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[†] Portions of work taken from a Ph.D thesis submitted by L. J. Rodriguez to the Georgia Institute of Technology, 1973.

[1] L. Van Hove, Phys. Rev. **95**, 249 (1954).

[2] L. J. Rodriguez, H. A. Gersch, and H. A. Mook (unpublished).

[3] H. A. Mook, R. Scherm, and M. K. Wilkinson, Phys. Rev. A **6**, 2268 (1972).

[4] H. A. Gersch, L. J. Rodriguez, and P. N. Smith, Phys. Rev. A **5**, 1547 (1972).

[5] For instruction in the manipulation of time-ordered operators, we are indebted to Q. Bui Duy, J. F. Fernandez, and R. Fox.

[6] See H. Cramer, *Mathematical Methods of Statistics* (Princeton U.P., Princeton, N. J., 1951), p. 186. Cumulant expansions for *c*-number products in scattering theory have been previously utilized by R. J. Glauber, *Lectures in Theoretical Physics*, edited by W. E. Brittin and L. G. Dunham (Interscience, New York, 1959), Vol 1. Cumulant expansions have also been applied to time-ordered operators, for example, see R. Kubo, in *Fluctuation, Relaxation, and Resonance in Magnetic Systems*, edited by D. ter Haar (Oliver and Boyd, Edinburgh, Scotland, 1962).

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Influence of Vibrational, Rotational, and Reorientational Relaxation on Pulse Amplification in Molecular Amplifiers*

F. A. Hopf†
Optical Sciences Center, University of Arizona, Tucson, Arizona 85721

C. K. Rhodes
Lawrence Livermore Laboratory, Livermore, California 94550

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Short-pulse amplification in gaseous molecular amplifiers is complicated by many aspects of atomic and molecular interactions. Among these are the various vibrational, rotational, and reorientational relaxational processes which influence the coupling of the energy stored in the molecular radiators to the electromagnetic field. The properties of plane-wave pulse amplification, especially in the saturated regime, are examined numerically in order to quantitatively determine the detailed effects of these relaxational phenomena. As expected, the results for saturated amplification show that the amount of extracted energy decreases significantly when the rotational relaxation time is sufficiently long in comparison to the pulse width. We also observe the development of pulse-shape variations which are a direct result of the collisional phenomena and differ qualitatively from the results obtained for amplifying media without an energy reservior. There is a tendency for the pulse lengths to increase owing to the energy transfer, in contrast to the strong narrowing effects which occur in the absence of the collisional processes. The influence of reorientational collisions is found to be small, accounting for less than a 20% effect on the over-all conclusions. Finally, we present results concerning the development of an asymptotic pulse shape in high-gain amplifiers. In this case, the pulse shape clearly exhibits the competition between the stimulated rate, which scales with the optical flux, and the collisional rates which are determined by the particle density. Calculations of this nature may be applied directly to CO_2, CO, and HF molecular amplifiers for both the electrically and chemically driven systems.

I. INTRODUCTION

Electromagnetic pulse amplification in gaseous molecular amplifiers is complicated by many aspects of atomic and molecular interactions. Among these are the multitude of relaxational processes which couple the molecular systems to one another as well as influence the interaction of the molecular radiators with the electromagnetic field. The perturbing fields which operate on the quantum-mechanical systems generally have a very complicated structure. There is, in addition to the coherent electric field $\vec{E}(t,z)$ of the amplified wave, a component due to collisions from neighboring particles which is rapidly varying in space, time, and direction. If the possibility of significant correlations arising from the presence of a coherent optical field is ignored,[1] then the perturbing field due to collisions can be regarded as a stochastic variable.[2] We do not take this approach here. Instead, we represent the relaxational processes by the appropriate phenomenological parameters. This choice arises quite naturally from the strong identification of the particular parameters with the corresponding physical mechanisms and relaxational processes. The dynamics of the coherent electric field $\vec{E}(t,z)$ are treated semiclassically in the customary way.[3]

In this work we appraise the effect of molecular relaxational processes on electromagnetic pulse amplification. Specifically, we examine the roles played by vibrational relaxation, rotational relaxation, and reorientational relaxation. A vibrational-energy–translational-energy exchange (VT) process for species A is denoted by

$$A(\nu)+M\rightarrow A(\nu')+M+\Delta E_K, \tag{1}$$

where M in this example represents a structureless collision partner, ν and ν' designate the quantum number(s) of the molecular vibration(s), and ΔE_K corresponds to the required change in the kinetic energy of the colliding systems as a result of over-all energy conservation. Processes in which a fraction of the internal energy appears as radiation are entirely negligible[4] for the class of systems being considered. Rotational and reorientational relaxational processes involve transitions among molecular-rotational states. For a linear $^1\Sigma$ molecule[5] the rotational state is completely described by the state $|j,m\rangle$, where j designates the total[6] molecular angular momentum and m denotes the projection of j along an arbitrary[7] space-fixed axis. Thus, we represent collisions involving a change in rotational and kinetic energies (RT) as

$$A(j,m)+M\rightarrow A(j',m')+M+\Delta E_K\,. \tag{2}$$

Rotational relaxation refers to processes in which $j-j'\neq 0$, while reorientational relaxation pertains specifically to $j=j'$ and $m-m'\neq 0$. Since the m states are degenerate,[8] $\Delta E_K=0$ in the reorientational case, although in general the distribution of the total kinetic energy between the colliding particles changes during the collision.

Clearly the most general collision is appropriately designated by

$$A(\nu,j,m)+M\rightarrow A(\nu',j',m')+M+E_K\,, \tag{3}$$

in which all three indices (ν,j,m) are simultaneously affected. In our model we neglect an independent description of these mixed processes and effectively assume that the probability of these processes is adequately expressed by the products of the probabilities for the corresponding unmixed events.

In addition to the time scales governing the kinetic behavior, we include the contributions of inhomogeneous broadening[9] (described by the parameter T_2^*) and phase-changing collisions (represented by the time T_2) in a manner similar to previous studies.[10] The complicating effects of velocity changes due to collisions relevant to gaseous media are modeled in a simple manner which is described in Sec. III.

Of particular interest are the properties of pulse amplification in the saturated regime where the stimulated rates are comparable to the density-dependent relaxational rates. It is found that the molecular relaxational processes exercise a strong influence on the resulting pulse shape, the energy extraction efficiency, and the saturation energy density. We present results concerning these quantities studied over a wide range of the relevant parameters. With appropriate numerical values for the relaxation rates, these calculations may be applied directly to CO_2, CO, and HF molecular amplifiers for electrically and, with minor modifications, chemically driven systems.

Finally, we observe that for a sufficiently short pulse under the conditions in which the stimulated rate greatly exceeds all the relaxational rates, coherence effects dominate and we make contact with previous studies of attenuating and amplifying media.[3] In this situation severe pulse-shape distortions appear as a result of the nonlinear coherent interaction of the radiation field and the molecular systems.

The outline of this paper is as follows. In Sec. II we provide a brief discussion of the mechanisms governing the relaxational processes of interest, indicating the typical rates characteristic of a wide class of systems. Section III deals with the method of computation containing explicit statements of the approximations used in our approach. The numerical results are presented in Sec. IV, which is followed by a concluding summary, Sec. V. The Appendix explores the details of the phenomenological density matrix equations.

II. DESCRIPTION OF BASIC RELAXATIONAL PROCESSES

In this section we briefly review the nature of the various collisional processes governing the molecular relaxations. Although specific numerical values of collisional rates naturally depend upon the detailed molecular properties of the collision partners, it is possible to make some general statements concerning the properties of the molecular interactions causing the relaxation.

A. Molecular Reorientation

A free molecular system is characterized by a total angular momentum[11] vector $\vec{j}$ which is naturally a constant of the motion both classically and quantum mechanically.[12] Pure molecular reorientation corresponds to a change in the *direction* of $\vec{j}$ without a change in its magnitude; the transition $|j,m\rangle\rightarrow|j,m'\rangle$, $m'\neq m$ represents a transition between two degenerate eigenstates so that no transfer of internal energy occurs. Such a transition can only occur through a torque applied to the molecular frame with a nonvanishing component perpendicular to the original direction of the angular momentum $\vec{j}$. This collisionally induced torque is a measure of the strength of the anisotropic component of the molecular interaction. As a rough approximation to the actual dynamical picture, we use the classical equation of motion governing the rate of change of the molecular angular momentum $\vec{j}$,

$$\frac{d}{dt}\vec{j}=\vec{T}, \tag{4}$$

where $\vec{T}$ represents the torque applied during a collision. The torque generated by a force $\vec{F}$ is given by

$$\vec{T}=\vec{r}\times\vec{F}, \tag{5}$$

where $\vec{r}$ is the effective radius of interaction. Equivalently, this force may be expressed as the gradient of the appropriate potential-energy function[13] $V(\vec{r})$ so that

$$\vec{T}=\vec{r}\times\nabla V(\vec{r}). \tag{6}$$

Simple integration of Eq. (4) gives

$$\Delta\vec{j}=\int_{\text{collision}}\vec{r}\times\nabla V(\vec{r})\,dt, \tag{7}$$

where the integration is over the duration of the collision. If we now approximate the integral by a properly selected product of average values, Eq. (7) becomes

$$\Delta\vec{j}\cong a(\nabla V)_{\text{av}}\tau, \tag{8}$$

where the quantity a represents the effective force range of the potential, $(\nabla V)_{\text{av}}$ is the mean force, and τ is the duration of the collision. Furthermore, if we approximate $(\nabla V)_{\text{av}}$ as an interaction strength V_0 divided by the scale length (V_0/a) and the time of collision τ as a/v, where v is the mean relative molecular speed, we obtain

$$\Delta j\cong a\frac{V_0}{a}\frac{a}{v}=V_0\frac{a}{v}\,. \tag{9}$$

This simple picture shows the elementary and anticipated result that long-range intermolecular forces are the most effective in transferring angular momentum.

Experimentally, the rate of molecular reorientation can be determined through measurements of the pressure-broadened linewidth of depolarized Rayleigh scattering. It has been shown by Gordon[14] and Hess[15] that a measurement of this component determines the rate of reorientation of the molecular angular momentum by collisions. Such measurements have recently been reported[16] for self-broadening of CO_2, OCS, and CS_2 having the respective values for the cross sections of 65×10^{-16} cm^2, 94×10^{-16} cm^2, and 117×10^{-16} cm^2.

