ and $J = 19$. Table A3 gives the vacuum wavelength and wavenumber of the P and R branches of importance of the HF laser. These are accurate to about 0.1 cm^{-1} .

Table A1 — Dunham co-efficients used to calculate the spectrum of HF. They are equivalent, with a small correction, to the symbols used by Herzberg.

Symbol		Value
Dunham	Herzberg	
Y_{00}	T_e	0.0
Y_{10}	$-\omega_e$	4138.73
Y_{20}	$-\omega_e x_e$	-90.05
Y_{30}	$\omega_e y_e$	0.932
Y_{40}	$-\omega_e z_e$	-0.0142
Y_{50}	-	-0.00059
Y_{01}	B_e	20.9555
Y_{11}	$-\alpha_e$	-0.7958
Y_{21}	γ_e	0.01182
Y_{31}	-	-0.000311
Y_{41}	-	-0.0000058
Y_{02}	$-D_e$	-0.002153
Y_{12}	β_e	0.0000623
Y_{22}	-	-0.00000206
Y_{03}	H_e	1.68×10^{-7}
Y_{13}	-	-6.5×10^{-9}
Y_{04}	-	-1.9×10^{-11}

Table A6 - Vibrational-Rotational Term values (cm^{-1})
for Hydrogen Fluoride

HYDROGEN FLUORIDE VIBRATIONAL-ROTATIONAL TERMS (cm^{-1})					
J	V= 0	V= 1	V= 2	V= 3	V= 4
19	9562.14	13237.95	16748.85	20098.76	23291.13
18	8836.75	12540.45	16078.56	19455.11	22672.57
17	8144.31	11874.56	15438.57	18840.45	22083.75
16	7485.62	11241.07	14829.66	18255.57	21522.43
15	6861.46	10640.74	14252.56	17701.19	20990.31
14	6272.57	10074.29	13707.99	17177.99	20488.05
13	5719.65	9542.40	13196.60	16686.63	20016.31
12	5207.37	9045.73	12719.04	16227.72	19575.67
11	4724.35	8584.87	12275.87	15801.84	19166.71
10	4283.16	8160.39	11867.67	15409.52	18789.94
9	3880.34	7772.80	11494.92	15051.26	18445.86
8	3516.38	7422.60	11158.10	14727.51	18134.90
7	3191.73	7110.20	10857.63	14438.68	17857.46
6	2906.78	6835.99	10593.89	14185.15	17613.91
5	2661.88	6600.32	10367.22	13967.22	17404.56
4	2457.33	6403.47	10177.86	13785.19	17229.69
3	2293.39	6245.70	10026.09	13639.29	17089.51
2	2170.25	6127.20	9912.10	13529.74	16984.22
1	2088.08	6048.12	9836.02	13456.55	16913.95
0	2046.97	6008.55	9797.96	13419.96	16878.79

HYDROGEN FLUORIDE VIBRATIONAL-ROTATIONAL TERMS (cm^{-1})					
J	V= 5	V= 6	V= 7	V= 8	V= 9
19	26328.61	29213.25	31946.29	34528.12	36958.18
18	25736.75	28646.78	31405.00	34011.89	36467.04
17	25171.38	28105.54	30887.68	33518.39	35997.34
16	24633.23	27590.26	30395.05	33048.31	35549.79
15	24122.99	27101.61	29927.79	32602.31	35125.04
14	23641.32	26640.24	29486.52	32181.03	34723.72
13	23188.84	26206.77	29071.86	31785.06	34346.42
12	22766.16	25801.78	28684.38	31414.97	33993.69
11	22373.81	25425.81	28324.60	31071.28	33666.05
10	22012.32	25079.36	27993.03	30754.49	33363.99
9	21682.15	24762.89	27690.12	30465.03	33087.95
8	21383.74	24476.85	27416.29	30203.33	32838.34
7	21117.48	24221.60	27171.92	29969.76	32615.53
6	20883.73	23997.49	26957.35	29764.64	32419.84
5	20682.79	23804.83	26772.87	29588.28	32251.56
4	20514.93	23643.89	26618.75	29440.92	32110.95
3	20380.38	23514.86	26495.19	29322.79	31998.21
2	20279.31	23417.94	26402.37	29234.03	31913.51
1	20211.85	23353.25	26340.42	29174.79	31856.97
0	20178.10	23320.89	26309.42	29145.15	31828.68

Table A3 - P and R Branch Transitions in Hydrogen Fluoride

HYDROGEN FLUORIDE SPECTRUM FOR VIBRATIONAL-ROTATIONAL TRANSITIONS FROM $v=1$ TO $v=0$					
	P BRANCH WAVE NUMBER (/CM)	VACUUM WAVELENGTH (MICRONS)		R BRANCH WAVE NUMBER (/CM)	VACUUM WAVELENGTH (MICRONS)
P(1)	3920.47	2.55071	R(0)	4001.15	2.49928
P(2)	3877.86	2.57874	R(1)	4039.12	2.47579
P(3)	3833.81	2.60837	R(2)	4075.45	2.45372
P(4)	3788.37	2.63966	R(3)	4110.08	2.43304
P(5)	3741.60	2.67266	R(4)	4142.99	2.41372
			R(5)	4174.11	2.39572
P(6)	3693.54	2.70743	R(6)	4203.42	2.37902
P(7)	3644.26	2.74404	R(7)	4230.87	2.36358
P(8)	3593.81	2.78256	R(8)	4256.42	2.34939
P(9)	3542.25	2.82306	R(9)	4280.85	2.33642
P(10)	3489.64	2.86562	R(10)	4301.71	2.32466
P(11)	3436.04	2.91033	R(11)	4321.38	2.31408
P(12)	3381.50	2.95727	R(12)	4339.03	2.30466
P(13)	3326.08	3.00655	R(13)	4354.63	2.29640
P(14)	3269.83	3.05826	R(14)	4368.17	2.28929
P(15)	3212.03	3.11252	R(15)	4379.61	2.28331
P(16)	3155.12	3.16946	R(16)	4388.94	2.27846
P(17)	3097.76	3.22919	R(17)	4396.14	2.27472
P(18)	3037.80	3.29185	R(18)	4401.23	2.27211
P(19)	2978.31	3.35761	R(19)	4404.10	2.27061
P(20)	2918.34	3.42661	R(20)	4404.83	2.27024

HYDROGEN FLUORIDE SPECTRUM FOR VIBRATIONAL-ROTATIONAL TRANSITIONS FROM $v=2$ TO $v=1$					
	P BRANCH WAVE NUMBER (/CM)	VACUUM WAVELENGTH (MICRONS)		R BRANCH WAVE NUMBER (/CM)	VACUUM WAVELENGTH (MICRONS)
P(1)	3749.84	2.66678	R(0)	3827.47	2.61269
P(2)	3708.72	2.69627	R(1)	3863.98	2.58800
P(3)	3666.40	2.72747	R(2)	3898.89	2.56483
P(4)	3622.62	2.76044	R(3)	3932.15	2.54314
P(5)	3577.54	2.79522	R(4)	3963.73	2.52288
			R(5)	3993.57	2.50402
P(6)	3531.21	2.83189	R(6)	4021.64	2.48655
P(7)	3483.69	2.87052	R(7)	4047.91	2.47041
P(8)	3435.04	2.91118	R(8)	4072.32	2.45560
P(9)	3385.30	2.95395	R(9)	4094.86	2.44208
P(10)	3334.53	2.99892	R(10)	4115.49	2.42985
P(11)	3282.80	3.04618	R(11)	4134.17	2.41887
P(12)	3230.15	3.09584	R(12)	4150.88	2.40913
P(13)	3176.63	3.14799	R(13)	4165.59	2.40062
P(14)	3122.32	3.20275	R(14)	4178.28	2.39333
P(15)	3067.26	3.26024	R(15)	4188.92	2.38725
P(16)	3011.50	3.32061	R(16)	4197.50	2.38237
P(17)	2955.10	3.38398	R(17)	4204.00	2.37869
P(18)	2898.12	3.45051	R(18)	4208.40	2.37620
P(19)	2840.61	3.52037	R(19)	4210.69	2.37491
P(20)	2782.62	3.59374	R(20)	4210.85	2.37482

HYDROGEN FLUORIDE SPECTRUM FOR VIBRATIONAL-ROTATIONAL
TRANSITIONS FROM $V=3$ TO $V=2$

	P BRANCH WAVE NUMBER (1/CM)	VACUUM WAVELENGTH (MICRONS)		R BRANCH WAVE NUMBER (1/CM)	VACUUM WAVELENGTH (MICRONS)
P(1)	3583.94	2.79023	R(0)	3658.59	2.73329
P(2)	3544.46	2.82131	R(1)	3693.67	2.70733
P(3)	3503.60	2.85420	R(2)	3727.19	2.68299
P(4)	3461.43	2.88898	R(3)	3759.10	2.66021
P(5)	3417.99	2.92569	R(4)	3789.37	2.63896
			R(5)	3817.95	2.61921
P(6)	3373.34	2.96442	R(6)	3844.79	2.60052
P(7)	3327.51	3.00525	R(7)	3869.88	2.58406
P(8)	3280.58	3.04824	R(8)	3893.16	2.56861
P(9)	3232.59	3.09350	R(9)	3914.60	2.55454
P(10)	3183.59	3.14110	R(10)	3934.17	2.54183
P(11)	3133.65	3.19117	R(11)	3951.85	2.53046
P(12)	3082.80	3.24380	R(12)	3967.59	2.52042
P(13)	3031.12	3.29911	R(13)	3981.39	2.51169
P(14)	2978.64	3.35724	R(14)	3993.20	2.50426
P(15)	2925.43	3.41830	R(15)	4003.01	2.49812
P(16)	2871.53	3.48246	R(16)	4010.80	2.49327
P(17)	2817.00	3.54987	R(17)	4016.54	2.48970
P(18)	2761.90	3.62070	R(18)	4020.23	2.48742
P(19)	2706.26	3.69514	R(19)	4021.84	2.48643
P(20)	2650.15	3.77338	R(20)	4021.35	2.48672

HYDROGEN FLUORIDE SPECTRUM FOR VIBRATIONAL-ROTATIONAL
TRANSITIONS FROM $V=4$ TO $V=3$

	P BRANCH WAVE NUMBER (1/CM)	VACUUM WAVELENGTH (MICRONS)		R BRANCH WAVE NUMBER (1/CM)	VACUUM WAVELENGTH (MICRONS)
P(1)	3422.23	2.92207	R(0)	3493.99	2.86206
P(2)	3384.25	2.95486	R(1)	3527.66	2.83474
P(3)	3344.93	2.98960	R(2)	3559.81	2.80913
P(4)	3304.32	3.02634	R(3)	3590.40	2.78521
P(5)	3262.46	3.06517	R(4)	3619.37	2.76291
			R(5)	3646.69	2.74222
P(6)	3219.41	3.10616	R(6)	3672.31	2.72308
P(7)	3175.23	3.14938	R(7)	3696.21	2.70547
P(8)	3129.95	3.19494	R(8)	3718.35	2.68937
P(9)	3083.64	3.24293	R(9)	3738.68	2.67474
P(10)	3036.34	3.29344	R(10)	3757.19	2.66157
P(11)	2988.10	3.34661	R(11)	3773.83	2.64983
P(12)	2938.99	3.40253	R(12)	3788.58	2.63951
P(13)	2889.04	3.46136	R(13)	3801.42	2.63060
P(14)	2838.31	3.52322	R(14)	3812.31	2.62308
P(15)	2786.86	3.58826	R(15)	3821.24	2.61695
P(16)	2734.73	3.65666	R(16)	3828.18	2.61221
P(17)	2681.98	3.72859	R(17)	3833.11	2.60885
P(18)	2628.64	3.80424	R(18)	3836.02	2.60687
P(19)	2574.78	3.88382	R(19)	3836.87	2.60629
P(20)	2520.44	3.96756	R(20)	3835.67	2.60710

