

Laser-Induced Rate Processes in Gases: Dynamics, Unimolecular Decay, and Scattered Field

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We have recast a linear quantum-mechanical Boltzmann equation, describing the dynamics of a gas of N -level atoms absorbing light between an arbitrary pair of levels, into the form of a generalized master equation. The atoms are permitted to undergo both phase-changing and energy-changing collisions with a heat bath of inert molecules. The possibility of unimolecular decay is incorporated into the Boltzmann equation. The solutions of the generalized master equation give an accurate description of the system for short as well as long times and for arbitrary light-field intensity. Eigenvalues obtained from the solution of the N -level master equation are shown to have particular significance with regard to the scattered electromagnetic field, with the imaginary parts of the complex eigenvalues providing the location and the real parts of the eigenvalues giving the widths of scattered radiation bands. The dynamics and scattered field for a two-level system is discussed in detail. Two collision parameters giving the frequency of phase-changing and energy-changing collisions are important. For special values of these parameters, our results reduce to scattered field spectra calculated previously. When unimolecular decay is included, one identifies the smallest eigenvalue of the generalized master equation with the macroscopic rate constant. Observation of the scattered field for different incident field intensities would permit separation of radiative and thermal effects in an enhanced reaction rate, without requiring an accurate temperature measurement.

I. INTRODUCTION

One of the more exciting speculations following the development of the laser centered upon its potential use as a device to stimulate chemical reactions selectively. The intense monochromatic nature of the radiation appeared to be ideally suited for exciting characteristic bond frequencies and overtones. This excitation could result in a marked increase in the probability for the bond to rupture even under thermally unfavorable conditions.^{1,2} The realization of the laser as a tool in selective chemistry has not occurred primarily because of two factors: (i) the presence of anharmonicities which limit the coupling between the molecule and the field and (ii) thermalizing intermolecular interactions. What limited success has been achieved in utilizing the laser to stimulate chemical events occurs when activation-energy requirements are directly satisfied solely by radiative means, as is the case for most previously reported photochemical reactions.

The question of whether molecular-loss mechanisms severely restrict the potential use of the laser in selective chemistry applications has been considered classically.¹ In this paper we propose a quantum formalism that includes the effect of the absorption of laser radiation within the framework of a model for a chemical reaction. The chemical

reaction is accounted for by assuming a unimolecular decay of one or more quasistationary levels of an ensemble of N -level atoms immersed in a heat bath and undergoing both elastic and inelastic collisions with an excess of solvent molecules. The phase-changing and energy-changing collisions are independently accounted for by the introduction of a superoperator³ into a Boltzmann-equation^{4,5} formalism that reduces the off-diagonal density matrix elements to zero following each collision, whether or not a change in the diagonal matrix elements also occurs.

In Sec. III, we derive a generalized master equation for the N -level system in the presence of a monochromatic field, which includes the effect of unimolecular decay of some of the levels. Particular solutions to the generalized master equation involve a set of $N+2$ eigenvalues describing both the short- and long-time behavior of the system. In the case where one or more of the levels of the system undergoes unimolecular decay, the smallest eigenvalue is identified as the unimolecular rate constant.⁶ In the absence of a chemical reaction, and in the long-time limit, the generalized master equation reduces to an ordinary master equation valid for low-intensity driving fields. The existence of complex eigenvalues and an oscillatory approach to steady state is possible.

Sections IV and V are devoted to the special case of a two-level system. The behavior of the eigenvalues as a function of intensity is discussed. For off-resonance low- and high-intensity driving fields, there are two real and two complex eigenvalues, the real roots giving rise to elastic components and the complex roots to inelastic components in a measurement of the scattered radiation field. At intermediate values of intensity, all four roots are real. Section V contains a detailed calculation of the scattered field bands, and previous results are found from our model by taking specific values for the ratio of energy-changing to phase-changing collision frequencies. In the case of unimolecular decay of the second level, an observation of the scattered radiation at different incident light intensities allows a separation of thermal and radiative effects. The value of the rate constant in the case of slow unimolecular decay could be observed directly by the decrease of scattered band intensities with time.

A general discussion of the physical significance of the eigenvalues is contained in Sec. VI. The relationships of the eigenvalue spectrum to the scattered field for the N -level system and the oscillatory approach to steady state when several of the roots are complex are considered.

II. PHYSICAL MODEL

We consider a gas of infinitely dilute solute molecules immersed in an inert carrier gas which acts as a thermal bath.⁷ Both energy-changing and phase-changing collisions occur randomly between solute and surrounding solvent bath molecules. The time evolution of the density matrix is described by a quantum-mechanical Boltzmann equation. Consider the evolution of $\underline{\rho}$ over a small interval Δt ,

$$\underline{\rho}(t + \Delta t) = \left(1 - \frac{\Delta t}{\tau}\right) \left(\underline{\rho}(t) + \frac{i}{\hbar} [\underline{\rho}, \underline{H}] \Delta t\right) + \frac{\Delta t}{\tau} \underline{K} \underline{\rho}. \quad (1)$$

We assume that collisions occur randomly with $\Delta t/\tau$ equal to the probability of a collision occurring in any small time interval Δt . In Eq. (1) we calculate $\underline{\rho}(t + \Delta t)$ as the sum of two terms. The first term gives the dynamical evolution assuming that no collision has occurred; the second term describes the effect of collisions by operating on $\underline{\rho}$ with a linear superoperator \underline{K} .³ The collision term is linear in $\underline{\rho}$ because we assume that collisions occur only with the heat-bath molecules.⁸ The superoperator \underline{K} must preserve the constant trace, Hermitian, and positive semidefinite properties of the density matrix $\underline{\rho}$. In the limit $\Delta t \rightarrow 0$, we obtain a linear quantum-mechanical Boltzmann equation,

$$\frac{d\underline{\rho}}{dt} = \frac{i}{\hbar} [\underline{\rho}, \underline{H}] + \frac{1}{\tau} \underline{K} \underline{\rho} - \frac{1}{\tau} \underline{\rho}. \quad (1a)$$

This equation assumes that collisions are instanta-

neous events, an assumption that can only be justified if the duration of a collision is small compared to τ .