B. Rotational Relaxation

Rotational transitions and reorientational processes are related in that they both result from the torque generated by the anisotropic component of the intermolecular interaction. They differ in that the rotational transitions necessarily involve a change in the magnitude of the angular momentum vector $\vec{j}$ and thus require an exchange of internal energy. Since molecular-rotational energies scale according to $Bj(j+1)$ where B is the rotational constant[17] and j equals the magnitude of angular momentum $\vec{j}$, the transferred internal energy will tend to increase with j and the inverse of the molecular moment of inertia. For the majority of molecular systems at temperatures ~300°K, the exchanged internal energy is substantially less than $k\Theta$, where Θ represents the kinetic temperature of the gas.[18] However, for the light hydrides rotational energies are comparable to vibrational energies for $j\sim10$. Although we will not address such possibilities in this work, this can lead to interesting processes involving near-resonant exchanges of rotational and vibrational energy (RV) processes. Measurements[19] of the quenching of CO infrared fluorescence by H_2 show that para-H_2 quenches vibrationally excited CO more readily than normal-H_2. Calculations[20] indicate that a selective rotational-vibrational exchange reasonably accounts for this observation. Sharma[21] has also discussed the role of RV couplings in connection with the CO_2-H_2 and CO_2-D_2 systems.

From the previous simplified discussion of reorientation, we expect that rotational relaxation will be strongly influenced by the presence of long-range anisotropic molecular forces. Since we are primarily interested in the longer-range components, it is reasonable to approximate the interaction by a model based upon a multipole expansion of the charge distributions representing the two molecules. Of course, the van der Waals interaction involving a tensor polarizability should also be included. Such a treatment ignores, for example, short-range exchange forces which are operative when the molecular charge clouds overlap.[22]

Consider a polar molecule such as CO and HF which have, by their lack of symmetry, permanent electric dipole moments. At sufficiently long range, the principal interaction producing the required torque will be due to the coupling of the collisionally induced electric field with the static electric moment. In this case the interaction is similar to that involved in the pure rotational microwave spectrum of these molecules in that both derive their coupling through the permanent electric dipole moment.[23] Symmetric systems like CO_2, however, have a vanishing static electric dipole moment owing to considerations of symmetry, and therefore, must depend upon coupling to a higher multipole moment. In this case, the first nonvanishing electric moment is the quadrupole.

The validity of the picture founded on the multipole expansion rests largely on the assumption that the bulk of the interactions of interest occur at intermolecular distances sufficiently large in comparison to the molecular dimensions of the free system. Pressure-broadening data of infrared transitions can be used to establish the scale of the interaction range to test this premise. For the example of CO_2, the full pressure-broadened linewidth[24] of the 10.6-μ $P(20)$ transition is ~7.5 MHz Torr^{-1}, which corresponds to a 7 Å interaction radius for CO_2-CO_2 collisions. This is to be compared with a C-O distance of 1.16 Å and leads one to conclude that the multipolar representation of the molecular interactions is a reasonable starting point. Finally, we emphasize that these remarks are only approximate and are designed mainly to present a simple model with which one can visualize these complicated[25] interactions.

Rotational relaxation rates are generally rapid processes with characteristic cross sections usually not much less[26] than the gas kinetic value. Experimentally established values for several gases are compiled in Ref. 25. The rotational relaxation of CO_2 has been measured on the 00°1-10°0 10.6-μ transition with laser techniques.[27] The value obtained is on the order of $10^7\ \text{sec}^{-1}\text{Torr}^{-1}$.

C. Vibrational Relaxation

Vibrational transitions are induced in collisions by forces generated along the coordinates of the normal modes of the molecule. Since an exchange of angular momentum is not usually involved,[28] short-range as well as longer-range interactions can both play important roles. However, since the interaction should be diabatic for the transition probability to be appreciable,[29] the rapidly varying short-range contributions will exert a strong influence in a wide class of situations. Nevertheless, the longer-range components appear to be influential and there is recent experimental evidence[30] indicating their participation in vibrational-energy transfer processes.

Calculations of vibrational deactivation probabilities assuming a short-range repulsion of exponential form have been presented by several authors.[31] For a rather broad range of circumstances it is found that the transition probability is exponentially dependent on a factor proportional to $(\Delta E^2 m/\alpha^2 T)^{1/3}$, where ΔE is the energy transferred, m is the reduced mass of the colliding molecules, α^{-1} is the range of the exponential force, and T is the kinetic temperature.[32] The role of diabaticity is clearly seen in an examination of this term; high velocity (low m and high T) and short range (large α) all conspire collectively to decrease the exponential factor and lead to an increased transition probability.[31]

Vibrational relaxation rates are experimentally observed to have a large variation. However, it is generally true that resonant VV processes tend to be significantly faster than VT deactivation calling for large[33] energy transfer into the kinetic degree of freedom. Rates for VT processes, nevertheless, vary strongly from one system to another. For example, the $p\tau$ value for CO at ~300°K is approximately 1 sec atm while the corresponding parameter for HF is ~14 nsec atm.[34]

III. METHOD OF COMPUTATION

We are generally concerned with the response of a pair of degenerate eigenlevels under the simultaneous influence of a resonant optical field and collisional coupling to an energy reservoir of adjacent states. The energy reservoir may consist of nearby rotational levels, vibrational levels, or a combination of both. The over-all effect of rotational or vibrational levels is essentially the same (they both serve as a pool of stored energy which can be coupled to the radiation field), although the communication rates for the two generally differ substantially. In these calculations this merely influences the magnitude of the collisional rate governing the transfer of population from the energy reservior to the radiating states. With this in mind, we do not explicitly examine the vibra-

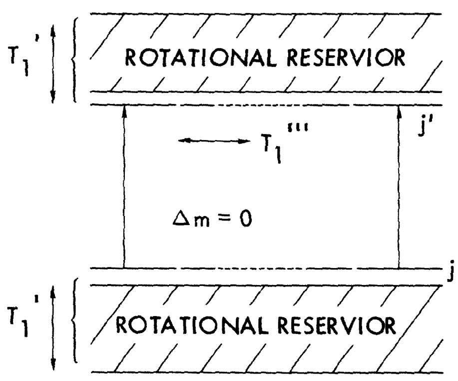

FIG. 1. Schematic of the level diagram indicating the radiating states designated by their angular momenta J (lower) and J' (upper) along with the reservoirs of rotational levels. Linearly polarized light polarized along the $\hat{z}$ axis is assumed so that the selection rule $\Delta m = 0$ holds. T_1' and T_1''' represent relaxation times defined in the text.

tional case, but rather use the example of rotational transfer to illustrate the general behavior.

A schematic of the relevant energy levels is shown in Fig. 1. In terms of the radiating levels J and J', we consider the radiation field to be exactly on resonance and linearly polarized along the $\hat{z}$ axis, as in previous treatments of degenerate transitions.[35,36] This choice of polarization leads to the selection rule $\Delta m = 0$. The self-consistent solution of the Maxwell and Schrödinger equations, which governs the behavior of the electromagnetic field and the active radiating levels (J, J'), is achieved in the manner described in earlier publications.[35,37] In order to incorporate the influence of the energy content of the adjacent levels, we modify the calculation as follows: Since it is assumed that the levels that comprise the reservoir do not interact directly with the radiation field, it is sufficient to describe these states by population densities[38] alone. These population densities are related to one another and to the population of the radiating states through a kinetic model representing the collisional coupling of reservoir states to the levels in direct interaction with the radiation field. In the absence of a stimulating field, the levels J and J' are assumed to be in equilibrium with the reservior states at the gas kinetic temperature. The presence of stimulated emission, however, will perturb the equilibrium situation and will consequently cause an energy exchange between the reservior states, which tends to restore the appropriate equilibrium condition. The communication between the individual energy states is characterized by a single inelastic relaxation time T_1'. The significance of this parameter and the conditions under which one may meaningfully describe the process by a single relaxation time are discussed in the Appendix. In addition to the relaxation time T_1', the other important property of the reservior is the ratio of its energy content to the energy stored in the active level. As we show later, it is appropriate to define this quantity as T_1''/T_1', the value[39] of which in any specific case is determined by the rotational partition function, the gas kinetic temperature, and the angular momentum of the radiating state.[5] We also account for the role of molecular reorientation, since this will modulate the coupling of the active levels to the radiation field because of the m dependence of the dipole matrix elements.[35,36] The time constant of molecular reorientation is characterized by the parameter T_1'''. In our model we assume that the probability of reorientation is independent of the projection change (Δm), a premise which presumably fails at sufficiently high angular momentum owing to the finite range of molecular interaction. However, since the results show that the influence or reorientation is relatively weak, we do not believe that this is a serious limitation. For the purpose of completeness we retain an inhomogeneous width described by the parameter T_2^*, although it is clear that the behavior of high-pressure[40] amplifiers will be independent of this quantity.

As stated earlier, these calculations involve a simultaneous and self-consistent solution of both Maxwell's and Schrödinger's equations. In this section we wish to discuss the particular differential equations that are solved numerically to describe the process of pulse amplification in molecular systems. It will be seen that the results are in contrast to those obtained with the two-level atom models. There are two reasons for this outcome. The first point relates to the fact that the coupling constant between the molecule and field is dependent on the angle between the angular-momentum vector and the electric vector. This is expressed as an m dependence of the matrix elements. This turns out to have only relatively minor consequences. The second more important factor is that the active level is closely coupled to nearby vibrational and rotational levels through collisional mechanisms. These act to repopulate the active level when it is depleted by radiative saturation. Previous amplifier treatments have not dealt with this situation. Furthermore, this adjacent set of molecular states represents a saturable reservoir of energy. This is another aspect of the theory which is absent in a two-level treatment. As a direct consequence of these energy-transfer processes the qualitative aspects of molecular amplification differ drastically from a two-level treatment. Although the model we use here is very simple, generalization to more complicated situations is straightforward.

The basic equations governing the dynamical response of the electromagnetic field and the medium are given below. These expressions represent the direct generalizations of those used in previous studies[35,37] appropriately modified to incorporate the influence of the relevant collisional processes. For the condition of exact resonance, and with both the rotating-wave and slowly-varying-envelope approximation (SVEA), the electromagnetic field $\vec{E}(t, z)$ may be completely described by a real amplitude $\mathcal{E}(t, z)$ in the form

$$\vec{E}(t, z) = \hat{\epsilon}\,\mathcal{E}(t, z)\cos(kz - \nu t), \tag{10}$$

where $\hat{\epsilon}$ is a unit polarization vector and the rapid optical variation is given by the cosine factor. The active level is generalized to include the fact that it is degenerate with respect to the magnetic quantum number m. We describe this situation with a set of density matrices[38] $\rho_i = \rho_i(\omega, t, z, \mathcal{P}_i)$

where the matrix elements $\mathcal{P}_i$ take on the set of values appropriate for the transition. We label the matrices $i=1,2,\ldots,$ according to the magnitude of the matrix element with the largest first and then in descending order, i.e., $\mathcal{P}_i > \mathcal{P}_j$ for $i<j$. We reserve the unsubscripted symbol $\mathcal{P}$ to refer to the largest of the dipole matrix elements.[41] We then define the ratio $r_i = \mathcal{P}_i/\mathcal{P}$. These ratios are evaluated differently according to whether one is amplifying with a Q-branch transition, in which case $r_i = (J-i+1)/J$, $i=1, J$, where J is the angular-momentum quantum number, or with a P- or R-branch transition, in which case $r_i = [j^2-(i-1)^2]^{1/2}/j$, $i=1, j$ and $j=J$, $J+1$, respectively. In addition, we use an index N_i that specifies the state to indicate whether there are one or two magnetic quantum states with the same dipoles. N_1 is different from unity only in the case of a P or R branch, in which case $N_1 = 0.5$. One notes that we have ignored the existence of the uncoupled levels. We do this since we intend to apply the theory for high-angular-momentum states ($J \gg 1$), where the problem is very nearly classical. In this limit, the approximation involves a very small error.

