

Non-Markovian dephasing of two-level resonance fluorescence in a strong radiation field

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A non-Markovian microscopic theory for the spontaneous emission spectrum of a two-level atom driven by a strong laser field and undergoing dephasing via the interaction with a thermal bath is developed. The present theory is valid for an arbitrary correlation time scale of the bath relative to the linewidth and interpolates from the Markovian to the static limits. Model calculations using the stochastic line-shape function of Kubo show how the characteristic triplet spectrum is modified by the interaction with the bath. The present results generalize our previous studies of resonance Raman scattering in a three-level system in a strong radiation field.

I. INTRODUCTION

The fluorescence spectrum of a two-level atom excited by a strong laser field has been the subject of numerous theoretical and experimental studies in recent years. A semiclassical theory which treats the laser field classically and the material system quantum mechanically was first developed,¹⁻³ and subsequently a full quantum-mechanical treatment was made.^{4,5} The theoretical results agree quantitatively with experiment.^{6,7} By introducing the notion of the physical spectrum,⁸ the detailed time-dependent behavior of the fluorescence spectrum was calculated.^{9,10} In addition, the effects of laser bandwidth and collisional broadening on the spectrum were studied.¹¹⁻¹⁴ The effects of dephasing processes on the fluorescence spectrum are commonly incorporated by introducing phenomenological dephasing (T_2) relaxation coefficients into the Bloch equations. This procedure is valid only in the Markovian limit whereby the correlation time of the bath (e.g., duration of a collision) is short compared with the inverse linewidth. A microscopic treatment of dephasing effects requires the introduction of a specific model for the bath "perturbers" and their interaction with the absorber.¹⁵⁻¹⁸ A general framework for the microscopic treatment of dephasing in multiphoton processes was developed recently.¹⁹ The formalism uses projection-operator techniques in Liouville space to perform selective averagings over the bath variables. We have applied it to two-photon processes (resonance fluorescence, Raman spectroscopy, and two-photon absorption),²⁰ nonlinear susceptibilities,²¹ and resonance fluorescence in a three-level system in a strong field.^{17,19} This general formalism is not restricted to the Markovian limit and we were able to discuss non-Markovian effects on all of these problems.

In this paper we develop a non-Markovian theory for dephasing effects on the resonance fluorescence of a two-level system in a strong field (the "Mollow spectrum"). We start with the total Hamiltonian of the system, the bath, and the radiation matter interaction. Utilizing ap-

propriate projection operators in Liouville space, the two-time correlation function of the atomic dipole operator is calculated. The fluorescence spectrum is then calculated as the Fourier transform of this two-time correlation function.^{3,5}

In Sec. II we present the model Hamiltonian which allows for a general dephasing process. In Sec. III we give a formal expression for the fluorescence spectrum using the tetradic scattering formalism. We then derive an approximate formula for the fluorescence utilizing the generalized single-photon line-shape function $I(\Delta)$. Finally, in Sec. IV we present and analyze some numerical results for typical Markovian as well as non-Markovian line shapes.

II. MODEL HAMILTONIAN

We consider a two-level system $|a\rangle$ and $|b\rangle$ interacting with a classical strong monochromatic radiation field with frequency ω_L , and with a thermal bath (Fig. 1). The bath is assumed to have only diagonal interactions with the system, i.e., it does not induce any relaxation of population (T_1 processes). The total Hamiltonian for the system plus bath plus the radiation field within the rotating wave approximation²² (RWA) is given by

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

where

$$H_0 = |a\rangle[\Delta_L + H_a(Q)]\langle a| + |b\rangle H_b(Q)\langle b| \quad (2)$$

and

$$V = \frac{1}{2}\mu(|a\rangle\langle b| + |b\rangle\langle a|). \quad (3)$$

The Hamiltonians H_a and H_b depend on the bath degrees of freedom (Q_B) and μ is the Rabi frequency representing the coupling of the system to the radiation field. Δ_L is the detuning of the radiation field from the two-level frequency ω_{ba} , i.e.,

$$\Delta_L \equiv \omega_L - \omega_{ba}. \quad (4)$$

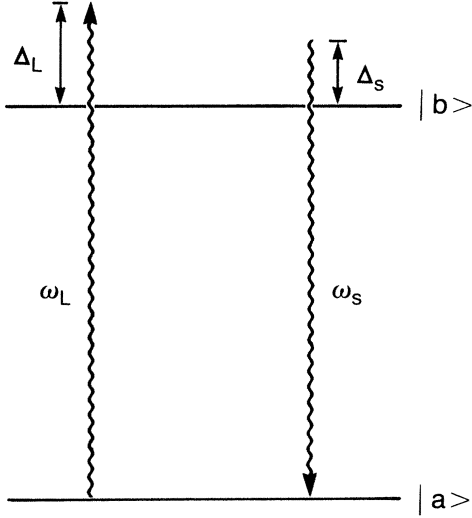


FIG. 1. Frequencies and detuning parameters for resonance fluorescence in a two-level system.