HYDROGEN FLUORIDE SPECTRUM FOR VIBRATIONAL-ROTATIONAL
TRANSITIONS FROM $v=5$ TO $v=4$

	P BRANCH WAVE NUMBER (1/CM)	VACUUM WAVELENGTH (MICRONS)		R BRANCH WAVE NUMBER (1/CM)	VACUUM WAVELENGTH (MICRONS)
P(1)	3264.15	3.06358	R(0)	3333.06	3.00084
P(2)	3227.63	3.09825	R(1)	3365.36	2.97145
P(3)	3189.80	3.13588	R(2)	3396.16	2.94450
P(4)	3150.70	3.17390	R(3)	3425.42	2.91935
P(5)	3110.37	3.21505	R(4)	3453.11	2.89594
			R(5)	3479.17	2.87425
P(6)	3073.88	3.25852	R(6)	3503.57	2.85423
P(7)	3026.27	3.30440	R(7)	3526.28	2.83585
P(8)	2982.59	3.35280	R(8)	3547.25	2.81908
P(9)	2937.88	3.40381	R(9)	3566.46	2.80390
P(10)	2892.21	3.45757	R(10)	3583.87	2.79028
P(11)	2845.61	3.51419	R(11)	3599.45	2.77820
P(12)	2798.14	3.57380	R(12)	3613.17	2.76765
P(13)	2749.85	3.63656	R(13)	3625.01	2.75861
P(14)	2700.79	3.70262	R(14)	3634.73	2.75108
P(15)	2651.01	3.77215	R(15)	3642.92	2.74505
P(16)	2600.55	3.84533	R(16)	3648.95	2.74051
P(17)	2549.47	3.92238	R(17)	3653.60	2.73748
P(18)	2497.81	4.00350	R(18)	3655.04	2.73595
P(19)	2445.62	4.08894	R(19)	3655.07	2.73593
P(20)	2392.95	4.17894	R(20)	3653.05	2.73744

HYDROGEN FLUORIDE SPECTRUM FOR VIBRATIONAL-ROTATIONAL
TRANSITIONS FROM $v=6$ TO $v=5$

	P BRANCH WAVE NUMBER (1/CM)	VACUUM WAVELENGTH (MICRONS)		R BRANCH WAVE NUMBER (1/CM)	VACUUM WAVELENGTH (MICRONS)
P(1)	3109.04	3.21643	R(0)	3175.15	3.14945
P(2)	3073.95	3.25315	R(1)	3206.09	3.11906
P(3)	3037.56	3.29211	R(2)	3235.55	3.09066
P(4)	2999.93	3.33341	R(3)	3263.50	3.06419
P(5)	2961.09	3.37713	R(4)	3289.90	3.03961
			R(5)	3314.70	3.01686
P(6)	2921.10	3.42336	R(6)	3337.87	2.99593
P(7)	2880.01	3.47221	R(7)	3359.36	2.97675
P(8)	2837.86	3.52378	R(8)	3379.16	2.95932
P(9)	2794.70	3.57820	R(9)	3397.21	2.94359
P(10)	2750.58	3.63560	R(10)	3413.49	2.92955
P(11)	2705.55	3.69611	R(11)	3427.97	2.91718
P(12)	2659.65	3.75989	R(12)	3440.61	2.90646
P(13)	2612.94	3.82711	R(13)	3451.40	2.89738
P(14)	2565.46	3.89794	R(14)	3460.29	2.88993
P(15)	2517.26	3.97258	R(15)	3467.27	2.88411
P(16)	2468.38	4.05124	R(16)	3472.32	2.87992
P(17)	2418.88	4.13415	R(17)	3475.40	2.87737
P(18)	2368.79	4.22156	R(18)	3476.50	2.87646
P(19)	2318.17	4.31374	R(19)	3475.60	2.87720
P(20)	2267.06	4.41100	R(20)	3472.67	2.87962

Appendix B — The Role of Numerical Stability in the Solution of Chemical Chain Reactions

This paper was presented at the 1971 Summer Computer Simulation Conference, Boston, Massachusetts, July 19-21, 1971, and appears in the proceedings. It attempts to illustrate in a simple manner the need for numerically stable schemes and the advantages.

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Lawrence Radiation Laboratory
UNIVERSITY OF CALIFORNIA
LIVERMORE
94550

**THE ROLE OF NUMERICAL STABILITY IN THE
COMPUTER SOLUTION OF CHEMICAL CHAIN REACTIONS**

John Creighton

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THE ROLE OF NUMERICAL STABILITY IN THE COMPUTER SOLUTION OF CHEMICAL CHAIN REACTIONS*

John Creighton

Lawrence Radiation Laboratory, University of California
Livermore, California

Summary

Chemical chain reactions are reviewed briefly. Numerical stability is defined and illustrated, mainly in pictorial form, and an example shows how considerations of numerical stability limit the maximum step size in systems of "stiff" differential equations such as chemical kinetic rate equations. Two methods that allow large time steps without introducing numerical instability are given.

Introduction

The need to calculate numerical solutions of chemical kinetic rate equations arose in trying to construct a numerical model of a chemical laser. In a fast exothermic chemical reaction, the product molecules may exist for a short time in vibrationally excited states, which can be used, under certain conditions, to create an infrared laser. The first step in calculating the laser output is to solve the chemical kinetic rate equations to obtain the rate of formation of excited product molecules. In doing this we found that numerical stability was crucial to obtaining efficient procedures. Discussions with other groups working on similar problems indicated that the need for numerical stability was common. A brief survey of the literature on detonation indicated that some attempts to solve kinetic rate equations had foundered on the rocks of numerical instability. It appeared, therefore, that our results would be applicable to a broad class of problems.

Although the phenomenon of numerical instability is well known to numerical analysts,¹⁻¹⁵ it does not seem to be familiar to people trained in other disciplines. Therefore, this paper is an attempt to present the subject of numerical stability in a simple manner, with apologies to the expert who is likely to see little that is new. As an aid to understanding, the topic has been developed largely in pictorial terms. More rigorous derivations can be found in the standard references on numerical analysis and in the literature.¹⁻¹⁵

The presentation is divided into four sections: a brief review of chemical chain reactions; the definition and illustration of numerical stability; an example of the need for numerical stability, to obtain large time steps; and suggested techniques for obtaining the required stability.

A Brief Review of Chemical Chain Reactions

An example of a gas phase chemical chain reaction frequently found in textbooks is the

photochemical reaction of hydrogen and bromine.¹⁶ The overall reaction is

If we break the reaction up into steps corresponding to chemically reactive collisions of molecules in a gas, the following steps turn out to be the dominant reactions:

where I_a represents the density of absorbed photons and M is any third body that does not react chemically in a three-body collision. The third body is necessary in recombination reactions, to conserve energy and momentum. The reaction rates (e.g., k_2) depend on the frequency of collision and the probability of reaction during a collision. The principle feature to be noted is the chain formed by Eqs. 3 and 4. Equation 2 produces a bromine atom (Br) that is captured in Reaction 3 but in the process produces a hydrogen atom (H) that in being captured produces a new bromine atom. If Reactions 5 and 6 were not occurring, the reaction would loop continuously through Reactions 3 and 4 until the H_2 or Br_2 were used up. However, Reactions 5 and 6 provide alternative reactions for the hydrogen and bromine atoms, removing them from the chain. In those reactions characterized as chain reactions, the rate of removal by Reactions 5 and 6 is usually relatively small, with the result that for every bromine atom created by absorption of one photon there may be 10^2 to 10^6 HBr molecules formed before the hydrogen and bromine atoms are removed. The ratio of HBr molecules to absorbed photons is called the "chain length."

Work performed under the auspices of the U. S. Atomic Energy Commission.

To calculate the concentrations as a function of time, we must obtain rate equations. Using the example above and letting $[X]$ be the number of molecules of type X per unit volume, we can write the following equations for the rate of change of number density (or concentrations, in an ideal gas mixture):

$$\frac{d[H_2]}{dt} = -k_2[Br][H_2] + k_{-2}[HBr][H] \quad (7)$$

$$\begin{aligned} d[Br_2] &= -k_1[I_2][Br_2] - k_3[H][Br_2] \\ &+ k_4[Br]^2[M] - k_{-4}[Br_2][M] + 1/2 k_5[Br] \quad (8) \end{aligned}$$

$$\begin{aligned} \frac{d[H]}{dt} &= k_2[Br][H_2] - k_{-2}[HBr][H] \\ &- k_3[H][Br_2] \quad (9) \end{aligned}$$

$$\begin{aligned} \frac{d[Br]}{dt} &= 2k_1[I_2][Br_2] - k_2[Br][H_2] \\ &+ k_{-2}[HBr][H] + k_3[H][Br_2] \\ &- 2k_4[Br]^2[M] + 2k_{-4}[Br_2][M] - k_5[Br] \quad (10) \end{aligned}$$

$$\begin{aligned} \frac{d[HBr]}{dt} &= k_2[Br][H_2] - k_{-2}[HBr][H] \\ &+ k_3[Br_2][H]. \quad (11) \end{aligned}$$

In these equations we have assumed that

$$[M] = [H_2] + [H] + [Br_2] + [Br] + [HBr]. \quad (12)$$

These are coupled first-order nonlinear differential equations with the number densities of the various species as variables. If the equations were linear they could be solved by straightforward matrix methods,⁵ but since the terms contain products of two variables this cannot be done. (The often-used steady-state approximation linearizes the equations by holding some concentrations constant, making the equations linear.) Since there is no general method for solving nonlinear differential equations, we must resort to numerical methods.

The obvious advantages of a computer code to solve these equations are that it is usually more economical than an experiment, and it can be used for design of hardware systems. It also reduces the necessity for handling materials that may be dangerous. An important advantage of the numerical solution that may not be obvious is that it can yield a qualitative understanding

of the reaction. It may be very difficult experimentally to measure the concentration of some intermediate species such as $[H]$, but the numerical solution gives this as a matter of course. Examination of a few computer printouts can rapidly indicate which features of the reaction are dominant.

In view of these advantages, computer solution of equations such as 6 through 11 ought to be commonplace, but there are some problems. There are often insufficient data on the chemical kinetic rates (k_1 , etc.),⁶ and the large effect of trace impurities in experiments can cause large discrepancies between calculated and experimental results. However, I wish to concentrate on a third problem: numerical instability.

The Nature of Numerical Stability

Numerical instability is the generation of erroneous solutions to differential equations because of deficiencies in the numerical scheme. The errors are frequently catastrophic in that they generate erroneous numbers approaching infinity. We must also be clear about what is not meant by numerical instability. In particular, it is not a matter of an instability of the system being simulated; we can assume the system to be stable and yet obtain erroneous solutions due to numerical instability. Also, numerical instability is not a programming "bug"; a procedure that is programmed completely without bugs can have numerical instability. Numerical instability is not the round-off error of the computer, or the truncation error of a series expansion, though it is related to these errors. I wish to illustrate this pictorially, give the conditions for numerical stability, and briefly discuss two methods that are numerically stable for large time steps.

Numerical instability is analogous to the instability of an amplifier with feedback. In an unstable numerical method, the truncation and round-off errors constitute "noise" that is amplified by the numerical scheme so that the erroneous output destroys the correct response. The existence of numerical instability depends on the numerical method and the time increment that is used.

When we solve the differential equation $dy/dt = -y$, we get a family of solutions of the form $y = y_0 e^{-t}$, with each curve in the family characterized by a different value of the parameter y_0 . A few of these curves are shown in Fig. 1. Since y_0 is a continuous variable there is, of course, an infinite number of intermediate curves lying between those shown in Fig. 1. When we set y_0 equal to some initial value we select one curve out of the family of solutions as our solution—as we selected the curve for $y_0 = 0.5$, shown in Fig. 1. A numerical solution is shown for comparison.

⁶Note, however, the recent extensive tables of kinetic rate data in Refs. 17 through 19, and the methods for estimating rate constants given by Benson.²⁰

Fig. 1. The solutions of the equations $dy/dt = -y$, for several values of y_0 . The solution for $y_0 = 0.5$ is shown with the corresponding numerical solution for $\Delta t = 0.5$.

The simple method used for this solution consists of calculating the derivative at a point $y(t_k)$ and drawing a short line at that slope over a time step Δt to the point $y(t_k + \Delta t)$, then repeating the process. That is,

$$y(t_k + \Delta t) = y(t_k) + \Delta t \{dy(t_k)/dt\} \quad (13)$$

Note that in the first step the new point lies on a curve (not shown) that is not the exact solution for $y_0 = 0.5$ but that is the solution for a slightly smaller value of y_0 . At each point the new $y(t_k)$ lies on a different solution curve from the previous one; but the error in the numerical solution remains small because each new point gives a value of the derivative, which forces the numerical solution back toward the true solution.

