QUANTUM-BEAT SPECTROSCOPY WITH COHERENT AND INCOHERENT RADIATION FIELDS

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The effects of partial or complete incoherence in the radiation field on quantum-beat spectroscopy of intermediate-size molecules are analyzed. A unified expression which interpolates between the coherent and the incoherent limits is derived for a radiation field whose phase undergoes a stochastic random modulation. The quantum-beat pattern is broadened and partially eroded as the degree of incoherence increases, but it does not diappear even in the extreme incoherent case, where simple rate equations apply. The effects of incoherence vanish completely if the excitation pulse has a sufficiently short duration.

The time evolution of intermediate-size molecules with a "sparse manifold" of energy levels, interacting with a coherent radiation field is well understood theoretically [1–4] as well as experimentally [5–10]. Both time-resolved (quantum beats) and frequency-resolved (absorption, dispersed fluorescence) experimental observables have been thoroughly discussed and analyzed. In this paper, we consider the effects of partial or complete incoherence in the radiation field on these spectra. Our model consists of a molecular system interacting with a light beam whose phase undergoes a stochastic random modulation. This is realistic model for laser pulses [11,12]. Closed expressions are derived for the time-resolved and frequency-resolved spectra, which interpolate between the completely coherent and completely incoherent limits. We predict that quantum beats will not be completely eroded, even in the extreme incoherent case. We shall first present the model and the completely coherent solution, then the incoherence will be introduced and finally, we present some numerical calculations.

Our model is shown in fig. 1. A single "doorway state" $|s\rangle$ carries all the oscillator strength from the ground state $|g\rangle$ and is quasi-degenerate with a sparse manifold of levels $\{|l\rangle\}$ [4]. The $\{|l\rangle\}$ states carry no oscillator strength and are not directly optically accessible, but they are coupled to the state $|s\rangle$ through the intramolecular interaction H'. The molecule is excited by a photon of frequency ω_L to the state $|s\rangle$ which subsequently fluoresces into the state $|g'\rangle$, emitting a photon of frequency ω_s. The total Hamiltonian which describes this process within the rotating-wave approximation is

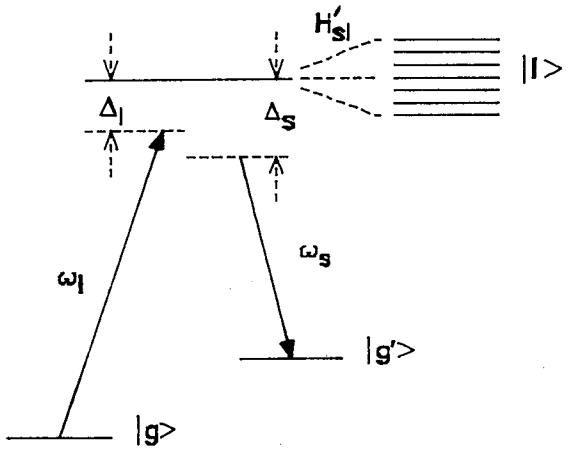

Fig. 1. Energy scheme and photon frequencies corresponding to the Hamiltonian (eq. (1)).

$$H = H_0 + V(t)\,, \tag{1a}$$

$$H_0 = |g\rangle(E_g + \omega_L)\langle g| + |g'\rangle(E_{g'} + \omega_s)\langle g'| + |s\rangle(E_s - \tfrac{1}{2}i\gamma_s)\langle s| + \sum_l |l\rangle(E_l - \tfrac{1}{2}i\gamma_l)\langle l| + H'\,, \tag{1b}$$

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$$H' = \sum_l (H'_{sl}|s\rangle\langle l| + H'_{ls}|l\rangle\langle s|)\,, \tag{1c}$$

$$V(t) = |s\rangle V_{sg}\phi(t)\langle g| + |g\rangle V_{gs}\phi^*(t)\langle s| + |s\rangle V_{sg'}\langle g'| + |g'\rangle V_{g's}\langle s|\,, \tag{1d}$$

$$\phi(t) = \phi_0(t)\exp[\mathrm{i}\textstyle\int_0^t \mathrm{d}\tau\,\alpha(\tau)]\,. \tag{2}$$