The time evolution of the entire (system plus bath) density matrix ρ is given by the Liouville equation

$$\frac{d\rho}{dt} = -iL\rho, \quad (5)$$

where L is the Liouville operator

$$L \equiv [H, \cdot] + \tilde{L}. \quad (6)$$

\tilde{L} is a phenomenological T_1 relaxation matrix given by

$$\tilde{L}_{bb,bb} = -\tilde{L}_{aa,bb} = -i\gamma, \quad (7a)$$

$$\tilde{L}_{aa,aa} = -\tilde{L}_{bb,aa} = 0, \quad (7b)$$

$$\tilde{L}_{ab,ab} = \tilde{L}_{ba,ba} = -i\frac{1}{2}\gamma. \quad (7c)$$

\tilde{L} can arise from spontaneous emission, coupling to another bath, etc. We assume that initially ($t \rightarrow \infty$) the system is in the ground state $|a\rangle$ so that

$$\rho(-\infty) = \rho_B^0 \rho_S^0, \quad (8)$$

where

$$\rho_S^0 = |a\rangle\langle a| \quad (9)$$

and the bath is in canonical equilibrium

$$\rho_B^0 = \exp(-H_B/KT) / [\text{Tr}_B \exp(-H_B/KT)], \quad (10)$$

Tr_B being the trace over the bath degrees of freedom. In Sec. III we shall use the tetradic (Liouville space) scattering formalism to solve for the steady-state fluorescence rate for the system described by the present Hamiltonian.

III. TETRADIC FORMULATION OF THE FLUORESCENCE LINE SHAPE

Our calculation of the fluorescence spectrum will start from the following expression which relates it to the Fourier transform of the two-time correlation function of

the dipole operator^{3,5}

$$\hat{I}(\omega_S) = \text{Re} \int_0^\infty d\tau \exp(-i\omega_S\tau) \langle \sigma_{ba}(\tau) \sigma_{ab}(0) \rangle. \quad (11)$$

Here $\sigma_{ab} \equiv |a\rangle\langle b|$ and $\sigma_{ba} \equiv |b\rangle\langle a|$ represent the atomic dipole operator and

$$\langle \sigma_{ba}(\tau) \sigma_{ab}(0) \rangle \equiv \text{Tr}[\sigma_{ba}(\tau) \sigma_{ab}(0) \hat{\rho}]. \quad (12)$$

$\hat{\rho}$ is the steady-state density matrix of the system plus bath plus the ω_L radiation field, and Tr represents the quantum-mechanical expectation value of the system and the statistical average over the bath. It will be more convenient to work in the interaction representation. To that end we define

$$d_{ba}(t) \equiv \sigma_{ba}(t) \exp(-i\omega_L t) \quad (13a)$$

and

$$d_{ab}(t) \equiv \sigma_{ab}(t) \exp(i\omega_L t). \quad (13b)$$

The fluorescence spectrum can then be rewritten in the form

$$\hat{I}(\Delta_L, \Delta_S) = \text{Re} \int_0^\infty d\tau \exp(i\Delta\tau) \langle d_{ba}(\tau) d_{ab}(0) \rangle, \quad (14)$$

where

$$\Delta_S \equiv \omega_S - \omega_{ba}, \quad (14a)$$

$$\Delta \equiv \Delta_L - \Delta_S = \omega_L - \omega_S, \quad (14b)$$

and

$$\langle d_{ba}(\tau) d_{ab}(0) \rangle \equiv \text{Tr}[d_{ba} \exp(-iL\tau) d_{ab} \hat{\rho}]. \quad (15)$$

Introducing the tetradic (Liouville space) notation,¹⁹ Eq. (14) may be written in the form

$$\begin{aligned} \hat{I}(\Delta_L, \Delta_S) = & -\text{Im} \text{Tr}[\langle\langle ab | (\Delta - L)^{-1} | aa \rangle\rangle \langle\langle ba | \hat{\rho} \rangle\rangle \\ & + \langle\langle ab | (\Delta - L)^{-1} | ab \rangle\rangle \langle\langle bb | \hat{\rho} \rangle\rangle]. \end{aligned} \quad (16)$$

Here $\hat{\rho}$ is the stationary density matrix given by¹⁹

$$\hat{\rho} = [1 + G(0)\mathcal{V}] |aa\rangle, \quad (17)$$

where

$$\mathcal{V} \equiv [V, \cdot \cdot \cdot],$$

where the initial condition Eq. (9) is used and $G(\Delta)$ is the resolvent operator in Liouville space given by

$$G(\Delta) \equiv (\Delta - L)^{-1}. \quad (18)$$

Equation (17) is the tetradic Liouville space analog of the Lippman-Schwinger equation of scattering theory and it simply implies that ρ may be obtained by starting at $t \rightarrow -\infty$ with the equilibrium density matrix [Eq. (8)] and switching on adiabatically the radiative interaction \mathcal{V} . Using the tetradic scattering formalism,¹⁹ we trivially have

$$\mathcal{V} |aa\rangle = \frac{1}{2} \mu (|ab\rangle - |ba\rangle), \quad (19)$$

and

$$\langle\langle ij | kl \rangle\rangle = \delta_{ik} \delta_{jl}, \quad (20)$$

so that

$$\langle\langle ij | \rho_S \rangle\rangle = \frac{1}{2} \mu [\langle\langle ij | G(0) | ba \rangle\rangle - \langle\langle ij | G(0) | ab \rangle\rangle]. \quad (21)$$

