

Collisional perturbations of time-resolved photon scattering from molecular levels

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(Received 6 August 1974; revised manuscript received 28 April 1975)*

A theoretical study is presented of the effects of collisional perturbations on the time-resolved resonant and near-resonant photon scattering from a molecular system. The photon counting rate is formulated in terms of tetradic Green's functions in Liouville space. The collisional and radiative damping effects are handled by an effective-Liouillian formalism. The formal expressions are disentangled by invoking a series of successive approximations, assuming short correlation times of the thermal bath, neglecting relaxation processes in the ground electronic state, considering rotational relaxation as providing the dominant damping mechanism in the excited electronic manifold, specializing to weak electromagnetic fields, neglecting some off-resonance processes and disregarding collision-induced radiative processes. The photon counting rate is expressed as a triple convolution of the photon counting rate for the free molecule with the Doppler Gaussian profile and with a Lorentz profile. The latter incorporates purely collisional effects due to intrastate cross relaxations and proper T_2 processes. The theory accounts well for the recent experimental data of Williams, Rousseau, and Dworetzky on collisionally perturbed I_2 molecules.

I. INTRODUCTION

Recent experiments by Williams, Rousseau, and Dworetzky¹ (WRD) have monitored the transition from resonance fluorescence to near-resonance Raman scattering in time-resolved photon-counting experiments from a single rotational-vibrational level of the $B^3\Pi$ state of the I_2 molecule. A subsequent theoretical study² pointed out that the experimental time-resolved decay pattern of an "isolated," collision-free, molecular level is characterized just by two types of lifetimes, that specifying the width of the molecular resonance, and those characterizing the light pulse. No new observable decay modes are exhibited when the excitation energy is tuned away from the molecular resonance. The off-resonance energy parameter affects the total intensity of the scattered photons and the relative intensities of the different decay components. The details of the latter effect are determined by the specific energetic spread of the exciting photon wave packet. This treatment² pertained to the decay characteristics of a single molecule and should be extended to handle the interesting effects of collisional damping on the time-resolved decay pattern. From the experimental work of WRD¹ some interesting information concerning this problem emerges. When the off-resonance energy increment Δ (i.e., the separation between the energies of the centers of the molecular resonance and the photon wave packet) is large (in comparison to the Doppler width, the energetic spread of the photon wave packet, and the radiative width of the molecu-

lar resonance), the following features are exhibited:

(a) At moderately low pressures (~ 0.03 Torr), the relative contribution of the long-lived decay component to the total intensity off resonance is slowly decreasing with Δ , becoming constant at large values of Δ .

(b) Increasing the total I_2 pressure results in a dramatic enhancement of the long-lived molecular component.

These interesting experimental results cannot be elucidated by a naive extension of the theory advanced for the "isolated" molecule,^{1,2} simply modifying the molecular radiative-decay width by the addition of a pressure-dependent term.³ The calculation of the photon-counting rate, which (to lowest order in the radiation field) depends on a second-order radiative perturbation, involves both T_1 (level-relaxation) and T_2 (line-broadening) processes. The latter include interference effects between the lower and the upper molecular states due to phase shifts, which cannot be expressed as additive contributions of the levels.

In view of the current interest in collisional quenching effects on radiative and nonradiative decay characteristics of electronically excited molecular states,⁴ this problem merits a theoretical study. In the present work we consider the effects of collisional perturbations on the transition between time-resolved resonance fluorescence and near-resonance Raman scattering from a molecular system. Section II is devoted to the general formulation of the collisional and the radiative damping effects in terms of tetradic

Green's functions. A solution is obtained (see Appendix) to second order in the applied field which, under appropriate conditions, is a generalization of the equivalent solution of the Bloch-Redfield equation, incorporating radiative as well as collisional damping effects. A specific model of the damping matrices is presented in Sec. III. In Sec. IV the model is applied to the experimental data.¹ Numerical results are presented and their physical interpretation is described. We conclude that, under realistic conditions pertaining to the excitation of an isolated molecule, the ratio of the intensity of the long-lived component to the total intensity is asymptotically proportional to Δ^{-2} at large Δ , while collisional-damping effects will result in a negligible variation of this ratio with Δ in the off-resonance situation. We were thus able to elucidate the quantitative features of the effect of collisional perturbations on the transition from resonance fluorescence to near-resonance Raman scattering.

II. TIME EVOLUTION OF A COLLISIONALLY PERTURBED MOLECULE

We shall now consider the time evolution of the density matrix of a molecular ensemble interacting with a light pulse at a moderately low pressure, incorporating both the electromagnetic interactions and the molecule-molecule collisional effects. It is assumed that the molecules are embedded in a sufficiently large bath and that the interactions are sufficiently weak to prevent departures of the bath from thermal equilibrium at any time. One can thus consider the subpart of the system consisting of the molecule and the radiation field (the mr system) by averaging the density matrix of the total system over the states of the "bath".⁵⁻⁷ The resulting reduced density matrix will be utilized to describe the photon-emission rate from the collisionally perturbed molecule.

It is later intended to treat the interaction with the external field by perturbation methods. In order to include spontaneous-emission effects to arbitrary orders, we resolve the radiation-matter interaction H'_{mr} into two parts—one pertaining to the set of modes contributing to the applied pulse (V) and the other pertaining to the rest (H_{mr}). Since the pulse is usually confined to a very small part of the photon phase space (e.g., by a very narrow angular distribution), there is only a small error in omitting these modes from the total contributions to radiative damping.⁸

The Hamiltonian of the system consisting of a single molecule embedded in a gas of (optically inactive) atoms in the presence of the radiation field is

$$H = H' + H_1 + V \equiv H_0 + V, \quad (1)$$

where

$$H' = H_m + H_b + H_r \quad (2)$$

and

$$H_1 = H_{mr} + H_{mb}.$$

Here H_m is the molecular Hamiltonian, H_r is the Hamiltonian of the free electromagnetic field, H_b is the Hamiltonian of the perturbing atoms, (i.e., the "bath"), and H_{mb} the molecule-bath interaction. The eigenstates of the zero-order Hamiltonian H' will be labeled $|mrb\rangle$, where $|m\rangle = |g\rangle, |s1\rangle, |s2\rangle, \dots, |sn\rangle$ corresponds to the molecular levels. $|r\rangle = |\text{vac}\rangle$ and $|\vec{k}\rangle$ correspond to the vacuum and one-photon states, respectively, while $|b\rangle$ labels the states of the perturbing atoms. Concerning the molecular levels, we shall consider only a single initial state (the ground state) $|g\rangle$ and a manifold of bound excited states $|s1\rangle, |s2\rangle, \dots, |si\rangle$, etc. Each of the excited levels is characterized by a radiative width Γ_{si}^r , and we assume that the separation of the levels exceeds their radiative width, i.e., $|E_{si} - E_{sj}| \gg \Gamma_{si}^r + \Gamma_{sj}^r$ for all $|si\rangle$ and $|sj\rangle$, so that no radiative interference effects are exhibited. The joint states of $(H_m + H_r)$ are supposed to be the continuum of the one-photon states $|g, \vec{k}\rangle$ and the zero-photon states $|si, \text{vac}\rangle$. We shall neglect off-resonance high-order electromagnetic interactions and disregard excited one-photon states $|si, \vec{k}\rangle$, etc. For the sake of convenience, let us now introduce the abbreviated notation $|\vec{k}\rangle \equiv |g, \vec{k}\rangle$ and $|i\rangle \equiv |si, \text{vac}\rangle$.