Here H_0 is the molecular Hamiltonian dressed by the radiation field, H' is the intramolecular coupling between $|s\rangle$ and $\{|l\rangle\}$, and γ_s, γ_l are the inverse lifetimes of these states. $V(t)$ is the radiation–matter coupling and $\phi(t)$ is the amplitude of the incident radiation field. $\phi(t)$ was decomposed into a product of two functions, an envelope function $\phi_0(t)$ and a random phase part which describes the fluctuations (incoherence) in the laser field. We assume that the phase modulation $\alpha(t)$ is a stationary stochastic Gaussian process.

Let us start by considering a completely coherent field with no fluctuations ($\alpha = 0$). We further assume that the molecule is initially in the ground state; then, to lowest order in perturbation theory, the transition amplitude from $|g\rangle$ to $|g'\rangle$ is [4]

$$\begin{aligned} C_{g'g} = &\int_{-\infty}^{t} \mathrm{d}t_1 \int_{-\infty}^{t_1} \mathrm{d}t_2\, \langle g'|\exp[-\mathrm{i}H_0(t-t_1)] \\ &\times V(t_1)\exp[-\mathrm{i}H_0(t_1-t_2)] \\ &\times V(t_2)\exp(\mathrm{i}H_0 t_2)|g\rangle \\ = &\, V_{g's}V_{sg}\int_{-\infty}^{t} \mathrm{d}t_1 \int_{-\infty}^{t_1} \mathrm{d}t_2\phi_0(t_2) \\ &\times \exp[-\mathrm{i}\Delta_L t_2 - \mathrm{i}\Delta_s(t-t_1)]\,\langle s|s(t_1-t_2)\rangle\,, \end{aligned} \tag{3}$$

where

$$\Delta_L = E_g + \omega_L - E_s\,, \tag{3a}$$

$$\Delta_s = E_{g'} + \omega_s - E_s \tag{3b}$$

and

$$\langle s|s(t)\rangle \equiv \exp(\mathrm{i}E_s t)\langle s|\exp(-\mathrm{i}H_0 t)|s\rangle\,. \tag{4}$$

The emission rate of ω_s photons at time t is then given by

$$\hat{I}(\Delta_L, \Delta_s, t) = \mathrm{d}|C_{g'g}(t)|^2/\mathrm{d}t\,. \tag{5}$$

$\hat{I}$, as defined in eq. (5), is not an experimental observable since it implies an infinite temporal and spectral resolution of the scattered photon ω_s. The result of any realistic experiment may be, however, calculated from $\hat{I}$ by convoluting it with a detector function with the appropriate resolution in Δ_s and t [12]. Let us consider an extreme situation in which we do not spectrally resolve the emission at all, but merely detect the total emission as a function of time. The photon counting rate is then given by

$$\begin{aligned} I(\Delta_L, t) &= \int_{-\infty}^{\infty} (\mathrm{d}|C_{gg'}|^2/\mathrm{d}t)\mathrm{d}(\Delta s) \\ &= \left| V_{g's}V_{sg}\int_{-\infty}^{t} \mathrm{d}\tau\phi_0(\tau)\exp(-\mathrm{i}\Delta_L\tau)\langle s|s(t-\tau)\rangle \right|^2 \end{aligned} \tag{6}$$

To proceed further, we must evaluate $\langle s|s(t)\rangle$ (eq. (4)). This is done by diagonalizing the molecular Hamiltonian H_0. Since H_0 is non-Hermitan, we have to find its right and left eigenstates, i.e.