Making use of Eqs. (17) and (19), we can rewrite Eq. (16) in the form

$$\begin{aligned} \hat{I}(\Delta_L, \Delta_S) = & \frac{1}{2} \mu \text{Im Tr} [\langle\langle ab | G(\Delta) | aa \rangle\rangle \langle\langle ba | G(0) | ab \rangle\rangle - \langle\langle ab | G(\Delta) | aa \rangle\rangle \langle\langle ba | G(0) | ba \rangle\rangle \\ & + \langle\langle ab | G(\Delta) | ab \rangle\rangle \langle\langle bb | G(0) | ab \rangle\rangle - \langle\langle ab | G(\Delta) | ab \rangle\rangle \langle\langle bb | G(0) | ba \rangle\rangle]. \end{aligned} \quad (22)$$

At this stage we introduce the tetradic projection operator^{17,19}

$$P \equiv |ab\rangle\rangle \langle\langle ab| + |ba\rangle\rangle \langle\langle ba| \quad (23)$$

and its complementary projection operator

$$Q \equiv 1 - P. \quad (24)$$

Using these definitions we may rewrite Eq. (22) in the form

$$\begin{aligned} \hat{I}(\Delta_L, \Delta_S) = & \frac{1}{2} \mu \text{Im Tr} [\langle\langle ab | PG(\Delta)Q | aa \rangle\rangle \langle\langle ba | PG(0)P | ab \rangle\rangle - \langle\langle ab | PG(\Delta)Q | aa \rangle\rangle \langle\langle ba | PG(0)P | ba \rangle\rangle \\ & + \langle\langle ab | PG(\Delta)P | ab \rangle\rangle \langle\langle bb | QG(0)P | ab \rangle\rangle - \langle\langle ab | PG(\Delta)P | ab \rangle\rangle \langle\langle bb | QG(0)P | ba \rangle\rangle], \end{aligned} \quad (25)$$

where¹⁹

$$PG(\Delta)P = \frac{1}{\Delta - L_0 - \tilde{L} - PR(\Delta)P}, \quad (26a)$$

$$QG(\Delta)P = Q \frac{1}{\Delta - QLQ} Q \mathcal{V} PG(\Delta)P, \quad (26b)$$

$$PG(\Delta)Q = PG(\Delta)P \mathcal{V} Q \frac{1}{\Delta - QLQ} Q. \quad (26c)$$

Here R is the "self-energy" in the Liouville space, given by

$$R(\Delta) \equiv P \mathcal{V} Q \frac{1}{\Delta - QLQ} Q \mathcal{V} P. \quad (27)$$

Equation (27) may be expanded in powers of μ :^{17,19}

$$R = \mu^2 \chi^{(2)} + \mu^4 \chi^{(4)} + \dots \quad (28)$$

The expression (28) is exact and, in general, $\chi^{(n)}$ involves n -time correlation functions of the dipole operator and its calculation is quite tedious. It has been shown previously^{17,19} that for the medium field-strength case, defined by the condition

$$\mu_L \ll \tau_c^{-1}, \quad (29)$$

where τ_c is the bath correlation time, the lowest-order terms $\chi^{(2)}$ in the expansion of Eq. (28) are dominant. In this case Eq. (28) becomes

$$R = P \mathcal{V} Q G^0(\Delta) Q \mathcal{V} P, \quad (30)$$

where

$$G^0(\Delta) \equiv \frac{1}{\Delta - L_0 - \tilde{L}}. \quad (31)$$

Equation (25) provides a formal expression for the fluorescence line-shape function in terms of appropriate

matrix elements of the tetradic Green's function G . We shall now provide approximate expressions for these matrix elements. To that end we shall introduce the ordinary (single-photon) line-shape function for the ab transition, i.e.,

$$I(\omega) = G_{ab,ab}^0(\omega) = i \int_0^\infty d\tau \exp[i\omega\tau - \frac{1}{2}\gamma\tau - g(\tau)]. \quad (32)$$

Note that by using the Liouville conjugation symmetry¹⁹ we have

$$I(\omega) = -I^*(-\omega). \quad (33)$$

The function $g(\tau)$ is the line-broadening function which arises from the interaction with the bath. All the relevant information regarding the bath dynamics and the system-bath interaction is contained in $g(\tau)$. The methods for the evaluation of $g(\tau)$ are well established for collisional broadening, phonon broadening in solids, density fluctuations in liquids, etc.¹⁹ In Appendices A–C we evaluate all the necessary Green's-function elements in terms of $I(\omega)$. Our final result for the fluorescence line shape is then obtained by substituting these matrix elements into Eq. (25), resulting in

$$\hat{I}(\Delta_L, \Delta_S) = \frac{1}{4} \mu^2 \text{Im} \frac{A(B+C)}{DE}, \quad (34)$$

where

$$A \equiv I(-\Delta_S) I(2\Delta_L - \Delta_S), \quad (34a)$$

$$B \equiv [I(\Delta_L) + I(-\Delta_L)] [I(2\Delta_L - \Delta_S)]^{-1} \times (\Delta_L - \Delta_S + i\gamma) - \frac{1}{2} \mu^2, \quad (34b)$$

$$C \equiv i\gamma I(2\Delta_L - \Delta_S)^{-1} I(\Delta_L) [1 + i\gamma(\Delta_L - \Delta_S)]^{-1}, \quad (34c)$$

$$D \equiv (\Delta_L - \Delta_S + i\gamma) - \frac{1}{2} \mu^2 [I(-\Delta_S) + I(2\Delta_L - \Delta_S)], \quad (34d)$$

$$E \equiv i\gamma - \frac{1}{2}\mu^2[I(-\Delta_L) + I(\Delta_L)] . \quad (34e)$$

Equation (34) is our general expression for the fluorescence spectrum. In Sec. IV we shall present some model calculations and analyze the resulting spectra.