The response of the macroscopic system to the applied field can be formulated in terms of tetradic Green's functions in Liouville space.^{5-7,9} The time evolution of the total density matrix is given by

$$\rho(t) = \exp[-iL(t-t')]\rho(t'), \quad (3)$$

where L is the Liouville operator, or Liouvillian, of the total system, defined as

$$LA = [H, A], \quad (4)$$

given any ordinary (dyadic) operator A . We can now impose initial conditions on the solution, requiring $\rho(t')$ to be independent of V for sufficiently early times, $t' \rightarrow -\infty$, i.e.,

$$\rho(t') \rightarrow \rho_0(t') \equiv \exp(-iL_0 t')\rho_0(0), \quad (5)$$

where ρ_0 is independent of the interaction V . We have partitioned the Liouvillian into

$$L = L_0 + W, \quad (6)$$

L_0 and W being the Liouville operators corresponding to H_0 and V , respectively. Owing to the presence of the nonstationary pulse,

$$L_0 \rho_0 = L_r \rho_0 \neq 0, \quad (7)$$

where L_r corresponds to $H_r [(L - L_r)\rho_0 = 0$ since the gas is in thermal equilibrium].

Neglecting statistical correlations between the mr system and the bath, we can write

$$\rho_0(0) = \rho_{mr}(0) \rho_b. \quad (8)$$

We now assume, for the sake of simplicity, that all the radiative widths of all the $|i\rangle$ states are identical, i.e., $\Gamma_{s_1}^r = \Gamma_{s_2}^r = \dots = \Gamma_s^r$. Then, the photon-counting rate is given by

$$\bar{F}(\Delta, \Gamma_s^r, t) = \Gamma_s^r P_e(t), \quad (9)$$

where

$$P_e(t) = \text{tr}_b \text{tr}_i \langle i, \text{vac}, b | \rho_{mr_b}(t) | i, \text{vac}, b \rangle \quad (10)$$

is the total population of the excited molecular manifold $\{|i\rangle\}$. The experimental photon-counting rate may be obtained from Eq. (9) by integrating over the distribution of Doppler-shifted molecular frequencies. The mr subsystem at $t=0$ is assumed to be given (up to a trivial normalization constant) by¹⁰

$$\rho_{mr}(0) = \int \int dk dk' A_k A_k^* |k\rangle \langle k'|, \quad (11)$$

where the amplitude-modulation parameters $\{A_k\}$ of one-photon states are normalized so that their Fourier transform assumes the maximum value of unity. Assuming that the pulse modes are uni-

directional, we can decompose the field amplitude by the one-dimensional Fourier transform.

$$\varphi(t) = \int dk \exp[i(\bar{k} - k)t] A_k, \quad (12)$$

where \bar{k} is the mean photon energy in the pulse. The reduced density matrix for the mr system can be expanded in the double-bracket notation of Liouville space.⁹ Let us reduce the relevant mr space into four subspaces spanned by the respective projection operators,

$$\hat{P}_1 = \sum_{ij} |ij\rangle \langle ij|, \quad (13a)$$

$$\hat{P}_0 = \int \int dk dk' |kk'\rangle \langle kk'|, \quad (13b)$$

$$\hat{P}_2 = \int dk' |ik'\rangle \langle ik'|, \quad (13c)$$

$$\hat{P}'_2 = \int dk |ki\rangle \langle ki|, \quad (13d)$$

where $|ij\rangle\rangle$ is the Liouville-space vector representing the operator $|i\rangle\langle j|$, etc. In the case of a sharp resonant transition $|k\rangle \rightarrow |j\rangle$, which is well isolated from other resonances, and with \bar{k} lying close to $E_{sj} - E_g$, we may ignore the interaction of the light pulse with all states $|i\rangle$ ($i \neq j$), and after some manipulation (see Appendix) we finally arrive, to second order in the applied field, at the following expression for $P_e(t)$:

$$P_e(t) = -2R_e \sum_i |V_{j\bar{k}}|^2 \int \int d\tau d\tau' \Theta(t - \tau) \Theta(t - \tau') \varphi(\tau) \varphi^*(\tau') \langle ij | G_1(t - \tau) | jj \rangle \langle j\bar{k} | G_2(\tau - \tau') | j\bar{k} \rangle. \quad (14)$$

Here $V_{jk} = \langle k | V | j \rangle$ is the electromagnetic interaction matrix element (assumed to be practically independent of k around \bar{k}). Θ is the Heavyside step function, and φ is defined by Eq. (12). $G_1(t)$ and $G_2(t)$ are retarded propagators of linear-response theory, given by

$$G_1(t) = (2\pi)^{-1} \int dE e^{-iEt} [E - \hat{P}_1 L_m \hat{P}_1 - R_1]^{-1},$$

$$G_2(t) = (2\pi)^{-1} \int dE e^{-iEt} [E - \hat{P}_2 (L_m + L_r) \hat{P}_2 - R_2]^{-1}. \quad (15)$$

R_1 and R_2 are non-Hermitian matrices defined as the appropriate projections of a general level-shift operator R , defined in the Appendix

$$R_1 = \hat{P}_1 R \hat{P}_1, \quad R_2 = \hat{P}_2 R \hat{P}_2. \quad (16)$$

The Hermitian parts of R_1 and R_2 are the shift matrices, while their antiHermitian parts correspond to relaxation matrices. In many cases the shift can be neglected, compared to the relaxation coefficients, whereupon the matrices R_1 and R_2 will be written as

$$R_a = -i\Gamma_a \quad (a = 1, 2). \quad (17)$$

Each of the elements of Γ_a contains both radiative and collisional contributions. A diagonal element of R_1 in this manifold is the level-decay rate, and the element combining $|ii\rangle\rangle$ with $|jj\rangle\rangle$ ($i \neq j$) is a cross-relaxation coefficient. Γ_1 is conventionally referred to as the T_1 relaxation matrix.^{11,12} Note that the matrix $\hat{P}_1 L_0 \hat{P}_1$ vanishes under the present conditions. G_2 involves the manifold $\{|ik\rangle\rangle\}$, which corresponds to the linear-response polarization in the exciting field. This propagator is encountered

in calculations of resonance absorption. $\underline{\Gamma}_2$ is conventionally referred to as the T_2 relaxation matrix.^{11,12} The operators $G_1(t)$ and $G_2(t)$ are thus the Fourier transforms of the resolvents for T_1 and T_2 processes, respectively. Whenever the correlation time for the molecular interactions is short compared to the relaxation times (as is the case in dilute gases) the E dependence of R_1 and R_2 can be disregarded.⁶ Under the conditions leading to (17) with R_1 and R_2 practically independent of E , we get

$$G_a(t) = -i\Theta(t) \exp(-i\Omega_a t - \underline{\Gamma}_a t) \quad (a=1, 2), \quad (18)$$

where $\Omega_1 = 0$, and $\Omega_2 = \hat{P}_2(L_m + L_r)\hat{P}_2$ is the (diagonal) matrix of resonance frequencies for the T_2 processes.