Under the stated circumstances, Maxwell's and Schrödinger's equations reduce to the following set of expressions. Maxwell's equation reads

$$\frac{\partial \mathcal{E}}{\partial z} + \frac{1}{c}\frac{\partial \mathcal{E}}{\partial t} = \alpha \sum_i r_i^2 N_i \int_{-\infty}^{t} dt'\, \mathcal{E}(t',z) \times e^{-(t-t')/T_2} \chi_i(t-t',t',z), \tag{11}$$

where T_2 is the phase-memory time and the gain coefficient α is given by

$$\alpha = \mathcal{P}^2 \nu N \pi \sigma(\nu)/2\hbar c \epsilon_0 . \tag{12}$$

Here $N \times N_i$ is the excitation density of the molecules in the ith state, ϵ_0 is the dielectric constant, and $\sigma(\nu)$ is the frequency distribution of the molecules owing to the Doppler effect. The generalized susceptibility χ_i is defined to be

$$\chi_i(T,t,z) = 2\pi\sigma(\nu)^{-1} \int_{-\infty}^{\infty} d\omega\, \sigma(\omega) [\rho_{aa}(\omega,t,z,\mathcal{P}_i) - \rho_{bb}(\omega,t,z,\mathcal{P}_i)] \cos(\omega-\nu)T, \tag{13}$$

where a and b refer to the upper and lower states, respectively. The equation of motion $\chi_i(T,t,z)$ written below is based on two major approximations. The first is that the upper and lower levels can be regarded as being entirely equivalent kinetically and with respect to degeneracy. This latter point means that the rotational temperatures of the two levels are identical and that the angular momenta of the molecular states are sufficiently large so that one can ignore the uncoupled levels in either the upper or lower active states. This approximation allows us to write all variables as differences between the upper and lower states. The second approximation is essentially a statement that we treat all the rotational states in the upper and lower levels as a single reservoir that repopulates (depopulates) the upper (lower) active levels. We define as N the inversion represented by the reservoir (normalized to unity in the absence of the field), that is, the inversion of the entire ensemble of states excluding the active levels.

The equations of motion for the active medium are then

$$\frac{\partial \chi_i(T,t,z)}{\partial t} = \frac{D(T)-\chi_i(T,t,z)}{T_1} + \frac{ND(T)-\chi_i(T,t,z)}{T_1'} + \left(\frac{\sum_{i=1}^{j} \chi_i(T,t,z) N_i}{\sum_{i=1}^{j} N_i} - \chi_i(T,t,z) \right) \Big/ T_1''' - \frac{\mathcal{P}^2 r_i^2}{2\hbar^2} \int_{-\infty}^{t} dt'\, \mathcal{E}(t,z)\, \mathcal{E}(t',z)\, e^{-(t-t')/T_2} [\chi_i(T+t-t',t',z) + \chi_i(T-t+t',t',z)], \tag{14}$$

and the equation for the reservoir is

$$\frac{\partial N}{\partial t} = \frac{1-N}{T_1} + \left(\frac{\sum_i \chi_i(0,t,z) N_i}{\sum_i N_i D(0)} - N \right) \Big/ T_1'' . \tag{15}$$

The function $D(T)$ is given by the Fourier transform, normalized to unity, of the function $\sigma(\omega)$ and is given by

$$D(T) = (\pi^{1/2} T_2^*)^{-1} e^{-T^2/T_2^{*2}}, \tag{16}$$

for Doppler broadening where the time T_2^* is the dephasing time due to molecular motion.

The first term in the right-hand side of Eqs. (14) and (15) is the ordinary pump term that has been discussed in other cases. We include conceptually VV collisions in this part of the equation. However, for the purpose of these calculations, we ignore the VV term by setting $T_1 \to \infty$ in all calculations, and taking as our initial condition

$$\chi_i(T,t_0,z) = D(T) \tag{17}$$

and

$$N=1, \tag{18}$$

where t_0 is the time at which the pulse arrives at the position z. These vibrational interactions are not included, since they differ from the rotational interaction only in the characteristic times of interaction and not in their qualitative effect on the development of pulses. If the VV collisions need to be added, it is a simple matter to include another reservoir variable incorporating the corresponding T_1 terms in a manner similar to the rotational reservoir.

The third term in Eq. (14) represents the effect of collisions which reorient the angular momentum of the molecule without changing its magnitude. This term has been the subject of recent controversy over the hypothesis that T_1''' could be very short without affecting the phase-memory time T_2. Although T_1''' is treated as a free parameter (as, of course, are T_1' and T_1''), it is always implicit that we intend, in any real application, for T_1''' to contribute to T_2. For reasons of simplicity only, we have assumed that the velocities are unchanged by these collisions. Since reorientation is shown to have a relatively weak influence, the error introduced by this assumption is negligible. In this case, as for inelastic collisions, the influence of velocity changes is unimportant provided that the momentum transfer is accompanied by a destruction of the phase memory (i.e., represents a contribution to T_2). Under these circumstances, the details that arise from the Doppler effect are minor in comparison to the large-scale changes in pulse waveform that are generated through repopulation from the reservoir. The final term in Eq. (14) is the interaction of the active level with the radiation field. This term has been discussed in detail elsewhere.[10,35]

The second terms in both Eqs. (14) and (15) represent the inelastic interrotational collisions, that is, collisions which transfer energy from the active level to the reservoir. In order to avoid complications arising from the velocity-changing effects of collisions, we have effectively assumed a hard-collision model in which the velocity of a molecule is completely randomized as the result of a transition from an active level to the reservoir. This appears reasonable as long as it is much more probable that the molecule will reside in the reservoir rather than the active level. Since $\chi_i(0,t,z)$ is just the total inversion in the ith level, and since $D(0)$ is included to normalize this inversion in the same fashion as N, the complicated term in expression (15) can be seen to have a simple interpretation. T_1' is the average time required for an atom in the active level to make a transition to the reservoir, and T_1'' is the time required for an atom in the reservoir to migrate to an active level. Since T_1' and T_1'' represent the same basic collision process, it follows that

$$T_1''/T_1' = N_r/N_a\,, \tag{19}$$

where N_r is the number of atoms in the reservoir in the absence of the optical field, N_a is the number of atoms in the active level in the absence of the optical field, and

$$1/T_1' + 1/T_1'' = 1/T_c\,, \tag{20}$$

where T_c is the inelastic collision time. This will be discussed in greater detail in the Appendix. Under normal circumstances, $T_1'' \gg T_1'$ in which case $T_1' \cong T_c$. Thus, we can usually refer to T_1' as the inelastic-collision time. In this limit, T_1'' is the time needed to bring the entire rotational set into equilibrium with itself. Consequently, it is referred to as the reservoir-equilibration time.

The most fundamental differences between the two-level atom and molecular models lie in the complicated terms which mutually link the reservoir and active level. There is, nevertheless, a relatively simple analysis that helps motivate both the significance and use of the time constant T_1'' and which also illustrates why the molecular and the two-level-atom models result in different behavior for the amplification of pulses. To examine this point we rewrite the equations of motion for the medium in the case of constant electric field in the limit $T_2 \ll T_2^*$ (i.e., pressure broadened). We eliminate the effects of degeneracy by letting $T_1''' \to 0$ so that each level behaves identically. The inversion is then represented in terms of the variable n where $nD(0) = \chi_i(0,t,z)$. Note that n is the total (integrated) inversion which is the proper variable to use in this limit. The equations then reduce to

$$\frac{dN}{d\mu} = \frac{n-N}{T_1''} \tag{21}$$

and

$$\frac{dn}{d\mu} = \frac{N-n}{T_1'} - T_2 (r^2)_{\text{av}} I n, \tag{22}$$

where

$$(r^2)_{\text{av}} = \sum_i N_i r_i^2 \Big/ \sum_i N_i$$

and

$$I(\mu, z) \equiv \mathcal{P}\mathcal{E}(\mu, z)^2/\hbar\,. \tag{23}$$

For convenience in later discussions we have written the equation in terms of the retarded time $\mu = t - z/c$. In these expressions note that the equations for a two-level atom relate to these by setting T_1'', $T_1' \to \infty$ and $(r^2)_{\text{av}} = 1$. In the limit in which the field varies slowly compared to an atomic-coherence time, the equation of motion for the electromagnetic field becomes insensitive to the phase of the field, and can be rewritten in terms of the intensity $I(\mu, z)$ such that

$$\frac{\partial I}{\partial z} = 2gIn. \qquad (24)$$

The constant g is the small-signal amplitude-gain constant which will be discussed in more detail at the end of this section. The statement of conservation of energy for this system can be found simply by substituting expression (22) into Eq. (21) and then substituting that result into the equation of motion for the field, thus obtaining

$$\frac{\partial I(\mu, z)}{\partial z} = -\frac{2g}{T_2 (r^2)_{\text{av}}} \frac{\partial}{\partial \mu} \left(n(\mu) + \frac{T_1''}{T_1'} N(\mu) \right). \qquad (25)$$

It is observed from this equation that the ratio T_1''/T_1' amplifies the contribution from the reservoir, and therefore, represents the ratio of the energy stored in the reservoir to the energy contained in the active level as stated in expression (19). The energy extracted from the molecules as a function of time can be found by integrating both sides of this equation with respect to the retarded time μ, so that

$$\frac{\partial}{\partial z} \int_0^{\mu} d\mu' \, I(\mu', z) = \frac{2g}{T_2 (r^2)_{\text{av}}} \left([1 - n(\mu)] + \frac{T_1''}{T_1'} [1 - N(\mu)] \right), \qquad (26)$$

with both N and n set to unity at the point $\mu = 0$ according to the appropriate initial conditions stemming from the definitions of these variables. Note that in the limit $\mu \to \infty$ both N and n tend to zero, indicating an equality between the upper- and lower-state populations. This point will be examined explicitly again in Sec. IV. Thus, the total available energy that can be extracted from the levels by the field is half of the energy stored in the system [the stored energy can be found by setting n, $N \to -1$ for the limit $\mu \to \infty$ in Eq. (26)].