Contrast this with the situation in Fig. 2, which shows the solutions, $y = y_0 e^t$, of the differential equation $dy/dt = y$. Once again each step from $y(t_k)$ to $y(t_k + \Delta t)$ moves the numerical solution from one curve to another on the family of analytic solutions. Now, however, the slope on the new curve forces the numerical solution further from the true solution, and in a few cycles the numerical solution will be nowhere near the true solution. This is numerical instability. These illustrations can be generalized to a rule for numerical stability: when the family of analytic solution curves is converging toward some single curve, we have numerical stability; if the family of curves is not converging, we do not have numerical stability. This can be stated more accurately and concisely in algebraic form: we have numerical stability when

$$\partial y / \partial y < 0, \quad (14)$$

where:

$$y' = dy/dt,$$

in the region where we seek the solution; otherwise, we do not have numerical stability. Note that this condition is precisely what we have in

Fig. 2. The solutions of the equation $dy/dt = y$, for several values of y_0 . The solution for $y_0 = 0.005$ is shown with the corresponding numerical solution for $\Delta t = 0.5$.

Fig. 1, where we showed geometrically that we had numerical stability. This criterion is valid for the present method and other popular ones. We shall see later that the criterion may be that $\partial y' / \partial y$ is less than some constant D .

In the case where $\partial y' / \partial y > 0$, as in Fig. 2, all is not lost. If we keep the time step very small, we can keep our numerical solution on curves that lie very close to the exact solution, and the numerical error will be small even after many time steps. In particular, if $\Delta y(t)$ is the difference between the numerical and true solutions at time t , we say that we have "relative stability" if the ratio $\Delta y(t)/y(t) < \epsilon$ over the entire range of t where we seek a solution, and ϵ is some constant. We usually wish to keep ϵ small compared with $y(t)$; or, more colloquially, we have "relative stability" if we keep our percentage error small.

One other type of instability is relevant to the problem of chemical chain reactions.

In Fig. 3 we return to the equation of Fig. 1, which was shown to be numerically stable because the family of solutions converged toward zero. Assume that we are interested only in the solution for $t \gg 1$, so we plot the solution on a different scale, and to save computer time we take a larger time step. The numerical solution, using the same method as Fig. 1 with Δt increased to 2.2, is shown for comparison. The solution oscillates with growing amplitude and in a few more steps would "blow up" completely.

This oscillation occurs because we have approximated the exact solution by a Taylor series, which for the method we used is terminated after the second term; that is,

$$y(t + \Delta t) = y(t) + \Delta t \{dy(t)/dt\} + \dots \quad (15)$$

In this example we have taken Δt so large that the error of order $(\Delta t)^2$ is large compared to the solution, resulting in oscillations. Some authors call this "partial instability".

The numerical method we have chosen is a poor one for actual calculations, but it illustrates

Fig. 3. An example of "partial instability" due to an excessively large time step, for the equation $dy/dt = -y$. The exact solution for $y_0 = 0.5$ is shown with the corresponding numerical solution for $\Delta t = 2.2$.

in simple form behavior that is common to most methods. References on numerical analysis¹⁻⁷ and the literature⁸⁻¹⁵ give a number of methods for numerical solution of differential equations. Most authors prefer multipoint methods and implicit methods. Implicit methods use information about the new point, to obtain the value of the new point. This often results in algebraic equations that must be solved by iterative techniques. For example, we could average the slopes at t_k and $t_k + \Delta t$ as follows:

$$y(t_k + \Delta t) = y(t_k) + 1/2 \Delta t \times \left[y'(t_k) + y'(t_k + \Delta t) \right]. \quad (16)$$

This must be solved iteratively. We can use our former method to obtain a trial value of $y(t_k + \Delta t)$. This is called the "predictor" step and usually requires an explicit formula. This new trial value is substituted in the right hand side of Eq. 16, and the process is repeated until two successive trial values agree within some small error limit. This is the "corrector" phase of the calculation. This is one of the simplest implicit methods. A simple multipoint formula is

$$y(t_k + \Delta t) = y(t_k) + 1/2 \Delta t \times \left[3y'(t_k) - y'(t_k - \Delta t) \right]. \quad (17)$$

In the multipoint method, previously calculated values of the derivative are used to obtain either a better prediction of the new point or a smaller truncation error in the corrector. Equation 17 approximates the derivative by a parabola, whereas the method used in the previous examples approximated it by a straight line. In most cases, the parabola will give a more accurate prediction.

The advantages of these methods are greater accuracy and stability, which permit larger time

steps. However, all these methods are characterized by a certain domain of stability.^{2,3,8,9}

The domain of stability for several popular methods is shown in Fig. 4. The figure represents the complex $\Delta t(dy'/dy)$ plane that corresponds to solutions of the form $e^{x+iy}t$. The factor e^{yt} represents oscillatory solutions; e^{xt} is the damping factor if x is negative, and the amplification factor if x is positive.

In many references Δt is represented as h , dy/dt is represented as $f(x, y)$, and stability is expressed in terms of the parameter $h(df/dy)$. If we have a system of several differential equations in variable y_k , stability is determined by the Jacobian matrix $(\partial y'_k / \partial y_j)$. If we call its eigenvalues λ_i , we must have $h\lambda_i$ lying in the stability domain for all the eigenvalues λ_i .

The Relationship between Time Step Size and Numerical Stability

When one attempts to solve chemical kinetic rate equations, he finds that he generally has a system of "stiff equations." This simply means that the solution has several time constants, some of which are orders of magnitude faster than others. This causes stability problems that can best be illustrated by an example.

The motion of a damped harmonic oscillator can be described by the pair of equations:

$$(dy/dt) - v = 0 \quad (18)$$

$$(dv/dt) + \gamma v + \omega^2 y = 0, \quad (19)$$

Fig. 4. Domain of stability for three popular numerical schemes. The domain is plotted on the complex $\Delta t(dy'/dy)$ plane, with the imaginary part representing oscillatory solutions and the real part representing exponentially decaying or growing factors. Based on data provided in Ref. 9.

where y can represent displacement, and v the velocity. For simplicity let $\gamma = 10.1$ and $\omega = 1$, an overdamped case. If we let $y(0) = 0$ and $v(0) = 9.9$, the solutions are (to a good approximation)

$$y = -e^{-10t} + e^{-0.1t} \quad (20)$$

$$v = 10e^{-10t} - 0.1e^{-0.1t} \quad (21)$$

This is shown in Fig. 5.

Fig. 5. The solution of the overdamped harmonic oscillator equations $dy/dt = v$ and $dv/dt = -y - 10.1v$, with initial conditions $y(0) = 0$, $v(0) = 9.9$. Exact solutions are shown along with numerical solutions, using exact values at $t = 5$ for starting values. The time step, $\Delta t = 0.22$, was large enough to cause the oscillations shown.

The solutions show that, for $t > 1$, only the second term in each solution is significant, because the first term has died down. Therefore, it would seem natural in doing a numerical solution for times $t > 1$ to use a time step appropriate to the slowly varying term, i.e., $\Delta t \sim 10$. It turns out, however, that we are forced to use a time step such that $\Delta t \sim 0.1$. To illustrate this point, a numerical solution of Eqs. 18 and 19 is shown in Fig. 5. The time step, Δt , was 0.22; for the last term, $-e^{-10t}$, this time step corresponds to the $\Delta t = 2.2$ in Fig. 3. The numerical solution was started at $t = 5$, using the analytic solution for starting values. The growth of the instability is clear from the figure. This illustrates the point that the size of the time step is controlled by the fastest terms in the solution. If we had chosen $\gamma = 1000 \omega^2$ in Eqs. 18 and 19, it would take on the order of a million time steps to reach the point where the slowly varying term was one-tenth its maximum. On all but the fastest computers this might take an hour.

Two Methods for Obtaining Large Time Steps

There are two ways to get around this problem: and obtain rapid numerical solutions of systems of "stiff equations."

One method is to build into the computer program logic that notes the fact that some terms in the solution are no longer important and then modifies or eliminates certain equations from the system. In our example this would be done by setting dv/dt to zero in Eq. 19, solving the equation for v , and substituting the value in Eq. 18 to give

$$dy/dt = -\omega^2 y / \gamma \approx -0.1y. \quad (22)$$

The solution of this equation is the second term of Eq. 20, so we have a stable method that can use time steps with $\Delta t \sim 10$ and with negligible error for $t > 1$. The stability for $\Delta t = 10$ and 15 was verified by a numerical calculation. It is not a trivial task to program this for large systems of equations, but it has been done successfully by G. Emanuel in the NEST chemical kinetics code, 21, 22.

Another approach is to use a method that includes large negative values of $\Delta t(dy/dt)$ in its domain of stability. In this case the rapidly decaying terms in the solution do not cause instability, and large time steps can be taken once these transients have died out. C. W. Gear has written a FORTRAN subroutine that does just this, 12-14.

The stability domain of the Gear method is shown on the complex $h\lambda$ plane in Fig. 6. Remembering that h is the time step and λ the eigenvalues of $(\partial y_k / \partial y_j)$, we see that the method is stable (shown by the shaded region) only for values to the left of the vertical line $\text{Re}(h\lambda) = -D$, but extends to minus infinity. Comparing this with Fig. 4, we see that stability in the region $-D \leq \text{Re}(h\lambda) \leq 0$ is sacrificed to extend the domain to minus infinity. Within the small, cross-hatched rectangle there is only "relative stability," which means that the error must be kept small in this region. The error will be small if we keep the quantity $h\lambda$ small.

In the Gear technique, the parameters determining the size of the rectangle— D , 0, and α —are chosen so that any value of $h\lambda$ lying in the rectangle will give an accurate solution. The time step h can now be chosen so that $h\lambda$ for the slowly varying terms in the solution lie in the rectangle, but those corresponding to rapidly decaying terms lie in the region of absolute stability and do not limit the size of the time step. This was precisely our goal: to have the time step controlled by the slowly varying terms. The subroutine has automatic error and time step controls that are interconnected to give the largest time step that will keep the error within acceptable limits.

We have used this subroutine to solve the $\text{H}_2 + \text{Br}_2$ reaction (Eqs. 2-6), which has time constants that differ by a factor on the order of 10^6 . The solution was carried out to 10^4 sec in 560 time steps, which requires less than a minute of computer time. The error limit was one part in 10^5 .

Fig. 6. Domain of stability for C. W. Gear's method plotted on the complex $h\lambda$ plane. The crosshatched rectangle indicates the area of relative stability. The shaded area is the region of absolute stability.

per step. Figure 7 is a plot of $\log \Delta t$ vs $\log t$, which shows how the time step increases as the transients die out. This subroutine is available in general use.

Conclusion

In conclusion, let us review briefly the importance of numerical stability to the numerical solution of chemical chain reactions. The rate equations are "stiff" in the sense that they have characteristic times that vary by several orders of magnitude. The shortest of these times will control the size of the maximum time step unless special methods are used. One method is to force certain derivatives to be zero (the steady-state approximation), and another is to use numerical techniques that are stable even when these fast terms are included.

Acknowledgments

I would like to thank Drs. R. Gelinas and A. Hindmarsh for bringing C. W. Gear's routine to my attention and for implementing it at our laboratory. They have also been of assistance in understanding the nature of numerical stability. I also am indebted to C. W. Gear, whose subroutine has made my work so much easier.

Appendix

Rapid Computer Evaluation of Rate Equation

In a practical problem there may be as many as 100 equations of the form of Eqs. (2)-(6), involving 20 molecular species. Fortunately, in the interests of accuracy and our sanity, a simple computer algorithm can derive the rate equations of the form of Eqs. (7)-(12).

There are two sources for this subroutine.^{23,24}

Fig. 7. A log-log plot of time step vs time for the $H_2 + Br_2$ reaction, using the Gear numerical scheme. The upper limit is arbitrarily set at 12 sec.