III. SPECIFIC MODEL FOR COLLISIONAL BROADENING

Equation (14) provides an approximate solution to the problem of the effect of collisional perturbations on the time-resolved decay rate of an excited molecular state, which is valid to second order in the interaction with the applied field. This result is similar to a second-order-perturbation solution of the Bloch-Redfield master equation.¹² However, the systematic derivation presented in the Appendix has the advantage of treating collisional and radiative damping in a combined manner. To apply our theory to real-life situations, we have to assume a specific model for the damping matrices $\underline{\Gamma}_1$ and $\underline{\Gamma}_2$ and for the light pulse $\varphi(t)$.

Let us take $\underline{\Gamma}_1$ to be an $n \times n$ matrix of the form

$$\langle\langle jj | \underline{\Gamma}_1 | ii \rangle\rangle = \Gamma'_1 \delta_{ij} - \Gamma''_1 (1 - \delta_{ij}) \quad (i, j = 1, \dots, n). \quad (19)$$

We thus assume that all the n levels of the excited manifold have the same damping rates Γ'_1 , and that the cross-relaxation rates Γ''_1 between all pairs of levels are identical. The negative sign of Γ''_1 results from general unitarity properties.⁷ This model treats all levels on the same footing and

introduces the notion of "level democracy." It incorporates minimum physical information concerning the excited band and is adequate in view of our current ignorance regarding the details of the individual relaxation terms in the band. In the absence of collisions we expect that $\Gamma''_1 = 0$ and $\Gamma'_1 = \Gamma'_s$. When radiative damping can be neglected with respect to collisional broadening at high pressures, and all relaxation processes occur within the $\{|ii\rangle\}$ manifold, we have $\Gamma'_1 = (n-1)\Gamma''_1$.

An important property of the $\underline{\Gamma}_1$ matrix, as given by Eq. (19), is that it has an eigenvector $\langle\langle \alpha | = \sum_i \langle\langle ii |$ with the eigenvalue

$$\Gamma_1 = \Gamma'_1 - (n-1)\Gamma''_1. \quad (20)$$

But this eigenvector is just the dyadic bra vector closing on G_1 on its left side in Eq. (14). G_1 is thus diagonalized, with the eigenvalue $(E + i\Gamma_1)^{-1}$ replacing the matrix G_1 . In the case where there is no collisional relaxation from the band, Γ_1 is then practically the radiative width of the band Γ'_s .

We shall now consider the T_2 propagator G_2 . In the case of a sharp resonance, we have to consider in G_2 only the single diagonal term $\langle\langle j\bar{k} | \underline{\Gamma}_2 | j\bar{k} \rangle\rangle \equiv \Gamma_2$. This term includes T_1 processes, in addition to "proper" T_2 processes which result from interference effects (phase shifts). Generally, we can write⁹

$$\Gamma_2 = \frac{1}{2}(\Gamma_{jj} + \Gamma_{\bar{k}\bar{k}}) + \Gamma'_2, \quad (21)$$

where Γ_{jj} and $\Gamma_{\bar{k}\bar{k}}$ are the damping rates of the levels $|j\rangle$ and $|\bar{k}\rangle$, respectively, and Γ'_2 stands for the "proper" T_2 processes. In our model we assume $\Gamma_{\bar{k}\bar{k}} = 0$, and $\Gamma_{jj} = \Gamma'_1$. In the limit of zero pressure,

$$\Gamma_2 \rightarrow \frac{1}{2}\Gamma'_s, \quad (22)$$

since Γ'_2 does not have radiative terms.

Equation (14) can now be expressed in the form

$$P_e(t) = |V_{j\bar{k}}|^2 \int_{-\infty}^t \int_{-\infty}^{\tau} d\tau d\tau' \varphi(\tau) \varphi^*(\tau') \exp[-\frac{1}{2}\Gamma'_1(2t - \tau - \tau')] \exp[(i\Delta - \hat{\Gamma})(\tau' - \tau)], \quad (23)$$

where

$$\hat{\Gamma} = \Gamma_2 - \frac{1}{2}\Gamma'_1. \quad (24)$$

Equations (23) and (24) are independent of the details of the model for the relaxation of the electronically excited manifold. It is important to notice that $\hat{\Gamma}$ incorporates only relaxation pro-

cesses within the excited manifold together with proper T_2 processes, and does not involve relaxation coefficients which lead to the depletion of the excited electronic manifold. In our special model,

$$\hat{\Gamma} = \frac{1}{2}(n-1)\Gamma''_1 + \Gamma'_2, \quad (25)$$

which incorporates purely collisional effects and

does not include radiative damping.

In the absence of collisions, $\Gamma_1 = \Gamma_s^r$ and $\hat{\Gamma} = 0$. Thus Eq. (23) can be written as an absolute square of an amplitude,

$$P_e(t) = \left| V_{jk} \int_{-\infty}^t d\tau \varphi(\tau) \exp[-\frac{1}{2}\Gamma_1(t-\tau) - i\Delta\tau] \right|^2 \equiv F(\Delta, \Gamma_1, t)/\Gamma_1, \quad (26)$$

where now $\Gamma_1 = \Gamma_s^r$, and F is the previously derived photon-counting rate for the isolated molecule.² Note, however, that when $\hat{\Gamma} \neq 0$, Eq. (23) cannot be written as the absolute square of an amplitude.

The effect of the collision-broadening factor in Eq. (23) can be elucidated if we note that the retarded propagators obey the identity

$$2\pi\Theta(\tau) \exp[-i\Delta - \hat{\Gamma}]\tau = \int_{-\infty}^{\infty} d\Delta' \exp(-i\Delta'\tau) [-i(\Delta - \Delta') + \hat{\Gamma}]^{-1}. \quad (27)$$

Inserting in Eq. (23), we get for the photon-counting rate \bar{F} in the presence of collisional perturbations

$$\bar{F}(\Delta, \Gamma_1, t) = \int_{-\infty}^{\infty} d\Delta' \hat{L}(\Delta - \Delta') F(\Delta', \Gamma_1, t) \equiv \hat{L} * F, \quad (28)$$

where

$$\hat{L}(\Delta) = (\hat{\Gamma}/\pi)(\Delta^2 + \hat{\Gamma}^2)^{-1} \quad (29)$$

is a Lorentz profile for the purely collisional intraband relaxation and the proper T_2 processes. Collisions thus affect the counting rate by a homogeneous "smearing" of the Δ dependence.

Finally, we have to incorporate the effect of the inhomogeneous Doppler broadening. First, let us consider the idealized situation¹³ in which the two broadening effects are totally independent of each other. This, is the case, e.g., when the radiating molecule is much heavier than the molecules of a foreign gas with which it collides.^{7,9} The radiating molecule will then be scattered mostly in the forward direction, thus affecting only slightly the velocity distribution. The collision-damping rates will depend essentially only on the perturber velocity, and will thus be independent of the velocity of the radiator. Doppler broadening will then ex-

press itself by convoluting (28) with the Doppler profile

$$\mathcal{F}(\Delta) = (\pi\beta^2)^{-1/2} \exp(-\Delta^2/\beta^2) \quad (30)$$

resulting in the final form for the photon-counting rate under conditions of pressure broadening:

$$\{F(\Delta, \Gamma_1, t)\} = \int \int \mathcal{F}(\Delta - \Delta') \hat{L}(\Delta' - \Delta'') \times F(\Delta'', \Gamma_1, t) d\Delta' d\Delta'' \equiv \mathcal{F} * \hat{L} * F. \quad (31)$$

The generalization to the case when the two broadening mechanisms do affect each other can now be easily envisioned. All we have to do to include such effects as Dicke narrowing, etc.,¹³ is to replace $\mathcal{F} * \hat{L}$ in (31) by the line-shape profile (from which interband processes have been deconvoluted). $\mathcal{F} * \hat{L}$ is thus the collision-broadened line-shape function, which can be obtained from absorption spectroscopy.