The effect of the operation of \underline{K} on the density matrix (in the energy representation) is to reduce all off-diagonal matrix elements to zero.⁹ The matrix elements of \underline{K} then have the form

$$K_{ij, k1} = P_{i-k} \delta_{ij} \delta_{k1}, \quad (2)$$

with

$$P_{i-i} = 1 - \sum_{j \neq i} P_{j-i}.$$

The matrix elements of $\underline{\rho}' = \underline{K} \underline{\rho}$ are given by

$$\underline{\rho}'_{ij} = \sum_{k, 1} K_{ij, k1} \rho_{k1}.$$

The fact that $\underline{K} \underline{\rho}$ is diagonal in the energy representation implies that a collision is equivalent to a perfect measurement of the energy. This assumption can be true only if¹⁰

$$\hbar/\Delta E \ll \tau, \quad (3)$$

where $\hbar/\Delta E$ is the Heisenberg uncertainty time for an accurate energy measurement of a level separated from its closest adjacent energy level by an increment in energy ΔE .

When \underline{H} contains a time-dependent driving term, representing the effect of a radiation field in semiclassical radiation theory, the collision superoperator destroys the phase relation between the molecule and the radiation field on every collision. Following a collision the molecule either remains in its initial state with probability P_{i-i} or is transferred to state j with probability P_{j-i} .

We note that our form of the Boltzmann equation, including both energy- and phase-changing collisions, is accurate even when $(\underline{\rho} - \underline{\rho}_{\text{equil}})$ is large. As one consequence, there exists a correspondence between the Boltzmann equation and the usual master equation describing the time evolution of the diagonal elements ρ_{ii} in the $t \rightarrow \infty$ limit.

We can extend the formalism to allow for unimolecular decay from one or more of the levels of the solute molecules. The Hamiltonian for an N -level system in which a unimolecular chemical reaction proceeds via decay from levels J through N is

$$\underline{H} = \underline{H}_1 - i \sum_{n=1}^N \Gamma_n \underline{P}_n, \quad \Gamma_n = 0 \quad \text{for } 1 \leq n < J. \quad (4)$$

Here $\underline{H}_1 = \underline{H}_1^\dagger$ is Hermitian, \underline{P}_n is the projection operator onto the n th chemically reactive state, and Γ_n is the width of the n th reactive state. $2\Gamma_n/\hbar$ is the microscopic unimolecular decay constant for the n th state.¹¹

When the Hamiltonian is non-Hermitian, the Liouville equation is

$$\frac{d\rho}{dt} = \frac{i}{\hbar} (\rho \underline{H}^\dagger - \underline{H} \rho), \quad (5)$$

and the Boltzmann equation is then

$$\frac{d\rho}{dt} = \frac{i}{\hbar} [\rho, \underline{H}_1] + \frac{1}{\tau} \underline{K} \rho - \frac{1}{\tau} \rho - \frac{1}{\hbar} \sum_{n=1}^N \Gamma_n (\rho \underline{P}_n + \underline{P}_n \rho). \quad (6)$$

III. GENERALIZED MASTER EQUATION

Equation (6) is quite general. In the presence of a coherent electromagnetic field, absorption and stimulated emission of radiation are handled, in the semiclassical approximation, by including appropriate time-dependent driving terms in the Hamiltonian \underline{H}_1 . The special case of a perfectly monochromatic field is of particular interest in laser phenomena. We assume that the radiation field induces transitions between levels r and s of the solute molecules. The energy-representation matrix elements of \underline{H}_1 are then

$$(\underline{H}_1)_{ii} = \epsilon_i, \quad (\underline{H}_1)_{sr} = (\underline{H}_1)_{rs} = \alpha A \sin \chi t. \quad (7)$$

All other off-diagonal matrix elements are zero. Here A specifies the amplitude and χ the frequency of the laser field. α is a dipole coupling matrix element. We assume that the laser frequency is on or near resonance for the r - s transition, so that

$$\hbar \chi \cong \epsilon_s - \epsilon_r = \hbar \omega. \quad (8)$$

Recalling the definition of the superoperator given in Eq. (2) and using the Hamiltonian defined in Eq. (7), we see that Eq. (6) implies the following explicit equation for the time dependence of the diagonal elements:

$$\begin{aligned} \frac{d\rho_{ii}}{dt} = & \frac{i}{\hbar} \alpha A \sin \chi t (\rho_{rs} - \rho_{sr}) (\delta_{ir} - \delta_{is}) \\ & + \frac{1}{\tau} \sum_{j \neq i} P_{i-j} \rho_{jj} - \frac{\rho_{ii}}{\tau} \sum_{j \neq i} P_{j-i} - \frac{2\Gamma_i}{\hbar} \rho_{ii}. \end{aligned} \quad (9)$$

For convenience, the decay term $-(2\Gamma_i/\hbar)\rho_{ii}$ is included for all levels, and Γ_i defined to be zero for levels which do not decay. The diagonal elements ρ_{ii} specify the fraction of molecules in the i th energy state. In the absence of the laser field ($A=0$), Eq. (9) is simply the familiar master equation describing the relaxation to thermal equilibrium of a dilute system coupled to a heat bath.

From a computational point of view, Eq. (9) is more complicated than the master equation because of the dependence on the off-diagonal elements ρ_{rs} and ρ_{sr} . Equation (6) gives for the time dependence of these elements

$$\frac{d\rho_{rs}}{dt} = i\omega \rho_{rs} + \frac{i\alpha A}{\hbar} \sin \chi t (\rho_{rr} - \rho_{ss})$$

$$- \frac{1}{\tau} \rho_{rs} - \frac{(\Gamma_r + \Gamma_s)}{\hbar} \rho_{rs}, \quad (10)$$

$$\begin{aligned} \frac{d\rho_{sr}}{dt} = & -i\omega \rho_{sr} + \frac{i\alpha A}{\hbar} \sin \chi t (\rho_{ss} - \rho_{rr}) \\ & - \frac{1}{\tau} \rho_{sr} - \frac{(\Gamma_r + \Gamma_s)}{\hbar} \rho_{sr}. \end{aligned}$$

Particular solutions to Eqs. (9) and (10) are obtained by assuming, with a *posteriori* justification,

$$\rho_{rr} = c_r e^{-\lambda t}, \quad \rho_{ss} = c_s e^{-\lambda t}. \quad (11)$$

