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Optical Hartmann–Hahn resonance and the spatial correlation of inhomogeneous broadening in molecular solids

Jeffrey A. Cina and Robert Silbey

Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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We propose the use of optical Hartmann–Hahn resonance between guest molecules in a solid in order to study the extent of spatial correlation of site energies in the inhomogeneous distribution. The correlation length and the form of the interaction which mediates the resonance between guest molecules can be determined from the time development of fluorescence.

I. INTRODUCTION

Inhomogeneous broadening of spectral lines is an ubiquitous phenomenon in the optical spectroscopy of solids, arising from the fact that the molecules in a solid do not have identical physical environments. Since a spectral transition measures the difference between two energy levels and each energy level is affected differently by the environment, the understanding of such inhomogeneities can be difficult. One important question, which has been discussed lately,¹ is the correlation of the energies in the broadened line with the relative positions of the molecules. That is, do molecules near one another in the solid have similar absorption frequencies or not? At one extreme is the answer that each molecule's absorption is completely uncorrelated with those of its neighbors, so that the environmental variations which give rise to inhomogeneous broadening vary from site to site in a microscopically random way. At the other extreme is the idea of macroscopic domains of homogeneity, so that all molecules in a large volume have identical absorption frequencies.

These two extremes² and intermediate possibilities¹ have been treated by Root and Skinner in their discussion of photon echo decay in solids. By analysis of the frequency dependence of photon echo decay, they suggested that, at least in one case, microscopic inhomogeneity was the more likely possibility. On the other hand, two-photon absorption experiments on ion pairs in solids³ have been interpreted as demonstrating that there are strong correlations between the inhomogeneous distributions of the two successive transitions needed to doubly excite next nearest neighbor pairs—evidence that spatial gradients of crystal distortions are small. Gulotty *et al.*⁴ have recently asserted that their photon echo results on pentacene in *p*-terphenyl suggest that excitation energies in that system are locally homogeneous.

In the present paper, we suggest a method for studying this question, based on the ideas of NMR spectroscopy applied to optical studies, as exemplified by the work of Warren and Zewail.⁵ The suggestion is to perform a double resonance experiment to determine whether sets of molecules with different absorption frequencies are close to one another in space. The experiment is difficult, but with the development of optical pulse techniques and the ability to change the phase of these optical pulses, we may hope that

the experiment is not impossible.

The paper is laid out in the following way: In Sec. II, the Hamiltonian for the model system is presented and discussed, and then transformed to a (pseudo) spin representation; in Sec. III, the pulse sequence, its effects on the density matrix of the system, and the experimental observable are described. In Sec. IV, a simple model is proposed which exhibits, perhaps in a clearer and more familiar way, the effects presented in Sec. III; finally, in Sec. V are the concluding remarks. Applicability of the proposed experiment to specific systems is considered in Appendix B.

II. HAMILTONIAN

We consider a system consisting of a number of absorbing molecules embedded in a host crystal. Each of these molecules has two electronic states, the ground state $|g\rangle$ and the excited state $|e\rangle$. Labeling each by an index for the site, we find the Hamiltonian for a single molecule at site n to be (in the absence of intermolecular interactions)

$$\begin{aligned} h_n &= E_g |g_n\rangle\langle g_n| + E_e |e_n\rangle\langle e_n| \\ &= \frac{1}{2} (E_g + E_e) + \frac{1}{2} (E_e - E_g) [|e_n\rangle\langle e_n| - |g_n\rangle\langle g_n|] \\ &\equiv \bar{\epsilon} 1_n + \omega \frac{1}{2} \sigma_n^{(z)}, \end{aligned} \quad (2.1)$$

where we have used the fact that $|e_n\rangle\langle e_n| + |g_n\rangle\langle g_n|$ is the unit operator in the space of the molecule at n , and that $|e_n\rangle\langle e_n| - |g_n\rangle\langle g_n|$ is proportional to the Pauli spin matrix $\sigma^{(z)}$ in this representation.

The intermolecular interactions lead to a number of effects: (1) The excitation energy will depend on the site index, and also on whether nearby molecules are in their ground state or their excited state; (2) there will be excitation exchange or transfer processes between molecules. The latter are governed by matrix elements V_{nm} , where

$$V_{nm} = \langle e_n g_m | \hat{V} | g_n e_m \rangle. \quad (2.2)$$

Note that doubly excited states interact with nonexcited states with the same element:

$$\langle e_n e_m | \hat{V} | g_n g_m \rangle = V_{nm}.$$

(We are, of course, assuming that the overlap and electron exchange integrals are negligible.) These terms contribute to the Hamiltonian in the form

$$\begin{aligned}\hat{V} &= \sum_{n>m} V_{nm} [|e_n\rangle \langle g_n| + |g_n\rangle \langle e_n|] \\ &\quad \times [|e_m\rangle \langle g_m| + |g_m\rangle \langle e_m|] \\ &= \sum_{n>m} V_{nm} \frac{1}{4} \sigma_n^{(x)} \sigma_m^{(x)}.\end{aligned}\quad (2.3)$$

In order to make an estimate of the first effect, we assume that the intermolecular coupling leading to it is from van der Waals interactions. Then the normal solvent shift D_n , which is the difference between the excitation energy at site n and the gas phase value, is given by⁶

$$D_n = \sum_m (\phi_{ne,mg} - \phi_{ng,mg}), \quad (2.4)$$

where $\phi_{ng,mg}$ is the van der Waals interaction ($\sim R_{nm}^{-6}$) between two ground state molecules and $\phi_{ne,mg}$ is the van der Waals interaction (also $\sim R_{nm}^{-6}$) between an excited molecule at n and the ground state molecule at m . This by itself leads to a term in the Hamiltonian

$$\hat{D} = \sum_n D_n \frac{1}{2} [\sigma_n^{(z)} + 1]. \quad (2.5)$$

If the excitation density is low, this is the whole story, and from experiment and theory, we know that D_n is of the order of a few hundred cm^{-1} in molecular crystals. However, if the excitation density is high, then we must worry about terms like $\phi_{ne,me}$, i.e., the excitation energy at site n will change when m is excited. Since the van der Waals coupling is short range, only very near molecules can have this effect, and so the size of the shift is likely to be $\sim D_n/100$ where 100 is an estimate of the number of molecules contributing to the shift in Eq. (2.4).