Equation (31) will be used to describe the photon-counting rate, incorporating both collisional and Doppler broadening. It has the form of a triple convolution of the photon-counting rate for the isolated molecule (F) with the Gaussian (inhomogeneous) distribution (\mathcal{F}) of Doppler-shifted molecular frequencies and with a Lorentz (homogeneous) profile \hat{L} . Equation (31) will be utilized in the discussion of the experiment¹ in Sec. IV.

IV. COMPARISON WITH EXPERIMENT

We are now in a position to compare our result, Eq. (31), with the experimental work of Williams *et al.*¹ In accordance with Fig. 1 of Ref. 1, we assume the following model shape for the pulse amplitude²:

$$\varphi(t) = \begin{cases} \exp(\frac{1}{2}\gamma_1 t) & (t < 0) \\ 1 & (0 < t < T) \\ \exp[-\frac{1}{2}\gamma_2(t-T)] & (t > T) \end{cases} \quad (32)$$

We thus consider here a photon wave packet specified by the following parameters: (1) the pulse rise time γ_1^{-1} , (2) the pulse duration T , and (3) the fall time of the pulse γ_2^{-1} .

The photon-counting rate in the case of an isolated molecule ($\hat{\Gamma} = 0$), given the pulse shape (32), has been investigated recently in detail.² For $t > T$, it is given by

$$F(\Delta, \Gamma_s^r, t) = \Gamma_s^r |V_{gs}|^2 \{ |A_s|^2 \exp[-\Gamma_s^r(t-T)] + |A_p|^2 \exp[-\gamma_2(t-T)] - 2R_e A_p^* A_s \exp[i\Delta(t-T)] \exp[-\frac{1}{2}(\gamma_2 + \Gamma_s^r)(t-T)] \}, \quad (33)$$

where

$$A_p = [\Delta + \frac{1}{2}i(\Gamma_s^r - \gamma_2)]^{-1} \quad (33a)$$

and

$$A_s = [\Delta + \frac{1}{2}i(\Gamma_s^r - \gamma_2)]^{-1} - [\Delta + \frac{1}{2}i\Gamma_s^r]^{-1} + \exp(-\frac{1}{2}\Gamma_s^r T + i\Delta T) \{ [\Delta + \frac{1}{2}i\Gamma_s^r]^{-1} - [\Delta + \frac{1}{2}i(\Gamma_s^r + \gamma_1)]^{-1} \}. \quad (33b)$$

The first term in (33) is characterized by the molecular decay time, the second term is characterized by the pulse decay time, while the third term involves an interference contribution. For the physically relevant case, $\gamma_2 \gg \Gamma_s^r$, the latter term is dominated by the pulse decay time. The relative contribution of the long-lived molecular component to the total photon-counting rate at $t = T$ in (33) is given by the ratio

$$R = I_M(\Delta)/I_T(\Delta), \quad (34)$$

where

$$I_M(\Delta) = |A_s|^2, \quad (34a)$$

$$I_T(\Delta) = |A_s|^2 + |A_p|^2 - 2R_e A_p^* A_s.$$

In order to simulate a real-life situation pertaining to the isolated molecule, we have to perform integration over the Doppler profile. The relative contribution of the molecular long-lived component at $t = T$ is thus

$$\langle R \rangle = \langle I_M \rangle / \langle I_T \rangle, \quad (35a)$$

where

$$\langle I_M \rangle = I_M * \mathcal{F}, \quad (35b)$$

$$\langle I_T \rangle = I_T * \mathcal{F},$$

and $\langle \dots \rangle$ denotes Doppler-integrated quantities.

Finally, in order to discuss the features of the time-resolved decay pattern, including combined Doppler and pressure broadening, we define the relative contribution of the long-lived component (with respect to the total intensity) at $t = T$ as

$$\{R\} = \{I_M\} / \{I_T\}, \quad (36a)$$

where

$$\{I_M\} = I_M * \mathcal{F} * \hat{L} = \langle I_M \rangle * \hat{L}, \quad (36b)$$

$$\{I_T\} = I_T * \mathcal{F} * \hat{L} = \langle I_T \rangle * \hat{L}.$$

Photon-counting rates for collisionally perturbed molecules have been calculated using Eq. (31) for the pulse shape given by Eq. (32). In order to simulate the experimental situation,¹ the following parameters (in units of Γ_1) were used: $\gamma_1 = \gamma_2 = 100$, $T^{-1} = 2$. The Doppler width is taken as $\beta = 500$ in the same units. In our model $\Gamma_1 = \Gamma_s^r$; the value of Γ_1 estimated from the long-decay

component in Ref. 1, is approximately 10^6 sec^{-1} , and is pressure independent.

In Fig. 1, we portray numerical results of the calculation of the isolated-molecule photon-counting rate $\langle F(\Delta, \Gamma_s^r, t) \rangle$.

Since $\beta \gg \Gamma_s^r$ the decay pattern corresponds to the resonance situation as long as $\Delta \lesssim \beta$ and, under these circumstances, only the molecular long-lived component is exhibited. When Δ exceeds 2β , both short and long components are exhibited. We also notice that the oscillating-type interference contribution is smeared out due to the Gaussian integration. Figure 2 exhibits the effects of collisional perturbations at relatively

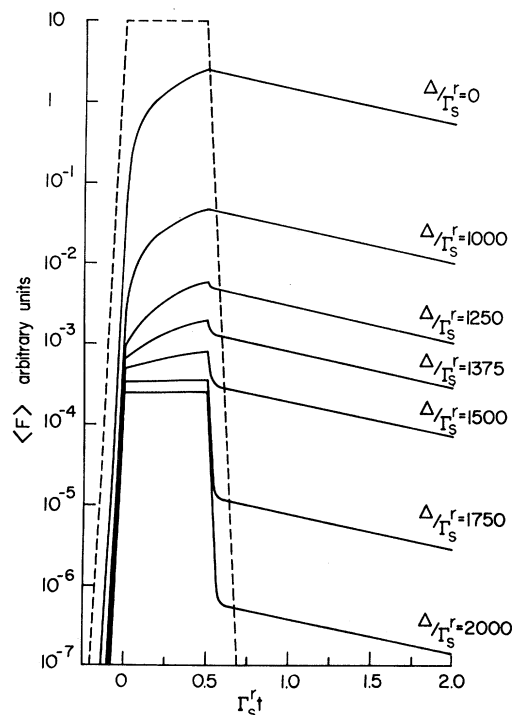


FIG. 1. Time resolution of the photon-counting rate $\langle F \rangle$ (in arbitrary units) in the absence of collisions for various values of the off-resonance energy Δ , the Doppler width (in units of the radiative damping) is $\beta/\Gamma_s^r = 500$; the rise and fall times of the pulse are $\gamma_1/\Gamma_s^r = \gamma_2/\Gamma_s^r = 100$; the inverse duration of the pulse is $T^{-1}/\Gamma_s^r = 2$. The dotted line is proportional to the pulse time-resolved intensity.

low values of Δ ($\Delta = 2\beta = 1000$ and $\Delta = 3\beta = 1500$) [see Fig. 2(a)] and at $\Delta = 4\beta = 2000$ [see Fig. 2(b)].