$$H_0|j\rangle = (\epsilon_j - \tfrac{1}{2}\mathrm{i}\gamma_j)|j\rangle \equiv E_j|j\rangle\,, \tag{7a}$$

$$\langle\bar{j}|H_0 = \langle\bar{j}|(\epsilon_j - \tfrac{1}{2}\mathrm{i}\gamma_j) \equiv \langle\bar{j}|E_j\,, \tag{7b}$$

with the normalization

$$\langle\bar{j}'|j\rangle = \delta_{jj'}\,. \tag{8}$$

Using eqs. (7), we may rewrite eq. (4) in the form [4]

$$\langle s|s(t)\rangle = \sum_j (\langle s|j\rangle)^2 \exp(-\mathrm{i}E_j t)\,. \tag{9}$$

Note the appearance of $(\langle s|j\rangle)^2$ and not $|\langle s|j\rangle|^2$, due to the non-Hermitean character of the Hamiltonian.

This model of an intermediate level structure was extensively studied both theoretically and experimentally. It is well known that the presence of the interaction between the $|s\rangle$ and the $\{|l\rangle\}$ levels results in dilution of the oscillator strength and long lifetimes of the excited states of the order of N/γ_s where $1/\gamma_s$ is the lifetime of the state $|s\rangle$ in the absence of H'. This arises from the mixing of the $|s\rangle$ state with the $\{|l\rangle\}$ states. Additionally, if the duration of the exciting pulse is very short, it is possible to observe a fast initial decay in the fluorescence emission with a time

scale of the order $\hbar/\Delta E$ where ΔE is the spectral range of the excited states [2,3]. We are now in a position to consider the effects of fluctuations in the radiation field on these observables. To that end, we shall replace the field amplitude $\phi_0(t)$ in eq. (6) with

$$\phi(t) \equiv \phi_0(t) \exp[\mathrm{i}\textstyle\int_0^t \mathrm{d}\tau\alpha(\tau)] \,, \tag{10}$$

where α is a stochastic Gaussian random process with the correlation function

$$\langle\alpha(0)\alpha(\tau)\rangle = \delta^2 \exp(-\Lambda\tau) \,. \tag{11}$$

Here $\langle\ \rangle$ denotes ensemble average over the stochastic variable α. The parameters δ and Λ represent the magnitude and the inverse time scale, respectively, of the phase fluctuations of the radiation field. The correlation function of ϕ is then given by [13,14]

$$\langle\phi(t+\tau)\phi(t)\rangle = \phi_0^*(t+\tau)\phi_0(\tau)J(\tau) \,, \tag{12}$$

where

$$J(\tau) = \exp[-\textstyle\int_0^\tau \mathrm{d}\tau_1(\tau-\tau_1)\langle\alpha(0)\alpha(\tau_1)\rangle] \,. \tag{13}$$

Making use of eqs. (13) and (11) we get

$$J(\tau) = \exp[-(\delta^2/\Lambda^2)(\mathrm{e}^{-\Lambda\tau} - 1 + \Lambda\tau)] \,. \tag{14}$$

Let us further introduce the spectral density of the field:

$$J(\omega) \equiv (2\pi)^{-1} \int_{-\infty}^{\infty} \mathrm{d}\tau \exp(-\mathrm{i}\omega\tau)J(\tau) \,. \tag{15}$$

$J(\omega)$ has the following continued-fraction representation [13]:

$$J(\omega) \equiv \frac{1}{\pi}\mathrm{Re}\,\cfrac{1}{\mathrm{i}\omega + \cfrac{\delta^2}{\mathrm{i}\omega + \Lambda + \cfrac{2\delta^2}{\mathrm{i}\omega + 2\Lambda + \ldots}}} \tag{16}$$