At this point we discuss certain characteristic parameters related to the performance and interpretation of these calculations. It is assumed that we are dealing with a plane-wave amplifier whose input and output planes are located at $z = 0$ and $z = L$, respectively. The given input data consist of an input pulse-amplitude function $\mathcal{E}(t, 0)$, the relaxation rates and linewidths characteristic of the medium, a parameter related to the low-signal gain coefficient, and the angular momenta of the upper (J') and lower (J) levels. For convenience we use the retarded time $\mu = t - z/c$, since it allows us to locate the leading edge of the pulse at $\mu = 0$. The output amplitude waveform then appears as $\mathcal{E}(\mu, L)$. Since one does not directly measure the pulse envelope $\mathcal{E}(\mu, z)$, it is often convenient to deal with certain functionals of this envelope which have a clearer physical significance. For our purposes these are the pulse area $\theta(z)$, the pulse energy $\mathcal{T}(z)$, the full width at half-maximum of the amplitude $\hat{t}_A(z)$ or intensity $\hat{t}_I(z)$, and the peak intensity $I_{\max}(z)$. The area $\theta(z)$ is defined through the relation involving the dipole moment[41] $\mathcal{P}$

$$\theta(z) = (\mathcal{P}/\hbar) \int_{\text{pulse}} \mathcal{E}(t, z) \, dt, \qquad (27)$$

and is used primarily as a parameter of the input pulse. For a fixed functional form of the envelope function $\mathcal{E}(t, z)$, the area clearly scales directly with the peak amplitude. The energy is defined through

$$\mathcal{T}(z) = (\mathcal{P}^2/\hbar^2) \int_{\text{pulse}} \mathcal{E}^2(t, z) \, dt. \qquad (28)$$

With the choice of units, the energy $\mathcal{T}(z)$ has the dimensions of inverse time. The actual energy can then be determined by application of the appropriate scale factor $c\hbar^2/8\pi\mathcal{P}^2$, where c represents the speed of light. In all calculations the unit of time is taken as T_2^* and the medium is then characterized by the time scales previously discussed. We have found, however, that it is somewhat inconvenient to describe the gain parameter in terms of the customary α usually rendered in cm^{-1}. As an alternative we introduce the small-signal coefficient g, defined through the expression

$$\mathcal{T}(z) = \mathcal{T}(0) e^{2gz}. \qquad (29)$$

It is easily shown, that in the limit of small-pulse energy and area for a pulse whose width $\hat{t}_A(z)$ is much greater than the inverse bandwidth of the amplifier, that $\chi_i(T, t, z) = D(T)$. Under these circumstances Eq. (11) leads directly to expression (29) above, with the coefficient g given by

$$g = \sum_{i=1} r_i{}^2 N_i \, \alpha \int_0^{\infty} D(T) e^{-(T/T_2)} \, dT. \qquad (30)$$

The small-signal enhancement of the amplified pulse is given by the factor e^{2gL}, which we then use as a characteristic of the medium.

IV. NUMERICAL RESULTS

In this section we present and explore various aspects of the numerical results derived from these calculations. Basically, the issues that are examined concern (a) in the role of the parameter T_1' on the efficiency of energy extraction from the amplifier, (b) the effect of the energy-transfer processes on the output pulse shape, (c) the influence of the reorientational parameter T_1''', and (d) the development of an asymptotic pulse shape for very-high gain systems. Experimental data relevant to this latter point have been observed in a hydrogen fluoride (HF) amplifier system.

A. T_1' Dependence of Energy Extraction

An important determinant of amplifier performance is the efficiency with which the stored energy can be extracted in the form of coherent radiation. In this connection it is of substantial interest to determine the relationship, for fixed amplifier input conditions,[42] between the output pulse energy and the relaxation time T_1'. In order to isolate the influence of this factor, we regard the other relevant parameters describing the amplifying medium as fixed.[43]

Figure 2 illustrates the influence of the rotational relaxation parameter T_1' on the extracted energy[44] $\mathcal{T}_{\text{out}}$. In all four curves (a)–(d) the incident pulses had identical waveforms with a width given by $\hat{t}_I(0)=21.6$. Curves (a) and (b) correspond to input areas $\theta(0)=\pi$, while those for (c) and (d) have the value $\theta(0)=2\pi$. The effect of saturation causes curves (c) and (d) to lie below (a) and (b). $T_1''/T_1'=10$ for cases (a) and (c), while for (b) and (d) the corresponding value is unity. This accounts for the fact that the curves (a) and (c) lie above their respective counterparts (b) and (d) at small values of T_1'. An essential point illustrated by Fig. 2 is that the pairs of curves coincide for $T_1'>\hat{t}_I(0)$ and increase significantly only if T_1' is considerably less than $\hat{t}_I(0)$. This is clearly due to the increased effectiveness of the rotational energy transfer for small T_1'. The splitting of the curve pairs arises from the differences in the reservoir energy content for the two values of T_1''/T_1'.

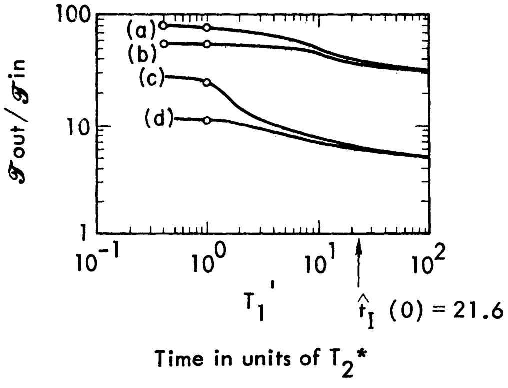

FIG. 2. Ratio of the pulse energy out to the pulse energy in ($\mathcal{T}_{\text{out}}/\mathcal{T}_{\text{in}}$) vs T_1' for pulses with an initial width given by $\hat{t}_I(0)=21.6$. In all cases $T_1'''=10^6$, with the remaining parameters given as follows: (a) $\theta(0)=\pi$, $T_1''/T_1'=10$; (b) $\theta(0)=\pi$, $T_1''/T_1'=1$; (c) $\theta(0)=2\pi$, $T_1''/T_1'=10$; (d) $\theta(0)=2\pi$, $T_1''/T_1'=1$. Complete extraction only occurs for T_1' significantly less than $\hat{t}_I(0)$. All times are in units of T_2^*.

The magnitude of the over-all influence of the rotational relaxation is most clearly shown in an examination of curve (c). This case corresponds to a strongly saturating input pulse propagating through an amplifier whose energy is stored mainly in the reservoir states ($T_1''/T_1'=10$). This is essentially the situation for the 10.6-μ transition of CO_2 at ~300°K. The extracted energy is considerably less than optimal unless T_1'' is of the same order as the pulse width $\hat{t}_I(0)$. The behavior of the amplifier efficiency exhibits several differences in the comparison of the present case to the two-level-atom model. In the latter, either of two situations generally occurs; the efficiency is independent of the pulse width,[45] as in the case where the width is much shorter that T_2, or the efficiency increases[46] with decreasing pulse width, as observed in the example of a Doppler broadened transition.[10] In contrast to the above, the inclusion of a collisionally coupled energy reservoir leads to an efficiency which grows with increasing pulse width.

There is a fairly simple exercise that illustrates why the molecular and two-level-atom models result in different behavior for the amplification of pulses. For an examination of this point we use the simplified forms of the equations of motion for the field and the medium equations (21), (22), and (24), which are valid under the assumptions that the field amplitude varies negligibly in the time T_2 and that medium degeneracy is unimportant, enabling T_1''' to be set to zero. We then consider the response of the molecular system to an incident constant-intensity monochromatic wave which is introduced at time $\mu=0$. Since the power is a constant, expressions (21) and (22) are simple differential equations with initial conditions $N=1$ and $n=1$. These equations are then solved to give

$$n(\mu)=\frac{\lambda_-(1+\lambda_+T_1'')e^{\lambda_+\mu}-\lambda_+(1+\lambda_-T_1'')e^{\lambda_-\mu}}{\lambda_- -\lambda_+}\,, \tag{31}$$

$$N(\mu)=\frac{\lambda_- e^{\lambda_+\mu}-\lambda_+ e^{\lambda_-\mu}}{\lambda_- -\lambda_+}\,, \tag{32}$$

with

$$\lambda_\pm=\frac{1}{2}\left\{-\left(\frac{1}{T_1'}+\frac{1}{T_1''}+T_2(\gamma^2)_{\text{av}}I\right)\right. \pm\left.\left[\left(\frac{1}{T_1'}+\frac{1}{T_1''}+T_2(\gamma^2)_{\text{av}}I\right)^2-\frac{4T_2}{T_1''}\right]^{1/2}\right\}. \tag{33}$$

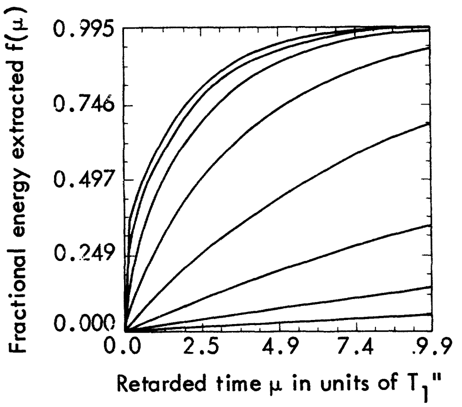

FIG. 3. Extracted energy from a molecular system vs retarded time μ. The higher curves represent greater optical intensities interacting with the active levels. The top curve represents limiting behavior and illustrates the time delay due to the finite rate of molecular relaxation. The time scale of the transfer is given essentially by T_1''.

The interaction of the field with the molecule causes energy to be extracted from the system until eventually both n and N tend to zero. Because of our approximations, only half of the energy stored in the molecule can be extracted. We then look at the fraction of energy that has been extracted from the atom at a time μ after the field has been energized. This fraction, which is given by

$$f(\mu)=1-\frac{T_1' n(\mu)}{T_1'+T_1''}-\frac{T_1'' N(\mu)}{T_1'+T_1''}\,, \tag{34}$$

is appropriately defined to account for the fact that only half of the stored energy can be extracted.

In Fig. 3 we display the function $f(\mu)$ vs μ for various values of the intensity I. The higher curves represent greater values of intensity. For low intensity the extraction is relatively gradual. It is observed that at the higher intensities, although some of the energy is extracted essentially instantaneously, there is a fraction of the energy that comes out at a rate determined by the collision time and is *independent* of the optical flux. In the limit of very large intensity the fraction of energy left in the molecular reservoir becomes

$$f(\mu)=1-\frac{T_1'}{T_1'+T_1''}\,e^{-T_2\langle r^2\rangle_{\mathrm{av}}I\mu}-\frac{T_1''}{T_1'+T_1''}\,e^{-\mu/T_1''}\,. \tag{35}$$

It is only the energy that is stored in the active level at $\mu=0$ which is extracted rapidly. The energy stored in the reservoir must wait for a time T_1'', the reservoir-equilibration time, until collisions transfer the molecules to the state in resonance with the field. This, of course, is in contrast with the two-level-atom model for which all of the energy can be extracted rapidly. It is essentially the confluence of two effects that leads to the continual narrowing seen in the two-level-atom case; first, that the energy is extracted ever more rapidly with increasing intensity, and second, that this energy adds to the intensity. However, in the molecular situation only the (usually small) percentage of the energy in the active level can contribute to the narrowing. The bulk of the energy must feed into the trailing edge of the pulse and results in a tendency to increase the pulse width. As we show later, it is also this division of the available energy into rapid and slow extraction that leads to a two-time-scale effect in the development of an asymptotic pulse waveform.