The particular solution to Eq. (10) is then

$$\begin{aligned} \rho_{rs} = & (c_r - c_s) \frac{\alpha A}{2\hbar} e^{-\lambda t} \left(\frac{e^{i\chi t}}{1/\tau + (\Gamma_r + \Gamma_s)/\hbar - \lambda - i(\omega - \chi)} \right. \\ & \left. - \frac{e^{-i\chi t}}{1/\tau + (\Gamma_r + \Gamma_s)/\hbar - \lambda - i(\omega + \chi)} \right), \quad (12) \\ \rho_{sr} = & (c_s - c_r) \frac{\alpha A}{2\hbar} e^{-\lambda t} \left(\frac{e^{i\chi t}}{1/\tau + (\Gamma_r + \Gamma_s)/\hbar - \lambda + i(\omega + \chi)} \right. \\ & \left. - \frac{e^{-i\chi t}}{1/\tau + (\Gamma_r + \Gamma_s)/\hbar - \lambda + i(\omega - \chi)} \right). \end{aligned}$$

Using the result given in Eq. (12), one finds

$$\frac{i\alpha A}{\hbar} \sin \chi t (\rho_{rs} - \rho_{sr}) = (c_s - c_r) W(\lambda) e^{-\lambda t}, \quad (13)$$

$$W(\lambda) = \frac{\alpha^2 A^2}{2\hbar^2} \frac{1/\tau + (\Gamma_r + \Gamma_s)/\hbar - \lambda}{[1/\tau + (\Gamma_r + \Gamma_s)/\hbar - \lambda]^2 + (\omega - \chi)^2}. \quad (14)$$

In arriving at Eq. (13), we have dropped terms which make a contribution to the solution $1/\tau\omega$, that are smaller than the retained terms. The condition $1/\tau\omega \ll 1$ is implied by the fundamental restriction on the Boltzmann equation stated in Eq. (3).

Using Eqs. (11) and (13), we can put Eq. (9) in the form

$$\begin{aligned} \frac{d\rho_{ii}}{dt} = & \frac{1}{\tau} \sum_{j \neq i} P_{i-j} \rho_{jj} - \frac{\rho_{ii}}{\tau} \sum_{j \neq i} P_{j-i} \\ & - \frac{2\Gamma_i}{\hbar} \rho_{ii} + W(\lambda) (\rho_{rr} - \rho_{ss}) (\delta_{is} - \delta_{ir}). \end{aligned} \quad (15)$$

Equation (15) formally resembles a master equation with radiative-transition terms between levels r and s . Note that because of the λ dependence of $W(\lambda)$ these are not differential equations in the ordinary sense, but are correct when one assumes

$$\rho_{ii} = c_i e^{-\lambda t} \quad (16)$$

and solves the resulting eigenvalue-eigenvector problem for λ and the eigenvector \underline{c} . Since this is the standard way to find particular solutions to a master equation, we feel justified in using the name "generalized master equation" for Eq. (15). It should also be noted that the "approximation" $W(\lambda) = W(\lambda=0)$ reduces Eq. (15) to an ordinary

master equation that is valid for sufficiently small A^2 .

It is convenient to define a matrix \underline{R} , containing thermal relaxation and unimolecular decay terms, with elements

$$R_{ij} = -\frac{1}{\tau} P_{i-j} + \delta_{ij} \left(\frac{1}{\tau} + \frac{2\Gamma_i}{\hbar} \right). \quad (17)$$

We also define a projection operator \underline{T} with elements

$$T_{ss} = T_{rr} = \frac{1}{2}, \quad T_{sr} = T_{rs} = -\frac{1}{2}, \quad (18)$$

and all other elements zero. Substituting Eq. (16) into Eq. (15) gives the following determinant equation for the eigenvalues λ :

$$|\underline{R} + 2W(\lambda)\underline{T} - \lambda\underline{T}| = 0. \quad (19)$$

The similarity transformation $\underline{S}^{-1}\underline{T}\underline{S}$, where

$$S_{rr} = S_{rs} = S_{sr} = 1/\sqrt{2}, \quad S_{ss} = -1/\sqrt{2},$$

and all other elements are zero, diagonalizes \underline{T} . Equation (19) can then be written as

$$|\underline{S}^{-1}\underline{R}\underline{S} - \lambda\underline{I}| + 2W(\lambda)|\underline{S}^{-1}\underline{R}\underline{S} - \lambda\underline{I}|_{ss} = 0. \quad (20)$$

The symbol $| \cdot |_{s,s}$ denotes the co-factor obtained by eliminating the s row and column. The eigenvalues of \underline{R} are, of course, the same as the eigenvalues of $\underline{S}^{-1}\underline{R}\underline{S}$. It is well known that microscopic reversibility

$$P_{j-i} = P_{i-j} e^{-(\epsilon_j - \epsilon_i)/kT}$$

implies that the eigenvalues of \underline{R} are real.¹² Equation (20) is a polynomial of order $N+2$; hence there are $N+2$ eigenvalues for the generalized master equation. Complex eigenvalues can occur.

IV. TWO-LEVEL SYSTEM

In this section we consider specific results for a two-level system, levels zero and one, and laser-induced transitions between these levels. We assume unimolecular decay from level one. We postpone a complete discussion of physical significance to Secs. V and VI, but do note that the existence of complex eigenvalues for the generalized master equation is of particular importance. For two levels, Eq. (15) becomes

$$\begin{aligned} \frac{d\rho_{00}}{dt} &= \frac{1}{\tau} P_{0-1}\rho_{11} - \frac{1}{\tau} P_{1-0}\rho_{00} + W(\lambda)\rho_{11} - W(\lambda)\rho_{00}, \\ \frac{d\rho_{11}}{dt} &= \frac{1}{\tau} P_{1-0}\rho_{00} - \frac{1}{\tau} P_{0-1}\rho_{11} + W(\lambda)\rho_{00} \\ &\quad - W(\lambda)\rho_{11} - \frac{2\Gamma_1}{\hbar}\rho_{11}, \end{aligned} \quad (21)$$

$$P_{1-0} = P_{0-1}e^{-\Theta}, \quad \Theta = \frac{\epsilon_1 - \epsilon_0}{kT}.$$

In the absence of the light field ($A=0$) and chemical reaction ($\Gamma_1=0$), these equations give the sim-

ple description of the approach to equilibrium of a two-level system with random phase, undergoing energy-changing collisions. The integrated solution is

$$\begin{aligned} \rho_{00} &= \frac{1}{1+e^{-\Theta}} + B e^{-t/\tau'}, \quad \rho_{11} = \frac{e^{-\Theta}}{1+e^{-\Theta}} - B e^{-t/\tau'}, \\ \frac{1}{\tau'} &= \frac{1}{\tau} P_{0-1}(1+e^{-\Theta}). \end{aligned} \quad (22)$$