$J(\omega)$ depends crucially on the parameter $\kappa \equiv \Lambda/\delta$. When $\kappa \gg 1$, $J(\omega)$ assumes a Lorentzian form

$$J(\omega) = \frac{1}{\pi}\frac{\Gamma/2}{\omega^2 + (\Gamma/2)^2} \,, \tag{17a}$$

where

$$\Gamma = 2\delta^2/\Lambda \,, \tag{17b}$$

whereas, when $\kappa \ll 1$ it reduces to a Gaussian

$$J(\omega) = (2\pi\delta)^{-1/2} \exp(-\omega^2/2\delta^2) \,. \tag{17c}$$

Upon the substitution of eq. (10) in eqs. (5) and (6) and performing the ensemble averaging we then get for the ensemble-averaged quantities

$$\langle\hat{I}(\Delta_\mathrm{L}, \Delta_s, t)\rangle = \int_{-\infty}^{\infty} \mathrm{d}\omega J(\omega)\hat{I}(\Delta_\mathrm{L} - \omega, \Delta_s, t) \tag{18}$$

and

$$\begin{aligned}\langle I(\Delta_\mathrm{L}, t)\rangle &= |V_{g's}|^2|V_{sg}|^2 \\ &\times \int_{-\infty}^{\infty} \mathrm{d}\omega J(\omega) \int_{-\infty}^{t} \mathrm{d}t_1 \int_{-\infty}^{t} \mathrm{d}t_1' \phi_0(t_1)\phi_0^*(t_1') \\ &\times \exp[(-\mathrm{i}\Delta_\mathrm{L} - \omega)(t_1 - t_1')] \\ &\times \langle s|s(t-t_1)\rangle\langle s(t-t_1')|s\rangle \\ &= \int_{-\infty}^{\infty} \mathrm{d}\omega J(\omega) I(t, \Delta_\mathrm{L} - \omega) \,. \end{aligned} \tag{19}$$

The intensity of the emitted light in the presence of fluctuations in the radiation field is just the convolution of the field spectral density $J(\omega)$ with the intensity spectrum from a completely coherent field.

We have made a computer calculation for a ten-level model system. The pulse envelope $\phi_0(t)$ was taken to be [4]

$$\begin{aligned}\phi_0(\tau) &= \exp(\gamma\tau) \,, && \text{if } \tau < 0 \,; \\ &= 1 \,, && \text{if } 0 \leqslant \tau \leqslant T \,; \\ &= \exp(-\gamma\tau) \,, && \text{if } \tau > T \,. \end{aligned} \tag{20}$$

The photon counting rates (eq. (6)) of a coherent excitation ($\alpha = 0$) for various detunings Δ_L is shown in fig. 2. The overall decay rate is $\approx$0.04, close to one tenth of the value of γ_s, which is to be expected from the dilution of oscillator strength.

We have studied the effects of laser field incoherence by performing the convolution (eq. (19)). In fig. 3A, we consider the $\kappa \gg 1$ case (eq. (17a)) where the field has a Lorentzian spectral density. The fwhm of $J(\omega)$ (Γ) is indicated in each panel. As Γ increases, the quantum-beat pattern broadens and undergoes averaging. This averaging, however, attains a limiting value and for $\Gamma \geqslant 10$ the beat pattern remains the