Let the concentration of each molecular species be a component y_i of a column vector $\bar{y}$, and let the stoichiometric number for the i th species on the left-hand side of the j th reaction be the matrix element r_{ij} of the matrix R . If we form a similar matrix P for the stoichiometric number of the products on the right-hand side, we can write equations similar to Eqs. (2) in matrix form as

$$(R)\bar{y} \rightarrow (P)\bar{y}.$$

For example, Eqs. (2)-(6) would be written

$$\begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix} \cdot \begin{pmatrix} H_2 \\ Br_2 \\ H \\ Br \\ HBr \\ M \\ Ia \end{pmatrix} =$$

$$\begin{pmatrix} 0 & 0 & 0 & 2 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 1 & 0 \\ 0 & 1/2 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \cdot \begin{pmatrix} H_2 \\ Br_2 \\ H \\ Br \\ HBr \\ M \\ Ia \end{pmatrix}$$

If there are I molecular species and J reactions, the matrices will have I columns and J rows.

Now the computer goes through the matrices row by row and for the j th row obtains a term

$$T_j = k_j \prod_{i=1}^I y_i^{r_{ij}} - k_{-j} \prod_{i=1}^I y_i^{p_{ij}},$$

where k_j and k_{-j} are the forward and reverse rate constants. Note that these terms are the same as the individual terms on the right-hand side of the rate Eqs. (7)-(12).

The rate equation for the i th molecular species is now obtained from

$$dy_i/dt = \sum_{j=1}^J (r_{ij} T_j - p_{ij} T_j),$$

which gives a total of I rate equations with I unknowns. These rate equations are evaluated numerically at each time step. If a matrix element is zero, no operation is required except a test for zero and incrementing the index to test the next matrix element. This type of evaluation of derivatives is therefore nearly as fast as evaluating the rate equations, yet it greatly reduces the chance of human error.

If modifications are made to the algorithm to manipulate labels of the molecular species instead of numerical values, the computer can be made to print out the derived rate equations.

To read in the reactions in this form, it is necessary to punch the matrix elements on cards. It is possible to write a subroutine of a few hundred FORTRAN statements that will read reactions punched in approximately the format of Eqs. (2)-(6) and convert these data into the appropriate matrix form.

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MEMORANDUM - July 27, 1971

TO: Distribution

FROM: J. Creighton

This memo is a technical addendum to UCRL 73106, "The Role of Numerical Stability in the Computer Solution of Chemical Chain Reactions." You may wish to file this with the original report.

Professor A. K. Oppenheim suggested that I use the oscillator problem of eqs 18-21 as an illustration of the power of Gear's method to solve stiff equations. The results are shown in the upper half of Figure A. For this problem the Gear method required 200 time steps to solve the system to the point where y was less than .001. It took 1460 time steps to achieve the same result using the Adam's Predictor-Corrector option in the Gear subroutine, with automatic time step control. Both methods were started with a very small time step which grew roughly exponentially until the time corresponding to the peak value of y . This required 150 time steps, after that the time step for the Gear method continued to grow exponentially* while the time step for the Adam's method stayed nearly constant. A detailed examination showed that under the Adam's method the time step increased until excessive error developed; at that point the time step was cut an order of magnitude, and would again increase until excess error developed. However, when the step size was averaged over tens of steps it remained constant for 1000 steps.

To obtain a more dramatic example I increased the damping factor γ to 100 so that the equivalent of equation 19 was

$$dv/dt + 100 v + y = 0, \quad (A1)$$

with the solution

$$y = e^{-.01t} - e^{-100t} \quad (A2)$$

As shown in the lower half of Figure A, the Gear method completed the problem in 255 time steps. The Adam's method was terminated after 5000 time steps

* This behavior is illustrated in Fig. 7 of the original paper (UCRL 73106).

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because of excess printer output. Using the average time step it was estimated that it would take over 100,000 time steps to complete the problem.

Robert J. Gelinac¹ has furnished a practical example of the power of Gear's method in a photo-chemical smog calculation. This is shown in Figure B. The Adam's method was terminated for budgetary reasons. If the time step were to remain constant for the rest of the problem it would require millions of minutes of computer time to reach completion. Since nobody has that sort of computer time it is clear that the problem requires a method that can handle stiff systems of equations. I believe that these examples show the power of Gear's method and the seriousness of the problem of stiffness.

¹ Robert J. Gelinac, "Stiff Systems of Kinetic Equations -- A Practitioner's View", University of California UCRL 73078 (to be published in *J. Comp. Phys*) 1971.

John Creighton
Chemistry Department
Organic Materials Division

THE GEAR METHOD RUNS MUCH FASTER
THAN THE ADAM'S PREDICTOR-CORRECTOR.

FIGURE A

A PHOTOCHEMICAL SMOG CALCULATION
RUNS FASTER BY GEAR'S METHOD ON CDC 7600

FIGURE B

Appendix C — Commutators for the Hamiltonian of Equation 6.1

In order to solve the Heisenberg equations of motion, Eq. 6.2, it is necessary to evaluate commutators for the Hamiltonian given in Eq. 6.1. These commutators have not been previously evaluated for the 3-level system of Section 6. The commutators were calculated from the matrix representations of Section 6.1, and are given below.

1. Radiation Creation and Annihilation Operators

The operators a^+ and a commute with all the molecular operators, σ and n . The operators a_1^+ and a_1 commute with a_2^+ , a_2 , a_3^+ , and a_3 because they span a different space. The non-vanishing commutators are

$$[a_k, a_k^+] = 1 = -[a_k^+, a_k] . \quad (C-1)$$

Other useful commutators are

$$[a_k, a_k^+ a_k] = a_k, [a_k^+, a_k^+ a_k] = -a_k^+ . \quad (C-2)$$

The subscript k refers to one transition, but the commutators vanish if k is not the same for all oscillators.

11. Molecular Raising and Lowering Operators

The raising operators σ_1^+ and σ_2^+ occur in the Hamiltonian (Eq. 6.1) as do the lowering operators. In evaluating commutators we obtain a new lowering operator

$$\sigma_3^- \equiv [\sigma_2^-, \sigma_1^-] .$$

We also obtain a raising operator

$$\sigma_3^+ \equiv [\sigma_2^+, \sigma_1^+] .$$

These two operators would appear in the Hamiltonian if b_3 were not zero.

The raising and lowering operators commute with radiation operators. In general $[A, B] = -[B, A]$, which implies $[A, A] = 0$. Commutation of raising and lower operators with population operators will be considered in the next section.

The commutators of raising and lowering operators with others are given below

$$[\sigma_1^-, \sigma_2^-] = \sigma_3^- = -[\sigma_2^-, \sigma_1^-]$$

$$[\sigma_1^-, \sigma_3^-] = 0 = -[\sigma_3^-, \sigma_1^-]$$

$$[\sigma_2^-, \sigma_3^-] = 0$$

$$[\sigma_1^-, \sigma_1^+] = n_1 - n_2$$

$$[\sigma_1^-, \sigma_2^+] = 0, [\sigma_1^-, \sigma_3^+] = \sigma_2^+$$

$$[\sigma_2^-, \sigma_1^+] = 0$$

$$[\sigma_2^-, \sigma_2^+] = n_2 - n_3, [\sigma_2^-, \sigma_3^+] = \sigma_1^+$$

$$[\sigma_3^-, \sigma_1^+] = -\sigma_2^-$$

$$[\sigma_3^-, \sigma_2^+] = \sigma_1^-, [\sigma_3^-, \sigma_3^+] = n_1 - n_3$$

$$[\sigma_1^+, \sigma_2^+] = -\sigma_3^+$$

III. Population Operators

The population operators n_1 , n_2 , and n_3 commute with all radiation operators and with each other; they do not commute with all of the raising and lowering operators.

Those commutators are

$$[n_1, \sigma_1^-] = \sigma_1^-$$

$$[n_1, \sigma_2^-] = 0$$

$$[n_1, \sigma_3^-] = \sigma_3^-$$

$$[n_1, \sigma_1^+] = -\sigma_1^+$$

$$[n_1, \sigma_2^+] = 0, [n_1, \sigma_3^+] = -\sigma_3^+$$

$$[n_2, \sigma_1^-] = -\sigma_1^-$$

$$[n_2, \sigma_2^-] = \sigma_2^-$$

$$[n_2, \sigma_3^-] = 0$$

$$[n_2, \sigma_1^+] = \sigma_1^+$$

$$[n_2, \sigma_2^+] = -\sigma_2^+, [n_2, \sigma_3^+] = 0$$

$$[n_3, \sigma_1^-] = 0$$

$$[n_3, \sigma_2^-] = -\sigma_2^-$$

$$[n_3, \sigma_3^-] = -\sigma_3^-$$

$$[n_3, \sigma_3^+] = 0$$

$$[n_3, \sigma_2^+] = \sigma_2^+, [n_3, \sigma_3^+] = \sigma_3^+$$

The physical significance of these commutators is clear. For example, the commutator $[n_j, \sigma_k^\pm]$ represents a raising or lowering operator on transition k interacting with level j .

If the interaction increases the value of n_j , then

$[n_j, \sigma_k^\pm] = -\sigma_k^\pm$. If there is no change in n_j the commutator is zero. The commutator of the raising and lowering operators for a single transition is the inversion, and the commutator of two lowering operators $[\sigma_1^-, \sigma_2^-]$ is σ_3^- which is an equivalent operation. If we had understood the physical significance beforehand we could have written the commutators by inspection, and we can now use our physical insight to check our algebra.

Appendix D -- A Simple Analytic Model for Rotational Relaxation

When this work began there was one set of experimental data relevant to the question of the dependence of the rotational relaxation rate on rotational quantum number in HF. That was a chemiluminescence experiment of Polanyi and Woodall (1972a). They reacted F with H₂ in a flowing system and observed the populations at several downstream stations by means of chemiluminescence. Starting with the initial distribution they calculated the downstream distributions using a master equation and different models for the dependence of the rate on rotational quantum number J. The best model was $P_J = 1.42 \exp(-.0085 \Delta E)$, where ΔE was the change in rotational energy. To use this data for HF it was necessary to know what physical parameters were important in causing rotational relaxation. Some form of theory was necessary.

The theoretical literature on rotational relaxation is oriented towards ultrasonics and other applications involving the specific heat. Some papers concentrated on the theory of averaging to obtain macroscopic parameters from microscopic models (Brau & Jonkman, 1970; de Boer & Uhlenbeck, 1964; Ruff & Winter, 1968). Another group of papers used models such as rough sphere, and prolate and oblate spheroids (Sather & Dahler, 1961 & 1962; Widom, 1960). These "mechanical" models don't seem very realistic, even for nonpolar molecules. A few papers considered molecules with imbedded dipole moments or diatomic molecules with forces between all four

atoms (Brout, 1954; Cross & Gordon, 1966; Nyeland, 1967; Parker, 1959; Zelevnik, 1967, 1970, 1971). These seemed a better model for HF, but they all assumed no initial rotation, so were useless for calculating rotational dependence.

It seemed appropriate, therefore, to calculate rotational relaxation based on a simple model using imbedded dipoles in hard spheres with initial rotation. Before the model was completed I observed that linewidths in HF (Meredith, 1972) varied with rotational quantum number and the variation was quite similar to the rotational relaxation in HCl observed by Polanyi and Woodall (1972a). The Anderson theory of line broadening (Anderson, 1949; Tsao & Curnutte, 1962) and similar theories (Murphy & Boggs, 1967 to 1969) are in fact theories of rotational relaxation assuming multipole interactions between molecules. When rotational frequencies are in the microwave region, the relaxation is entirely due to rotational relaxation. In the visible a large fraction of the linewidth is due to phase changing collisions where the phase of the oscillation is perturbed, but the quantum numbers are unchanged. In the infrared, where energy differences are comparable to kT , the importance of phase changing collisions is unclear. In the IXION code the rotational relaxation rate was set proportional to the measured linewidth in HF. Good agreement with experiment was obtained when it was assumed that at least one half of all line broadening transitions involved a change of rotational state.

The correlation between linewidth and rotational relaxation made the simple model somewhat superfluous. The Murphy and Boggs (1967 to 1969) theory of linewidth gives values accurate to a few percent. However, the simple model gives insight into the physical processes. In other models I find that I lose the physical picture in the mathematical detail.