The value of the collision-broadening parameter $\hat{\Gamma}$ has been varied from zero to unity (in Γ_1 units). These results clearly demonstrate that up to about $\Delta = 3\beta$, the effects of collisions are insignificant. However, at $\Delta = 4\beta$, we notice a most dramatic enhancement of the slowly decaying component as the pressure is increased. This is observed at values of $\hat{\Gamma}$ as low as a few hundredths of Γ_1 . Figure 3 portrays the ratio $\{R\} = \langle I_M \rangle / \langle I_T \rangle$, defined by Eq. (36), between the long-lived intensity and the total intensity, as a function of Δ , calculated for various values of $\hat{\Gamma}$. We note that, first, at values of $\Delta \lesssim 3\beta$, $\{R\}$ is practically unity at all pressures and, second, at $\Delta \gtrsim 4\beta$, $\{R\}$ increases with increasing pressure from a small value ($\approx 10^{-3}$), with the most dramatic enhancement occurring with $\hat{\Gamma} \approx 0.025$. For this small $\hat{\Gamma}$ value, $\{R\}$ exhibits a weak variation with Δ in the

range $4\beta - 10\beta$. Also, note that at higher pressures ($\hat{\Gamma} \gtrsim 0.25$), the value of $\{R\}$ becomes practically independent of Δ at values of $\Delta \gtrsim 4\beta$. In order to gain a qualitative understanding of these features, let us study separately $\langle I_M \rangle$ and $\langle I_T \rangle$, shown in Fig. 4. At zero pressure ($\hat{\Gamma} = 0$) the two intensity components start from the same value at $\Delta = 0$, both decreasing rapidly with increasing Δ . At $\Delta \gtrsim 3\beta$ they separate, with $\langle I_M \rangle$ exhibiting a much steeper drop. Increasing $\hat{\Gamma}$ results in an appreciable enhancement in $\langle I_M \rangle$, while $\langle I_T \rangle$ is only slightly affected by increasing the pressure. The asymptotic behavior of $\{R\}$ is independent of Δ (for $\hat{\Gamma} > 0$).

Consider now the asymptotic Δ dependence of the photon-counting rate under the experimental conditions $\beta \gg \gamma_1 + \gamma_2 \gg \Gamma_s^r$.

At large values of Δ , the total intensity of the isolated-molecule decay rate at $t = T$ is, as seen from Eq. (34a), $I_T \propto \Delta^{-2}$, falling off as a tail of a Lorentzian. Incorporating Doppler broadening (again in the isolated molecule) results in a convolution with the Gaussian distribution (30), which still retains the Δ^{-2} asymptotic dependence in $\langle I_T \rangle$. The asymptotic expression for the long-lived molecular component in the isolated-molecule case (in the absence of Doppler broadening) is, as seen from Eq. (34a), $I_M \propto \Delta^{-4}$, and its convolution with a Gaussian results in the same asymptotic form $\langle I_M \rangle \propto \Delta^{-4}$, falling off much more rapidly than a Lorentzian. This analysis shows that the asymptotic behavior of the ratio (at $\Delta \gg \beta$) is

$$\langle R \rangle \propto \Delta^{-2} \quad (37)$$

as illustrated in Fig. 1.

This result for the isolated molecule is in var-

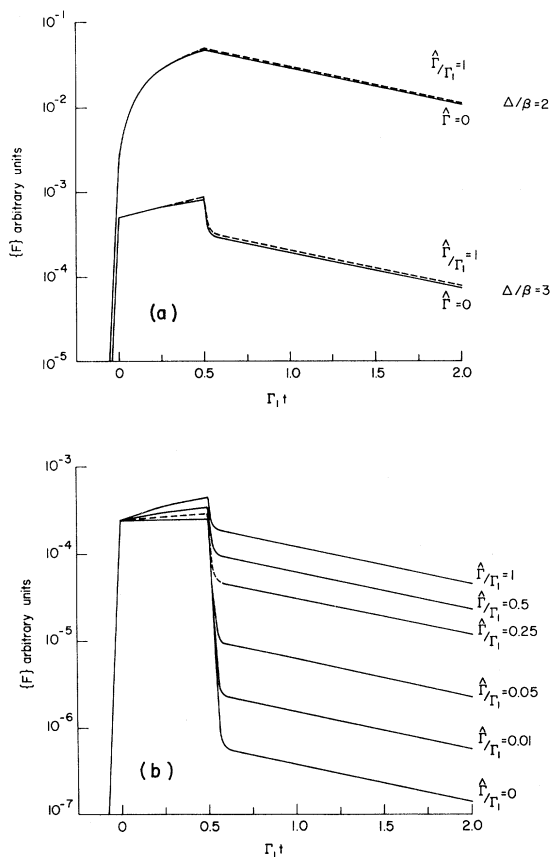


FIG. 2. Effect of collision broadening on the photon-counting rates (a) at values of the off-resonance parameter $\Delta/\Gamma_1 = 2\beta/\Gamma_1 = 1000$, and $\Delta/\Gamma_1 = 3\beta/\Gamma_1 = 1500$; (b) at $\Delta/\Gamma_1 = 4\beta/\Gamma_1 = 2000$, showing the dramatic effect of pressure broadening ($0 < \hat{\Gamma} \leq \Gamma_1$) at high Δ values. Pulse parameters same as in Fig. 1. Note that $\Gamma_1 \approx \Gamma_s^r$.

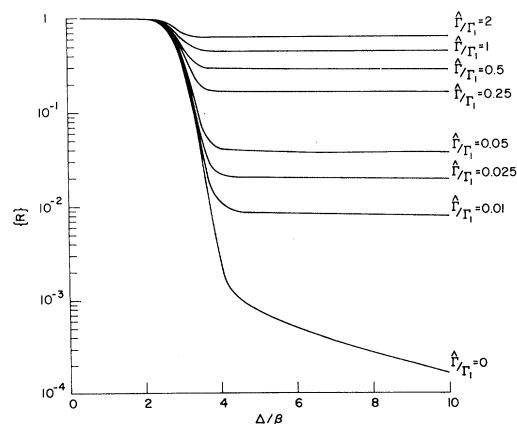


FIG. 3. Intensity ratio $\{R\}$ between the slowly decaying component and the total photon-counting rate, evaluated at $t = T$, as a function of the off-resonance parameter Δ , at different values of the collision-broadening rate $\hat{\Gamma}$. Other parameters same as in Fig. 1.