Other interactions can also cause the excitation energy at site n to be dependent on the presence of nearby excitations. For example, if upon excitation a molecule distorts its local environment (excitation-phonon coupling), it will change the excitation frequency of nearby molecules. Thus we find we must add to the Hamiltonian a term:

$$\hat{Q} = \sum_{n>m} \frac{1}{4} Q_{nm} [\sigma_n^{(z)} + 1] [\sigma_m^{(z)} + 1]. \quad (2.6)$$

The form is dictated by the fact that the effect is present only when both molecules are excited.

The total Hamiltonian is then given by the sum of Eqs. (2.6), (2.5), (2.3), and (2.1):

$$\begin{aligned}\hat{H} &= \sum_n \frac{1}{2} \omega_n \sigma_n^{(z)} + \sum_{n>m} \frac{1}{4} V_{nm} \sigma_n^{(x)} \sigma_m^{(x)} \\ &\quad + \sum_{n>m} \frac{1}{4} Q_{nm} \sigma_n^{(z)} \sigma_m^{(z)}.\end{aligned}\quad (2.7)$$

For an optically allowed transition, V_{nm} is given to lowest order by the dipole-dipole interaction, and so is proportional to R_{nm}^{-3} and, as we pointed out above, Q_{nm} is short ranged, possibly varying as R_{nm}^{-6} . In Eq. (2.7) we have neglected a constant term independent of the excitation operators.

We have written the final form of the Hamiltonian, Eq. (2.7), to make clear the similarity to a spin Hamiltonian, in order to facilitate our later discussion. This form is valid strictly at low temperatures where fluctuations due to ther-

mal motions can be neglected.

If we now make the substitution of S_n for $\frac{1}{2} \sigma_n$, we find

$$\hat{H} = \sum_n \omega_n S_{zn} + \sum_{n>m} \{ V_{nm} S_{nx} S_{mx} + Q_{nm} S_{nz} S_{mz} \}. \quad (2.8)$$

III. OPTICAL HARTMANN-HAHN RESONANCE

A model Hamiltonian of the form (2.8) applies to a dilute substitution of guest molecules in a host crystal whose transitions are well separated in energy from those of the guests. In such a system the slightly different environment of each guest molecule leads to a distribution of excitation energies ω_n . (The coupling elements V_{nm} and Q_{nm} are regarded as functions only of the distance vector $\mathbf{R}_n - \mathbf{R}_m$.) The proportion of molecules with energy ω leads to a distribution function $P(\omega)$, peaked at $\bar{\omega}$, the center of the inhomogeneously broadened absorption line, and normalized to unity,

$$\int P(\omega) d\omega = 1. \quad (3.1)$$

The spatial distribution of molecules of different site energies determines a joint probability function $P(\omega, \omega', \mathbf{R})$. The number $P(\omega, \omega', \mathbf{R}) d\omega d\omega'$ is the probability that the first of two guest molecules separated by \mathbf{R} will have frequency within $d\omega$ of ω and the second will be within $d\omega'$ of ω' . Root and Skinner¹ have proposed a specific form for $P(\omega, \omega', \mathbf{R})$ which depends only upon $R = |\mathbf{R}|$, $|\omega - \bar{\omega}|$, $|\omega' - \bar{\omega}|$, the function $P(\omega)$, and a correlation length. If inhomogeneous broadening is macroscopic, or by domains, the correlation length will be large compared with the lattice constants; microscopic inhomogeneous broadening corresponds to a small correlation length.

The optical effect we want to consider is mediated by the Q_{nm} interaction between a pair of molecules of different frequencies. Because Q_{nm} falls off rapidly with distance, the effect depends on spatial proximity of pairs of molecules of different frequencies and offers a way to determine the joint probability function experimentally.

This double resonance is effected with two narrow-band lasers within the inhomogeneous line. Their interactions with the two-level molecules are described by the operator

$$\hat{H}_L = -2\mu \sum_n S_{xn} [E_a \cos(\omega_a t + \phi) + E_b \cos \omega_b t]. \quad (3.2)$$

Laser powers are adjusted so that

$$\omega_a, \omega_b, |\omega_a - \omega_b| \gg \mu E_a, \mu E_b \gg |V_{nm}|, |Q_{nm}| \quad (3.3)$$

and it must be possible to shift the phase ϕ of the ω_a light in a time much shorter than the free induction decay time $1/\mu E_a$ of the ω_a molecules.

The ω_a light will interact strongly with molecules belonging to the narrow piece of the inhomogeneous line of width $\sim \mu E_a$ centered at ω_a . Molecules with energies well outside of this band will not be excited by the ω_a laser. Since we are interested in the evolution of those molecules within this narrow band which have Q_{nm} interactions with molecules with site excitation energies in the vicinity of ω_b , well separated from ω_a , we ignore spectral diffusion. It is as-

sumed that interactions between molecules directly excited by the lasers and those which are not directly excited make no essential contribution to the time development of the molecules within the narrow ω_a band. Moreover, it is assumed that molecules in the region of frequency of width $\mu E_{a(b)}$ centered at $\omega_{a(b)}$ behave as if they were all directly on resonance with the $\omega_{a(b)}$ laser.