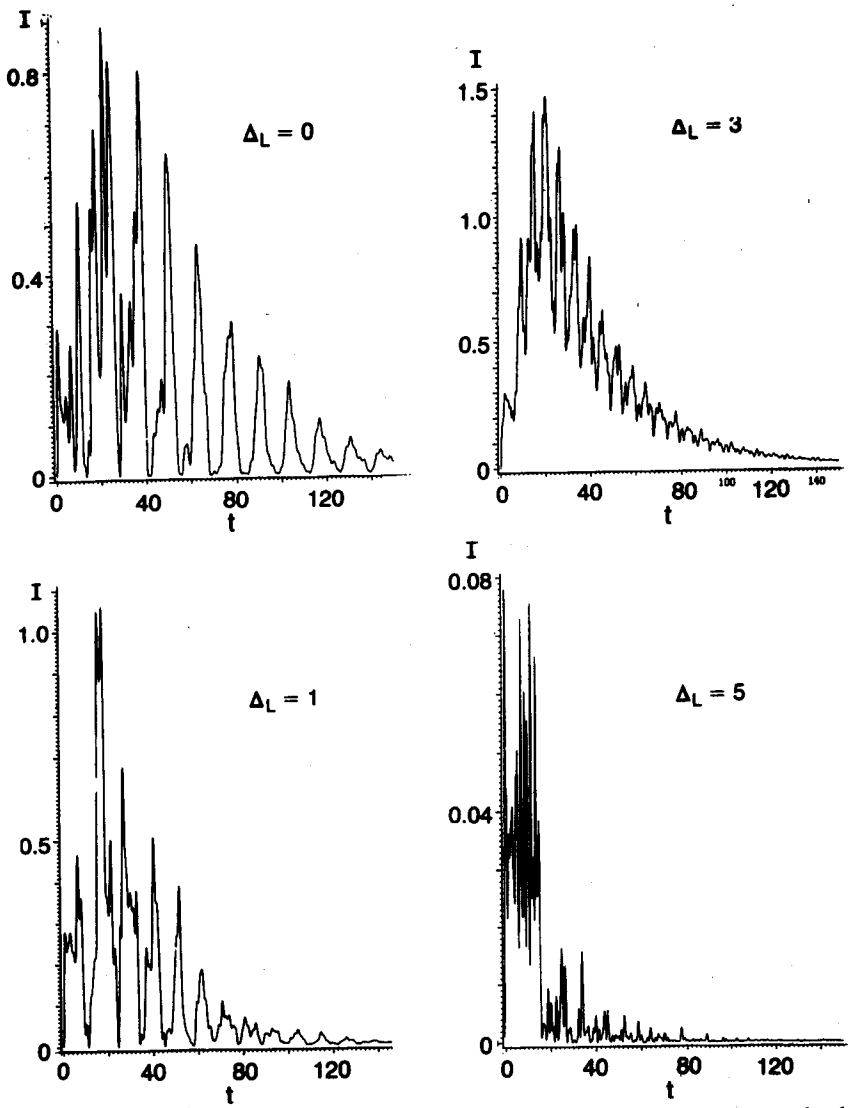

Fig. 2. The quantum-beat pattern $I(\Delta_L, t)$ (eqs. (6), (9) and (20)) of a coherent exciting pulse with a ten-level system. The parameters were $E_S = 0$; $E_1 = 0, \pm 0.45, \pm 1, \pm 1.73, \pm 2.83$; $\gamma_S = 0.4$; $H_{sl} = 0.6$; $T = 15$; $\gamma = 15$.

same. A similar behavior is shown in fig. 3B in which we chose $\kappa \ll 1$ (eq. (17c)) and $J(\omega)$ has a Gaussian spectrum, with the same values of fwhm as in fig. 3A. The Gaussian spectrum is, however, less effective than the Lorentzian in the averaging due to its sharper cut-off in frequency. The limiting value obtained for highly incoherent field (broad-band $J(\omega)$) may be calculated as follows: In the limit of broad-band noise where $J(\omega)$ is more or less constant over the range of integration where $I(\Delta_L - \omega, t)$ is appreciable, we may make the approximation

$$\langle I(\Delta_L, t)\rangle = \int_{-\infty}^{\infty} d\omega J(\omega) I(\Delta_L - \omega, t)$$

$$\approx J(\Delta_L) \int_{-\infty}^{\infty} I(\omega, t)\, d\omega$$

$$= J(\Delta_L) \int_{-\infty}^{t} d\tau |\langle s|s(t-\tau)\rangle|^2 |\phi_0(\tau)|^2 . \qquad (21)$$