A classical model will be used and then correlated with the quantized rotational levels, similar to Landau-Teller theory for vibrational relaxation (Landau & Teller, 1936; Herzfeld & Litovitz, 1959; Rapp, 1960). The classical theory will be shown to give results similar to a quantum theory.

The model assumes two hard spheres with imbedded ideal dipoles. When they are separated by a distance R , molecule 1 exerts a torque

$$\tau_2 = \frac{-\mu_1 \mu_2}{R^3} [2 \cos \theta_1 \sin \theta_2 - \sin \theta_1 \cos \theta_2] \quad (D-1)$$

on molecule 2, where μ_1 and μ_2 are the dipole moments and the angles are shown in Fig. D1. For simplicity we will set $\theta_1 = 0$ and let $\theta_2 = (\omega_0 t + \delta)$, where $t = 0$ at the instant of closest approach. The angle δ , therefore, is the angle between the dipoles at the instant of closest approach. The simplest model for translational motion, a straight line trajectory at constant velocity will be used. The distance between dipoles at any time is given by $R^2 = v^2 t^2 + b^2$.

The dipoles exert torques on each other, leading to a change in rotational energy

$$\Delta E = \int \tau d\theta.$$

With the above assumptions the rotational energy change in molecule 2 is

$$\Delta E = -2\mu_1\mu_2 \int_{-\infty}^{\infty} \frac{\sin(\omega t + \delta)}{(\sqrt{t^2 + b^2})^{3/2}} \omega dt. \quad (D-2)$$

This is the net energy change in a collision. The energy at some instant t_1 is obtained by letting t_1 be the upper limit in the integral. This instantaneous value of the rotational energy change is a rapidly oscillating function, and has a large magnitude when t_1 is small. As the two molecules approach, the instantaneous energy change becomes large, but as they separate most of this change is cancelled by the symmetry of the trajectory. It is also interesting to note that the collision is nonadiabatic even for molecules with thermal velocities. In vibrational relaxation only fast molecules contribute. Slow molecules have adiabatic collisions where the molecules can readjust easily during the time of encounter. In the case of rotational relaxation, even a slowly moving molecule has a nonadiabatic collision in the sense that the rotational energy change near the instant of closest approach can be very large, equivalent to a change of several quantum numbers. There is, therefore, an appreciable probability of its being in some other quantum state.

This occurs because the dipole interaction energy is larger than the rotational energy levels.

Before integrating Eq. D-2, we expand $\sin(\omega t + \delta)$ to $\cos \delta \sin \omega t + \sin \delta \cos \omega t$. The first term vanishes on integration because it is odd. After re-arranging the integrand we get

$$\Delta E = \frac{-2\mu_1\mu_2}{v^3} \frac{\omega \sin \delta}{\int_{-\infty}^{\infty} \frac{\cos \omega t \, dt}{(t^2 + b^2/v^2)^{3/2}}} \quad (D-3)$$

The integration gives a modified Bessel function of the second kind (Abramowitz & Stegun, 1964).

$$\Delta E = - \left(\frac{4\mu_1\mu_2}{b^3} \right) \left(\frac{\omega^2 b^2}{v^2} \right) \sin \delta K_1 \left(\frac{\omega b}{v} \right) \quad (D-4)$$

The first term is the electrostatic energy of the dipole-dipole interaction at a separation equal to the impact parameter, b . The ratio $\frac{\omega b}{v}$ is related to the ratio of the rotational energy to the kinetic energy. The rotational energy of an HF molecule is approximately $E_{\text{rot}} \approx 1/2 m_H \omega^2 r_e^2$, where m_H is the mass of the hydrogen atom and r_e is the equilibrium separation. Similarly, $1/2 M v^2$ is the kinetic energy. Both the energies are proportional to k_1 , and $b > 2r_e$. Therefore, the quantity $\omega^2 b^2/v^2$ is proportional to the ratio of the rotational to the kinetic energies multiplied by the ratio M/m_H , which is about 20 in the case of HF. The quantity $\omega b/v$ will range from about 3 to 40 as J goes from 1 to 15 if v is the average velocity. The asymptotic form of $k_1(x)$ is $\sqrt{\pi/2x} e^{-x} [1 + O(1/x)]$. Using the asymptotic form gives

$$\Delta t = \left(\frac{4\mu_1\mu_2}{3} \right) \left(\frac{\omega b}{v} \right)^{3/2} \sqrt{\pi/2} \sin \delta \exp(-\omega b/v). \quad (D-5)$$

The angle, δ , is the angle between the two dipoles at the instant of closest approach. It is necessary to average over δ , b , and v .

The average over δ is the trickiest. At $t = -\infty$ the phase angles are random, but the dipole forces tend to align the dipoles so that certain values of δ are preferred over others. This implies that the instantaneous value of ω changes when the dipoles approach each other. It is difficult to calculate the average value of $\sin \delta$ accurately but it is easily estimated. Because of the dipole forces the molecule will rotate slower than average over half a cycle, and faster during the other half. Let the corresponding times be t_1 and t_2 , then $t_1 + t_2 = 2\pi/\omega_0$, where ω_0 is the average rotational frequency. The average over δ will be approximately $\langle \sin \delta \rangle = (t_1 - t_2)/(t_1 + t_2)$ with $t_1 = \pi/(\omega_0 - \Delta\omega)$ and $t_2 = \pi/(\omega_0 + \Delta\omega)$, so that $\langle \sin \delta \rangle$ is approximately $\Delta\omega/\omega_0$. We can estimate $\Delta\omega$ by considering the angular acceleration due to dipole-dipole forces

$$\frac{d}{dt} = \tau/I = \frac{2\mu_1\mu_2}{3r^3} \sin \omega t, \quad (D-6)$$

where τ is the torque and I the moment of inertia. Then

$$\Delta\omega = 1/2 \int_{-\pi/2}^{\pi/2} \tau/I dt = \frac{\mu_1\mu_2}{3r^3} \int_{-\pi/2}^{\pi/2} \sin \omega t \omega dt,$$

where the $1/2$ represents an approximate average over the instantaneous values of $\Delta\omega$. This gives

$$\langle \sin \delta \rangle \sim \frac{\Delta\omega}{\omega_0} = \frac{2\mu_1\mu_2}{b^3 + \omega_0^2}, \quad (D-7)$$

which is the ratio of the dipole energy at closest approach to the rotational energy. Our estimate has implicitly assumed $\Delta\omega/\omega_0 \ll 1$. The upper limit of $|\langle \sin \delta \rangle|$ is 1. For small values of b the dipole energy is large, so we can approximate $\langle \sin \delta \rangle = 1$. This approximation is valid except when ωb is very large, but then the energy change is small because of the exponential term in Eq. D-5. We now have

$$\Delta E \sim - \frac{4\mu_1\mu_2}{b^3} \left(\frac{\omega b}{v} \right)^{3/2} \sqrt{\pi/2} \exp(-\omega b/v), \quad (D-8)$$

which must be averaged over b and v . The average over b can be expressed as an incomplete gamma function, and taking the leading term of the asymptotic expansion simply results in using b_0 , the minimum impact parameter, for b in Eq. D-8. The average over v is the same as in the Landau-Teller theory except for a different power of v in front of the exponential. The result is similar with the average value of v being $(kT \omega b_0/M)^{1/3}$, with M the reduced mass of the two molecules. Substituting in Eq. D-8 gives

$$\langle \Delta E \rangle \sim \frac{4\mu_1\mu_2}{b_i^3} \omega b_0 \sqrt{\frac{\pi M}{2kT}} \exp[-(\omega^2 b_0^2 - M/kT)^{1/3}]. \quad (D-9)$$

This is the classical average energy loss. This can be related to the quantum mechanical probability in a simple

manner (Rapp & Kassal, 1969). A classical ensemble of n collisions would have an energy loss $n \langle \Delta E \rangle$. A corresponding quantum ensemble would have an energy loss $n P_J (E_J - E_{J-1})$, where P_J is the probability of the transition from J to $J-1$. For rotational transitions, $E_J - E_{J-1} = 2B_0 J$, where B_0 is the rotational constant of the molecule. Thus we have the simple relationship between the quantum probability and the classical average energy loss

$$P_J = \langle \Delta E \rangle / 2 B_0 J. \quad (D-10)$$

Substituting this in Eq. D-9 gives

$$P_J = \frac{2\mu_1 \mu_2}{b_o^3 B_o J} \sqrt{\frac{\pi M \omega^2 b_o^2}{2 kT}} \exp \left[- \left(\frac{M \omega^2 b_o^2}{kT} \right)^{1/3} \right] \quad (D-11)$$

The first term is the ratio of the maximum dipole interaction energy to the change in rotational energy. For highly polar molecules this can be considerably larger than one. The other terms contain an expression which is dimensionally equivalent to a rotational energy divided by the average thermal energy. However, this expression doesn't represent an actual rotation. The frequency is the initial rotational frequency of one molecule, the distance is the minimum impact parameter, and the mass is the reduced mass of the colliding molecules. The expression is proportional to the initial rotational energy. Assuming that most of the rotational energy of HCl is the motion of the light-hydrogen atom about the heavy chlorine, the initial rotational energy is $1/2 m_H \omega^2 r_e^2$, where m_H is a proton mass and r_e is the equilibrium separation. Thus

$$M \omega_{b_0}^2 = \left(\frac{M}{m_H} \frac{b_0^2}{r_e^2} \right) m_H \omega_{r_e}^2.$$

The mass ratio, in the case of HCl is 18 and b_0 3 to 4 r_e , so the term in parenthesis is about 200. The greatest uncertainty is in the value of b_0 , and exceeds the error made by neglecting the motion of the chlorine atom about the center of mass. Quantum mechanically the initial rotational energy is approximately equal to $1/2 m_H \omega_{r_e}^2$. Thus $M \omega_{b_0}^2 \sim 400 B_0 J(J+1)$. For HCl B_0 is about 10 cm^{-1} and at $300 \text{ K } kT \sim 200 \text{ cm}^{-1}$, so

$$M \omega_{b_0}^2 / kT \approx 20 J(J+1).$$

The dipole moment of HCl is approximately 1 Debye and if b_0 is $3.5 \text{ \AA}$, the dipole interaction energy is 137 cm^{-1} .

Calculated probabilities using these numbers are shown in Table D1 and Fig. D2, where they are compared with Polanyi's fit to the experimental data,

$$P = 1.42 \exp (-.0085 \Delta E).$$

Clearly Eq. D-11 gives a probability which is much too low at high J . The main problem is in the exponent. Numerical evaluation of the integrals doesn't remove the discrepancy. The error appears to be due to assuming that the target molecule is not rotating at any time. In reality, it will experience torques and begin to rotate. The torques will then oscillate at the difference frequency and reduce the exponent. To calculate this frequency would require more sophisticated mathematical techniques. It is also clear

that a quantum treatment would not solve the problem. First-order perturbation theory gives the probability as the Fourier transform of the interaction potential. This gives roughly the same integrals as the classical theory. Dillon and Stephenson (1973) have shown that the straight path assumption can cause calculated probabilities to be too small, and that the error increases with increasing rotational energy.

This simple theory seems to give the appropriate magnitude for the rotational relaxation at $J = 2$. The cross-section decreases with increasing J in agreement with experiment, but the decrease is much too rapid. The error appears to be due to the approximation of assuming a straight path and that the target molecule remains stationary. Some numerical calculations with the same physical model show that the target molecule does in fact rotate. The physical picture - rotational relaxation due to dipole-dipole interaction - is probably correct, because the same picture has been used successfully to calculate line broadening in several molecules (Murphy & Boggs, 1967-79; Meredith, 1972; Tsau & Curnutte, 1962). Apparently the failure of the model is due to mathematical difficulties.

<u>.t</u>	<u>Equ. D-11</u>	<u>$1.42 \exp(-.0085\Delta E)$</u>
1	7.1	1.19
2	1.32	1.01
3	.36	.85
4	.11	.72
5	.037	.61
7	.0038	.43
10	.00037	.26
15	7.2 E-6	.11
20	2.4 E-7	.047

Table III Comparison of calculated rotational relaxation rate (Eq. D-11) with experimental curve fit for HCl, i.e. $1.42 \exp(-.0085\Delta E)$.