IV. MODEL CALCULATIONS

In order to explore Eq. (34) further we need to construct a specific model for the bath which will result in explicit expressions for $g(\tau)$ and for the single-photon line-shape function $I(\omega)$ [Eq. (32)]. For our present discussion, however, it will be sufficient to use a simple stochastic model developed by Kubo²³ for single-photon line shapes. This model has been applied to a variety of multiphoton line-shape problems¹⁹ following its first application to strong field line shapes.²⁴

The model assumes that the two-level frequency undergoes a stationary Gaussian-Markovian process. The resulting line shape has the following two-parameter expression for $g(\tau)$:

$$g(\tau) = (\delta^2/\Lambda^2)[\exp(-\Lambda\tau) - 1 + \Lambda\tau] . \quad (35)$$

Here δ is a measure of the interaction strength responsible for the line broadening, whereas $\tau_c = \Lambda^{-1}$ is the correlation time of the bath (e.g., the duration of a collision). The nature of the ordinary line-shape function [Eq. (32)] is governed by the dimensionless parameter $\kappa \equiv \Lambda/\delta$. When $\kappa \gg 1$ we get the Markovian limit whereby

$$\exp[-g(\tau)] \cong \exp(-\hat{\Gamma}\tau) , \quad (36)$$

where

$$\hat{\Gamma} = \delta^2/\Lambda , \quad (37)$$

and the line-shape function $I(\Delta)$ assumes a Lorentzian form

$$I(\Delta) = \frac{1}{\Delta + i\Gamma} . \quad (38)$$

Here Γ is the total dephasing rate of the optical transition defined by

$$\Gamma \equiv \frac{1}{2}\gamma + \hat{\Gamma} . \quad (39)$$

In the other extreme $\kappa \ll 1$ we have

$$\exp[-g(\tau)] \cong \exp(-\delta^2\tau^2/2) \quad (40)$$

and $I(\Delta)$ assumes a Voigt profile (a convolution of a Lorentzian and a Gaussian). A convenient continued fraction representation of $I(\Delta)$ was also developed by Kubo:²³

$$I(\Delta) = \frac{1}{\Delta + \frac{1}{2}i\gamma - \frac{\delta^2}{\Delta + \frac{1}{2}i\gamma + i\Lambda - \frac{2\delta^2}{\Delta + \frac{1}{2}i\gamma + i2\Lambda + \dots}}} . \quad (41)$$

We are now in a position to discuss the fluorescence line shape, Eq. (34). We first note that in the weak field ($\mu \rightarrow 0$) limit, the fluorescence spectrum of the two-level

system is similar to the three-level system, i.e.,

$$\hat{I}(\Delta_L, \Delta_S) = \frac{1}{4}\mu_L^2 \left[\frac{2}{\gamma} I''(\Delta_L) I'''(-\Delta_S) + \text{Im} \left[\frac{1}{\Delta_L - \Delta_S} I(-\Delta_S) I(\Delta_L) \right] \right] , \quad (42)$$

where $I = I' - iI''$. In the Markovian limit Eq. (42) reduces further to

$$\hat{I}(\Delta_L, \Delta_S) = \frac{\mu^2/4}{\Delta_L^2 + \Gamma^2} \left[\pi\delta(\Delta_S - \Delta_L) + \frac{2\hat{\Gamma}}{\gamma} \frac{\Gamma}{\Delta_S^2 + \Gamma^2} \right] . \quad (43)$$

These are the well-known Raman and the dephasing-induced (redistribution) components.¹⁹ In the strong field Markovian limit, substituting Eq. (38) into Eq. (34) we get

$$\hat{I}(\Delta_L, \Delta_S) = \frac{-1}{(\Delta_L^2 + \Gamma^2)\gamma + \mu^2\Gamma} \frac{A+B}{C} , \quad (44)$$

where

$$A \equiv 2\Gamma[(-\Delta_S + i\gamma)(\Delta_L - \Delta_S + i\gamma) - \frac{1}{2}\mu^2] , \quad (44a)$$

$$B \equiv (2\Delta_L - \Delta_S + i\Gamma)(\Delta_L - \Delta_S + i\Gamma) \times (-\Delta_L + i\Gamma)\gamma/(\Delta_L - \Delta_S) , \quad (44b)$$

and

$$C \equiv (\Delta_L + i\Gamma)(\Delta_L - 2\Delta_S + i\Gamma)(\Delta_L - \Delta_S + i\gamma) - \mu^2(\Delta_L - \Delta_S + i\Gamma) . \quad (44c)$$

Equation (44) contains a term with $(\Delta_L - \Delta_S)^{-1}$ which diverges when $\Delta_L - \Delta_S = 0$; we shall rewrite Eq. (44) in the form

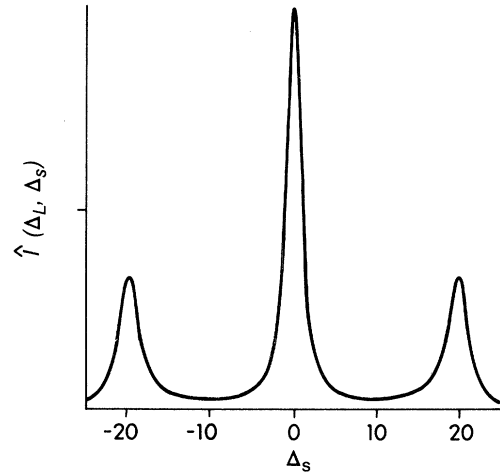


FIG. 2. Fluorescence spectrum (Mollow triplet) in the absence of dephasing [Eq. (34)]. $\Delta_L = 0$, $\mu = 20$, $\gamma = 2$. The elastic scattering δ function at $\Delta_S = \Delta_L$ [Eq. (45)] is not shown in this figure.