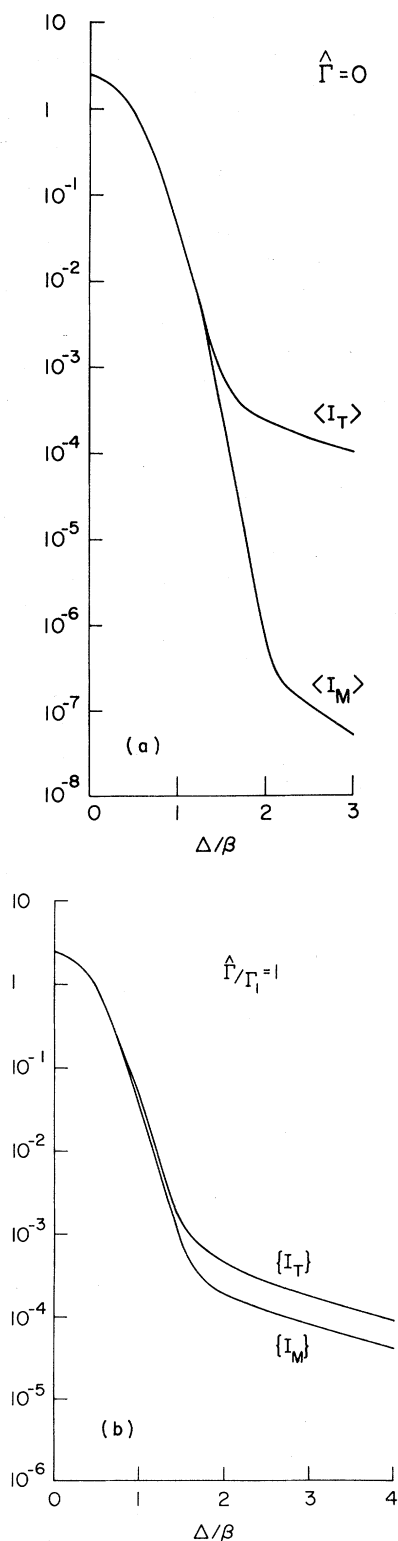


FIG. 4. Total intensity and the slow-component intensity (evaluated as $t = T$) as a function of Δ , at (a) $\hat{\Gamma} = 0$ (zero pressure), and (b) $\hat{\Gamma}/\Gamma_1 = 1$ (i.e., $\hat{\Gamma} \approx \Gamma_1^*$). Other parameters same as in Fig. 1.

iance with the "low" pressure experimental data of WRD.¹ We conclude that even under such low pressures (0.03 Torr I_2), collisional effects are already of considerable importance, and we proceed to discuss the finite-pressure results required for the understanding of time-resolved photon scattering by a collisionally perturbed molecule. Pressure broadening amounts to convolution with the Lorentzian (29) which, although being extremely narrow, will make the long-lived component drop off asymptotically as $\{I_M\} \propto \Delta^{-2}$, whereas the asymptotic form of the total intensity $\{I_T\} \propto \Delta^{-2}$ is unaffected by pressure.

In summary, we note that for the case of a pulse characterized by short exponential rise and fall times (compared to the radiative time), the following asymptotic forms are obtained:

$$\{I_T(\Delta)\} \sim \langle I_T(\Delta) \rangle \propto \Delta^{-2}, \quad (38a)$$

$$\{I_M(\Delta)\} \sim (\hat{\Gamma}/\pi\Delta^2) \int d\Delta' \langle I_M(\Delta') \rangle. \quad (38b)$$

Notice the following three characteristics: Firstly, the total intensity is not changed by collision broadening. Secondly, the intensity of the long-lived molecular component is proportional to $\hat{\Gamma}$ and thus to the pressure. Thirdly, $\{R\}$ is Δ independent at large Δ . The last two conclusions hold regardless of the details of the pulse shape, while the first is specific to exponential rise and decay of the pulse.

We can extend this discussion to other pulse shapes. For example, when the pulse rise and decay are faster than exponential, we expect that both $I_M(\Delta)$ and $I_T(\Delta)$ will decrease faster than Δ^{-2} at large Δ . In this case Eq. (38b) still holds, while the total intensity at $t = T$ is now

$$\{I_T(\Delta)\} = (\hat{\Gamma}/\pi\Delta^2) \int d\Delta' \langle I_T(\Delta') \rangle \quad (39)$$

and, again, cancellation of the Δ dependence occurs in $\{R\}$. Notice that when collision-broadening effects persist, then (even with small $\hat{\Gamma}$ values) $\{R\}$ is asymptotically pressure independent for this pulse shape.

A qualitative physical distinction between the short- and the long-lived components of the photon-counting rate can be made in stating that the latter involves a scattering process, which has to be handled as a single quantum-mechanical process, while the long-lived component constitutes a decay of a metastable state, where excitation and decay processes can be segregated. Different Fourier components of the exciting pulse contribute to the resonant-scattering and to the direct-scattering processes.² At zero pressure, those Fourier components of the pulse which are close

to resonance excite the long-lived component, while other Fourier components are directly scattered. In the extreme off-resonance situation, pressure broadening results in a dominating contribution to $\{I_M(\Delta)\}$ from $\{I_M(0)\}$, i.e., from near resonance. The collisionally broadened line spans a larger fraction of the Fourier components of the pulse than does the isolated molecule, whereupon the decay of metastable states is enhanced, becoming comparable to the contribution of direct scattering. Thus, the collisional perturbation can be considered as exerting a "memory-erosion" effect on the molecule, increasing the role of excited molecules which have lost their memory concerning the time evolution of the light pulse.

The theory developed in this paper provides an adequate interpretation of the experimental data of WRD.¹ The dramatic effect of low values of $\hat{\Gamma}/\Gamma_1$ as small as 0.025 on the decay features makes it exceedingly difficult to perform such experiments on an "isolated" (collision-free) molecule. The "low" pressure experiments of WRD¹ performed with 0.03 Torr of I_2 result in an asymptotic value of $\{R\} \approx 0.1$ off-resonance. This value, with the help of the data in Fig. 4, implies that $\hat{\Gamma}/\Gamma_1 \approx 0.15$ and, taking $\Gamma_1 = 10^6 \text{ sec}^{-1}$, we estimate $\hat{\Gamma} \approx 10^5 \text{ sec}^{-1}$ for this pressure. This implies an average cross section of $\sim 50 \text{ \AA}^2$ for the relaxation processes embedded in $\hat{\Gamma}$, which is close to a gas-collisional cross section. The increase of $\{R\}$ with pressure is adequately accounted for. In the experimental work, a dramatic enhancement was reported by increasing the pressure from 0.03 to 0.25 Torr. Taking $\hat{\Gamma}/\Gamma_1 = 0.15$ at 0.03 Torr and assuming $\hat{\Gamma}$ to vary linearly with pressure, we expect that $\hat{\Gamma}/\Gamma_1 = 1.2$ at 0.3 Torr, whereupon from Fig. 4 we see that this enhancement should amount to an increase of $\{R\}$ from 0.1 at 0.03 Torr to the value of 0.5 at 0.25 Torr.

It will be useful to comment on the hidden assumptions involved in the present treatment. Concerning the ground state, we have neglected any relaxation processes in this manifold. As we have already pointed out, the extension of the present formalism to handle these processes is straightforward. Regarding the excited electronic manifold, we have adopted a simple model of n levels characterized by identical relaxation rates. We have disregarded any T_2 contributions to the Γ_1 matrix, Eq. (19). This is appropriate for rotational relaxation, which is probably the dominant damping mechanism, but has to be modified in order to incorporate vibrational relaxation. The Γ_2 matrix, Eq. (21), was simplified by application of the rotating wave (or frame) approximation,¹⁴ neglecting off-resonance processes, which is a

reasonable assumption. We have specialized to weak electromagnetic fields, so that field-matter coupling was handled to second order. Collision-induced radiation processes were disregarded. Concerning the general aspects of collisional perturbations, the pressure was considered to be sufficiently low so as to make the binary-collision approximation valid, making possible neglect of correlation effects and separating radiative and collisional contributions to Γ_1 and Γ_2 . All these assumptions are reasonably applicable to the problem at hand. We would also like to point out that we have disregarded the role of intermolecular resonance electronic energy-transfer processes, which may play a role in the system studied by WRD.¹ Our formalism leads to the conclusion that $\hat{\Gamma}$ incorporates only relaxation processes within the excited electronic manifold, and therefore the electronic energy transfer process (which depletes the excited state) does not contribute to $\hat{\Gamma}$.