Here B is a constant depending on $\rho_{00}(t=0)$. The parameter τ' is seen to be a relaxation time associated with energy-changing collisions. Since in the absence of a light field, the off-diagonal density matrix elements relax to zero with relaxation time τ , this parameter is associated with phase-changing collisions. The situation is analogous to NMR phenomena with τ' corresponding to the longitudinal relaxation time and τ corresponding to the transverse relaxation time.¹³

It is also interesting to examine Eq. (21) in the special case of no chemical reaction and with the approximation

$$W(\lambda) \cong W(\lambda=0) = \frac{\alpha^2 A^2}{2\hbar^2} \frac{1/\tau}{1/\tau^2 + (\omega - \chi)^2}. \quad (23)$$

$W(\lambda=0)$ is exactly the radiative-transition rate one finds using first-order perturbation theory and including collisional broadening in a straightforward way.¹⁴ For this reason Eq. (21), or equally well Eq. (15), has the familiar form of an ordinary master equation when one approximates $W(\lambda) \cong W(\lambda=0)$. With this approximation, and still ignoring chemical reaction, the eigenvalues for Eq. (21) are

$$\begin{aligned} \lambda &= 0, \\ \lambda &= \frac{1}{\tau'} + \frac{\alpha^2 A^2}{\hbar^2} \frac{1/\tau}{1/\tau^2 + (\omega - \chi)^2}. \end{aligned} \quad (24)$$

This result allows us to state precisely, the conditions under which the ordinary master equation will accurately describe the approach to equilibrium for the two-level system. Recalling Eq. (14), we see that the approximation $W(\lambda) = W(\lambda=0)$ requires a sufficiently small amplitude so that

$$W(\lambda=0) \ll \frac{1}{2}(1/\tau - 1/\tau'). \quad (25)$$

Mollow⁵ assumes $1/\tau = 1/\tau'$, and this condition is never satisfied.

The generalized master equation (21) has a total of four eigenvalues. The two eigenvalues not found in the ordinary master equation are of the order $1/\tau$ for small A . These two eigenvalues, therefore, must describe short-time behavior of the density matrix. The condition that the ordinary master equation describes the approach to equilibrium only in a long-time limit, that is, when

$$t \gg 1/\tau, \quad (26)$$

is contained in the generalized-master-equation formalism.

Let us now consider the eigenvalues of the generalized master equation. These can be found by solving Eq. (20). For the two-level system, we find

$$\frac{1}{2W(\lambda)} = \frac{\lambda - \Gamma_1/\hbar}{(\lambda - \delta_-)(\lambda - \delta_+)} \equiv F(\lambda), \quad (27)$$

$$\delta_{\pm} = \frac{1}{2\tau'} + \frac{\Gamma_1}{\hbar} \pm \left[\left(\frac{1}{2\tau'} \right)^2 + \frac{\Gamma_1}{\hbar} \frac{P_{0-1} - P_{1-0}}{\tau} + \frac{\Gamma_1^2}{\hbar^2} \right]^{1/2}.$$

It is clear that

$$\delta_- \leq \Gamma_1/\hbar < \delta_+. \quad (28)$$

A schematic plot of the function $F(\lambda)$ is shown in Fig. 1.

Consider first the solution to Eq. (27) when the driving frequency is on resonance, that is $\omega = \chi$. For the resonance case we find

$$\frac{1}{2W} = \frac{\hbar^2}{\alpha^2 A^2} \left(\frac{1}{\tau} + \frac{\Gamma_1}{\hbar} - \lambda \right), \quad (29)$$

so that Eq. (27) reduces to a cubic. It is easy to show, by considering Eq. (27) for small $(\omega - \chi)^2$, that

$$\lambda = 1/\tau + \Gamma_1/\hbar + O[(\omega - \chi)^2] \quad (30)$$

is an eigenvalue. This root plus the three solutions to the cubic give the four required eigenvalues. Consider the intersection of the straight line given by Eq. (29) with the function $F(\lambda)$. For small A , the slope in Eq. (29) is almost infinite and there will in general be three intersections with the curve $F(\lambda)$. There are then a total of four real and positive eigenvalues. As the amplitude of the light field increases, the slope in Eq. (29) approaches negative zero, and we find that for amplitudes greater than some particular A , only one intersection exists. For this large-amplitude case, we have two real eigenvalues and two complex conjugate eigenvalues.

In the one special case where

$$1/\tau + \Gamma_1/\hbar = \delta_+, \quad (31)$$

the above argument does not hold, since clearly there are now two real roots and two complex conjugate roots for all amplitudes.

The above argument about the existence of complex roots is easily verified when chemical reaction is absent. For $\Gamma_1 = 0$, we easily compute explicit solutions to Eq. (27). These solutions are

$$\lambda = 0, \quad (32)$$

$$\lambda = \frac{1}{2} \left\{ \frac{1}{\tau} + \frac{1}{\tau'} \pm \left[\left(\frac{1}{\tau} - \frac{1}{\tau'} \right)^2 - \frac{4\alpha^2 A^2}{\hbar^2} \right]^{1/2} \right\}.$$

Here the existence of complex roots requires that

$$\frac{\alpha^2 A^2}{\hbar^2} > \frac{1}{4} \left(\frac{1}{\tau} - \frac{1}{\tau'} \right)^2. \quad (33)$$

The exceptional case mentioned under Eq. (31) exists when $1/\tau = 1/\tau'$. It should be noted that this exceptional case is just the one treated by Mollow in his paper on the scattered field with collisional damping.⁵

When the light-field frequency is off resonance, the discussion of the existence of four real eigenvalues is more complicated. It is possible, however, to give a quantitative description when $\Gamma_1 = 0$. In this case one eigenvalue is zero and the other three eigenvalues are solutions of a cubic equation, whose discriminant is

$$Q = \frac{1}{27} \left[\Omega^2 - \frac{1}{3} (1/\tau - 1/\tau')^2 \right]^3 + \frac{1}{4} (1/\tau - 1/\tau')^2 \left[\frac{2}{27} (1/\tau - 1/\tau')^2 - \frac{1}{3} \Omega^2 + \Delta^2 \right]^2, \quad (34)$$

$$\Omega^2 = (\omega - \chi)^2 + \alpha^2 A^2/\hbar^2, \quad \Delta^2 = (\omega - \chi)^2.$$

If $Q < 0$, there are three real and different roots.