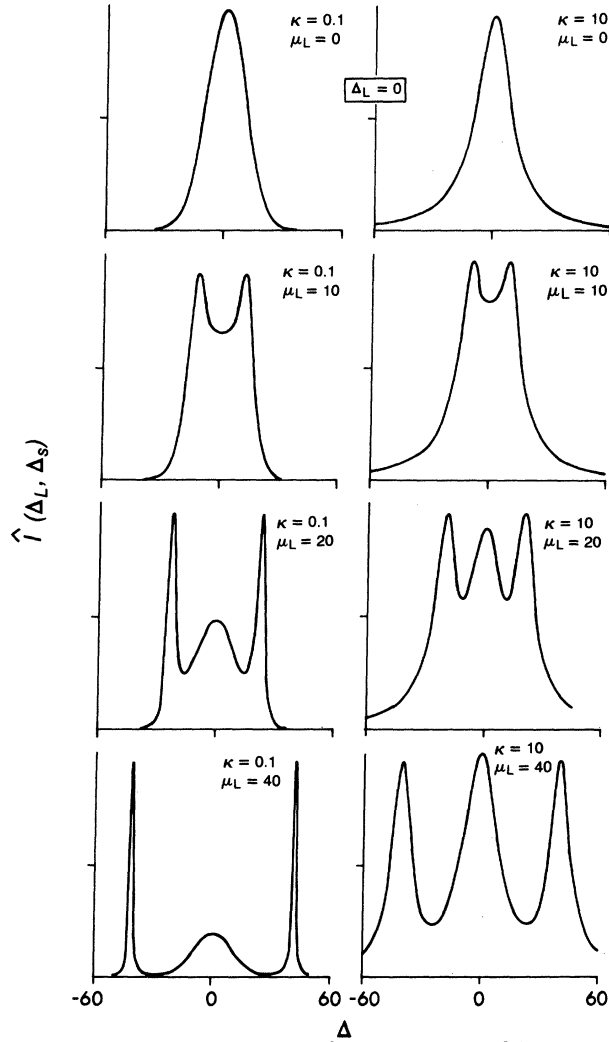


FIG. 3. Saturation behavior of the resonance fluorescence spectrum $\hat{I}(\Delta_L, \Delta_S)$ Eq. (34) together with Eq. (41). $\Delta_L=0$, $\gamma=1$. The $\kappa=10$ lines (impact limit) were calculated using $\delta=100$ and $\Lambda=1000$, whereas the $\kappa=0.1$ lines (Gaussian limit) were calculated using $\delta=10$ and $\Lambda=1$, so that $I(\Delta_L)$ has approximately the same width in both cases. The elastic scattering δ function at $\Delta_S=\Delta_L$ [Eq. (45)] is not shown in this figure.

$$\hat{I}(\Delta_L, \Delta_S) = -\pi\delta(\Delta_L - \Delta_S)F + J(\Delta_L, \Delta_S), \quad (45)$$

where

$$F \equiv [(\Delta_L - \Delta_S)\hat{I}(\Delta_L, \Delta_S)]_{\Delta_L=\Delta_S} \quad (46)$$

and

$$J(\Delta_L, \Delta_S) \equiv \hat{I}[(\Delta_L - \Delta_S)] - \frac{F}{\Delta_L - \Delta_S}. \quad (47)$$

In the absence of proper dephasing $\hat{\Gamma}=0$ and $\Gamma=\gamma/2$. Equation (44) then gives the conventional Mollow spectrum³ as shown in Fig. 2. The triplet results from a dynamical Stark splitting of our two-level system. We have calculated the fluorescence spectrum [Eq. (45) together with Eq. (41)] both in the Markovian and the non-Markovian limits, and for medium field strength and arbitrary