Fig. 21 Schematic showing the parameters of a dipole-dipole interaction model.

Fig. D2 Comparison of calculated probability of rotational relaxation (Eq. D11) with experimentally based curve fit $[1.42 \exp(-.00854E)]$.

Appendix E — Subroutines DIFFUN and THERMO from the
MINOTAR Computer Code

These two subroutines form the core of the MINOTAR code when used in conjunction with C. W. Gear's subroutines for integrating stiff differential equations (Gear, 1971a). The remainder of the code handles input/output and terminates the code at a preselected time.

Subroutine DIFFUN computes the rate equations for the density of each species. Some of Gear's original arguments in the subroutine call have been transferred to COMMON block PRINC.

Subroutine THERMO calculates the temperature and the thermodynamics of each species. It also calculates the forward and reverse rate coefficients at the current temperature.

SUBROUTINE DIFFUN(CONC,DCDT)
 11 AUG 72
 COMMENT CARDS REVISED * SEPT 1973

 THIS SUBROUTINE CALCULATES THE TIME DERIVATIVE OF THE
 DENSITY OF EACH CHEMICAL SPECIES. THIS SUBROUTINE IS
 INTENDED TO BE CALLED BY C.W. GEAR'S SUBROUTINE STIFF.

INPUT ARGUMENT
 CONC(I) THE VALUE OF THE DENSITY (MOLES/CC) OF CHEMICAL SPECIES I.
 OUTPUT ARGUMENT
 DCDT(I) THE TIME DERIVATIVE OF CONC(I).
 OTHER VARIABLE, AS NOTED BELOW, ARE TRANSMITTED VIA LABELLED COMMON.

THIS SUBROUTINE CALLS SUBROUTINE THERMO WHICH RETURNS THE VALUES
 OF THE FOLLOWING ARRAYS IN COMMON/THERM/
 RATEFW(J) THE FORWARD REACTION RATE FOR REACTION J
 RATEVR(J) THE CORRESPONDING REVERSE RATE.

THE FOLLOWING ARRAYS, IN COMMON/CHEM/, MUST HAVE BEEN SET BY
 THE INPUT ROUTINES
 SR(I,J) THE NUMBER OF MOLECULES OF SPECIES I IN REACTION J
 ON THE REACTANT SIDE OF THE EQUATION
 SP(I,J) THE SAME ON THE PRODUCT SIDE OF THE REACTION
 CAT(I,M) THE NUMBER OF MOLECULES OF SPECIES I IN CATALYST M.
 VALUES OTHER THAN 1.0 OR 0.0 SPECIFY THE RELATIVE
 EFFICIENCY OF SPECIES I, BUT DO NOT AFFECT THE BALANCE.

THE FOLLOWING INTEGERS, IN COMMON/PRINC/, MUST HAVE BEEN SET BY
 THE INPUT ROUTINES.

KHEM THE TOTAL NUMBER OF CHEMICAL SPECIES PRESENT.
 KMIN = KHEM+1
 IMAX = KHEM PLUS THE NUMBER OF DEFINED CATALYSTS.
 JMAX THE TOTAL NUMBER OF CHEMICAL REACTIONS FOR THE PROBLEM.

SUBROUTINE DIFFUN CALCULATES THE AUXILIARY ARRAY
 RATE

WHICH IS TRANSMITTED TO THE OUTPUT ROUTINES VIA COMMON/CHEM/.
 IT IS NOT OTHERWISE USED IN OTHER SUBROUTINES.

 REAL CONC(20), DCDT(20)
 THE FOLLOWING LABELED COMMON BLOCKS MUST BE CONTAINED IN THE CALLING
 SUBROUTINES AND IN SUBROUTINE THERMO.
 COMMON/PRINC/ Y(20,13), TIME, KHEM, KMIN, IMAX, JXT, JMAX
 COMMON/THERM/ DENSITY, PRESSUR, TEMP, RATEFW(100), RATEVR(100),
 X EQUILK(100)

COMMON/CHEM/ SR(20,100), SP(20,100), RATE(100), CAT(20,20), ISO

 SECTION I

CALCULATE THE CONCENTRATION OF THE CATALYSTS.
 DEFINED AS THE ATOMS IN A THREE-BODY COLLISION WHICH DO NOT REACT.
 THE FORMULA IS

$$CONC(M) = \text{SUM}(I=1 \text{ TO } IMAX) (CAT(I,M)) * CONC(I)$$

WHERE *M* IS THE CATALYST SPECIES INDEX
 AND RANGES FROM KMIN TO IMAX.

DO 127 MI = KMIN, IMAX

CONC(MI) = 0.0

DO 125 I = 1, IMAX

125 CONC(MI) = CONC(MI) + CAT(I,MI) * CONC(I)

127 CONTINUE

```

C -----
C                               SECTION II
C CALCULATE THE NET RATE FOR EACH REACTION
C AND STORE IT IN *RATE(J)*, USING THE FORMULA
C
C      RATE(J) = RATERV(J)*PRODUCT([=1,IMAX)(CONC(I))*SP(I,J) -
C              -RATEF(J)*PRODUCT([=1,IMAX)(CONC(I))*SR(I,J)
C
C WHERE THE VARIABLES ARE DEFINED ABOVE.
C -----
C
C CALL THERMO
C      TO OBTAIN PATEFH AND RATERV
C
DO 50 J = 1,IMAX
  FMD = -RATERV(J)
  REV = RATERV(J)
  DO 40 I = 1,IMAX
    SRA = SR(I,J)
    IF(SRA.EQ.0.) GO TO 30
    IF(SPA.EQ.1.) GO TO 29
    IF(SRA.EQ.2.) GO TO 27
    FMD = FMD*(CONC(I))*SRA
    GO TO 30
  27 FMD = CONC(I)*CONC(I)*FMD
    GO TO 30
  29 FMD = FMD*CONC(I)
  30 SPA = SP(I,J)
    IF(SPA.EQ.0.) GO TO 40
    IF(SPA.EQ.1.) GO TO 39
    IF(SPA.EQ.2.) GO TO 37
    REV = REV*(CONC(I))*SPA
    GO TO 40
  37 REV = REV*CONC(I)*CONC(I)
    GO TO 40
  39 REV = REV*CONC(I)
  40 CONTINUE
  RATE(J) = FMD + REV
50 CONTINUE
C -----
C                               SECTION III
C CALCULATE THE TIME DERIVATIVE OF THE CONCENTRATION
C *DCDT(I)* FOR EACH SPECIES, TAKING THE SUM OVER J OF
C (SR(I,J)-SP(I,J)) TIMES THE NET REACTION RATE, *RATE(J)*,
C FOR THE JTH REACTION.
C -----
DO 70 I = 1,KHEM
  DCDT(I) = 0.0
  DO 60 J = 1,IMAX
    DCDT(I) = DCDT(I) + (SR(I,J) - SP(I,J))*RATE(J)
  60 CONTINUE
70 CONTINUE
C
RETURN
END
C -----

```

```

C-----
C SUBROUTINE THERMO
C.... REVISED 30 AUG 1973 BY J. CREIGHTON
C.... THIS SUBROUTINE CALCULATES THE TEMPERATURE AND KINETIC RATE
C.... CONSTANTS FOR A HOMOGENEOUS GAS PHASE REACTION AT CONSTANT
C.... VOLUME. THE REACTION CAN BE ADIABATIC OR ISOTHERMAL AND
C.... A SIMPLE MODIFICATION PERMITS NON-ISOTHERMAL CALCULATIONS WITH
C.... HEAT LOSS (OR GAIN) FROM THE SYSTEM.
C.... THIS SUBROUTINE IS INTENDED TO BE CALLED BY #SUBROUTINE DIFFUND,
C.... WHICH IN TURN IS CALLED BY C.W.GEAR'S #SUBROUTINE STIFFA.
C.... ALL COMMUNICATION WITH OTHER SUBROUTINES IS VIA LABELED COMMON
C.... INDEX VARIABLES
C.... I IS THE INDEX USED TO DENOTE CHEMICAL SPECIES.
C.... J IS THE INDEX USED TO DENOTE REACTION NUMBER.
C.... THE FOLLOWING COMMON VARIABLES MUST BE SET BY THE INPUT ROUTINES
C
C      IN COMMON/TABLE/
C      CPIN(I) A SET OF 7 COEFFICIENTS FOR THE SPECIFIC HEAT PER MOLE
C      AT CONSTANT PRESSURE FOR CHEMICAL SPECIES I. THE SPECIFIC HEAT
C      IS CALCULATED FROM THE FORMULA
C      CSUBP(I) = CP(1,I) + CP(2,I)*TEMP + CP(3,I)/TEMP
C      + CP(4,I)*TEMP**2 + CP(5,I)/TEMP**2
C      + CP(6,I)*TEMP**3 + CP(7,I)/TEMP**3
C      GFORMIN(I) A SET OF COEFFICIENTS TO DETERMINE THE GIBBS
C      FREE ENERGY PER MOLE (KCAL/MOLE) FOR CHEMICAL SPECIES I.
C      IT IS DETERMINED FROM THE FORMULA
C      GIBBS(I) = SUMMATION(L=1 TO 7) OF GFORMIN(L,I)*TEMP**(L-1)
C      HFORM(I) THE STANDARD ENTHALPY OF REACTION PER MOLE
C      (KCAL/MOLE) AT 298.15 K FOR THE CHEMICAL SPECIES I.
C      RATECON(I,J) 3 COEFFICIENTS PER REACTION FOR THE
C      FORWARD RATE CONSTANT IN THE ARRHENIUS FORM,
C      K(I) = A*(T**S)*EXP(-EA/RT)
C      WITH A = RATECON(1,J)
C      S = RATECON(2,J)
C      EA = RATECON(3,J)
C
C      IN COMMON/PRINC/
C      KMEX THE NUMBER OF CHEMICAL SPECIES PRESENT (20 OR LESS)
C      JMAX THE TOTAL NUMBER OF CHEMICAL REACTIONS (100 OR LESS)
C      JXT THE NUMBER OF CHEMICAL REACTIONS WITH CONSTANTS THAT
C      ARE NOT IN THE ARRHENIUS FORM. THESE ARE DETERMINED BY
C      SUBROUTINE XRATE, TO BE FURNISHED BY THE USER.
C      XRATE CALCULATES RATES FOR REACTIONS 1 TO JXT.
C      THERMO CALCULATES ARRHENIUS RATES FOR REACTIONS JMIN (=JXT+1)
C      TO JMAX.
C
C      IN COMMON/CHEM/
C      SR(I,J) IS THE STOICHIOMETRIC NUMBER OF SPECIES I ON THE
C      REACTANT SIDE OF REACTION J.
C      SP(I,J) IS THE STOICHIOMETRIC NUMBER OF SPECIES I ON THE
C      PRODUCT SIDE OF REACTION J.
C      ISO IS A FLAG FOR ISOTHERMAL OR ADIABATIC RUNS
C      ISO = 1 -- ISOTHERMAL
C      ISO = 0 - ADIABATIC