If $Q = 0$, there are three real roots, at least two of which are equal. If $Q > 0$, there is one real root and two complex conjugate roots. In Fig. 2 we exhibit a plot of the function $Q=0$. The shaded region indicates the presence of three real roots. In qualitative terms, we find that three real roots exist at intermediate amplitudes and not too far off resonance. This same qualitative statement holds when chemical reaction is included.

We easily compute the "eigenvectors" of the generalized master equation. The eigenvector elements are the coefficients c_i of Eq. (16). For the two-level system, Eq. (21) implies

$$\frac{c_0}{c_1} = \frac{(1/\tau)P_{0-1} + W(\lambda)}{(1/\tau)P_{1-0} + W(\lambda) - \lambda} = \frac{2\Gamma_1}{\hbar\lambda} - 1. \quad (35)$$

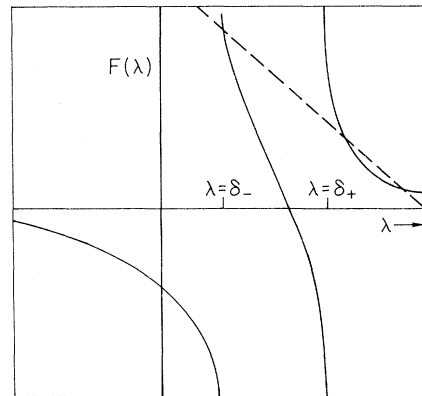


FIG. 1. Schematic plot of the function $F(\lambda)$. The dashed line gives the function $1/2W$ on resonance, and for large A . The three intersections give three real positive eigenvalues for the generalized master equation.

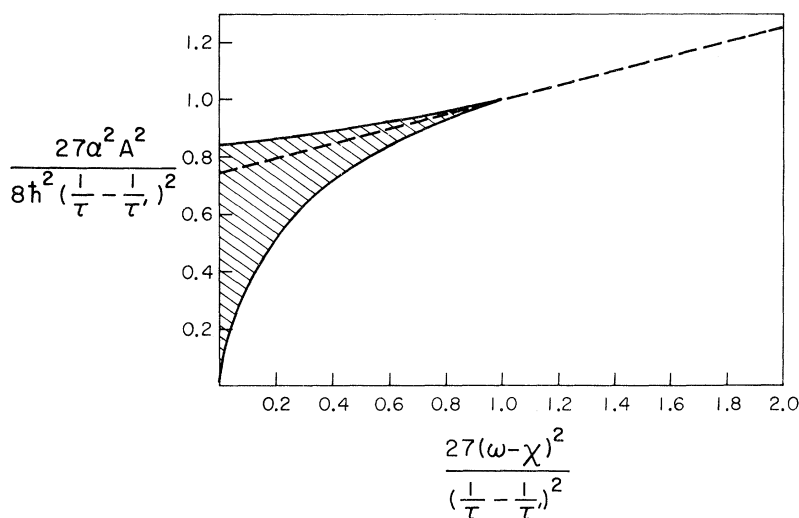


FIG. 2. Light-field parameters A^2 and $(\omega - \chi)^2$ that give rise to complex eigenvalues for the two-level system without chemical reaction. In the shaded region all four eigenvalues are real. In the unshaded region there are two real eigenvalues and a pair of complex conjugate eigenvalues. In the unshaded region above the dashed line, the system shows an oscillatory approach to equilibrium if $1/\tau > 1/\tau'$.

The second equality in Eq. (35) makes use of Eq. (27) for the eigenvalues. Recalling Eqs. (11) and (12), we are now in a position to write down particular solutions for all four density matrix elements of the two-level system. These solutions are

$$\underline{\rho}_\lambda = \begin{bmatrix} \left(1 - \frac{2\Gamma_1}{\hbar\lambda}\right) e^{-\lambda t} & \left(1 - \frac{\Gamma_1}{\hbar\lambda}\right) \frac{(\alpha A/\hbar) e^{(-\lambda + i\chi)t}}{1/\tau + \Gamma_1/\hbar - \lambda - i(\omega - \chi)} \\ \left(1 - \frac{\Gamma_1}{\hbar\lambda}\right) \frac{(\alpha A/\hbar) e^{(-\lambda - i\chi)t}}{1/\tau + \Gamma_1/\hbar - \lambda + i(\omega - \chi)} & -e^{-\lambda t} \end{bmatrix} \quad (36)$$

In writing down Eq. (36), we have retained only the dominant term, with resonance denominator, in Eq. (12). Since we have four eigenvalues for the generalized master equation, Eq. (36) gives four independent solutions to the Boltzmann equation. In the special case when two eigenvalues, e.g., λ and λ' , are equal, one can find a fourth independent solution,

$$\underline{\rho}' = \frac{d}{d\lambda} \underline{\rho}_\lambda \quad (37)$$

The diagonal elements of $\underline{\rho}'$ have a time dependence $te^{-\lambda t}$.

The four particular solutions allow us to write a general solution to the linear Boltzmann equation:

$$\underline{\rho} = \sum_{i=1}^4 \alpha_i \underline{\rho}_{\lambda_i} \quad (38)$$

The four coefficients α_i allow one to match the general solution to an arbitrary Hermitian density matrix specified at time $t=0$.

In the absence of chemical reaction, $\Gamma_1=0$ and one eigenvalue vanishes. Equation (36) is inconvenient in this case, but one easily calculates

$$\underline{\rho}_{\lambda=0} = \frac{1}{1/\tau' + 2W(\lambda=0)} \begin{bmatrix} \frac{1}{\tau} P_{0-1} + W(\lambda=0) & \frac{\alpha A}{2\hbar} \frac{1}{\tau} P_{0-1} (1 - e^{-\infty}) \frac{e^{i\chi t}}{1/\tau - i(\omega - \chi)} \\ \frac{\alpha A}{2\hbar} \frac{1}{\tau} P_{0-1} (1 - e^{-\infty}) \frac{e^{-i\chi t}}{1/\tau + i(\omega - \chi)} & \frac{1}{\tau} P_{0-1} e^{-\infty} + W(\lambda=0) \end{bmatrix} \quad (39)$$

In this case the density matrix approaches a steady-state value,

$$\underline{\rho} = \underline{\rho}_{\lambda=0} \text{ as } t \rightarrow \infty, \Gamma_1=0 \quad (40)$$

The steady-state populations $\rho_{00}(\lambda=0)$ and $\rho_{11}(\lambda=0)$

are identical to those predicted by the ordinary master equation, (21) with $W(\lambda) = W(\lambda=0)$.