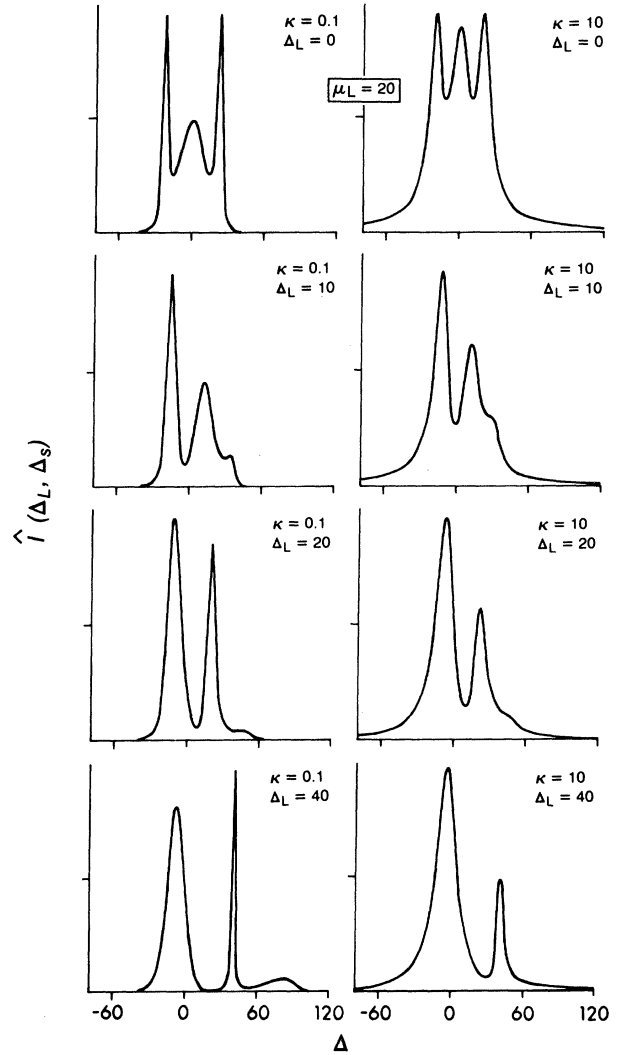


FIG. 4. Variation of the resonance fluorescence spectrum $\hat{I}(\Delta_L, \Delta_S)$ with the detuning Δ_L for a fixed Rabi frequency $\mu_L=20$. Other parameters same as in Fig. 3.

detuning. The results are shown in Figs. 3–5. Figure 3 shows the variation of the fluorescence spectrum with the pump intensity for resonance pumping ($\Delta_L=0$). The right ($\kappa=10$) column is in the Markovian limit and the left ($\kappa=0.1$) column is in the static limit. The strong field limit is obtained whenever the generalized Rabi frequency

$$\theta = (\Delta_L^2 + 4\mu_L^2)^{1/2} \quad (48)$$

is the largest parameter in the problem (except for the inverse correlation time of the bath). The spectrum separates in this case into three (non-Lorentzian) peaks centered at

$$\Delta_S = \Delta_L (\Delta_L \pm \theta). \quad (49)$$

The difference between the Markovian and non-Markovian lines is in the shape of the peaks. We note that when μ_L is large the two sidebands are much narrower in the non-Markovian ($\kappa=0.1$) case. This may be

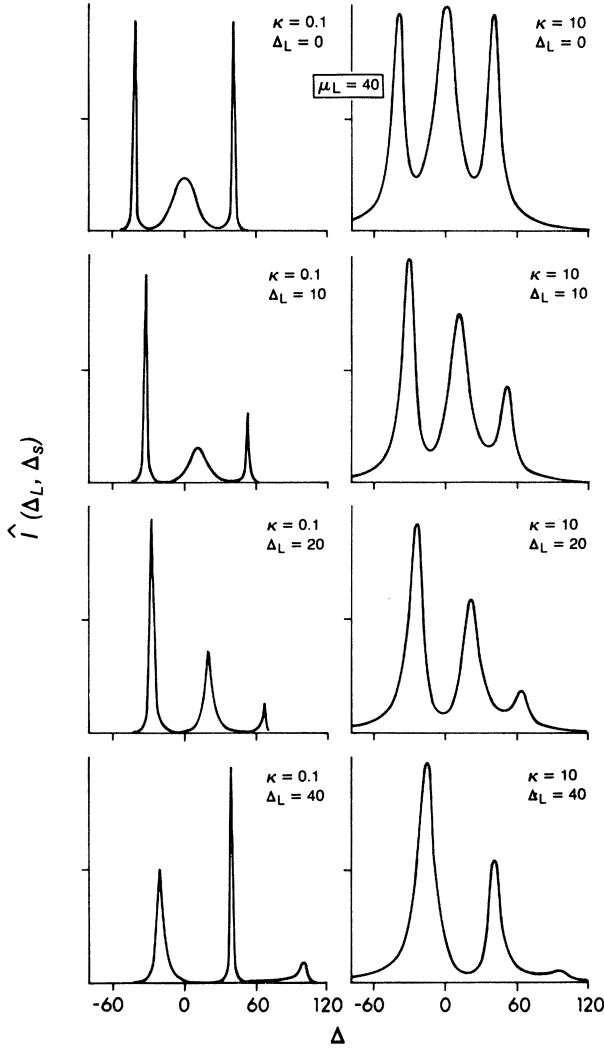


FIG. 5. Variation of the resonance fluorescence spectrum $\hat{\Gamma}(\Delta_L, \Delta_S)$ with the detuning Δ_L for a fixed Rabi frequency $\mu_L = 40$. Other parameters same as in Fig. 3.

interpreted by invoking the frequency dependence of $\hat{\Gamma}$ [$\hat{\Gamma}(\Delta) \rightarrow 0$ at large Δ] which exists at large detunings in this case but is absent, by assumption, in the Markovian ($\kappa = 10$) case.¹⁹ When the field intensity is increased, from Eq. (43) we know that there always exists a $\delta(\Delta_S - \Delta_L)$ elastic scattering component. In the three-level system on the other hand¹⁹ the δ function disappears as the field strength increases. This difference can be interpreted by noting that in the two-level system, the population excited from the state $|a\rangle$ will return to $|a\rangle$ via spontaneous emission, so that the modulation of $|a\rangle$ due to the laser field does not affect the elastic scattering. In contrast, the population excited from the initial state $|a\rangle$ in the three-level system will go to some other final state $|c\rangle$, so that the modulation of the state $|a\rangle$ by the laser will be reflected in the emission spectrum. Figures 4 and 5 show the variation of the fluorescence spectra with the detuning of the pump field, for finite intensities $\mu_L = 20$ and $\mu_L = 40$, respectively. Our results indicate that fluores-

cence line shapes in strong fields contain very useful dynamical information [i.e., the $g(\tau)$ bath correlation function]. Precise line shape measurements, especially at large detunings Δ_L and Δ_S are needed in order to extract this information.