Molecules outside these two ranges are treated as if they were completely off resonance with both lasers. Since interactions between excited and unexcited molecules are assumed to be of negligible importance, these molecules may be dropped from further consideration. The initial ground state density matrix

$$\rho(0) = \prod_n^{(a)} \prod_m^{(b)} \left(\frac{1}{2} - S_{zn} \right) \left(\frac{1}{2} - S_{zm} \right) \quad (3.4)$$

develops according to

$$i \frac{d\rho(t)}{dt} = [H_0 + H_1 + H_L, \rho(t)], \quad (3.5)$$

where

$$H_0 = \omega_a \sum_n^{(a)} S_{zn} + \omega_b \sum_m^{(b)} S_{zm}, \quad (3.6)$$

$$H_1 = \sum_n^{(a)} \sum_m^{(b)} \{ V_{nm} S_{xn} S_{xm} + Q_{nm} S_{zn} S_{zm} \}, \quad (3.7)$$

and H_L comprises those terms from \hat{H}_L pertaining only to (a) and (b) molecules.

The Liouville equation may be simplified with the transformation

$$\tilde{\rho}(t) = R(t)\rho(t)R^\dagger(t), \quad (3.8)$$

$$R(t) = \exp \left\{ it \left(\omega_a \sum_n^{(a)} S_{zn} + \omega_b \sum_m^{(b)} S_{zm} \right) \right\}, \quad (3.9)$$

yielding

$$i \frac{d\tilde{\rho}(t)}{dt} = [\tilde{H}_1(t) + \tilde{H}_L(t), \tilde{\rho}(t)] \quad (3.10)$$

with

$$\tilde{\rho}(0) = \rho(0).$$

We call $\tilde{\rho}(t)$ the density matrix in the rotating frame. The largest terms in the rotating frame Hamiltonian are of size $\sim \mu E$. Since

$$\mu E_a, \mu E_b \ll \omega_a, \omega_b, |\omega_a - \omega_b|,$$

the rate of change of $\tilde{\rho}$ is much slower than the frequency of oscillation of the time dependent terms in the rotating frame Hamiltonian. These may be averaged over several periods⁷ (the rotating wave approximation). The averaged Hamiltonian becomes

$$\begin{aligned} \tilde{H}_1 + \tilde{H}_L \cong & -\mu E_a \sum_n^{(a)} S_{xn} \cos \phi + S_{yn} \sin \phi - \mu E_b \sum_m^{(b)} S_{xm} + \frac{1}{2} \sum_n^{(a)} \sum_m^{(a)} \frac{V_{nm}}{2} (S_{xn} S_{xm} + S_{yn} S_{ym}) + Q_{nm} S_{zn} S_{zm} \\ & + \frac{1}{2} \sum_n^{(b)} \sum_m^{(b)} \frac{V_{nm}}{2} (S_{xn} S_{xm} + S_{yn} S_{ym}) + Q_{nm} S_{zn} S_{zm} + \sum_i^{(a)} \sum_j^{(b)} Q_{nm} S_{zn} S_{zm}. \end{aligned} \quad (3.11)$$

The dipolar interactions between (a) and (b) molecules average to zero in the rotating wave approximation, as do the off-resonance interactions of (b) molecules with the ω_a laser and vice versa. The equations of motion can be further simplified by anticipating the fact, proven in Appendix A, that with the sequence of laser pulses employed here, the interactions among the (a) molecules do not lead, by themselves, to a fluorescence signal. So the double sum over (a) sites in Eq. (3.11) can be omitted.

We shall consider the situation where (b) molecules are less numerous and further separated from each other on the average than are the (a) molecules. This can be achieved by taking ω_b away from the center of the inhomogeneous line, unless broadening is strictly macroscopic. In any case, dephasing of the (b) molecules does not concern us here, so we drop the double sum over (b) sites from the Hamiltonian as well.

The simplified Liouville equation in the rotating frame becomes

$$\begin{aligned} i \frac{d\tilde{\rho}(t)}{dt} = & \left[-\mu E_a \sum_n^{(a)} S_{xn} \cos \phi + S_{yn} \sin \phi - \mu E_b \right. \\ & \left. \times \sum_m^{(b)} S_{xm} + \sum_n^{(a)} \sum_m^{(b)} Q_{nm} S_{zn} S_{zm}, \tilde{\rho}(t) \right]. \end{aligned} \quad (3.12)$$

The experiment begins with a laser pulse at ω_a long

enough to equalize the ground and excited state populations of the (a) molecules. Such a pulse takes a time $\tau = \pi/2\mu E_a$ regardless of the initial phase. We take $\phi = \pi/2$. Interactions can be ignored during the pulse, since $\tau|Q_{nm}| \ll 1$, and $E_b = 0$, so

$$\begin{aligned} \tilde{\rho}(\tau) = & \exp \left\{ i(\pi/2) \sum_n^{(a)} S_{yn} \right\} \tilde{\rho}(0) \exp \left\{ -i(\pi/2) \sum_n^{(a)} S_{yn} \right\} \\ = & \prod_n^{(a)} \prod_m^{(b)} \left(\frac{1}{2} + S_{xn} \right) \left(\frac{1}{2} - S_{zm} \right). \end{aligned} \quad (3.13)$$

During this laser pulse the dipole moments of the (a) molecules follow the external electric field by 90° (see Sec. IV). At the end of the pulse the ω_a laser is left on, but phase shifted to $\phi = 0$, bringing the oscillation of its electric field into phase with those of the molecular dipoles.