V. SCATTERED FIELD

In this section we generalize some of Newstein's¹⁵

and Mollow's⁵ results for the spectrum of the scattered field from a two-level system. The intensity of the scattered field is proportional to

$$g(\nu, t) = \int_{-\infty}^{\infty} dl e^{i\nu l} g(t, l), \quad (41)$$

$$g(t, l) = \langle a^\dagger(t) a(t+l) \rangle, \quad (42)$$

where a^\dagger and a are atomic-raising and -lowering operators, respectively. Mollow has shown that the function $g(t, l)$ can be expressed as

$$g(t, l) = U_{\alpha\alpha}(l, t)\rho_{11}(t) + U_{\alpha m}(l, t)\rho_{01}(t). \quad (43)$$

$U_{\alpha\alpha}$ and $U_{\alpha m}$ are matrix elements of an operator which relates the density matrix at time $t+l$ to the density matrix at time t . The expression

$$\begin{aligned} \rho_{10}(t+l) = & U_{\alpha m}(l, t)\rho_{11}(t) + U_{\alpha\alpha}(l, t)\rho_{10}(t) \\ & + U_{\alpha\alpha}^*(l, t)\rho_{01}(t) + U_{\alpha m}(l, t)\rho_{00}(t) \end{aligned} \quad (44)$$

defines the elements $U_{\alpha\alpha}$ and $U_{\alpha m}$.

We compute $U_{\alpha\alpha}$ and $U_{\alpha m}$ by expressing the density matrix as a sum of the four particular solutions found in Sec. IV:

$$\underline{\rho}(t+l) = \sum_{i=1}^4 \alpha_i \underline{\rho}_{\lambda_i}(t+l). \quad (45)$$

Setting $l=0$ in Eq. (45) allows one to invert Eq. (45) and obtain α_i as a linear combination of density matrix elements at time t . Substitution of these α_i 's into Eq. (45) yields expressions of the form given in Eq. (44), and permits one to identify the required coefficients $U_{\alpha\alpha}$ and $U_{\alpha m}$.

The actual computation of $U_{\alpha\alpha}$ and $U_{\alpha m}$ is quite lengthy and we have carried it through in complete generality only for the case without chemical reaction. The results of this calculation are

$$\begin{aligned} U_{\alpha\alpha}(l) = & \frac{e^{i\chi l}}{2D} [R_1(\lambda_2 - \lambda_3) e^{-\lambda_1 l} + R_2(\lambda_3 - \lambda_1) e^{-\lambda_2 l} \\ & + R_3(\lambda_1 - \lambda_3) e^{-\lambda_3 l}], \end{aligned} \quad (46)$$

$$R_i = \frac{\alpha_i^2 A^2}{\hbar^2} + 2a_i a_i' - 2i\Delta a_i',$$

$$U_{\alpha m}(l, t) = \frac{e^{-i\chi(l+t)}}{D} (c_{23} e^{-\lambda_1 t} + c_{31} e^{-\lambda_2 t} + c_{12} e^{-\lambda_3 t}) + S_{10} e^{-i\chi t}, \quad (47)$$

$$\begin{aligned} c_{ij} = & (\lambda_i - \lambda_j) \left(\frac{\alpha A}{\hbar} \frac{S_{11}(a_i^2 + \Delta^2)(a_j^2 + \Delta^2)(a_{6-i-j} - i\Delta)}{(a_i a_j + \Delta^2)^2 + \Delta^2(\lambda_i - \lambda_j)^2} \right. \\ & \left. + \frac{\alpha^2 A^2}{2\hbar^2} (S_{01} e^{-i\chi t} - S_{10} e^{i\chi t}) - S_{10} e^{i\chi t} (a_{6-i-j}' - i\Delta) \right), \end{aligned}$$

where

$$D = \lambda_1^2(\lambda_2 - \lambda_3) + \lambda_2^2(\lambda_3 - \lambda_1) + \lambda_3^2(\lambda_1 - \lambda_2),$$

$$\Delta = \omega - \chi,$$

$$a_i = 1/\tau - \lambda_i,$$

$$a_i' = \frac{1}{\tau'} - \lambda_i,$$

$$S_{01} = S_{10}^* = \frac{(\alpha A/2\hbar) P_{0-1}(1 - e^{-\Theta}) e^{i\chi t}}{1/\tau' + 2W_{0,1}(\lambda=0)} \frac{1/\tau}{1/\tau - i\Delta},$$

$$S_{11} = \frac{(1/\tau) P_{0-1} e^{-\Theta} + W_{0,1}(\lambda=0)}{(1/\tau) P_{0-1}(1 + e^{-\Theta}) + 2W_{0,1}(\lambda=0)}. \quad (48)$$

In using the above results to calculate the scattered field spectrum via Eqs. (41) and (43), there are two points to note. In Eq. (43) steady-state values can be used for $\rho_{01}(t)$ and $\rho_{11}(t)$ to get the steady-state spectrum. These are

$$\rho_{01}(t) = S_{01} \quad \text{and} \quad \rho_{11}(t) = S_{11} \quad \text{as } t \rightarrow \infty. \quad (49)$$

Also the calculation of $U_{\alpha\alpha}$ and $U_{\alpha m}$ assumes that $l > 0$. For negative l one uses the relationship⁵

$$g(-l) = g^*(l). \quad (50)$$

It is clear that at steady state and in the absence of chemical reaction, the correlation function has the form

$$g(t, l) = g(l) = \sum_{i=1}^4 c_i e^{-\lambda_i l - i\chi l}, \quad (51)$$

with $\lambda_4 = 0$. The scattered field spectrum is

$$\begin{aligned} g(\nu) = & \sum_{i=1}^3 \frac{2\text{Re}\lambda_i \text{Re}c_i - 2(\nu - \chi - \text{Im}\lambda_i) \text{Im}c_i}{(\text{Re}\lambda_i)^2 + (\nu - \chi - \text{Im}\lambda_i)^2} \\ & + (\text{Re}c_4) 2\pi\delta(\nu - \chi). \end{aligned} \quad (52)$$