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APPENDIX A: EVALUATION OF $PG(\Delta)P$

According to Eq. (26a) PGP is given by

$$PG(\Delta)P = \frac{1}{\Delta - L_0 - \tilde{L} - PR(\Delta)P} \quad (\text{A1})$$

and it is clear in ab, ba space we have

$$PR(\Delta)P = \begin{bmatrix} R_{ab,ab} & R_{ab,ba} \\ R_{ba,ab} & R_{ba,ba} \end{bmatrix}, \quad (\text{A2})$$

$$\Delta - L_0 - \tilde{L} = \bar{G}^0(\Delta) = \begin{bmatrix} \bar{G}_{ab,ab}^0 & 0 \\ 0 & \bar{G}_{ba,ba}^0 \end{bmatrix}, \quad (\text{A3})$$

where $\bar{G}^0 \equiv (G^0)^{-1}$ and $\bar{G}_{ab,ba}^0 = \bar{G}_{ba,ab}^0 = 0$ are used. Since we only keep the lowest term in Eq. (28), from Eq. (30) we have

$$R_{ab,ab}(\Delta) = \frac{1}{4}\mu^2(G_{aa,aa}^0 + G_{bb,bb}^0 - G_{aa,bb}^0 - G_{bb,aa}^0). \quad (\text{A4})$$

In bb, aa space \bar{G}^0 becomes

$$\bar{G}^0(\Delta) = \Delta - L_0^S = \begin{bmatrix} \Delta + i\gamma & 0 \\ -i\gamma & \Delta \end{bmatrix} \quad (\text{A5})$$

and its inversion gives

$$G^0(\Delta) = \frac{1}{\Delta(\Delta + i\gamma)} \begin{bmatrix} \Delta & 0 \\ i\gamma & \Delta + i\gamma \end{bmatrix}. \quad (\text{A6})$$

Using (A4) and (A6) we have

$$R_{ab,ab}(\Delta) = \frac{\mu^2}{2(\Delta + i\gamma)} \quad (\text{A7})$$

and the same procedure gives

$$R_{ba,ba}(\Delta) = R_{ab,ab}(\Delta). \quad (\text{A8})$$

For $\Delta - L_0^S - R$ we have

$$\Delta - L_0 - \tilde{L} - R(\Delta) = \begin{bmatrix} \bar{G}_{ab,ab}^0 - R_{ab,ab} & R_{ab,ba} \\ R_{ba,ab} & \bar{G}_{ba,ba}^0 - R_{ba,ba} \end{bmatrix}. \quad (\text{A9})$$

When inverting this matrix we get

$$\frac{1}{\Delta - L_0^S} = \frac{1}{\bar{G}_{ab,ab}^0 \bar{G}_{ba,ba}^0 - R_{ab,ab}(\bar{G}_{ab,ab}^0 + \bar{G}_{ba,ba}^0)} \begin{bmatrix} \bar{G}_{ba,ba}^0 - R_{ba,ba} & -R_{ab,ab} \\ -R_{ab,ab} & \bar{G}_{ab,ab}^0 - R_{ab,ab} \end{bmatrix}, \quad (\text{A10})$$

where Eq. (A8) is used. Substituting (A7) and (A8) into (A10) and expressing (A10) in terms of the line-shape function given by Eq. (32) we finally have

$$\langle\langle ab | PG(\Delta)P | ab \rangle\rangle = \frac{I(\Delta - \Delta_L)}{(\Delta + i\gamma) - \frac{1}{2}\mu^2[I(\Delta - \Delta_L) + I(\Delta + \Delta_L)]} [(\Delta + i\gamma) - \frac{1}{2}\mu^2 I(\Delta + \Delta_L)], \quad (\text{A11})$$

$$\langle\langle ba | pG(0)P | ab \rangle\rangle = \frac{I(-\Delta_L)I(\Delta_L)}{i\gamma - \frac{1}{2}\mu^2[L(-\Delta_L) + L(\Delta_L)]} (-\frac{1}{2}\mu^2), \quad (\text{A12})$$

$$\langle\langle ba | PG(0)P | ba \rangle\rangle = \frac{I(\Delta_L)}{i\gamma - \frac{1}{2}\mu^2[I(-\Delta_L) + I(\Delta_L)]} [i\gamma - \frac{1}{2}\mu^2 I(-\Delta_L)]. \quad (\text{A13})$$