Next, the ω_b laser is turned on for a time t_1 . To study the time development, we make a second transformation:

$$\tilde{\rho}(t_1 + \tau) = S(t_1)\tilde{\rho}(t_1 + \tau)S^\dagger(t_1) \quad (3.14)$$

with the operator

$$S(t_1) = \exp \left\{ -it_1 \left(\mu E_a \sum_n^{(a)} S_{xn} + \mu E_b \sum_m^{(b)} S_{xm} \right) \right\}.$$

The transformed Liouville equation is

$$i \frac{d\tilde{\rho}(t_1 + \tau)}{dt_1} = \left[\sum_n^{(a)} \sum_m^{(b)} Q_{nm} (S_{zn} \cos \mu E_a t_1 - S_{yn} \sin \mu E_a t_1) \times (S_{zm} \cos E_b t_1 - S_{ym} \sin \mu E_b t_1), \tilde{\rho}(t_1 + \tau) \right]. \quad (3.15)$$

With the Hartmann-Hahn condition⁸

$$\mu E_a = \mu E_b,$$

the Hamiltonian can be averaged with another rotating wave approximation, yielding

$$i \frac{d\tilde{\rho}(t_1 + \tau)}{dt_1} \cong \left[\sum_n^{(a)} \sum_m^{(b)} \frac{Q_{nm}}{2} (S_{yn} S_{ym} + S_{zn} S_{zm}), \tilde{\rho}(t_1 + \tau) \right]. \quad (3.16)$$

The solution is

$$\tilde{\rho}(t_1 + \tau) = U(t_1) \tilde{\rho}(\tau) U^\dagger(t_1), \quad (3.17)$$

where

$$U(t_1) = \exp \left\{ -it_1 \sum_n^{(a)} \sum_m^{(b)} \frac{Q_{nm}}{2} (S_{yn} S_{ym} + S_{zn} S_{zm}) \right\}. \quad (3.18)$$

In the original rotating frame, the density operator is

$$\tilde{\rho}(t_1 + \tau) = S^\dagger(t_1) U(t_1) \tilde{\rho}(\tau) U^\dagger(t_1) S(t_1). \quad (3.19)$$

At this time, the ω_b laser is turned off and the ω_a laser is phase shifted to $\phi = -\pi/2$ for the duration of another $\pi/2$ pulse:

$$\begin{aligned} \tilde{\rho}(\tau + t_1 + \tau) &= \exp \left\{ -i(\pi/2) \sum_i^{(a)} S_{yi} \right\} S^\dagger(t_1) U(t_1) \tilde{\rho}(\tau) U^\dagger \\ &\quad \times (t_1) S(t_1) \exp \left\{ i(\pi/2) \sum_i^{(a)} S_{yi} \right\}. \end{aligned} \quad (3.20)$$

The excited state population among the (a) molecules is proportional to the fluorescence at ω_a . This population is given by

$$\begin{aligned} I &= \left\langle \sum_i^{(a)} \left(\frac{1}{2} + S_{zi} \right) \right\rangle \\ &= \text{tr} \left\{ \sum_i^{(a)} \left(\frac{1}{2} + S_{zi} \right) \tilde{\rho}(\tau + t_1 + \tau) \right\}. \end{aligned} \quad (3.21)$$

By cyclic permutation of operators in the trace this is found to be

$$I = \text{tr} \left\{ \sum_i^{(a)} U^\dagger(t_1) \left(\frac{1}{2} - S_{xi} \right) U(t_1) \tilde{\rho}(\tau) \right\}. \quad (3.22)$$

In order to evaluate this expression, we consider the form of the propagator $U(t_1)$; Eq. (3.18). The magnitude of Q_{nm} drops precipitously with distance and the average number of (a) molecules between R and $R + 1$ lattice spacings away from a (b) molecule,

$$4\pi R^2 f |\mu E| \frac{P(\omega_a, \omega_b, R)}{P(\omega_a)} < 4\pi R^2 f |\mu E| P(\omega_a) \quad (3.23)$$

does not exceed one before $R = 4$ or 5. (f is the fraction of lattice sites occupied by guest molecules.) So the (b) molecule of index m can, in this dilute system, have a significant interaction only with the (a) molecule [of index $n = n(m)$] closest to it. The propagator (3.18) therefore becomes

$$U(t_1) \cong \exp \left\{ -it_1 \sum_m^{(b)} \frac{Q_{n(m)m}}{2} (S_{yn} S_{ym} + S_{zn} S_{zm}) \right\} \quad (3.24)$$

and operators in the exponent corresponding to different m commute because the (b) molecules are spatially disperse. With the help of the relation for spin $\frac{1}{2}$ operators:

$$\begin{aligned} &\exp \{ i\alpha (S_{yn} S_{ym} + S_{zn} S_{zm}) \} S_{xn} \\ &\quad \times \exp \{ -i\alpha (S_{yn} S_{ym} + S_{zn} S_{zm}) \} \\ &= S_{xn} \cos^2(\alpha/2) + S_{xm} \sin^2(\alpha/2) \\ &\quad + (S_{zn} S_{ym} - S_{zm} S_{yn}) \sin \alpha, \end{aligned} \quad (3.25)$$

$$\begin{aligned} I &= \frac{1}{2} \sum_m^{(b)} \sin^2 \frac{Q_{n(m)m} t_1}{4} = \frac{1}{2} \sum_n^{(a)} \sum_m^{(b)} \sin^2 \frac{Q_{nm} t_1}{4} \\ &= \frac{N f^2 |\mu E|^2}{2} \sum_j P(\omega_a, \omega_b, \mathbf{R}_j) \sin^2 \frac{Q(\mathbf{R}_j) t_1}{4}, \end{aligned} \quad (3.26)$$

where N is the number of sites within the crystal. The sum is over all sites and \mathbf{R}_j is the vector to the j site from an origin within the crystal. It is evident that the optical Hartmann-Hahn resonance will produce no effect if the correlation length for inhomogeneous broadening significantly exceeds the range of $Q(\mathbf{R})$.