Each term in the sum is, for all practical purposes, a Lorentzian with a center displaced from the driving frequency χ by $\text{Im}\lambda_i$ and a width given by $\text{Re}\lambda_i$. The center and width of the lines in the scattered field spectrum are just the eigenvalues of the generalized master equation. When a pair of complex conjugate eigenvalues exists, there will be in general a pair of unequal intensity lines displaced symmetrically from the central peaks. The sidebands are not present when all four eigenvalues are real. In Sec. IV, we have shown that at low intensities and slightly off resonance there are always two complex eigenvalues. The sidebands disappear, however, at some intermediate value of field intensity when all four eigenvalues are real. For still higher incident intensity, the roots again divide into two real and two complex roots, and the sidebands return. The appearance of sidebands at high-field intensities occurs both off resonance and on resonance. On resonance, the appearance of sidebands requires the Rabi frequency Ω to exceed a collisional-loss frequency

$$\Omega^2 = \alpha^2 A^2 / \hbar^2 > \frac{1}{4} (1/\tau - 1/\tau')^2. \quad (53)$$

It is of interest to examine the spectrum in the limit of low-field intensity. The eigenvalues that are correct through order A^2 are found to be

$$\lambda_1 = \frac{1}{\tau'} + \frac{\alpha^2 A^2}{\hbar^2} \frac{1/\tau - 1/\tau'}{\Delta^2 + (1/\tau - 1/\tau')^2}, \quad (54)$$

$$\lambda_2 = \lambda_3^* = \frac{1}{\tau} + i\Delta - \frac{\alpha^2 A^2}{2\hbar^2} \frac{1/\tau - 1/\tau' - i\Delta}{\Delta^2 + (1/\tau - 1/\tau')^2}.$$

The values of $U_{\alpha\alpha}$ and $U_{\alpha m}$, from Eqs. (46)–(48) are

$$U_{\alpha\alpha} = e^{-(\lambda_2 + i\chi)t} + \frac{\alpha^2 A^2}{2\hbar^2} \frac{1}{(1/\tau - 1/\tau' + i\Delta)^2} \times (e^{-(\lambda_2 + i\chi)t} - e^{-(\lambda_1 + i\chi)t}) + O(A^4), \quad (55)$$

$$U_{\alpha m} = S_{10} (e^{-i\chi t} - e^{-(\lambda_2 + i\chi)t}) + O(A^3).$$

Using Eq. (55) and neglecting terms of order A^4 , $e^{-\circ} A^2$, and $(e^{-\circ})^2$, one obtains the following result for the scattered field spectrum:

$$g(\nu) = \frac{\alpha^2 A^2 / 4\hbar^2}{1/\tau^2 + \Delta^2} 2\pi\delta(\chi - \nu) + \left(\frac{(\alpha^2 A^2 / 4\hbar^2) / (2/\tau - 1/\tau')\tau'}{1/\tau^2 + \Delta^2} + \frac{e^{-\circ}}{1 + e^{-\circ}} \right) \times \left(\frac{2/\tau}{1/\tau^2 + (\nu - \omega)^2} \right). \quad (56)$$

Thus in the case of low-field intensity, the scattered field contains a line at the driving frequency χ and a band of width $1/\tau$ at the atomic resonant frequency ω . The band associated with the λ_3 root is of order A^4 . In his paper on the scattered field with collision damping, Mollow⁵ uses a Boltzmann equation which is identical to our Eq. (21) when one takes

$$P_{1-0} = \frac{e^{-\circ}}{1 + e^{-\circ}}, \quad P_{0-1} = \frac{1}{1 + e^{-\circ}}, \quad \text{and } \Gamma_1 = 0.$$

Recalling the definition of $1/\tau'$ given in Eq. (22), we see that Mollow assumes

$$1/\tau = 1/\tau'. \quad (57)$$

As it must, Eq. (56) agrees exactly with Mollow's low-intensity result when one assumes Eq. (57).

Mollow's radiation-damped equations⁵ are also a special case of Eq. (21), with

$$P_{0-1} = 2, \quad e^{-\circ} = 0, \quad \text{and } \Gamma_1 = 0.$$

This means

$$1/\tau' = 2/\tau.$$

The sideband in the low-intensity spectrum disappears in this case. Mollow has shown that the spectrum is symmetric in the radiation-damped case with both sidebands having intensity of order A^4 .

The eigenvalues can be computed exactly when the incident field oscillates at the atomic resonance frequency $\chi = \omega$. These eigenvalues are given in

Eqs. (30) and (32). The calculation of the scattered field in this case is simplest and most interesting in the limit of high-field intensity. The result is¹⁶

$$g(\nu) = \frac{1/2\tau}{1/\tau^2 + (\nu - \omega)^2} + \frac{\frac{1}{8}(1/\tau + 1/\tau')}{\frac{1}{4}(1/\tau + 1/\tau')^2 + (\nu - \omega - \delta)^2} + \frac{\frac{1}{8}(1/\tau + 1/\tau')}{\frac{1}{4}(1/\tau + 1/\tau')^2 + (\nu - \omega + \delta)^2}, \quad (58)$$

$$\delta = [\alpha^2 A^2 / \hbar^2 - \frac{1}{4}(1/\tau - 1/\tau')^2]^{1/2}.$$

In the special case $1/\tau' = 1/\tau$, this spectrum agrees with results given earlier by both Mollow and Newstein. $1/\tau' = 2/\tau$ gives agreement with Mollow's radiation-damped results.

The scattered field calculation for a stable two-level atom can be applied directly to the case of a two-level atom undergoing unimolecular decay from the upper level provided that the unimolecular-decay rate is slow compared with the thermal plus radiative upward transition rates $[(1/\tau)P_{1-0} + W_{0,1}]$. Because of the steady depletion of scatterers due to unimolecular decay, there is no equilibrium solution for the diagonal density matrix elements. The magnitude of the smallest eigenvalue is the observed unimolecular rate constant for the reaction. If

$$\Gamma_1/\hbar \ll (1/\tau)P_{1-0} + W_{0,1},$$

then the density matrix elements given in Eq. (36) approach their nonreaction counterparts. The matrix for the smallest eigenvalue approaches the steady-state counterpart, Eq. (39), with each element multiplied by the decay factor $e^{-\lambda_0 t}$,

$$\rho_{ij} = \rho_{ij}(\Gamma_1 = 0) e^{-\lambda_0 t}, \quad i, j = 1, 2. \quad (59)$$

The spectrum of scattered radiation is the same as before, except that the band intensities decay in time by the factor $e^{-\lambda_0 t}$, which enters as the time dependence of $\rho_{11}(t)$ and $\rho_{01}(t)$ in Eq. (43).