```

```

C      IN COMMON/THERM/
C      TEMP MUST BE SET TO THE INITIAL VALUE OF THE TEMPERATURE
C      BY THE INPUT ROUTINE. THEREAFTER IT IS CONTROLLED BY RATHERMO.
C.... THE FOLLOWING VARIABLES MUST HAVE BEEN SET BY THE CALLING
C      SUBPROGRAMS AND MAY HAVE DIFFERENT VALUES AT EACH CALL.
C      IN COMMON/PRINC/
C      Y(I,J) IS THE DENSITY (MOLES/CC) OF THE CHEMICAL SPECIES I
C      CONC(I) FOR NOTATIONAL CONVENIENCE CONC IS EQUIVALENCED TO Y
C      TIME THE CURRENT VALUE OF THE TIME, SET BY STIFF.
C      IN COMMON/STIFF/
C      JPC AN INITIALIZATION FLAG
C      JPC .LT. 0 -- SET ERZERO
C      JPC .GE. 0 -- CALCULATE CURRENT TEMPERATURE AND RATES
C.... SUBROUTINE THERMO SETS THE VALUES OF THE FOLLOWING VARIABLES
C      IN COMMON/THERM/
C      DENSITY THE TOTAL DENSITY (MOLES/CC) OF THE GAS MIXTURE.
C      PRESSUR THE TOTAL PRESSURE (TORR) OF THE GAS MIXTURE.
C      TEMP THE CURRENT VALUE OF THE TEMPERATURE (KELVIN).
C      THE INITIAL VALUE OF TEMP MUST BE SET BY THE INPUT ROUTINE.
C      RATEF(J) THE VALUE OF THE FORWARD RATE CONSTANT(CC/MOLE-SEC)
C      FOR REACTION J AT THE CURRENT TEMPERATURE.
C      RATERV(J) THE CORRESPONDING REVERSE RATE.
C      EQUILK(J) THE CURRENT VALUE OF THE EQUILIBRIUM CONSTANT FOR
C      REACTION J.
C      EQUILK(J) = RATEF(J)/RATERV(J)
C.... NOTE: IF THIS SUBROUTINE IS USED ON A COMPUTER WITH WORDS SHORTER
C      THAN 36 BITS, SOME VARIABLES MAY HAVE TO BE DOUBLE PRECISION.
C      -----
C.... THE CALLING SUBROUTINES MUST CONTAIN THE FOLLOWING LABELED
C      COMMON BLOCKS.
C
COMMON/TABLE/CP(7,20),GFORM(7,20),HFORM(20),RATECON(3,100)
COMMON/PRINC/ Y(20,13), TIME,KHEM,KMIN,IMAX,JXT,JMAX
REAL CONC(20)
EQUIVALENCE (Y,CONC)
COMMON/CHEM/ SR(20,100), SP(20,100), RATE(100), CAT(20,20),ISO
COMMON/THERM/ DENSITY,PRESSUR,TEMP,RATEF(100),RATERV(100),
X EQUILK(100)
COMMON/STIFF/YMAX(20),ERROR(20),EPS,M,KMIN,MMAX,JPC

C      LOCAL ARRAYS
C      REAL C(7), DG(885(100)), DGRT(20)
C
C      SUBROUTINE CALLED BY THIS SUBROUTINE
C      EXTERNAL XRATE
C      -----
C      INITIALIZE PARAMETERS
C      R IS THE UNIVERSAL GAS CONSTANT IN CAL/MOLE-KELVIN.
DATA R / 1.98717 /
C      RLOG IS THE NATURAL LOGARITHM OF 298.15
DATA RLOG / 5.69758671557 /
C      TREF IS THE STANDARD TEMPERATURE FOR THE ENTHALPY OF
C      FORMATION.
DATA TREF / 298.15 /
C      QEXT IS THE HEAT REMOVED FROM THE SYSTEM.
DATA QEXT / 0.0 /
DATA JPC / -1 /
C      NOTE: ANSI STD. FORTRAN REQUIRES THAT JPC BE SET BY AN
C      EXECUTABLE STATEMENT OR A BLOCK DATA SUBPROGRAM.

```

```

C -----
C          SECTION 1
C    CALCULATE THE TEMPERATURE AT THE PRESENT CONCENTRATIONS
C -----
C
C    CALCULATE THE TOTAL DENSITY AND ENTHALPY OF FORMATION AT 298 K,
C    FOR THE PRESENT CONCENTRATIONS.
C
C    ENTHLPY = 0.
C    DENSITY = 0.
C    DO 40 I = 1,KHEM
C      DENSITY = DENSITY + CONC(I)
C      ENTHLPY = ENTHLPY + HFORM(I)*CONC(I)*1.E3
C    40 CONTINUE
C
C      IN AN ISOTHERMAL PROBLEM RATES ARE CALCULATED ONLY ON FIRST
C      PASS
C      IF( 1150.EQ.1).AND.(JPC.GE.0) ) GO TO 97
C -----
C    CALCULATE THE COEFFICIENTS FOR THE TOTAL SPECIFIC HEAT
C -----
C
C    DO 60 N = 1,7
C      C(N) = 0.0
C      DO 50 I=1,KHEM
C        C(N) = CONC(I)*CP(N,I) + C(N)
C    50 CONTINUE
C    60 CONTINUE
C -----
C
C    CALCULATE THE COEFFICIENTS FOR
C    THE INTEGRAL(0 TO TEMP)(CSUBV*DT)
C    A1*TEMP + A2*TEMP**2 + A3*TEMP**3 + A4*TEMP**4
C    -A5/TEMP - A6/TEMP**2 + A7*ALOG(TEMP)
C -----
C
C    A1 = C(1) - R*DENSITY
C    A2 = C(2)*0.5
C    A3 = C(4)/3.
C    A4 = C(6)*0.250
C    A5 = C(5)
C    A6 = C(7)*0.5
C    A7 = C(3)
C
C    CALCULATE SPECIFIC HEAT (CONSTANT VOLUME) AND QREF--
C    THE INTEGRAL OF CSUBV FROM ZERO TO 298 K.
C    CSUBV = A1 + TEMP*(C(2) + TEMP*(C(4) + C(6)*TEMP))
C    = (( C(7)/TEMP + C(5)/TEMP + C(3)/TEMP
C    QREF = TREF*(A1) + TREF*(A2 + TREF*(A3 + TREF*(A4)))
C    = (A5/TREF + A5)/TREF + A7*ALOG
C    EX = ENTHLPY - DENSITY*R*TREF - QREF
C    IF(JPC.LT.0) GO TO 101
C -----
C
C    CALCULATE THE PRESENT TEMPERATURE BY THE NEWTON-RAPHSON METHOD
C -----
C
C    TCVG = 1.E-16
C    BEGIN ITERATIVE LOOP, MAXIMUM SIX ITERATIONS
C    DO 70 M=1,6
C      IF(TEMP.GT.0.0) TLOG = ALOG(TEMP)
C      ENERGY = EX + TEMP*(A1+TEMP*(A2+TEMP*(A3+TEMP*A4)))
C      = (A6/TEMP + A5)/TEMP + A7*TLOG
C      TC = (ZERO+DEXT-ENERGY)/CSUBV
C      TEMP = TEMP + TC
C
C    CHECKS AND WARNING DIAGNOSTICS MAY BE INSERTED
C    HERE IF TEMP EXCEEDS RANGE OF THERMODYNAMIC TABLE
C    (APPROX. 100 TO 6000 K.)
C    IF((TC*TC).LE.TCVG) GO TO 75
C    70 CONTINUE
C
C    PRINT DIAGNOSTIC BUT CONTINUE IF CONVERGENCE FAILS
C    TAPE 3 IS SET AS THE OUTPUT TAPE (OR DISK FILE)
C    71 WRITE(3,171) TEMP,GC
C    171 FORMAT(2*TEMP,CONVERGENCE PROBLEM AT,111.2,SHK,ERROR=,F12.3,1HK)

```

```

C -----
C
C      SECTION II
C      CALCULATE EQUILIBRIUM CONSTANT AND RATES FROM FREE ENERGY OF FORMATION
C -----
C      CALCULATE FREE ENERGY OF FORMATION FOR EACH SPECIES
75  BETA = 1.E3/(R*TEMP)
C      THE FACTOR, 1.E3, CONVERTS KCAL TO CAL.
      TLOG = ALOG(TEMP)
C      DGRT(I) IS THE GIBBS FREE ENERGY OF FORMATION TIMES BETA
C
      DO 80 I = 1,KHEM
        DGZERO = (((GFORM(7,I))*TEMP + GFORM(6,I))*TEMP
1         + GFORM(5,I))*TEMP + GFORM(4,I))*TEMP
2         + GFORM(3,I))*TEMP + GFORM(2,I))*TEMP + GFORM(1,I)
        DGRT(I) = DGZERO*BETA
80      CONTINUE
C -----
C      FOR EACH REACTION CALCULATE FORWARD RATE CONSTANT, EQUILIBRIUM
C      CONSTANT AND REVERSE RATE CONSTANT
C
C      CALCULATE RATES IN ARRHENIUS FORM
      DO 90 J = JMIN,JMAX
        DGIBBS(J) = 0.
        DO 88 I = 1,IMAX
90          DGIBBS(J) = (SP(I,J) - SR(I,J))*DGRT(I) + DGIBBS(J)
          EQUILK(J) = EXP(-DGIBBS(J))
          RATEFW(J) = RATECON(1,J)*EXP(TLOG*RATECON(2,J)
1          - RATECON(3,J)*BETA)
          RATERV(J) = RATEFW(J)/EQUILK(J)
90          CONTINUE
C -----
C      CALCULATE RATES REQUIRING EXTERNAL SUBROUTINE
C      97 IF(JMIN.GT.1) CALL XRATE(JMIN)
C
C      PRESSUR = 31382.6*DENSITY*R*TEMP
C      PRESSURE IS GIVEN IN TORR FOR DENSITY IN MOLES/CC.
C      RETURN
C -----
C
C      SECTION III
C      ON FIRST PASS THRU SUBROUTINE SET EZERO
C
101 IF(TEMP.GT.0.0) TLOG = ALOG(TEMP)
      EZERO = EX + TEMP*(A1*TEMP+A2*TEMP*(A3*TEMP+AN))
1         -1A6/TEMP + A51/TEMP + A7*TLOG
      JMIN = JKT + 1
      JPC = 0
      GO TO 75
C
C      IN ORDER TO CALCULATE RATES
C -----
C
C
      END

```

Appendix F — Subroutines DIFFUNB and CHEMIST from the IXION Code

These two subroutines form the core of the IXION code. Subroutine DIFFUNB is called by the Gear Subroutine, STIFFB, to evaluate the time derivatives. (STIFFB is a version of the Gear routine which takes advantage of the banded nature of the large Jacobian matrix (Hindmarsh, 1973). DIFFUNB evaluates the electric field, polarization and population equations. It calls subroutine CHEMIST to get many of the required co-efficients. CHEMIST calculates the rate of formation of HF assuming that the only important reaction is

It also simulates the dissociation of NF_3 to give F, and calculates co-efficients for the vibrational relaxation, rotational relaxation and line broadening terms. It assumes that the thermo-dynamic temperature remains constant.

SUBROUTINE DIFFUSION.TIME (Y, J, JPLAS)

12 APR 73

COMMENT CARDS UPDATED 2 JAN 75

A SUBROUTINE TO CALCULATE TIME DERIVATIVES FOR THE HF CHEMICAL LASER. IT CALCULATES POPULATIONS OF STATES OF HF, DIELECTRIC POLARIZATIONS AND ELECTRIC FIELDS FOR EACH LASER TRANSITION, USING SIMPLIFIED SEMI-CLASSICAL LASER EQUATIONS. IT TREATS 20 CASCADES WHICH INCLUDE 6 VIBRATIONAL LEVELS ALONG WITH THE POLARIZATION AND ELECTRIC FIELD FOR THE 5 LASER TRANSITIONS WHICH COUPLE THESE STATES.

THIS SUBROUTINE IS INTENDED TO BE CALLED BY *STIFFB*,
A VERSION OF C.W. GEAR'S ALGORITHM MODIFIED FOR Banded MATRICES.

DEFINITION OF VARIABLES

QUANTUM NUMBERS

V = VIBRATIONAL QUANTUM NUMBER

IV = V + 1

JVMAX = MAX VALUE OF IV--SET BY CALLING PROGRAM.

MUST BE ≤ 6

ROTATIONAL QUANTUM NUMBER IS NORMALLY J, HOWEVER IN THIS CODE
J = J + 1, I.E., ROTATIONAL GROUND STATE HAS J=1.

PRINCIPAL VARIABLES

Y IS AN ARRAY WHOSE FIRST COLUMN IS A VECTOR (LENGTH=320)
CONTAINING THE DEPENDENT VARIABLES (UNKNOWN).
IN STIFFB Y IS DIMENSIONED (320,13). WHERE THE ADDITIONAL
TWELVE VECTORS CONTAIN SCALED DERIVATIVES.
THE VECTOR, Y, IS ARRANGED BY CASCADES. EACH CASCADE INCLUDES
SIX VIBRATIONAL-ROTATIONAL STATES COUPLED BY P-BRANCH
LASING TRANSITIONS. THESE STATES ARE DESIGNATED YIM1 AND
YIM3). THE VARIABLE YIM1) IS THE DIELECTRIC POLARIZATION
FOR THE TRANSITION FROM YIM3) TO YIM1). YIM2) IS THE
CORRESPONDING ELECTRIC FIELD. EACH CASCADE CONTAINS 16
VARIABLES--6 POPULATIONS, 5 POPULATIONS, AND 5 ELECTRIC
FIELDS. THERE IS A CASCADE FOR EACH OF THE 20 ROTATIONAL
STATES OF THE LEVEL WITH V=0. THE INDEX, M, IS COMPUTED
FROM $MD = 16 * J0 - 15$, WHERE J0 IS THE ROTATIONAL QUANTUM
NUMBER FOR THE STATE WITH V=0. IN EACH CASCADE M ASSUMES
VALUES FROM MD TO MD+15 IN INCREMENTS OF 3.