IV. A SIMPLE MODEL

In the experiment described above, molecules with site energy ω_a undergo oscillation locking in a laser field of frequency $\omega = \omega_a$ and amplitude μE_a . Simultaneously, another laser of frequency ω_b and amplitude μE_b resonantly drives similar molecules of site energy ω_b . The amplitude μE_b is the Rabi frequency at which the ω_b molecules complete cycles of excitation and deexcitation. (a) and (b) molecules belong to different pieces of the inhomogeneously broadened absorption line. If they are nonetheless spatially proximate, Q_{nm} interactions will allow (a) molecules to experience the population oscillations of the (b) molecules provided that the Hartmann-Hahn condition $\mu E_b = \mu E_a$ is met.

The effect of the Hartmann-Hahn resonance on an (a) molecule can be likened to the effect on it of a low frequency oscillation in its site energy.⁸ The essential features of this interaction can be described by considering a one electron molecule with ground and first excited states ψ_g and ψ_e possessing even and odd symmetry, respectively. Neither state has a dipole moment, but the two are connected by a transition dipole moment

$$\mu = - \int dq \psi_e(q) q \psi_g(q). \quad (4.1)$$

The states may have different quadrupole moments. Let

$$\delta_{g(e)} = \int dq q^2 \psi_{g(e)}^2 \quad (4.2)$$

and assume $\delta_g \neq \delta_e$.

In spin operator notation, the Hamiltonian⁹ is

$$H_0 = \omega/2(|e\rangle\langle e| - |g\rangle\langle g|) = \omega S_z, \quad (4.3)$$

where ω is the site energy of the molecule. The dipole moment operator

$$\hat{\mu} = -|e\rangle \int dq \psi_e(q) q \psi_g(q) \langle g| - |g\rangle \int dq \psi_g(q) q \psi_e(q) \langle e| = 2\mu S_x \quad (4.4)$$

is the spin operator version of $-q$. The operator for its rate of change is

$$\frac{d\hat{\mu}}{dt} = \frac{1}{i} [\hat{\mu}, H_0] = -2\mu\omega S_y. \quad (4.5)$$

The quadrupole moment operator:

$$q^2 = (\delta_e - \delta_g) S_z \quad (4.6)$$

is proportional to the population difference $2S_z$.

The total Hamiltonian of the molecule in a resonant laser field linearly polarized in the q direction and a quadrupolar field of amplitude Q and frequency ϵ is given by

$$H = (\omega + Q \cos \epsilon t) S_z - 2\mu E S_x \cos(\omega t + \phi).$$

The quadrupolar field shifts the molecule on and off resonance with the laser at a frequency ϵ .

The initial ground state density matrix is

$$\rho(0) = \frac{1}{2} - S_z \quad (4.7)$$

and

$$i \frac{d\rho(t)}{dt} = [H, \rho(t)] \quad (4.8)$$

describes the time development. In the interaction representation:

$$\tilde{\rho}(t) = e^{iH_0 t} \rho(t) e^{-iH_0 t}; \quad \tilde{\rho}(0) = \rho(0) \quad (4.9)$$

and

$$i \frac{d\tilde{\rho}(t)}{dt} \cong [-\mu E S_x \cos \phi - \mu E S_y \sin \phi + Q S_z \cos \epsilon t, \tilde{\rho}(t)]. \quad (4.10)$$

Let us take the initial phase of the laser to be $\phi = \pi/2$ so that the electric field is $-E \sin \omega t$. The dipole moment of the molecule in its ground state is zero. After a short time ($\mu E \tau < \pi/2$, $Q\tau \ll 1$),

$$\tilde{\rho}(\tau) = e^{i\mu E \tau S_y} \tilde{\rho}(0) e^{-i\mu E \tau S_y} = \frac{1}{2} - S_z \cos \mu E \tau + S_x \sin \mu E \tau, \quad (4.11)$$

so that

$$\mu(\tau) = \text{tr}[2\mu S_x \rho(\tau)] = \mu \sin \mu E \tau \cos \omega \tau. \quad (4.12)$$

The dipole moment oscillates at frequency ω and follows the electric field by 90° of phase. Its amplitude, which grows

with an envelope $\mu \sin \mu E \tau$, reaches its maximum value μ at time $\tau = \pi/2\mu E$.