VI. COMMENTS ON EIGENVALUES

Most of the results obtained for the two-level system permit generalization to the N -level system with optical transitions between just two levels. In general there are $N+2$ eigenvalues for the generalized master equation and $N+2$ particular solutions to the Boltzmann equation. The general solution is a linear combination of these particular solutions that matches the $t=0$ values of the diagonal and two appropriate off-diagonal density matrix elements. In principle, then, a complete description of the time evolution of the density matrix and a complete calculation of the scattered field is possible. Such a calculation, however, is quite lengthy, and it is fortunate that a good deal of physical information is contained in just the eigenvalue spectrum of the generalized master equation.

In considering the time evolution of the system, the eigenvalues with small real parts are the most significant. In a system with chemical reaction, the smallest eigenvalue λ_1 is the chemical-rate constant for the system. To make this identification, one notes that

$$\underline{\rho} \cong \underline{\rho}(\lambda = \lambda_1), \quad (60)$$

when

$$[\text{Re}(\lambda_i - \lambda_1)]t \gg 1, \quad i = 2, 3, \dots, N+2.$$

In Eq. (60) each diagonal density matrix element has the time dependence

$$\rho_{ii} \sim e^{-\lambda_1 t}.$$

Therefore,

$$\frac{d\rho_{ii}}{dt} = -\lambda_1 \rho_{ii}$$

for all i , and λ_1 is the unimolecular-rate constant.

In a system without chemical reaction, there is always a zero eigenvalue. The system approaches a steady state, and the steady-state populations are given correctly by the ordinary master equation obtained by setting $W(\lambda) = W(\lambda = 0)$ in Eq. (15). This holds for the N -level system and for arbitrarily high light-field intensity. The approach to steady state is determined by the nonzero eigenvalue(s) with smallest real part. One has

$$\underline{\rho} = \underline{\rho}(\lambda = 0) + k \underline{\rho}(\lambda = \lambda_1),$$

for large t , where k is a constant. If the eigenvalues with smallest real part are a pair of complex conjugate eigenvalues, then one has the interesting case of an oscillatory approach to steady state.

The existence of this oscillatory approach to steady state is easily demonstrated in the two-level system. In the cubic equation that determines the three nonzero eigenvalues, one finds

$$\lambda_1 = \frac{1}{2}(\lambda_2 + \lambda_3), \quad (61)$$

if

$$\alpha^2 A^2 / \hbar^2 = 2\Delta^2 + \frac{2}{9}(1/\tau - 1/\tau')^2. \quad (62)$$

Equation (62) is indicated by the dashed line in Fig. 2. When complex eigenvalues exist, Eq. (61) can hold only if $\lambda_2 + \lambda_3$ are the complex roots. The requirement for an oscillatory approach to steady state is that

$$\lambda_1 > \frac{1}{2}(\lambda_2 + \lambda_3), \quad (63)$$

which in turn implies that

$$\frac{\alpha^2 A^2}{\hbar^2} > 2\Delta^2 + \frac{2}{9}(1/\tau - 1/\tau')^2, \quad 1/\tau > 1/\tau' \quad (64)$$

or

$$\frac{\alpha^2 A^2}{\hbar^2} < 2\Delta^2 + \frac{2}{9}(1/\tau - 1/\tau')^2, \quad 1/\tau < 1/\tau'. \quad (65)$$

In gases we expect that $1/\tau > 1/\tau'$, and so Eq. (64) requires that the Rabi frequency be large. Referring to Fig. 2, one has an oscillatory approach to steady state in and only in the unshaded region above the dashed line.

The eigenvalue spectrum also gives the positions and widths of the lines in the scattered field. Considering again the N -level problem, one notes that the spectrum $g(\nu)$ will be a sum of Fourier terms of the form

$$\int_0^\infty e^{-\lambda_i t} e^{i\nu t} dt + \text{c. c.}$$

It follows that each real eigenvalue provides a line centered at $\nu = \chi$ and of width λ_i . Each pair of complex conjugate eigenvalues will give two lines at $\nu = \chi \pm \text{Im}\lambda_i$ of width $\text{Re}\lambda_i$.

We expected to be able to show that in the N -level model there are at most one pair of complex conjugate roots. We have not been able to prove this result, which seems to require an N -level generalization of the interlacing property given in Eq. (28). The question of how many pairs of sidebands are possible in the scattered field of an N -level system remains an open question.

The calculation of intensity factors for the N -level system is too complicated to carry out in general. It is, however, physically obvious that, for small A^2 , only the sideband at $\nu = \omega$ will have a significant intensity, being of the order A^2 .

VII. DISCUSSION

We have considered the effect of a monochromatic driving field upon an N -level atomic system suffering thermalizing collisions with a heat bath and undergoing unimolecular decay. Detailed computations were presented for the case $N=2$ and consistency was demonstrated with previous calculations of the scattered field when special values were assigned to the elastic and inelastic collision rates.

An intuitive picture for the time evolution of the level populations follows from the derivation of a generalized master equation. The set of eigenvalues for the generalized master equation have particular significance in predicting the scattered field components and the approach of the N -level system to equilibrium. These eigenvalues for certain ranges in the incident field intensity are complex and in some cases give rise to an oscillatory approach of the diagonal density matrix elements towards steady state. Moreover, the imaginary part of the complex roots gives the location of the scattered field bands, and the real part of the roots determines the widths of these bands.

The N -level model with unimolecular decay can be used to predict the effect of radiative transitions upon the reaction rate. The scattered field solution is particularly useful here, since it distin-

guishes the thermal from radiative contributions to the reaction rate. The separation of the thermal from nonthermal-rate components is accomplished by observing the position of the sidebands relative to the central band as a function of light intensity. Let us assume for simplicity that

$$\frac{\alpha^2 A^2}{\hbar^2} \gg \frac{1}{4} \left(\frac{1}{\tau} - \frac{1}{\tau'} \right)^2. \quad (33')$$

Then as the light intensity is increased, the sidebands will move away from the central band and will show no appreciable increase in linewidth if the effect of the radiation is to populate the decaying atomic level directly. If, however, the increased radiation is partially absorbed by the solvent bath, and collisions with the hotter solvent molecules provide the major contribution to an increased population of the decaying atomic state,

then the sideband widths will broaden, while their positions will remain fixed. If the number of phase-changing collisions increased to the point where

$$\frac{1}{4} (1/\tau - 1/\tau')^2 \approx \alpha^2 A^2 / \hbar^2,$$

the sidebands would move towards the central band and their widths would broaden. We note that this method of separating the thermal from nonthermal components of the reaction rate does not require knowledge of the reaction temperature. This could be useful since an accurate measurement of temperature of a gas in the presence of an intense laser field is extremely difficult.

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