B. Influence on Output Pulse Shape

The energy-transfer processes exert an influence on the output-pulse waveforms. The resulting pulse-shape variations are a direct consequence of the collisional phenomena and differ qualitatively from the results obtained for amplifying media without an energy reservoir. As discussed earlier, the two-level model generally leads to a strong pulse narrowing,[10,47] as a result of the bootstrapping effect of the extracted energy on the stimulated rate. However, in the molecular case the finite relaxation rate introduces a delay in the

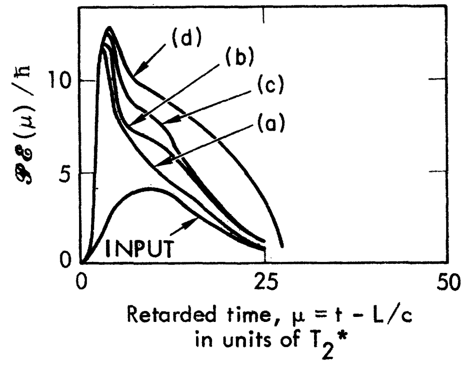

FIG. 4. Output-pulse amplitude waveforms in units of $\mathcal{P}\mathcal{E}(\mu)/h$ vs retarded time $\mu=t-L/c$: (a) $T_1'=100$, $T_1''/T_1'=1$; (b) $T_1'=10$, $T_1''/T_1'=1$; (c) $T_1'=2$, $T_1''/T_1'=1$; (d) $T_1'=2$, $T_1''/T_1'=10$. The corresponding input pulse, for which $\Theta(0)=2\pi$ and $\hat{\mathcal{E}}_I(0)=10.8$, is shown as the lowest curve. In all cases $T_1'''=10^6$, so that the reorientational processes are inoperative. The effects of energy transfer from the reservoir generate a substantial energy content in the tail of the pulse. All times are in units of T_2^*.

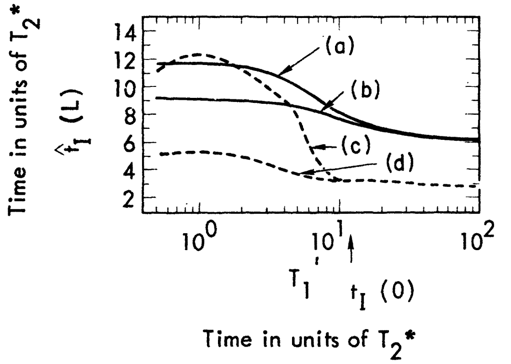

FIG. 5. Output-pulse width $\hat{t}_I(L)$ vs relaxation time T_1'. The fixed parameters for the curves are as follows: (a) $\theta(0)=\frac{1}{2}\pi$, $T_1''/T_1'=1$; (b) $\theta(0)=\frac{1}{2}\pi$, $T_1''/T_1'=1$; (c) $\theta(0)=2\pi$, $T_1''/T_1'=10$; (d) $\theta(0)=2\pi$, $T_1''/T_1'=1$. In all cases $T_1'''=10^6$ and $\hat{t}_I(0)=10.8$. Notice that curves (a) and (c) actually correspond to a pulse broadening as a result of the influence of the reservoir. All times are in units of T_2^*.

stimulated energy extraction process which counteracts the effectiveness of the mechanisms generating the pulse narrowing.

Examples of the influence of the energy transfer on the output pulse shape are illustrated in Fig. 4. Although some sharpening of the leading edge does occur, there is a clear tendency for a considerable fraction of the energy to appear in the trailing portion of the pulse. As the results show, for a fixed initial pulse width $\hat{t}_I(0)$ of 10.8, the effect is more prominent as T_1' is reduced and the ratio T_1''/T_1' is increased. This is essentially just a statement that the total pulse energy scales with both the relaxational rate coupling the reservoir states to the radiating levels and the energy content of the reservoir. As a consequence of this dynamical picture, we observe that the pulse evolution develops such that the initial peak contains only a relatively small fraction of the total energy. The tail of the pulse accounts for the remaining larger amount coming from the reservoir and the pulse actually broadens to greater values of $\hat{t}_I(z)$ during amplification. Under the conditions of strong saturation, the energy partitions itself approximately so that the ratio of the energy in the tail to the energy in the peak is given roughly by T_1''/T_1'.

Quantitative data concerning the influence of the collisional relaxation on the output pulse widths $\hat{t}_I(L)$ are shown in Fig. 5. For sufficiently long relaxation times T_1', the output pulse width $\hat{t}_I(L)$ is independent of the relaxation rate. This occurs approximately for $T_1'>\hat{t}_I(0)$ and results directly from the negligible energy transfer that takes place in this regime. For the shorter values of T_1' the magnitude of the pulse distortion depends upon the optical flux and the amount of energy available for transfer into the trailing edge of the pulse. Weakly saturating pulses will clearly be affected in a minimal way by the relaxation. Since such pulses are not effective in disturbing the equilibrium population densities of the states, they are not sensitive to the rate of energy transfer among the states.[48] On this basis we anticipate that the influence of T_1' should be larger for more strongly saturating pulses. The results illustrated in Fig. 5 confirm this conclusion. Curves (a) and (b) correspond to $\theta(0)=\frac{1}{2}\pi$, while the corresponding value for curves (c) and (d) is $\theta(0)=2\pi$. For the same ratio of T_1''/T_1', the total variation of $\hat{t}_I(L)$ is greater for the (c)-(d) curves than for the (a)-(b) pair. In addition, the curves for which $T_1''/T_1'=10$ [i.e., (a) and (c)] show a stronger effect than their counterparts [i.e., (b) and (d)] for which $T_1''/T_1'=1$ because of the greater energy available in the reservoir. Indeed, for a sufficiently small value of T_1' the curves (a) and (c) indicate that the output pulse length $\hat{t}_I(L)$ is greater than the input value $\hat{t}_I(0)$.

In conclusion we note that the over-all influence of the relaxational processes is to introduce a general tendency for pulses whose widths $\hat{t}_I$ are in the range T_1', $T_2 \lessgtr \hat{t}_I \ll T_1''$ to broaden upon amplification. Moreover, the trend is for maximum broadening to be associated with greater efficiencies. As observed earlier, this feature is distinguished from the result for the two-level-atom models in which increased efficiency is usually accompanied by some degree of pulse narrowing.[10,45]

C. Influence of Reorientational Processes

The rate of molecular reorientation in these calculations is given by the parameter $(T_1''')^{-1}$. Since the transition dipole matrix elements have an m dependence,[23] reorientation effectively modulates the coupling strength of the radiating ensemble with the electromagnetic field. We recall that in the absence of reorientation and phase-destructive processes, the polarizations of the independent coherently excited ensembles interfere and produce modulation of the pulse envelope. The effects have previously been examined for attenuators in both unbroadened[36] and inhomogeneously broadened[35] media.

These studies indicate that reorientational processes play a small role in the dynamics of pulse amplification. Figure 6 illustrates the typical effect of T_1''' under saturated conditions[48] on the

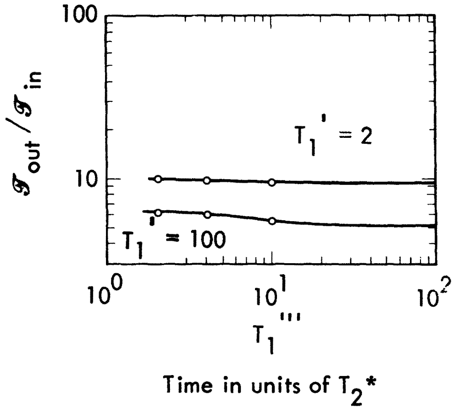

FIG. 6. Ratio of energy out to energy in $\mathcal{T}(L)/\mathcal{T}(0)$ vs the reorientational relaxation parameter T_1'''.

energy ratio $\mathcal{T}(L)/\mathcal{T}(0)$ which is seen to be quite weak. The slight increase in the extracted energy for short values of T_1''' arises from the fact that influence of the larger matrix elements, which produce a greater stimulated rate, is distributed over all magnetic sublevels and not restricted to a few. The effect of T_1''' on the output pulse width $\hat{t}_I(L)$ is also small, as Fig. 7 shows. The results also show that the role of T_1'' entirely negligible if $T_1''' \gg T_1'$, since in that case the excitation funnels into the more-strongly-coupled levels through collisional transfer in the reservoir.

D. Development of Asymptotic Pulse Shape in High-Gain Systems

It was observed in our calculations that the pulse had a tendency to develop a characteristic envelope largely insensitive to initial conditions (e.g., gain and amplifier bandwidth) after undergoing a sufficiently large degree of amplification. The general features of these pulses are shown in Fig. 8. These resulting pulse envelopes exhibit the presence of two phenomena, one radiative and the other collisional. The salient characteristics of the pulse illustrated in Fig. 8 are the intense and sharp initial peak and the broad trailing edge which contains the major fraction of the total energy.

The over-all behavior of the pulses is characterized by phenomena having two widely different time scales. The narrow initial peak is generated essentially by a coherent interaction of the radiation field with the resonant active levels. This type of response is directly related to the pulse narrowing effects normally associated with amplification in a two-level system.[10,37] However, the collisional processes act to stabilize the width of this component approximately to the value T_2.

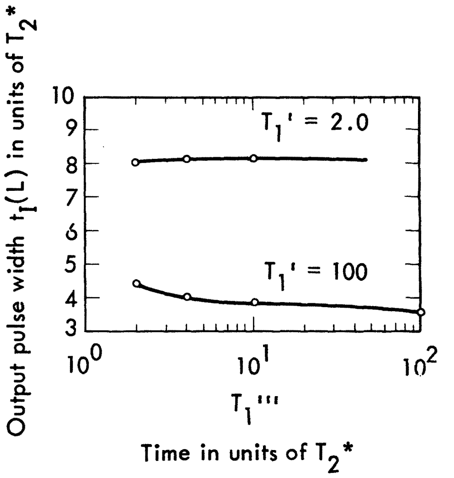

FIG. 7. Output-pulse widths $\hat{t}_I(L)$ vs the reorientational relaxation parameter T_1'''.