The population difference at this time is

$$\langle 2S_z \rangle = -\cos \mu E \tau = 0. \quad (4.13)$$

At this point the laser is brought into phase with the dipole moment of the molecule by shifting its phase to $\phi = 0$. This is oscillation locking. The equation of motion

$$i \frac{d\tilde{\rho}}{dt} = [-\mu E S_x + Q S_z \cos \epsilon t, \tilde{\rho}(t)] \quad (4.14)$$

may be transformed again by defining

$$\tilde{\tilde{\rho}}(t_1 + \tau) = e^{-i\mu E t_1 S_x} \tilde{\rho}(t_1 + \tau) e^{i\mu E t_1 S_x}; \quad \tilde{\tilde{\rho}}(\tau) = \frac{1}{2} + S_x. \quad (4.15)$$

Whence

$$i \frac{d\tilde{\tilde{\rho}}(t_1 + \tau)}{dt} = [Q \cos \epsilon(t_1 + \tau) (S_x \cos \mu E t_1 - S_y \sin \mu E t_1), \tilde{\tilde{\rho}}(t_1 + \tau)]. \quad (4.16)$$

If the Hartmann-Hahn condition

$$\epsilon = \mu E$$

is obeyed, the Liouville equation can be simplified with a rotating wave approximation to yield

$$i \frac{d\tilde{\tilde{\rho}}(t_1 + \tau)}{dt_1} = \left[\frac{Q}{2} S_y, \tilde{\tilde{\rho}}(t_1 + \tau) \right]. \quad (4.17)$$

The solution is

$$\tilde{\tilde{\rho}}(t_1 + \tau) = \frac{1}{2} + S_x \cos \frac{Q t_1}{2} - S_z \sin \frac{Q t_1}{2} \quad (4.18)$$

and

$$\tilde{\rho}(t_1 + \tau) = e^{-\mu E t_1 S_x} \tilde{\tilde{\rho}}(t_1 + \tau) e^{i\mu E t_1 S_x}, \quad (4.19)$$

from which we find the dipole moment to be

$$\begin{aligned} \mu(t_1 + \tau) &= \text{tr}(2\mu S_x e^{-i\omega(t_1 + \tau) S_z} \tilde{\rho}(t_1 + \tau) e^{i\omega(t_1 + \tau) S_z}) \\ &= \mu \left(\cos \omega t \cos \frac{Q t_1}{2} + \sin \omega t \sin \mu E t_1 \sin \frac{Q t_1}{2} \right). \end{aligned} \quad (4.20)$$

The population difference is

$$\langle 2S_z \rangle = -\cos \mu E t_1 \sin \frac{Q t_1}{2}. \quad (4.21)$$

If Q were zero, the populations of excited and ground states would remain equal and the molecular dipole $\mu(t_1 + \tau) = \mu \cos \omega t$ would still be in phase with the laser field. If the laser phase is dropped back now by another ninety degrees, the electric field will follow the dipole by a quarter cycle, damping its oscillations. The molecule will begin to lose energy, returning to its ground state at time $\tau + t_1 + \tau$.

Shifting the laser phase to $\phi = -\pi/2$ for the length τ of a $\pi/2$ pulse, we find in the general case of nonzero Q that

$$\tilde{\rho}(\tau + t_1 + \tau) = e^{-i(\pi/2) S_y} \tilde{\rho}(t_1 + \tau) e^{i(\pi/2) S_y}. \quad (4.22)$$

The population difference at this time is

$$\langle 2S_z \rangle = -\cos \frac{Q t_1}{2}. \quad (4.23)$$

As mentioned, the pulse returns the molecule to its ground state if $Q = 0$. A nonzero excited state population will manifest itself through fluorescence at frequency ω .

In the optical Hartmann–Hahn experiment proposed above, the interaction which prepares the molecule to emit or absorb radiation during the final pulse is provided by the population oscillations of a nearby molecule of different site energy rather than by an external quadrupolar field.

V. DISCUSSION

We have shown that fluorescence detected Hartmann–Hahn experiment can, in principle, reveal the nature of inhomogeneous broadening in an energetically disordered optical system. The optical transitions studied might be those of guest organic molecules in a glass or a host crystal.

The form of joint probability function which specifies the spatial correlation of inhomogeneous broadening is to be found from the time dependence of the fluorescence signal at frequency ω_a given by Eq. (3.26). We do not know the exact form of the $Q(\mathbf{R})$ interaction which mediates the Hartmann–Hahn resonance. But, because it is short range (possibly being dominated by a $\sim 1/R^6$ van der Waals contribution), significant contributions to the sum (3.26) will involve only several lattice vectors, and the frequencies of temporal oscillations of the fluorescence will reveal the form of $Q(\mathbf{R})$. The intermolecular coupling term [see Eq. (2.6)] of which $Q(\mathbf{R})$ is the coefficient, is of importance when considering interaction between two molecules, both excited.

Several approximations made here—the assumptions of square excitation profiles, long natural lifetimes, and the absence of spectral diffusion—exclude effects which might lead to non-null fluorescence even in the absence of Hartmann–Hahn resonance. While it is not evident that these would mimic the time development characteristic of such a resonance, they could probably be removed in large part by recording the difference between the signal as derived in Eq. (3.26) and that obtained when the phase of the final ω_a pulse is shifted by π radians.

In order for the theory presented here to be valid, inhomogeneous broadening must be large enough so that the inequalities (3.3) can be applied. In addition, if $Q(\mathbf{R})$ is to be determined, the natural lifetime of a single excitation must exceed the resonance time $\sim 2\pi/Q_{\max}$ [Eq. (3.26)] required to reach the first fluorescence maximum. These criteria and their consequences in phase-shifting rise time and laser power requirements are considered in Appendix B, for two typical mixed crystal systems. It is shown there that phase-shift rise times about two orders of magnitude faster than currently achieved by acousto-optic modulation (~ 4 ns) will probably be required. The theory presented here is immediately applicable to the Hartmann–Hahn resonance between transitions of two different molecular species in a solid. The resonance condition then is $\mu_1 E_1 = \mu_2 E_2$. It should be pointed out that the Hartmann–Hahn effect has recently been used to test for the spatial proximity of nuclear spins with different Larmor frequencies, belonging to different molecules in a disordered solid.¹⁰

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APPENDIX A: BEHAVIOR OF A COLLECTION OF INTERACTING MOLECULES OF EQUAL SITE ENERGY UNDER OSCILLATION LOCKING

It was shown in the model problem of Sec. II that, during oscillation locking and in the absence of other external fields, the dipole moment of a single two level molecule oscillates in phase with the locking laser field, so that

$$\mu(t) = \mu \cos \omega t. \quad (A1)$$

The dipole moment of the molecule would obey this same development (for $t \ll$ lifetime) if it were allowed to evolve freely after a $\pi/2$ pulse.