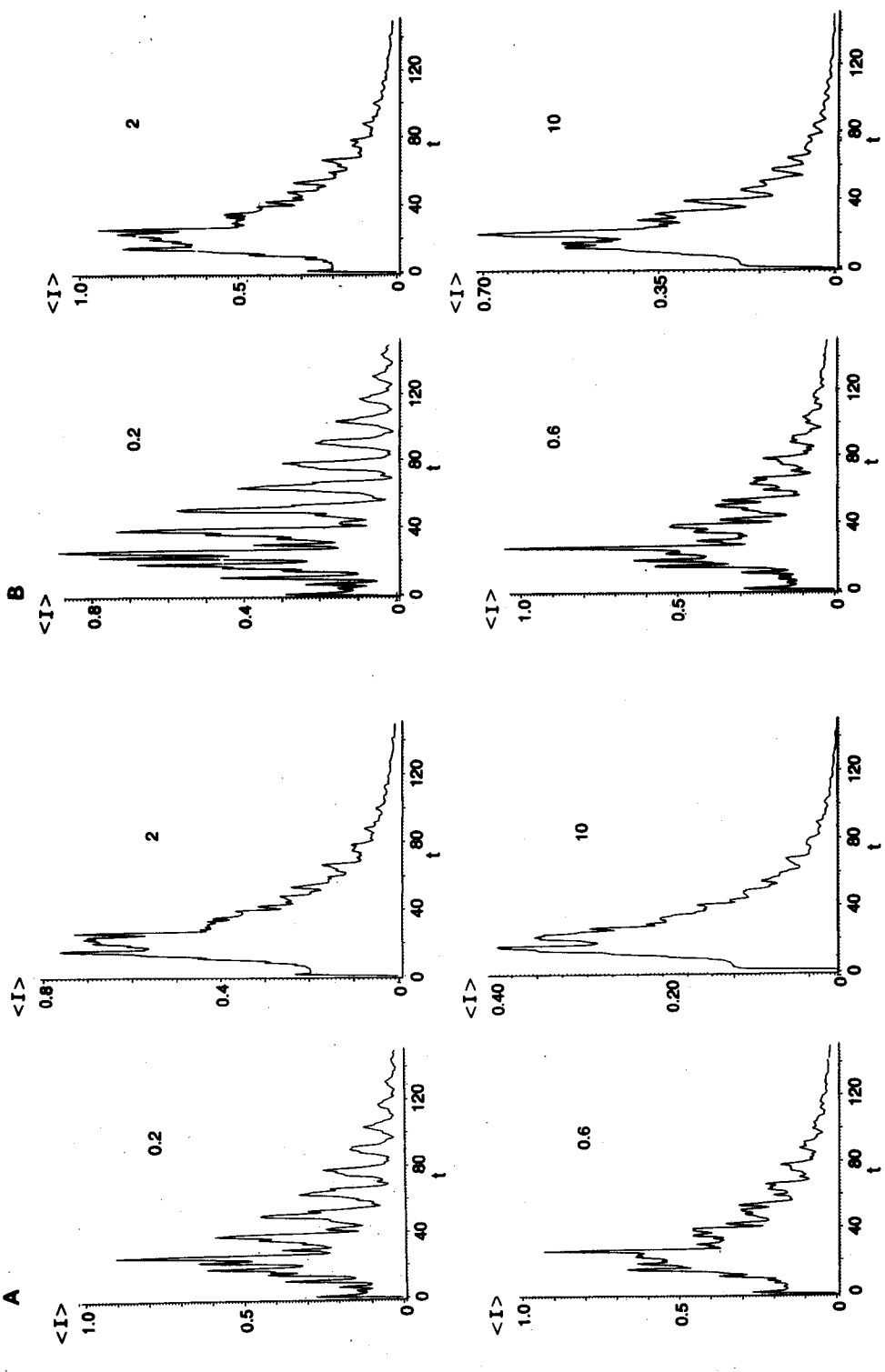

Fig. 3. The quantum-beat pattern $\langle I(\Delta_L, t)\rangle$ (eqs. (19) and (20)) obtained by convoluting $I(\Delta_L, t)$ of fig. 2 with $J(\omega)$ (eq. (16)). $\Delta_L = 0$, other parameters same as in fig. 2. (A) $\kappa \geq 1$. $J(\omega)$ given by eq. (17a). The fwhm of $J(\omega)$ (Γ) is indicated in each panel. (B) $\kappa \ll 1$. $J(\omega)$ given by eq. (17c). The fwhm of $J(\omega)$ $((8 \ln 2)^{1/2}\delta)$ is indicated in each panel.