In the limit $T_2^* \ll T_2$, the coherent pulse is not stabilized at the value of T_2^* and continues to narrow indefinitely as in the two-level model. On the other hand, the broad pulse tail is produced by energy transfer through collisional relaxation from the reservoir states. As shown earlier, the characteristic time scale for this process is given roughly by T_1''. These two phenomena are able to evolve essentially as independent entities, since the rate for the radiative process scales with the optical intensity, while the rate of the

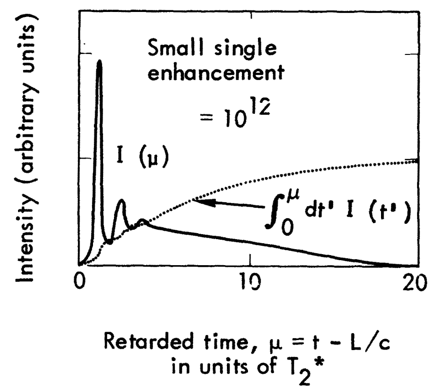

FIG. 8. Intensity $I(\mu)$ vs retarded time μ for the characteristic pulse envelope developed in a high-gain amplifier is given by the solid line. The dashed contour is the integrated energy of the pulse as a function of retarded time μ. The parameters corresponding to the calculation are: small signal enhancement $= 10^{12}$, $T_2^* = 1$, $T_2 = 1$, $T_1' = 2$, $T_1'' = 10$, and $T_1''' = 10^6$.

collisional mechanism scales with the particle density. While the latter is fixed, the former increases due to amplification enabling the radiative process to largely decouple itself from the effects of collisional relaxation. Thus, it is the competition between the collisional and radiative processes which is largely responsible for the two-time scale behavior of the pulse envelope. Effects of this nature have recently been observed experimentally in a high-gain high-frequency amplifier.[49] We note that this feature of the asymptotic pulse is only weakly influenced in the limit $T_2^* \lesssim T_2$. However, in the extreme inhomogeneously broadened limit, this effect will be significantly modified.

Having seen that the trailing edge effect of the asymptotic wave function is a slowly varying function of time, we can return to the previously stated working equations and derive this behavior as an analytic result.[50] We use Eqs. (21) and (22) for the medium and expression (24) for the intensity, a procedure which is valid in the limit that the field changes negligibly in the time T_2. We also note that in this limit, the degeneracy will no longer be important, so that we accordingly discuss the case of short T_1''' as well.

In the asymptotic limit, the intensity is so high that the active level is always nearly completely bleached; that is, n is nearly zero. This means that we can neglect n relative to N in Eq. (22), or rather

$$N(\mu) \cong e^{-\mu/T_1''} . \qquad (36)$$

If we again neglect $\dot{n}$ and n compared to N in Eq. (21) it follows that

$$n \cong [T_1 T_2 (r^2)_{\text{av}} I(\mu, z)]^{-1} e^{-\mu/T_1''} . \qquad (37)$$

Upon substitution into Eq. (24), we observe that the right-hand side no longer depends on either the field or the medium variables. It is therefore a straightforward matter to integrate this equation. The result is most conveniently written in terms of the retarded time μ, in which case

$$I(\mu, z) = I(\mu, 0) + [2gz / T_1 T_2 (r^2)_{\text{av}}] e^{-\mu/T_1''} . \qquad (38)$$

The initial condition $I(\mu, 0)$ here is fixed, so that ultimately the second term will dominate. This is precisely what happens in the development of the asymptotic waveform; the trailing edge very closely follows the exponential term $e^{-\mu/T_1''}$. In this process the field adiabatically follows the level population.

In this asymptotic limit we expect that the model will have serious flaws if it incorrectly describes the kinetics of the medium. Nevertheless, the model shows one important fact; namely, that a full solution of the wave equation is unnecessary in order to determine the trailing edge. One can always follow the much simpler procedure outlined above. Even if the result cannot be obtained in closed form, it will still be much easier to determine the behavior of the solution in this manner than by a solution of the full set of nonlinear equations.

V. SUMMARY AND CONCLUSIONS

The properties of saturated plane-wave short-pulse amplification in gaseous molecular amplifiers have been studied by numerical methods. Specifically, the influence of collisional phenomena on the amplification process has been examined. These calculations have been made within the framework of the slowly-varying-envelope assumption (SVEA) in conjunction with a description of an exactly resonant optical field in terms of a single real variable $\mathcal{E}(t, z)$. This procedure rigidly fixes the phase of the field and explicitly rules out an appraisal of dispersive effects. This issue will be addressed in a future publication.

One of the most important effects of molecular relaxation concerns the efficiency of energy extraction during pulse amplification. These results show that unless the pulse width is comparable to or greater than the total kinetic response time of the relaxing system, the extracted energy will be far less than the energy stored. In order to increase the collisional rate, one must increase the density. However, it may be possible to increase the effective rotational relaxation rate in polar systems through the use of stimulated radiative processes, since pure rotational transitions are strongly allowed in these molecules.[51] This possibility, of course, does not arise for symmetric systems like CO_2.

Another important influence of molecular relaxation on pulse amplification concerns modification of the pulse envelope. There is a general tendency for the development of substantial pulse tails due to the transfer of energy from the reservoir states. This is due entirely to the finite collisional communication time between the radiating levels and the reservoir states.

In spite of the many complications entering into this analysis, it was satisfying to observe that reorientational effects were typically sufficiently small to presumably justify the neglect of these processes for most applications.

The generation of an asymptotic pulse envelope in high-gain systems appears as a generic phenomenon in molecular amplifiers. The two observed time scales characterizing the pulse shape are due separately to a radiative process forming a narrow peak and a collisional process determining the formation of the relatively broad pulse tail. These two effects can become largely decoupled as a result of their different dynamical structure.

ACKNOWLEDGMENTS

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APPENDIX

In this appendix, we show how the working equations are derived from a more complete phenomenological description of the interrotational collision processes. The primary purpose of these equations is to show the sort of approximations that must be made in order to arrive at the phenomenological equations shown in the text. We will ignore the Doppler effect throughout, since it only serves to make the derivation more complicated. Also, for convenience, we will deal with the medium in the limit that the pulse width is much larger than T_2. We then define $\rho_{aa}(J,M)$, $\rho_{bb}(J,M)$ as the density matrix element for the upper or lower vibrational state with angular momentum J and magnetic quantum number M where $M=-J, -J+1, \ldots, J$. We will define a collision time $T^a_{JMJ'M'}$, $T^b_{JMJ'M'}$ as the collision times between the J, M and the $J'M'$ state for the upper and lower vibrational levels, respectively.

For each equation for the upper state, there is a similar equation for the lower state. We will, as long as feasible, write the equations for the upper level only, with the understanding that the equations for the lower level are identical with an interchange of the indices a and b.

The generalized phenomenological density-matrix equations can then be written

$$\begin{aligned}\dot{\rho}_{aa}(J,M) = {} & [\lambda_a(J) - \rho_{aa}(J,M)]/T_1 \\ & + \sum_{M'J'} [\rho_{aa}(J',M')(T^a_{J'M'JM})^{-1} \\ & \qquad - \rho_{aa}(J,M)(T^a_{JMJ'M'})^{-1}] \\ & - r^2_M \tfrac{1}{2}(T_2 I)[\rho_{aa}(J_a,M) - \rho_{bb}(J_b,M)]\,\delta_{J_a J}, \end{aligned} \tag{A1}$$

where J_a is the active upper state, J_b is the active lower state, and I is the instantaneous intensity defined in Eq. (23). For convenience we have restricted ourselves to the case of plane-polarized light for which the selection rules are $\Delta M=0$ (we have chosen the axis of quantization to be along the direction of polarization of the light). The value of r_M is the ratio between the matrix element of the Mth state and the maximum among the set M. However, the indexing is different for the moment, from the convention used in the text in that the $M=1$ level is not necessarily the maximum. We use throughout this paper the index M to refer to the magnetic sublevel, and the index i to refer to the special convention that is used in the text. From Eq. (A1), we obtain the equation for the active level as

$$\begin{aligned}\dot{\rho}_{aa}(J_a,M) = {} & \frac{\lambda_a(J_a) - \rho_{aa}(J_a,M)}{T_1} \\ & + \sum_{JM'}{}' \left(\frac{\rho_{aa}(J,M')}{T^a_{M'JMJ_a}} - \frac{\rho_{aa}(J_a,M)}{T^a_{MJ_aM'J}}\right) \\ & + \sum_{M'=-J_a}^{J_a} \left(\frac{\rho_{aa}(J_a,M')}{T^a_{M'J_aMJ_a}} - \frac{\rho_{aa}(J_a,M)}{T^a_{MJ_aM'J_a}}\right) \\ & - (\tfrac{1}{2}r^2_M)\,T_2 I\,[\rho_{aa}(J_a,M) - \rho_{bb}(J_b,M)], \end{aligned} \tag{A2}$$

where we use the summation convention $\sum'$ to refer to the case where the active level is excluded from the sum. We are trying to arrive at a formula in which all of the levels other than the active one is lumped into a single reservoir term. From the second collision term on the right-hand side of Eq. (A2) one sees that this comes about from the assumption

$$(T^a_{J'M'JM})^{-1} = (T^a_J)^{-1}. \tag{A3}$$

That is, we assume that the collision from $J'M'$ to JM is independent of $J'M'$ and is independent of M as well, since otherwise it would lead to a M dependent excitation in the absence of a field. We simplify the reorientation term in (A2) by setting

$$(T^a_{JM'JM})^{-1} = (T^a_{JJ})^{-1}. \tag{A4}$$

Equations (A3) and (A4) together mean that we are assuming that there are no selection rules to the collisions. The J dependence in Eq. (A3) is needed in order to fulfill the considerations of detailed balance. With these assumptions, the equation for the active level becomes

$$\begin{aligned}\dot{\rho}_{aa}(J_a,M) = {} & \frac{\lambda_a(J_a) - \rho_{aa}(J_a,M)}{T_1} \\ & + \left(\frac{1}{T^a_{J_a}} \sum_{JM'}{}' \rho_{aa}(J,M') - \rho_{aa}(J_a,M) \sum_{J}{}' \frac{2J+1}{T^a_J}\right) \\ & + \left(\frac{1}{T^a_{J_aJ_a}} \sum_{M=-J_a}^{J_a} \rho_{aa}(J_a,M') - \rho_{aa}(J_a,M) \frac{2J_a+1}{T^a_{J_aJ_a}}\right) \\ & - (\tfrac{1}{2}r^2_M)\,T_2 I\,[\rho_{aa}(J_a,M) - \rho_{bb}(J_b,M)]. \end{aligned} \tag{A5}$$