It should be pointed out that the present treatment apparently applies to a system where the levels of the bath molecules are off-resonance with respect to the excited state of the molecule that interacts with the radiation (foreign-gas broadening). However, it can be shown that resonance transfer, as occurs in the self-broadening of a pure gas, does not essentially alter this result. The whole framework of the theory has to be modified so as to take into account the indistinguishability of the molecules.¹⁵ Thus, instead of speaking about the single-molecule operators $|i\rangle\langle k|$ as defining the projection operator \hat{P}_2 , Eq. (13), we should consider the symmetrized form

$$\sum_{A=1}^N \{|i\rangle\langle k|\}_{A} \exp(i\vec{k} \cdot \vec{R}_A), \quad (40)$$

where the sum is carried over the N identical molecules. The exponential factor arises from the space variation of the pulse (which we have disregarded here), \vec{k} being the wave vector of the photon. This symmetrization results only in a small modification of the expressions for Γ_1 , Eq. (19), and for Γ_2 , Eq. (21), involving the resonance transfer rate. We note in passing that for our specific model, involving only a single ground state $|g\rangle$, Γ_1 and Γ_2 are independent of this energy-transfer process. Even when both Γ_1 and Γ_2 are slightly affected by resonance transfer, this correction is practically the same for both and will not affect $\hat{\Gamma}$.

ACKNOWLEDGMENT

The authors are grateful to Professor A. Szöke and Professor R. Bersohn for helpful discussions.

APPENDIX

Equation (3) can be expressed in terms of the Fourier transform of the retarded Green's function as

$$\rho(t) = (2\pi i)^{-1} \int_{-\infty}^{\infty} dE \exp[-iE(t-t')] G(E) \rho(t') \quad (t > t'). \quad (\text{A1})$$

Here

$$\rho(t) = \rho_0(t) + (2\pi i)^{-1} \int dE e^{-iEt} G(E) W \exp[i(E-L_r)t'] (E-L_r+i\eta)^{-1} \rho(0) \quad (t' \rightarrow -\infty), \quad (\text{A5})$$

where we have used Eq. (5). Utilizing the identity

$$\exp[i(E-L_r)t'] (E-L_r+i\eta)^{-1} = -i \int d\tau \Theta(\tau-t') \exp[i(E-L_r)\tau] \tau^{\frac{t'-\tau}{\eta}} - 2\pi i \delta(E-L_r) = G_r - G_r^\dagger \quad (\text{A6})$$

where Θ is the Heavyside step function, we can write (A5) in a form independent of t' , i.e.,

$$\rho(t) = \frac{1}{2\pi i} \int dE e^{-iEt} [G_r + GW(G_r - G_r^\dagger)] \rho(0). \quad (\text{A7})$$

The time evolution of the m_r system in the presence of the pulse can then be described by a retarded Green's function

$$\bar{G}(E) = \text{Tr}_b[\rho_b G(E)], \quad (\text{A8})$$

where the trace is taken over all the states of the bath. The probability $P_e(t)$ of the system being in any excited (zero-photon) state at the time t is then given by

$$P_e(t) = (2\pi i)^{-1} \int_{-\infty}^{\infty} dE e^{-iEt} \sum_i \langle i | \mathcal{G}(E) \rho_{m_r}(0) | i \rangle, \quad (\text{A9})$$

where

$$\mathcal{G}(E) \equiv \bar{G}(E) W (G_r - G_r^\dagger). \quad (\text{A10})$$

The expectation value in Eq. (A9) involves a vacuum expectation value in the radiation states.

A typical matrix element on the right-hand side of Eq. (A9) can be written in double-bracket notation as^{7,9}

$$\langle i | \mathcal{G}(E) \rho_{m_r}(0) | i \rangle = \int \int dk dk' A_k A_k^* \langle \langle ii | \mathcal{G}(E) | kk' \rangle \rangle. \quad (\text{A11})$$

Equation (9), together with Eqs. (A9) and (A11), provides us with the necessary formal expression

$$G(E) = (E - L + i\eta)^{-1} \quad (\eta \rightarrow +0) \quad (\text{A2})$$

is the retarded Green's function of the total system. Making use of the Dyson equation for G ,¹⁶ and of Eq. (7), we can write

$$G\rho_0(t') = (G_r + GWG_r)\rho_0(t'), \quad (\text{A3})$$

where

$$G_r = (E - L_r + i\eta)^{-1}. \quad (\text{A4})$$

Equation (A1) then attains the form

for the time-resolved radiative decay of a collisionally perturbed molecule. What is now required is the calculation of the matrix elements of $\mathcal{G}(E)$, which will be accomplished by the Fano-Zwanzig projection-operator techniques.⁵⁻⁷

To evaluate the Green's function we shall proceed in two stages. First, we adopt Fano's formalism⁶ to derive an effective Liouvillian in the m_r subspace, which is recast in terms of a level-shift operator. Second, we utilize projection operators in the m_r subspace to derive some formal expressions for the matrix elements of $\mathcal{G}(E)$. Systematic approximations are subsequently introduced to account (to lowest order) for weak electromagnetic interactions and for the effects of binary collisions.

Following (1) and (2), we may resolve the Liouvillian as follows:

$$\begin{aligned} L &= L_0 + W, \\ L_0 &= L' + L_1, \\ L' &= L_m + L_r + L_b, \\ L_1 &= L_{m_r} + L_{m_b}, \end{aligned} \quad (\text{A12})$$

where L_0 , etc., are the Liouville operators corresponding to H_0 , etc. Let us introduce the projection operators⁵

$$\begin{aligned} \hat{C} &= \rho_b \text{Tr}_b, \\ \hat{D} &= 1 - \hat{C}. \end{aligned} \quad (\text{A13})$$

Since V has only matrix elements combining the lower band $\{|k\rangle\}$ with the upper band $\{|i\rangle\}$, the transition from $|kk'\rangle$ to $|ii\rangle$ requires at least two applications of W , with $|ki\rangle$ or $|ik'\rangle$ as inter-

mediate steps. The second-order perturbation contribution to \mathfrak{g} can be written as

$$\mathfrak{g}^{(2)}(E) = \overline{GWG}W(G_r - G_r^\dagger), \quad (\text{A14})$$

where G is the retarded Green's function for the free system, and the bar is defined in (A8). So, to second order in W ,

$$\begin{aligned} \langle\langle ii | \mathfrak{g}(E) | kk' \rangle\rangle &= \langle\langle ii | \hat{C}GWG\hat{C}W(G_r - G_r^\dagger) | kk' \rangle\rangle \\ &= -2\pi i \langle\langle ii | \hat{C}GWG\hat{C}W | kk' \rangle\rangle \delta \\ &\quad \times (E - k + k'). \end{aligned} \quad (\text{A15})$$