YDOT(M) IS THE TIME DERIVATIVE CORRESPONDING TO Y(M).

THE FOLLOWING VARIABLES ARE SET BY THE CALLING PROGRAM

BSQ = THE VALUE OF THE LINESHAPE FUNCTION AT LINE
CENTER MULTIPLIED BY THE EINSTEIN COEFFICIENT, B(1,0).
CAV1 IS A CAVITY CONSTANT SET BY THE CALLING PROGRAM.

IT IS A FUNCTION OF CAVITY LENGTH AND MIRROR REFLECTIVITIES.
DETAIL(IV,J) = THE FRACTION OF THE LASING SPECIES CREATED
IN THE STATE (IV,J).

LIMIT VARIABLES

SOME TERMS IN THE YDOT RATE EQUATION CALL FOR TERMS
WITH QUANTUM NUMBERS EXCEEDING THE UPPER OR LOWER LIMITS.
THE FOLLOWING VARIABLES HAVE THE VALUE 1.0 EXCEPT
UNDER THE FOLLOWING CONDITIONS.

AV1 = 0. WHEN IV=1

AV5 = 0. WHEN IV=6

AJ = 0. WHEN J=20

OTHER CASES ARE HANDLED BY ZERO VALUES IN ARRAYS
BN, DJ, OR GR.

```

C
C   SET UP ARRAYS OF CONSTANTS
C   DIMENSION Y(320),VDO(320)
C   DIMENSION BN(1), DJ(21), GR(21)
C   COMMON/RAD/ BSO,CAVI,CAVLN,FILL,GAMMA2,NDIFN,IVMAX
C   COMMON/RATES/ DETAIL(6,20), EOK(6,20), HFDO(1),VDO(1),RDOT,TOLD
C   COMMON/EQL/ TERM(6,20),TEMP,R1,RVIB,PROT,P2,F0
C
C   R IS THE GAS CONSTANT IN UNITS 1/CH-K
C   DATA R / 0.695031 /
C
C   GR(I) IS THE DEGENERACY RATIO--(2J+1)/(2J'+1).
C   DATA GR / 0.0, .333333, .600000, .714285, .777777,
C   1 .818181, .846153, .866666, .882352, .894736,
C   2 .904761, .913043, .920000, .925925, .931034,
C   3 .935483, .939393, .942857, .945945, .948717, .951219 /
C
C   DJ(I) IS THE VARIATION OF ROTATIONAL RELAXATION RATE AND
C   COLLISIONAL BROADENING RATE WITH PUTATIONAL QUANTUM NUMBER, J.
C   DATA DJ / 0.0, 0.525, 0.515, 0.430, 0.346,
C   1 0.2382, 0.1668, 0.1169, 0.08187, 0.05735,
C   2 0.04017, 0.02814, 0.01971, 0.01381, 0.009673,
C   3 0.006776, 0.004746, 0.003325, 0.002329, 0.001632, 0.0 /
C
C   BN(I) GIVES THE VARIATION OF THE EINSTEIN COEFFICIENT WITH J;
C   I.E., BSO*IV*B(I) IS THE PRODUCT OF THE LINESHAPE
C   FUNCTION AND THE EINSTEIN COEFFICIENT FOR THE P(IV,J)
C   TRANSITION.
C   DATA BN / 0.0, 1.5325, 1.0789, 1.0236, 1.0267,
C   1 1.0501, 1.0833, 1.1225, 1.1657, 1.2121,
C   2 1.2408, 1.3127, 1.3662, 1.4224, 1.4782,
C   3 1.5394, 1.5986, 1.6626, 1.7274, 1.7944, 0.0 /
C
C   -----
C
C   CALL CHEMIST
C
C   TO OBTAIN THE FOLLOWING VARIABLES
C   HFDOOT = THE TOTAL RATE OF FORMATION OF THE LASING SPECIES.
C   VDOOT = THE VT (OR VV) RELAXATION KINETIC RATE TIMES
C   THE DENSITY OF THE RELAXING SPECIES.
C   RDOT = THE RT RELAXATION KINETIC RATE TIMES THE DENSITY OF
C   THE RELAXING SPECIES.
C   GAMMA2 = THE COLLISIONAL LINEWIDTH CONSTANT
C
C   CALCULATE DOPPLER COEFFICIENT
C   OPK = 2400.*SQRT(TEMP)
C
C   DIAGNOSTIC PRINTOUT
C   ITTY = 59
C   IF(NDIFN.LT.1) WRITE(ITTY,13) RDOT,VDOOT,HFDOOT
C   13 FORMAT(1* R,*,E10.2,* V,*,E10.2,* HF,*,E10.2)
C

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C -----
C
C
C      CALCULATE TIME DERIVATIVES
C
C      MAIN LOOP- CALCULATE 20 CASCADES
C      DO 200 J0=1,20
C      SET UP LIMIT VARIABLES AND QUANTUM NUMBERS
C      M0 = 16*J0 - 15
C      J = J0
C      AJ = 1
C      IF(J0.EQ.20) AJ=0.0
C      IV = 1
C      AV1 = 0.0
C      AV6 = 1.0
C      MU = M0 + 3*(1/VMAX-1)
C
C      INNER LOOP--CALCULATE ONE CASCADE
C      DO 100 M=M0,MU,3
C      SET APPROPRIATE CONSTANTS
C      V = FLOAT(1/V-1)
C      VP = V + 1
C      MAVNUM = TERM(IV+1,J-1) - TERM(IV,J)
C      CSQ = (GAMMA2*DJ(J+1))**2 + (DPK*WAVENUM)**2
C      DOMEGA = SQRT(CSQ)
C      CALCULATE EFFECTS OF DETUNING
C      TPH = (4.7124E10/CAVL)/((CAV1 + GAMMA2)
C      CSQ = 1./((1. + TPH**2)
C      CPH = SQRT(CSQ)
C
C      COMPUTE THE REQUIRED EQUILIBRIUM CONSTANT
C      EQK(IV,J) = THE EQUILIBRIUM CONSTANT FOR ROTATIONAL
C      RELAXATION FROM (IV,J+1) TO (IV,J).
C      TERM(IV,J) = THE TERM ENERGY OF STATE WITH (IV,J)
C      ARG = ( TERM(IV,J) - TERM(IV,J+1) )/(R*TEMP)
C      EQK(IV,J) = EXP(ARG)/GR(J+1)
C
C      COMPUTE RATE OF POPULATION CHANGE
C
C      IF(IV.EQ.6) AV6 = 0.0
C      YDOT(M) = 2.*CPH*(AV6*Y(M+1)*Y(M+2) - AV1*Y(M-2)*Y(M-1))
C      A      *DETAIL(IV,J)*MF00T
C      B      *VDOT*(VP*BN(J)*Y(M+3) - V*BN(J+1)*Y(M) )
C      C      *RDOT*( Y(M+16)*AJ*DJ(J+1)
C      D      -EQK(IV,J)*DJ(J+1) + DJ(J))*Y(M)
C      E      *EQK(IV,J-1)*Y(M-16)*DJ(J) )
C
C      COMPUTE THE POLARIZATION RATE
C
C      IF(M.EQ.MU) GO TO 200
C      YDOT(M+1) = -DOMEGA*Y(M+1) + VP*BN(J)*BSQ*MAVNUM*CPH
C      B      *1 Y(M+2)*( Y(M+3)-GR(J)*Y(M)) + Y(M+3))
C
C      COMPUTE ELECTRIC FIELD RATE OF CHANGE
C
C      YDOT(M+2) = -CAV1*Y(M+2) + FILL*Y(M+1)*CPH
C
C      RESET LIMIT VARIABLES AND QUANTUM NUMBERS
C      AV1 = 1
C      AV6 = 1
C      IV = IV+1
C      J = J-1
C      IF J .EQ. 0 WE HAVE REACHED THE TOP OF THE CASCADE
C      IF(J.LE.9) GO TO 200
C      100 CONTINUE
C      200 CONTINUE
C
C -----
C
C      INCREMENT A COUNTER
C      NDIFN = NDIFN + 1
C      RETURN
C      END

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SUBROUTINE CHEMIST
C 12 APR 78
C COMMENT CARDS UPDATED 2 JAN 75
C A SUBROUTINE TO CALCULATE
C HFODT = THE TOTAL RATE OF FORMATION OF THE LASING SPECIES.
C VDOT = THE VT (OR VV) RELAXATION KINETIC RATE TIMES
C THE DENSITY OF THE RELAXING SPECIES.
C ROOT = THE RT RELAXATION KINETIC RATE TIMES THE DENSITY OF
C THE RELAXING SPECIES.
C GAMMA2 = THE COLLISIONAL LINEWIDTH CONSTANT
C
COMMON/STCOM1/N,TIME,H,HMIN,HMAX,EPS,MF,KFLAG,JSTART,ML,MU
COMMON/RATES/ DETAIL(16,20),EOK(16,20),HFODT,VDOT,ROOT,TOLD
COMMON/EQL/ TERM(16,20),TEMP,R1,RVIB,ROOT,H2,F0
COMMON/RAD/ B50,CAVI,CAVLN,FILL,GAMMA2,NDIFN,IVMAX
C
C SET DEFAULT VALUES
C AVOGADRO'S NUMBER--CONVERT MOLES/CC TO MOLECULES/M**3
DATA AVM / 6.02252E29 /
DATA P1 / 3.14159 /
DATA F / 0. /
DATA HF / 0. /
DATA TOLD / 0. /
C
C ON NEW TIME STEP UPDATE FOLD, HFOLD, AND TPRV; OTHERWISE
C COMPUTE RATES. TOLD IS SET BY CALLING PROGRAM.
IF(TOLD.LE.TPRV) GO TO 10
FOLD = F
HFOLD = HF
TPRV = TOLD
C
C SET SOME CONSTANTS
10 TEMP = 300.
C FREQUENCY OF CURRENT PULSE
B = 1.25E7
C CONVERSION FROM TORR TO MOLES/CC
TORRC = 5.8741E-8*300./TEMP
C SET DENSITIES OF CHEMICAL SPECIES. F0 IS MAXIMUM
C F-ATOM DENSITY
F3N = 13.0*TORRC
H2 = 2.5*TORRC
HE = 0.0*TORRC
F0 = 0.0125*F3N
C SET RATE CONSTANTS
ERT = 855./TEMP
R1 = 1.2E14*EXP(1-ERT)
C GAS KINETIC RATE IS ABOUT 4.E13 AT 300K; LINE BROADENING IS
C SET AT ABOUT 10 TIMES GAS KINETIC.
WIDTH = 4.6E13*SQRT(TEMP)
ROOT = 0.50*WIDTH
C
C COMPUTE CURRENT RATES
C
C ROTATIONAL RELAXATION
ROOT = ROOT*(H2 + F3N + F0 + HE)
C COLLISIONAL BROADENING
GAMMA2 = WIDTH*(H2 + F3N + F0 + HE)
C SIMULATE HALF SINE WAVE CURRENT PULSE
PHI = B*TIME + 0.25*PI
IF(PHI.GT.PI) PHI = 0.
C F-ATOM DENSITY
FODT = F0*(B*(1.7071*SIN(PHI)) - HFODT/AVM)
F = FOLD + (TIME-TOLD)*FODT
C FORMATION OF HF, AND VIBRATIONAL RELAXATION
HF = HFOLD + (TIME-TOLD)*HFODT/AVM
VDOT = (7.1E9*H2 + 1.6E7*F3N + 5.E6*HE + .72E12*F
A * 1.4E12*HF)
HFODT = R1*H2*F*AVM
C
C RETURN
C END

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