The equation for the sum over all the inactive levels comes from summing over Eq. (A1). This gives

$$\sum_{JM}{}' \dot{\rho}_{aa}(J,M) = \Big(\sum_{J}{}' (2J+1)\lambda_a(J) - \sum_{JM}{}' \rho_{aa}(J,M)\Big)\Big/T_1 + \sum_{JM}{}' \sum_{J'M'} \left(\frac{\rho_{aa}(J',M')}{T_J^a} - \frac{\rho_{aa}(J,M)}{T_J^a}\right), \tag{A6}$$

where we have substituted the assumed form for the collision term. One sees that no further assumptions are needed in order that the collision term in (A6) can be written as a product of the sum over ρ_{aa} and the sum over $(T_J^a)^{-1}$. This term is further simplified by writing the sum over all levels as the active level plus the sum over the inactive levels. Then the double sum $\sum_{JM}' \sum_{J'M'}'$ vanishes identically. This reduces Eq. (A6) to

$$\sum_{JM}{}' \dot{\rho}_{aa}(J,M) = \Big(\sum_{J}{}' (2J+1)\lambda_a(J) - \sum_{JM}{}' \rho_{aa}(J,M)\Big)\Big/T_1 + \left(\sum_{M'} \rho_{aa}(J_a,M') \sum_{J}{}' \frac{2J+1}{T_J^a} - \frac{2J_a+1}{T_{J_a}^a} \sum_{JM}{}' \rho_{aa}(J,M)\right). \tag{A7}$$

Equations (A5) and (A7) are then combined with the corresponding equations for the lower level in order to write equations of motion for the population differences. These equations are

$$\begin{aligned}\frac{d}{dt}[\rho_{aa}(J_a,M) - \rho_{bb}(J_b,M)] = {}& \lambda_a(J_a) - \lambda_b(J_b) - \frac{\rho_{aa}(J_a,M) - \rho_{bb}(J_b,M)}{T_1} \\ &+ \left[\frac{1}{T_{J_a}^a} \sum_{JM}{}' \rho_{aa}(J,M) - \frac{1}{T_{J_b}^b} \sum_{JM}{}' \rho_{bb}(J,M) - \left(\rho_{aa}(J_a,M) \sum_{J}{}' \frac{2J+1}{T_J^a} - \rho_{bb}(J_b,M) \sum_{J}{}' \frac{2J+1}{T_J^b}\right)\right] \\ &+ \left[\frac{1}{T_{J_aJ_a}^a} \sum_{M'=-J_a}^{J_a} \rho_{aa}(J_a,M') - \frac{1}{T_{J_bJ_b}^b} \sum_{M'=-J_b}^{J_b} \rho_{bb}(J_b,M') - \left(\frac{2J_a+1}{T_{J_aJ_a}^a} \rho_{aa}(J_a,M) - \frac{2J_b+1}{T_{J_bJ_b}^b} \rho_{bb}(J_b,M)\right)\right] - r_M^2 T_2 I [\rho_{aa}(J_a,M) - \rho_{bb}(J_b,M)],\end{aligned} \tag{A8}$$

for the active level, and for the reservoir one has

$$\begin{aligned}\frac{d}{dt}\Big(\sum_{JM}{}' \rho_{aa}(J,M) - \sum_{JM}{}' \rho_{bb}(J,M)\Big) = {}& \left[\sum_{J}{}' (2J+1)\lambda_a(J) - \sum_{J}{}' (2J+1)\lambda_b(J) - \Big(\sum_{JM}{}' \rho_{aa}(J,M) - \sum_{JM}{}' \rho_{bb}(J,M)\Big)\Big/T_1\right] \\ &+ \left[\sum_{M'=-J_a}^{J_a} \rho_{aa}(J_a,M') \sum_{J}{}' \frac{2J+1}{T_J^a} - \sum_{M'=-J_b}^{J_b} \rho_{bb}(J_b,M) - \left(\frac{2J_a+1}{T_{J_a}^a} \sum_{JM}{}' \rho_{aa}(J,M) - \frac{2J_b+1}{T_{J_b}^b} \sum_{JM}{}' \rho_{bb}(J,M)\right)\right].\end{aligned} \tag{A9}$$

It is observed from an inspection of these equations what approximations need to be made in order to write each pair as a population difference. First, we note that in the case of a P- or R-branch transition, J_a and J_b will be different. Thus we note that we must approximate

$$J_a \cong J_b. \tag{A10}$$

Since J_a and J_b differ, at most by a factor of one, this will be reasonable provided that $J_a \gg 1$, $J_b \gg 1$. In practice, we set the two equal to $J_{\min}$, which is defined to be the smaller of the two. We discard the levels which are not dipole coupled (i.e., for which $r_M = 0$) to another level. For the time constants, we note that we must have

$$(T_{J_a}^a)^{-1} \cong (T_{J_b}^b)^{-1}, \tag{A11a}$$

$$\sum_{J}{}' \frac{2J+1}{T_J^a} \cong \sum_{J}{}' \frac{2J+1}{T_{J_b}^b}, \tag{A11b}$$

and

$$(T_{J_aJ_a}^a)^{-1} \cong (T_{J_bJ_b}^b)^{-1}. \tag{A11c}$$

There are a few subtle points contained in these approximations. The various time constants must be related to each other through detailed-balance considerations. Thus, where it is fairly reasonable to suppose Eq. (A11a) is true for J_a and J_b equal, it is a somewhat different matter to make the approximation for $J_a = J_b \pm 1$. The assumption implies also that the probability of being in the J_b, M state (in the absence of an electromagnetic field) is approximately the same as being in the $J_b \pm 1, M$ state. If one assigns a rotational temperature Θ_{rot} to the levels (equal to the translational temperature), this is equivalent to the assumption that the energy separation between the levels is much smaller than $k\Theta_{\text{rot}}$.

The various approximations that are made to write the equations as population differences are, in the final analysis, nowhere near as severe as the assumptions made in Eq. (A3), where it was necessary to assume that there were no selection rules. On the other hand, the approximations in Eq. (A11) only serve to decrease the number of equations by a factor of 2, whereas unless Eq. (A3), or some similar approximation, is made, the number of equations becomes infinite. As long as one wishes to deal with a noninfinite set of equations, one might as well make use of the extra saving of a factor of 2. The only occasion where this would not be suitable would be if one wanted to include the effect of a highly asymmetrical VV interaction, as is, for example, the case in CO_2.

There is a further assumption that must be included in order to use this model. This can be stated as

$$(T^a_{J_a})^{-1}[\lambda_a(J_a) - \lambda_b(J_b)]^{-1} \cong {\sum_J}' \frac{(2J+1)}{T^a_J} \Big/ {\sum_J}' (2J+1)[\lambda_a(J) - \lambda_b(J)] \,. \tag{A12}$$

That is, the pump and the interrotational collisions tend to maintain the same population distributions. This is the same as demanding that $\lambda_a(J)\,T^a_J$ is the same for every level. It is not necessary to make this assumption in the limit that T_1 is much longer than the pulse width. However, the normalization is awkward if one doesn't take Eq. (A12) to be valid.

With these approximations, we can define

$$W_M = \frac{\rho_{aa}(J_a, M) - \rho_{bb}(J_b, M)}{\lambda_a(J_a) - \lambda_b(J_b)} \,, \tag{A13}$$

$$N = \frac{{\sum_{JM}}' \rho_{aa}(J, M) - {\sum_{JM}}' \rho_{bb}(J, M)}{{\sum_J}'(2J+1)[\lambda_a(J) - \lambda_b(J)]} \,, \tag{A14}$$

where N is the same inversion as appears in the text. W_M differs from the n_i only in that the special convention for labeling the states has not yet been used. As noted before, we use J_{min}, the smaller of the J_a or J_b, as the new index for the active level. Then defining

$$(T_1')^{-1} = {\sum_J}' (2J+1)/T^a_J \,, \tag{A15}$$

$$(T_1''')^{-1} = (2J_{\text{min}} + 1)/T^a_{J_{\text{min}} J_{\text{min}}} \,, \tag{A16}$$

and

$$(T_1'')^{-1} = (2J_{\text{min}} + 1)/T^a_{J_{\text{min}}} \,, \tag{A17}$$

we find

$$\dot{W}_M = \frac{1 - W_M}{T_1} + \frac{N - W_M}{T_1'} - \left(\frac{1}{2J_{\text{min}} + 1} \sum_{M' = -J_{\text{min}}}^{J_{\text{min}}} W_{M'} - W_M\right) \Big/ T_1''' - r_M^2 T_2 I W_M \tag{A18}$$

and

$$\dot{N} = \frac{1 - N}{T_1} + \left(\frac{1}{2J_{\text{min}} + 1} \sum_{M' = -J_{\text{min}}}^{J_{\text{min}}} W_{M'} - N\right) \Big/ T_1'' \,. \tag{A19}$$

These equations are identical to the ones that appear in the text except for the inclusion of the coherence effects, which involve the last term on the right-hand side Eq. (A19), and the Doppler effect, which involves the use of the susceptibilities $\chi_M(T, t, z)$ rather than $W_M(t, z)$. The convention used in the text is motivated by the fact that $r_M^2 = r_{-M}^2$, so that half of the equations in the set of W_M equations are redundant (i.e., $W_M = W_{-M}$) under any circumstances when the initial conditions are independent of M. The interrelations between the JM subscripts and j, i used in the text are as follows: For a P or R branch, every state within the set $M = -J_{\text{min}}, J_{\text{min}}$ has a nonzero dipole matrix element. Furthermore, the $M = 0$ is the largest. Thus the index $i - 1$ corresponds to $M = 0$ and $j = J_{\text{min}} + 1$. Furthermore, the ordering will be determined by the fact that $r_M > r_{M'}$ for $|M| < |M'|$. Since the $M = 0$ state has no corresponding state at $-M$, we have $N_1 = 1$ for $i > 1$.

For a Q branch, the element $r_M = 0$ for $M = 0$. In most circumstances it is a minor approximation to ignore the $M = 0$ state altogether, and it does make for a much simpler numerical code. Therefore, we have $j = J_{\text{min}}$. In this case the maximum dipole occurs for $M = \pm J_{\text{min}}$. Thus, $i = 1$ corresponds to the largest value of M. In this case, we have $r_M < r_{M'}$ for $|M| < |M'|$, so that the states appear in decreasing order in terms of the magnetic quantum numbers. Since the $M = 0$ case does not appear explicitly in the set, all of the states are doubled. For that reason, we have $N_i = 1$ for all i.

With the convention established above, we note that the equations (without coherence or Doppler effect) are found by replacing W_M by the appropriate n_i in Eqs. (A18) and (A19), which correspond to Eqs. (14) and (15) in the text.

The collision times defined in Eqs. (A14)–(A16) are the same as are used in the text. Equation (A15) directly defined T_1''' as the total reorientational collision time, i.e., the time it takes a molecule in the state (J, M) to go to any member of the set $[J,M'; M' \epsilon (-J, J)]$. Similarly, the total inelastic collision time, which takes a molecule from the state J, M to any member of the rotational state is then

$$(T_c)^{-1} = \sum_J (2J+1)/T_J^a, \tag{A20}$$

where we note, of course, that T_J^a and T_J^b are the same via earlier approximations. Thus from the definitions of T_1' and T_1'', we have

$$(T_c)^{-1} = (T_1')^{-1} + (T_1'')^{-1}, \tag{A21}$$

and, using Eq. (A12), one sees that

$$T_1''/T_1' = \sum_J{}' \frac{(2J+1)[\lambda_a(J) - \lambda_b(J)]}{(2J_{\min}+1)[\lambda_a(J_{\min}) - \lambda_b(J_{\min})]}, \tag{A22}$$

which is the relationship stated in Eq. (19). In the case where Eq. (A12) is not taken to be true (i.e., in the limit $T_1 >>$ pulse width), then Eq. (A22) can be restated in terms of the detailed balance conditions within the rotational set. In that case, Eq. (19) must be understood as applying to the relative populations of the active levels and the rest of the rotational set as it is established by the rotational kinetics alone.