Since W does not depend on the bath,

$$\hat{C}GWG\hat{C} = \hat{C}G\hat{C}W\hat{C}G\hat{C} + \hat{C}G\hat{D}W\hat{D}G\hat{C}. \quad (\text{A16})$$

Using Zwanzig's projection-operator methods, we can write^{5,6}

$$\hat{C}G\hat{C} = (E - L_m - L_r - \hat{C}R\hat{C})^{-1}\hat{C}, \quad (\text{A17})$$

where

$$R = L_1 + L_1\hat{D}(E - \hat{D}\hat{L}\hat{D})^{-1}\hat{D}L_1 \quad (\text{A18})$$

is the non-Hermitian tetradic level-shift (self-energy) operator. Also,^{10,19}

$$\hat{C}G\hat{D} = \hat{C}G\hat{C}R\hat{D}(E - L_0 + i\eta)^{-1}\hat{D}. \quad (\text{A19})$$

However,

$$\langle\langle ii | \mathfrak{g}(E) | kk' \rangle\rangle = -2\pi i \delta(E - k + k') \langle\langle ii | \hat{P}_1\bar{G}\hat{P}_1W(\hat{P}_2\bar{G}\hat{P}_2 + \hat{P}'_2\bar{G}\hat{P}'_2)W | kk' \rangle\rangle, \quad (\text{A23})$$

where $\hat{P}_2\bar{G}\hat{P}_2$ and $\hat{P}'_2\bar{G}\hat{P}'_2$ are related, since

$$\langle\langle ik | \bar{G}(E) | jk \rangle\rangle = -\langle\langle ki | \bar{G}(-E) | kj \rangle\rangle^*. \quad (\text{A24})$$

Equation (A23) essentially involves two types of reduced Green's functions

$$G_1 = \hat{P}_1\bar{G}\bar{P}_1, \quad G_2 = \hat{P}_2\bar{G}\bar{P}_1, \quad (\text{A25})$$

with the appropriate level-shift operators

$$R_1 = \hat{P}_1R\hat{P}_1, \quad R_2 = \hat{P}_2R\hat{P}_2, \quad (\text{A26})$$

respectively.

The contributions to G_1 involve states in the excited electronic manifold (i.e., $|ii\rangle$, $|jj\rangle$, etc.). In general, this manifold includes also mixed terms such as $|ij\rangle$. However, in many cases, symmetry can considerably simplify matters, particularly dropping out all $|ij\rangle$ terms if $|i\rangle$ and $|j\rangle$ involve different rotational states.¹⁸ This

$$\hat{C}R\hat{C} = \hat{C}L_1\hat{C} + \hat{C}R\hat{D}(E - L_0 + i\eta)^{-1}\hat{D}L_1\hat{C}. \quad (\text{A20})$$

The magnitude of $\hat{C}G\hat{C}$ is bounded by the inverse of the anti-Hermitian part of $\hat{C}R\hat{C}$. Let the lowest upper bound be denoted Γ_0^{-1} . Likewise, $\hat{C}R\hat{C}$ can be written as $A_1^2G_1$, where G_1 is also a retarded Green's function,¹⁷ with a lowest upper bound Γ_1^{-1} , and A_1 is associated with the interaction $\hat{C}L_1\hat{D}$. It follows from (A19) and (A20) that, to order of magnitude,

$$\frac{O(\hat{C}G\hat{D})}{O(\hat{C}G\hat{C})} \approx \frac{A_1}{\Gamma_1} \approx \left(\frac{\Gamma_0}{\Gamma_1}\right)^{1/2}. \quad (\text{A21})$$

In dilute gases, where Γ_0 is an inverse relaxation time (of the order of MHz/Torr), and Γ_1 is an inverse collision time (typically $> 10 \text{ cm}^{-1}$), $\hat{C}G\hat{D}$ is negligible compared to $\hat{C}G\hat{C}$, and the bath average of the product of G 's can be replaced by the product of averages,

$$\hat{C}GWG\hat{C} \approx \hat{C}G\hat{C}W\hat{C}G\hat{C}. \quad (\text{A22})$$

By the exclusion of the external-field photon modes from L_m , $\hat{C}R\hat{C}$ is reduced to the four subspaces spanned by the respective projection operators, defined in Eq. (13).

We thus arrive at

is the relevant case for our problem in view of the predominant role of rotational relaxation within the excited electronic band. The reason is that in the calculation of populations, we implicitly introduce an averaging over the rotational-degeneracy M numbers, thus retaining only the monopole irreducible representation of the rotation symmetry group in the manifold $\{|ij\rangle\}$, which can have contributions only from $J_i = J_j$ where J_i and J_j correspond to the initial and final rotational quantum numbers. Under these conditions, G_1 involves only matrix elements in the manifold $\{|ii\rangle\}$.

The expression for the photon-counting rate, as can be seen from Eqs. (9) and (A9), is a Fourier transform of the E -dependent tetradic Green's function. Following (A9), (A11) and (A23), and introducing the assumptions made above, we can write

$$\begin{aligned} P_e(t) = & - \sum_i \int \int \int dE dk dk' e^{-iEt} A_k A_k^* \delta(E - k + k') \langle\langle ii | \bar{G}(E) | jj \rangle\rangle \\ & \times [|V_{jk'}|^2 \langle\langle jk' | \bar{G}(E) | jk' \rangle\rangle + |V_{jk}|^2 \langle\langle kj | \bar{G}(E) | kj \rangle\rangle]. \end{aligned} \quad (\text{A27})$$

Making use of (A24) and the integrations over k and k' , it follows that the two contributions (with P_2 and P_2' , respectively) to $P_e(t)$ are complex-conjugate, so that

$$P_e(t) = 2 \operatorname{Re} I(t), \quad (\text{A28})$$

where

$$I(t) = - \sum_i |V_{j\bar{k}}|^2 \int dE \int d\tau \langle \langle ii | G_1 | jj \rangle \rangle \varphi(\tau) \\ \times \exp[i(E - \bar{k})\tau - iEt] \\ \times \int dk' A_{k'}^* \langle \langle jk' | G_2 | jk' \rangle \rangle \exp(ik'\tau). \quad (\text{A29})$$

In the derivation of (A29) we neglected the weak k dependence of the electromagnetic coupling V_{kj} over the pulse modes, and carried out the integration over k . Consider now the integration over k' . Assuming (as is appropriate for this problem)

that $L_m |jk\rangle\rangle$ and $R_2 |jk\rangle\rangle$ vary insignificantly with k' around \bar{k} , one can write

$$\langle \langle jk' | G_2(E) | jk' \rangle \rangle \approx \langle \langle j\bar{k} | G_2(E - k' + \bar{k}) | j\bar{k} \rangle \rangle. \quad (\text{A30})$$

Introducing the inverse Fourier transform $G_2(\tau)$, we get

$$\int dk' A_{k'}^* \langle \langle jk' | G_2(E) | jk' \rangle \rangle \exp(ik'\tau) \\ \approx i \int d\tau' \varphi^*(\tau') \langle \langle j\bar{k} | G_2(\tau' - \tau) | j\bar{k} \rangle \rangle \\ \times \Theta(\tau' - \tau) \exp[-iE(\tau - \tau')]. \quad (\text{A31})$$

Using (A31), together with (A28) and (A29), we get Eq. (14) after performing the integration over E .

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