The same is not true of the total dipole moment of a collection of molecules of approximately equal site energies randomly distributed in a crystal and interacting with each other. In the absence of oscillation locking, following a $\pi/2$ pulse the dipole–dipole and Q_{nm} interactions among the resonant molecules will cause their individual dipolar oscillations to get out of phase with each other and to change in amplitude, leading to disappearance of the macroscopic dipole moment. With no macroscopic dipole oscillation, the molecules cannot be made coherently to lose energy during a final $\pi/2$ pulse and the system will fluoresce regardless of Hartmann–Hahn effects.

During oscillation locking, however, the coherence among the individual dipoles is maintained. After a $\pi/2$ pulse the density matrix (3.13) of the (a) molecules is

$$\tilde{\rho}_a(\tau) = \prod_n^{(a)} \left(\frac{1}{2} + S_{x_n} \right). \quad (A2)$$

Evolution proceeds according to

$$i \frac{d\tilde{\rho}_a(t_1 + \tau)}{dt_1} = \left[-\mu E_a \sum_n^{(a)} S_{x_n} + \frac{1}{2} \sum_n^{(a)} \frac{V_{nm}}{2} \right. \\ \left. \times (S_{x_n} S_{x_m} + S_{y_n} S_{y_m}) + Q_{nm} S_{z_n} S_{z_m}, \tilde{\rho}_a(t_1 + \tau) \right] \quad (A3)$$

during oscillation locking [see Eq. (3.11)].

Transforming to

$$i \frac{d\tilde{\rho}_a(t_1 + \tau)}{dt_1} = [\tilde{H}, \tilde{\rho}_a(t_1 + \tau)], \quad (A4)$$

[see Eq. (3.14)] where

$$\tilde{H} \cong \frac{1}{2} \sum_r^{(a)} \sum_j^{(a)} \frac{V_{nm}}{2} S_{x_n} S_{x_m} \\ + \left(\frac{V_{nm}}{4} + \frac{Q_{nm}}{2} \right) (S_{y_n} S_{y_m} + S_{z_n} S_{z_m}) \quad (A5)$$

and

$$\tilde{\rho}_a(\tau) = \bar{\rho}_a(\tau), \quad (\text{A6})$$

we have

$$\tilde{\rho}_a(t_1 + \tau) = e^{-it_1\tilde{H}}\bar{\rho}_a(\tau)e^{it_1\tilde{H}}. \quad (\text{A7})$$

The population difference following a $\pi/2$ pulse with $\phi = -\pi/2$, applied at $t = t_1 + \tau$, is [see Eq. (3.20)]

$$\left\langle 2 \sum_n^{(a)} S_{zn} \right\rangle \Big|_{t=\tau+t_1+\tau} = \text{tr} \left\{ -2 \sum_n^{(a)} S_{zn} \tilde{\rho}(t_1 + \tau) \right\}. \quad (\text{A8})$$

This is proportional to the component of the total dipole moment of the (*a*) molecules which is in phase with the locking laser at $t = t_1 + \tau$ [Eq. (4.20)].

The important quantity is

$$e^{it_1\tilde{H}} \sum_n^{(a)} S_{zn} e^{-it_1\tilde{H}} = \sum_n^{(a)} S_{zn} \quad (\text{A9})$$

by commutivity of \tilde{H} and $\sum_n^{(a)} S_{zn}$. Because of oscillation locking, interactions among the (*a*) molecules do not effect the in-phase component of the oscillating collective dipole moment of the (*a*) molecules. In the absence of a Hartmann-Hahn resonance, they will be driven back to their ground states by the final pulse.

APPENDIX B: APPLICABILITY OF THE THEORY TO REAL PHYSICAL SYSTEMS

In order for the optical Hartmann-Hahn resonance to be achieved, and used to test for spatial proximity of molecules with different site energies, the inequalities (3.3) must apply. Broadening of the main optical absorption line must be primarily inhomogeneous, so that two frequency packets within the line can be excited by narrow band lasers whose frequency separation and bandwidths exceed the magnitude, in frequency, of the energy transfer matrix elements.