In summary, the equations used in the text are derived from a more complete description of the interrotational kinetics through many approximations. Most of these approximations are minor in nature, and are needed to allow one to write the equations in terms of the population difference. These approximations will be reasonable so long as the matrix elements for the collisions are the same for both upper and lower state. Furthermore, they demand that the angular momenta be sufficiently large, and that the rotational temperature be high. These conditions are reasonable for most amplifier applications. The other approximation—namely that there be no selection rules to the collisions—is much more severe, since there is clear evidence that this is not true under many circumstances.[52] However, unless this approximation is made at some state, one is confronted with the necessity of an infinite set of reservoir equations to describe the rotational set. This would be very awkward to work with in practice, and would only serve to complicate the present discussion. Under conditions where rotational selection rules are important, this analysis must be modified in the obvious manner. Nevertheless, we anticipate that with a judicious choice of the ratio of T_1' to T_1'', one will be able to do a satisfactory job of matching experiment and theory in many practical situations.

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[1] Normally, the density of states of the total system is sufficiently large that this assumption is not an important limitation. Under these conditions the excited systems interact collisionally with a large uncorrelated bath and not with each other.

[2] A treatment of this genre for nuclear spin systems may be found in A. Abragam, *The Principles of Nuclear Magnetism* (Oxford U. P., London, 1961).

[3] This procedure is well documented in a multitude of publications. For example, see E. L. Hahn and S. L. McCall, Phys. Rev. **183**, 457 (1969); F. T. Arecchi, G. L. Masserini, and P. Schwendimann, Riv. Nuovo Cimento **1**, 181 (1969).

[4] The probability of such an event is anticipated to be extemely small. This probability, to a rough approximation, is given by the product of a rate characteristic of the spontaneous radiative decay of molecular vibrations ($\sim 10^3$ sec^{-1}) and the time duration of a molecular collision. This latter time is given approximately by a/v, where a represents the interaction range and v the mean relative molecular velocity. Under typical circumstances this results in a probability of $\sim 10^{-10}$, a negligible quantity in comparison to the normally observed V-T rates.

[5] For a complete description of molecular spectroscopic notation the reader is referred to the volumes G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* (Van Nostrand, New York, 1950); *Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1945); *Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules* (Van Nostrand, New York, 1966).

[6] For our purposes we ignore hyperfine effects and assume that all nuclei are spin zero. However, this does not mean that we disregard the relevant consequences of over-all symmetry properties on the molecular wave function when identical nuclei are involved. This latter consideration influences the statistical weight of molecular states and in the example of $C^{12}O_2^{16}$ causes the odd rotational states of the ground vibrational level to be missing.

[7] We assume that no external fields are present and that space is isotropic.

[8] Since space is assumed to be isotropic, the energy is invariant under spatial rotations.

[9] For our present purposes it is sufficient to assume that the

inhomogeneous width occurs from Doppler broadening.

[10] F. A. Hopf and M. O. Scully, Phys. Rev. **179**, 399 (1969).

[11] For a general molecule the total angular momentum is comprised of several components, including those due to rotation about the center of mass, electronic spin, electronic orbital motion, vibrational angular momentum, and intrinsic nuclear spins. However, for simplicity in our discussion we will assume that the only component of interest is that due to molecular rotation.

[12] For the majority of cases of interest, the rotational degree of freedom is highly excited so that $|\vec{j}| \gg h$. For this situation it is a good approximation to regard the molecular system as a classical rotator.

[13] We regard the potential energy function in the customary Born-Oppenheimer sense.

[14] R. G. Gordon, J. Chem. Phys. **44**, 3083 (1966).

[15] S. Hess, Z. Naturforsch. A **25**, 350 (1970); and in *Springer Tracts in Modern Physics* (Springer-Verlag, Berlin, 1970), Vol. 54, p. 136.

[16] R. A. J. Keijser, M. Jansen, V. G. Cooper, and H. F. P. Knaap, Physica (Utr.) **51**, 593 (1971).

[17] The rotational constant B is inversely proportional to the molecular moment of inertia. For the details of the relationship between the molecular structure and the rotational constant, see Ref. 5.

[18] For the example of CO_2 at room temperature, $B \simeq 0.39$ cm^{-1} and $kT_g \simeq 210$ cm^{-1} so that the level spacing is comparable to kT_g for $j \simeq 60$. Owing to the Boltzmann factor, the population of rotational states with $j > 60$ is extremely small.

[19] R. C. Millikan and L. A. Osburg, J. Chem. Phys. **41**, 2196 (1964).

[20] R. D. Sharma and C. W. Kern, J. Chem. Phys. **55**, 1171 (1971).

[21] R. D. Sharma, J. Chem. Phys. **50**, 919 (1969).

[22] For details concerning intermolecular forces see H. Margenau and N. R. Kestner, *Theory of Intermolecular Forces*, 2nd ed. (Pergamon, New York, 1971); *Intermolecular Forces*, edited by J. O. Hirschfelder (Interscience, New York, 1967). A general treatment of noncentral force scattering is contained in M. L. Goldberger and K. M. Watson, *Collision Theory* (Wiley, New York, 1964).

[23] For a discussion of microwave transitions in molecules see C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill, New York, 1955).

[24] C. Freed and A. Javan, Appl. Phys. Lett. **17**, 53 (1970).

[25] For further details the reader should consult H. S. W. Massey, E. H. S. Burhop, and H. B. Gilbody, *Electronic and Ionic Impact Phenomena* (Oxford U. P., London, 1971), Vol. III.

[26] The very light molecules like H_2 and D_2 which have large rotational spacings tend to have rates somewhat slower than most systems.

[27] P. K. Cheo and R. L. Abrams, Appl. Phys. Lett. **14**, 47 (1969); T. O. Carroll and S. Marcus, Phys. Lett. A **27**, 590 (1968).

[28] We ignore the quenching of vibrational angular momentum which is often present in excited degenerate vibrations.

[29] A discussion of these points is given by J. D. Lambert, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic, New York, 1962), p. 783.

[30] For a discussion of experimentally observed deviations from the Landau-Teller theory see J. C. Stephenson, R. E. Wood, and C. B. Moore, J. Chem. Phys. **54**, 3097 (1971).

[31] L. D. Landau and E. Teller, Phys. Z. Sowjetunion **10**, 34 (1936); C. Zener, Phys. Rev. **37**, 556 (1931); J. M. Jackson and W. F. Mott, Proc. R. Soc. A **137**, 703 (1932); R. N. Schwartz, Z. I. Slawsky, and K. F. Herzfeld, J. Chem. Phys. **20**, 1591 (1952). Also see Ref. 25.

[32] This form leads to a linear plot of the relaxation time versus $T^{-1/3}$.

[33] In this context, "large" generally means in comparison to kT.

[34] J. R. Airey and S. F. Fried, Chem. Phys. Lett. **8**, 23 (1971).

[35] F. A. Hopf, C. K. Rhodes, and A. Szoke, Phys. Rev. B **1**, 2833 (1970).

[36] C. K. Rhodes, A. Szoke, and A. Javan, Phys. Rev. Lett. **21**, 1151 (1968).

[37] G. L. Lamb, Jr., Rev. Mod. Phys. **43**, 99 (1971).

[38] In the language of the density matrix we consider only diagonal matrix elements; the off-diagonal terms for reservoir are zero.

[39] With this definition T_1'' is a measure, in units of T_1' of the significance of the reservoir states from the standpoint of energy content. In addition, it is shown later that T_1'' is the relevant coupling time for energy transfer from the totality of reservoir states to the active level.

[40] For example in CO_2 at 10.6 μ the pressure broadening coefficient is $\sim$ 7.5 MHz torr^{-1} and the Doppler width is $\sim$ 60 MHz so that this limit is essentially reached for pressures somewhat greater than 10 torr.

[41] The dipole moment has the dimensions electric charge times distance. Under circumstances in which several dipole moments are involved, we normalize to the largest value defined as $\mathcal{P}$.

[42] This refers, for example, to the input pulse energy and width.

[43] Of course, in following this procedure we cannot violate certain obvious constraints; for instance, the bandwidth of the system T_2^{-1} must not be less than $(T_1')^{-1}$. This is equivalent to the condition that $T_2 \le T_1$ in the language of Abragam, Ref. 2.

[44] The quantity $\mathcal{T}_{\text{out}} \equiv \mathcal{T}(L)$ where the position $z = L$ identifies the output plane of the amplifier.

[45] L. M. Frantz and J. S. Nodvik, J. Appl. Phys. **34**, 2346 (1963); N. G. Basov, R. V. Ambartsumyan, V. S. Zuev, P. G. Kryukov, and V. S. Letokhov, Zh. Eksp. Teor. Fiz. **50**, 23 (1966) [Sov. Phys.-JETP **23**, 16 (1966)].

[46] This discussion does not apply to situations in which the pulse bandwidth is much greater than the gain bandwidth of the medium.

[47] P. W. Hoff, H. A. Haus, and T. J. Bridges, Phys. Rev. Lett. **25**, 82 (1970).

[48] No dependence, of course, is expected for unsaturated amplification.

[49] F. A. Hopf, B. Krawetz, and C. K. Rhodes (unpublished).

[50] This procedure is valid only under circumstances in which the numerical calculational procedures have demonstrated their stability.

[51] Pure rotational transitions in optically pumped HF have been reported by N. Skribanowitz, I. P. Herman, R. M. Osgood, Jr., M. S. Feld, and A. Javan, Appl. Phys. Lett. **20**, 428 (1972).

[52] Recent linewidth measurements of H_2O indicate that rotational relaxation can be strongly inhibited for sufficiently high angular momentum. These results are reported in R. S. Eng., A. R. Calawa, T. C. Harman, P. L. Kelley, and A. Javan, Appl. Phys. Lett. **21**, 303 (1972). Other examples are known, for example, see R. G. Gordon, P. E. Larson, C. H. Thomas, and E. B. Wilson [J. Chem. Phys. **50**, 1388 (1969)] and R. M. Lees and T. Oka [J. Chem. Phys. **51**, 3027 (1969)] for experimental aspects as well as H. A. Rabitz and R. G. Gordon [J. Chem. Phys. **53**, 1815 (1970); and J. Chem. Phys. **53**, 1831 (1970)] for a theoretical analysis.