APPENDIX B: EVALUATION OF $PG(\Delta)Q$

To evaluate $PG(\Delta)Q$ given by Eq. (26c),

$$PG(\Delta)Q = PG(\Delta)P\mathcal{Y}Q \frac{1}{\Delta - QLQ} Q, \quad (\text{B1})$$

we only need to calculate $\mathcal{Y}(\Delta - QLQ)^{-1}$ since $PG(\Delta)P$ has been calculated in Appendix A. Keeping the lowest order in $(\Delta - QLQ)^{-1}$ we have

$$Q \frac{1}{\Delta - QLQ} Q = QG^0 Q. \quad (\text{B2})$$

Then $\langle\langle ab | PG(\Delta)Q | aa \rangle\rangle$ can be written in a more explicit form

$$\langle\langle ab | PG(\Delta)Q | aa \rangle\rangle = \frac{-\frac{1}{2}\mu(1 + i\gamma/\Delta)I(\Delta - \Delta_L)}{(\Delta + i\gamma) - \frac{1}{2}\mu^2[I(\Delta - \Delta_L) + I(\Delta + \Delta_L)]}, \quad (\text{B5})$$

where $G_{aa,aa}^0 = \Delta^{-1}$ is used.

APPENDIX C: EVALUATION OF $QG(\Delta)P$

$QG(\Delta)P$ is given by Eq. (24b)

$$QG(\Delta)P = Q \frac{1}{\Delta - QLQ} Q\mathcal{Y}PG(\Delta)P. \quad (\text{C1})$$

Keeping the lowest order as shown in Eq. (28), $(\Delta - QLQ)^{-1}$ becomes

$$(\Delta - QLQ)^{-1} = G^0. \quad (\text{C2})$$

$$\begin{aligned} \langle\langle ab | PG(\Delta)Q | aa \rangle\rangle &= \left[\frac{1}{\Delta - L_0^S - R} \right]_{ab,ab} (\mathcal{Y}G^0)_{ab,aa} \\ &+ \left[\frac{1}{\Delta - L_0^S - R} \right]_{ab,ba} (\mathcal{Y}G^0)_{ba,aa}. \end{aligned} \quad (\text{B3})$$

From (B2) we get

$$\begin{aligned} (\mathcal{Y}G^0)_{ab,aa} &= \langle\langle ab | \mathcal{Y} | aa \rangle\rangle G_{aa,aa}^0 + \langle\langle ab | \mathcal{Y} | bb \rangle\rangle G_{bb,aa}^0 \\ &= -\frac{1}{2}\mu(G_{aa,aa}^0 - G_{bb,aa}^0) = -\frac{1}{2}\mu G_{aa,aa}^0, \end{aligned} \quad (\text{B4a})$$

$$\begin{aligned} (\mathcal{Y}G^0)_{ba,aa} &= \langle\langle ba | \mathcal{Y} | aa \rangle\rangle G_{aa,aa}^0 + \langle\langle ba | \mathcal{Y} | bb \rangle\rangle G_{bb,aa}^0 \\ &= \frac{1}{2}\mu(G_{aa,aa}^0 - G_{bb,aa}^0) = \frac{1}{2}\mu G_{aa,aa}^0. \end{aligned} \quad (\text{B4b})$$

Substituting (B4) into (B3) and using (A10) we have

Since

$$\begin{aligned} (G^0\mathcal{Y})_{bb,ab} &= G_{bb,bb}^0 \langle\langle bb | \mathcal{Y} | ab \rangle\rangle + G_{bb,aa}^0 \langle\langle aa | \mathcal{Y} | ab \rangle\rangle \\ &= \frac{1}{2}\mu(G_{bb,bb}^0 - G_{bb,aa}^0) = \frac{1}{2}\mu \frac{1}{\Delta + i\gamma}, \end{aligned} \quad (\text{C3})$$

$$\begin{aligned} (G^0\mathcal{Y})_{bb,ba} &= G_{bb,bb}^0 \langle\langle bb | \mathcal{Y} | ba \rangle\rangle + G_{bb,aa}^0 \langle\langle aa | \mathcal{Y} | ab \rangle\rangle \\ &= -\frac{1}{2}\mu(G_{bb,bb}^0 - G_{bb,aa}^0) = -\frac{1}{2}\mu \frac{1}{\Delta + i\gamma}, \end{aligned} \quad (\text{C4})$$

where (A6) is used, we can then write Eq. (C1) more explicitly

$$\begin{aligned} \langle\langle bb | QG(0)P | ab \rangle\rangle &= (G^0 \mathcal{V})_{bb,ab} G(0)_{ab,ab} \\ &+ (G^0 \mathcal{V})_{bb,ba} G(0)_{ba,ab}, \quad (C5) \end{aligned}$$

$$\begin{aligned} \langle\langle bb | QG(0)P | ba \rangle\rangle &= (G^0 \mathcal{V})_{bb,ab} G(0)_{ab,ba} \\ &+ (G^0 \mathcal{V})_{bb,ba} G(0)_{ba,ba}. \quad (C6) \end{aligned}$$

By using (A10) we immediately get

$$\langle\langle bb | QG(0)P | ab \rangle\rangle = \frac{\frac{1}{2}\mu I(-\Delta_L)}{i\gamma - \frac{1}{2}\mu^2[I(-\Delta_L) + I(\Delta_L)]}, \quad (C7)$$

$$\langle\langle bb | QG(0)P | ba \rangle\rangle = \frac{-\frac{1}{2}\mu I(\Delta_L)}{i\gamma - \frac{1}{2}\mu^2[I(-\Delta_L) + I(\Delta_L)]}. \quad (C8)$$

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