This form does not change as the spectral width of J increases further. Upon comparison of eq. (21) with eq. (6) we note that eq. (6) is fully coherent; we calculate an amplitude and then square it. Eq. (21), on the other hand, is fully incoherent and may be obtained by a simple rate equation in which we consider only probabilities (not amplitudes). It is also clear from eq. (19) that the shorter the light pulse, the less effective will be the averaging due to the incoherence. The reason is that for short pulses, the $|j\rangle$ states do not have sufficient time to evolve during the pulse and the molecular state following the pulse is simply the doorway state $|s\rangle$ regardless of any incoherence. In the limit of δ function excitation we then have

$$\langle I(\Delta_L, t)\rangle \propto \left|\sum_j (\langle s|j\rangle)^2 \exp(-iE_j t)\right|^2 . \qquad (22)$$

This implies that under the same conditions required to observe the short component [2,3] (pulse duration $\ll \hbar/\Delta E$), the effects of incoherence will be insignificant. This effect is demonstrated in fig. 4 which uses

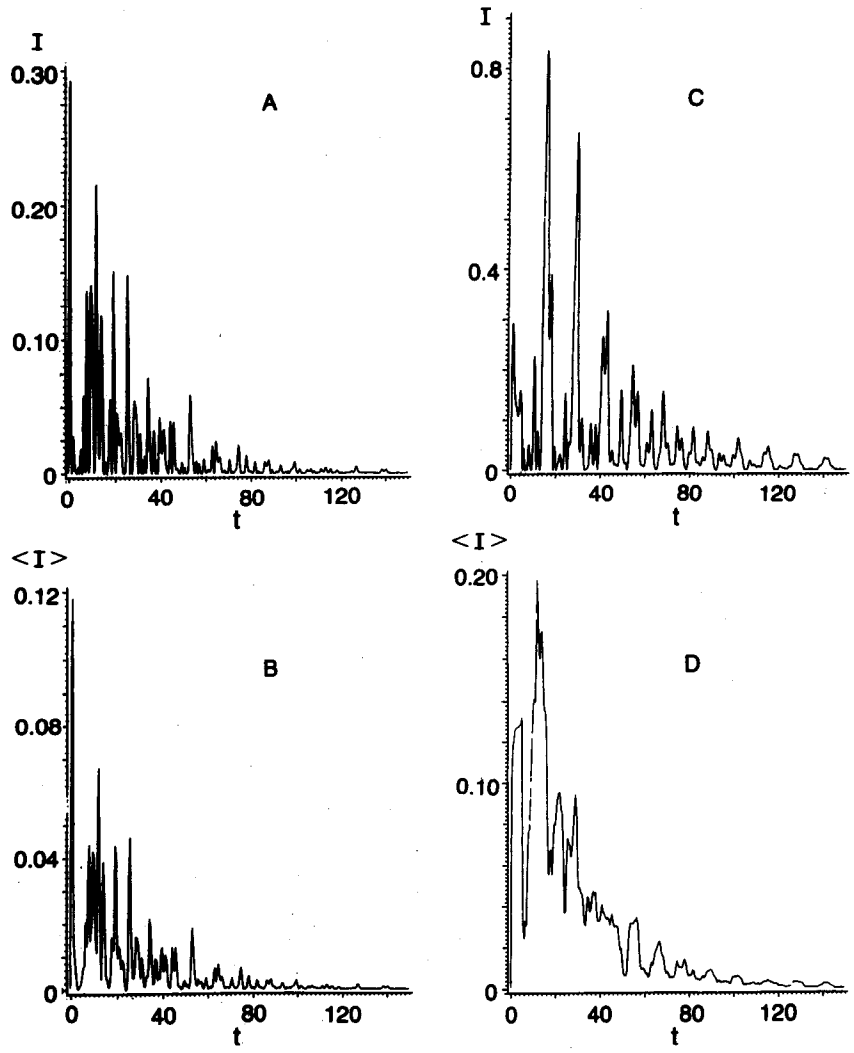

Fig. 4. The effect of the pulse duration T on the quantum-beat spectrum. $\Delta_L = 0$ in all cases. $\langle I\rangle$ was calculated using eq. (19) together with eq. (17a). (A) Coherent excitation (eq. (6)) $T = 1$. (B) Effect of field incoherence on (A) (eq. (19)) with $\Gamma = 10$, $T = 1$. (C) Coherent excitation (eq. (6)), $T = 5$. (D) Effect of field incoherence on (C) (eq. (19)) with $\Gamma = 10$, $T = 5$. Other parameters same as fig. 2.

the same parameters of fig. 3A but with shorter pulses ($T = 5$ and $T = 1$ compared with $T = 15$ in fig. 3A). $\Gamma = 10$ was taken in all cases. It is clear that the averaging in panel D ($T = 5$) is much more significant thant that of panel B ($T = 1$).