We consider first the well-characterized mixed crystal of naphthalene in durene¹¹ which has been the subject of photon-echo dephasing experiments.^{12,13} The naphthalene transition ${}^1B_{1u} \leftarrow {}^1A_{1g}$ (316.8 nm), with linewidth ~ 30 GHz at ~ 1.5 K, has a transition moment $\mu \sim 0.02$ D. The volume per molecule in the durene host¹¹ is $215 \text{ \AA}^3 \equiv a^3$. Excluding nearest neighbors, which absorb separately from the "monomer" line,¹² the matrix elements for energy transfer among guests are bounded roughly by

$$V \lesssim \frac{\mu^2}{h(2a)^3} = 35 \text{ MHz}. \quad (\text{B1})$$

This coupling strength and the inhomogeneous linewidth dictate an intermediate value for the Rabi frequency

$$\frac{\mu E}{h} \sim 1 \text{ GHz}. \quad (\text{B2})$$

The corresponding optical free induction decay time

$$\tau_{\text{FID}} = \frac{h}{2\pi\mu E} \sim 160 \text{ ps} \quad (\text{B3})$$

imposes the requirement that the rise time for phase shifting of the laser pulses be tens of picoseconds at most. This is two orders of magnitude faster than the shortest rise time reported to date.⁵

The laser power is given by

$$P = \frac{E^2}{4\pi} Ac, \quad (\text{B4})$$

where *A* is the illuminated area. The electric field amplitude is determined from the bandwidth and transition dipole moment to be $E \sim 330$ stat V cm⁻¹. To illuminate an area 100 μm in diameter requires a laser power

$$P \sim 4.1 \text{ kW} \quad (\text{B5})$$

during the polarization locking pulse.

The time scale of the polarization locking pulse is determined by the first maximum in the fluorescence signal, which occurs [Eq. (3.26)] at

$$t = \frac{h}{Q_{\text{max}}}. \quad (\text{B6})$$

The value of *Q* for next nearest neighbor naphthalene pairs in durene has not yet been measured. If it exceeds

$$Q/h \sim 100 \text{ MHz}, \quad (\text{B7})$$

Eq. (3.3) is not obeyed and the theory presented here is not applicable. The first fluorescence maximum occurs after 10 ns of polarization locking if a Hartmann-Hahn resonance with this maximum value of *Q*/*h* is present. If *Q*/*h* for next nearest neighbors has a smaller value, or if spatial correlation of site energies prevents spatial proximity of molecules with different energies, longer polarization locking pulses would be required. The fluorescence lifetime¹² (180 ns) of naphthalene in durene sets an absolute upper bound for polarization locking in this transition.

A similar analysis can be made of the ${}^7F_0 \leftrightarrow {}^5D_0$ transition of Eu^{3+} ions occupying sites of C_2 symmetry in Y_2O_3 , which has been studied by frequency-dependent photon echo.¹⁵

The inhomogeneous width, 10 GHz for 2% Eu^{3+} at 1.8 K, again implies a Rabi frequency $\mu E \lesssim 1$ GHz for narrow-band excitation. So a similar upper bound on the magnitude of *Q* measurable by Hartmann-Hahn resonance exists as in the previous case; the fluorescence lifetime $T_1 = 86$ ms is amply in excess of the corresponding resonance time of > 10 ns. Although no value of the transition dipole moment has been reported for this transition, to our knowledge, an upper bound can be determined by assuming that T_1 is strictly radiative and that decay to other than the ground state does not occur. (This is manifestly not the case experimentally.¹⁶) In this way we find that

$$\mu^2 < \frac{3h}{4} \left(\frac{\lambda}{2\pi} \right)^3 \frac{1}{2\pi T_1} = 7.27 \times 10^{-4} \text{ D}^2. \quad (\text{B8})$$

Here, $\lambda = 5808 \text{ \AA}$. Thus

$$\mu < 2.70 \times 10^{-2} \text{ D}. \quad (\text{B9})$$

The volume per C_2 cation site in Y_2O_3 is $a^3 \sim 50 \text{ \AA}^3$ so the next nearest neighbor dipole-dipole coupling between Eu^{3+} ions is

$$\frac{V}{h} = \frac{\mu^2}{h(2a)^3} < 280 \text{ MHz}. \quad (\text{B10})$$

Nearest neighbors are to be excluded, since such dimers absorb separately from the monomer line.

The upper bounds of the transition dipole moment [Eq.

(B9)] and of V/h for next nearest neighbors [Eq. (B10)] are probably considerably in excess of their actual values. From a fit of their theory to frequency-dependent photon echo data, Root and Skinner¹ obtain a value

$$V/h = 2.2 \text{ MHz} \quad (\text{B11})$$

for nearest neighbor pairs of Eu^{3+} ions in Y_2O_3 . In their analysis, however, no attempt is made to exclude dimers which absorb separately from the monomer line.

For the purposes of estimating power requirements and the limits of narrow-band excitation, we assume that

$$\mu \sim 0.01 \text{ D} \quad (\text{B12})$$

and correspondingly that

$$V/h \sim 39 \text{ MHz} \quad (\text{B13})$$

The electric field amplitude corresponding to a Rabi frequency $\mu E \sim 1 \text{ GHz}$ and a transition dipole moment [Eq. (B12)] leads to a power requirement

$$P \sim 17 \text{ kW} \quad (\text{B14})$$

for a $100 \mu\text{m}$ spot. This is to be maintained for the $\sim 10 \text{ ns}$ of cross polarization.

If the largest effective Q/h is less than the 100 MHz maximum [Eq. (B7)] measurable in this system, this and the next nearest neighbor V/h value (B13) may allow some latitude to decrease the Rabi frequency and hence the laser power and more importantly, to ease the phase-shifting rise time requirement.

We have already mentioned, in Sec. V, that the theory presented here is immediately generalizable to an optical Hartmann-Hahn resonance between two different guest species. This would ensure good frequency separation of the two transitions and would allow determination of the change

of the solvent shift of a transition in one molecule upon excitation of another in its vicinity. An orientationally disordered host crystal,¹⁷ such as 2,3-dimethylnaphthalene,¹⁸ would ensure such frequency separation in a single transition. Up to 300 cm^{-1} of (presumably microscopically broadened) inhomogeneous width¹⁹ have been reported in this host.

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