In summary, eq. (19) interpolates all the way from the coherent driving whereby $J(\omega) = \delta(\omega)$ and $\langle I(\Delta_L, t)\rangle$ reduces to $I(\Delta_L, t)$ (eq. (6)), to the complete incoherent excitation ($J(\omega) \approx$ const) (eq. (21)). It is clear that the quantum-beat pattern is averaged as the degree of incoherence increases, and this averaging depends crucially on the duration of the excitation pulse. We have also shown that the beats do not necessarily disappear in the extreme incoherent limit.

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References

[1] M. Bixon, J. Jortner and Y. Dothan, Mol. Phys. 17 (1969) 109.
[2] F. Lahmani, A. Tramer and C. Tric, J. Chem. Phys. 60 (1974) 4431;
A. Frad, F. Lahmani, A. Tramer and C. Tric, J. Chem. Phys. 60 (1974) 4419.
[3] R. van der Werf, E. Schutten and J. Kommandeur, Chem. Phys. 11 (1975) 281; 16 (1976) 125, 151.
[4] J. Jortner and S. Mukamel, in: The world of quantum chemistry, eds. R. Daudel and B. Pullman (Reidel, Dordrecht, 1973) pp. 145 ff.;
S. Mukamel and J. Jortner, in: Excited states, Vol. 3, ed. E.C. Lim (Academic Press, New York, 1977) pp. 57 ff.
[5] J. Chaiken, M. Gurnick and J.M. McDonold, J. Chem. Phys. 74 (1981) 106.
[6] W.R. Lambert, P.M. Felker and A.H. Zewail, J. Chem. Phys. 75 (1981) 5958;
P.M. Felker and A.H. Zewail, Chem. Phys. Letters 102 (1983) 113.
[7] B.J. van der Meer, H.Th. Jonkman, J. Kommandeur, W.L. Meerts and W.A. Majewski, Chem. Phys. Letters 92 (1982) 565;
J. Kommandeur, Rec. Trav. Chim. 102 (1983) 421.
[8] H. Henke, H.L. Selzle, T.R. Hays, S.H. Lin and E.W. Schlag, Chem. Phys. Letters 77 (1981) 448.
[9] S. Okajima, H. Sarbusa and E.C. Lim, J. Chem. Phys. 76 (1982) 2096.
[10] D.D. Smith, S.A. Rice and W. Struve, J. Chem. Phys., to be published.
[11] C. Cohen-Tannoudji, in: Frontiers in laser spectroscopy, eds. V.I.R. Balian, S. Haroche and S. Liberman (North-Holland, Amsterdam, 1977) pp. 5 ff.
[12] S. Mukamel, in: Procedings of the Rochester Conference on Coherence and Quantum Optics, eds. L. Mandel and E. Wolf (Plenum Press, New York, 1983).
[13] R. Kubo, Advan. Chem. Phys. 15 (1969) 101.
[14] S. Mukamel, Phys. Rept. 93 (1982) 1.