

# Intermolecular interaction dynamics and optical dephasing: Picosecond photon echo measurements in mixed molecular crystals

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(Received 4 October 1979; accepted 31 October 1979)

Picosecond optical coherence techniques are employed to study dynamical intermolecular interactions in low concentration mixed molecular crystals, i.e., pentacene in naphthalene at 1.4 K. A concentration-dependent broadening of the optical homogeneous line is observed. Stimulated photon echo measurements rule out excited state transport as the broadening mechanism. The photon echo results exhibit a linear concentration dependence and a theory is proposed that accounts for the broadening in terms of phonon-induced fluctuations in guest-guest dipole-dipole interactions. Detailed considerations indicate that the system is best described in terms of localized excitations rather than delocalized impurity band states. In the low concentration limit, there is additional broadening of the homogeneous line beyond that produced by the lifetime. A model is presented describing this broadening in terms of phonon-induced modulation of the guest-host van der Waals interactions, i.e., in terms of a fluctuating crystal shift.

## I. INTRODUCTION

In this paper we present a detailed study of the dynamical processes which influence low concentration guest molecules in a host crystal at very low temperatures. Several fundamental questions are answered pertaining to the dynamical nature of molecular electronic states in the "almost isolated" situation, i.e., the case in which the molecule of interest interacts weakly with its environment. Optical line shape analysis can provide information useful in understanding dynamics in molecular systems.<sup>1</sup> However, the information obtainable from the homogeneous optical absorption line is frequently masked by inhomogeneous line broadening. In the experiments described below it was possible to extract dynamical information from under the guest molecule's inhomogeneous  $S_0$  to  $S_1$  optical line using picosecond optical coherence techniques, i.e., photon echo<sup>2</sup> and stimulated photon echo<sup>3</sup> experiments.

The questions to be addressed involve the nature of the guest-lattice and guest-guest interactions in the mixed crystal system, pentacene in naphthalene. It will be demonstrated that even in a concentration range as low as  $10^{-6}$  mole/mole the  $S_0$ - $S_1$  homogeneous optical linewidth ( $1/\pi T_2$ ) displays a well-defined concentration dependence. If the excited states on the various guest molecules were truly degenerate and in a static lattice, the intermolecular interaction evidenced by the concentration-dependent  $T_2$  would result in eigenstates delocalized among the guest molecules. A narrow band of energy levels, an impurity band,<sup>4</sup> would be associated with the guest  $S_1$  state. The bandwidth is on the order  $\langle J \rangle$ , where  $\langle J \rangle$  is the concentration-dependent average guest-guest intermolecular interaction.

In a real mixed crystal there are static potential fluctuations (inhomogeneous broadening) and phonon-induced dynamical potential fluctuations which can destroy the impurity band. This is equivalent to an Anderson transition<sup>5</sup> and will occur when the magnitude of the potential

fluctuations,  $\Delta V$ , becomes comparable to  $\langle J \rangle$ . When  $\langle J \rangle < \Delta V$ , the excited state is localized on a single molecule, and the eigenstate is the guest molecular eigenstate.

Static descriptions in terms of impurity band states or isolated molecular states cannot explain the concentration-dependent optical dephasing (homogeneous line broadening). Dephasing requires dynamical processes. There are two possible concentration-dependent processes which could be responsible for the observed dephasing. The first involves electronic excited state energy transport.<sup>6</sup> As an excitation moves from molecule to molecule, it will sample a variety of transition frequencies due to the energy inhomogeneity of the ensemble of molecules. Increased concentration increases the rate of transport, producing a greater rate of frequency fluctuations and, thus, greater dephasing. If the transport were fast enough, the optical line would be motionally narrowed.<sup>1</sup> Transport could occur either in an impurity band or among isolated molecular states, depending on the relative magnitudes of  $\Delta V$  and  $\langle J \rangle$ .

The second possible concentration-dependent dephasing mechanism involves phonon-induced fluctuations in the guest-guest intermolecular interactions. Since the pentacene  $S_0$ - $S_1$  transition is a highly allowed electric dipole transition and we are dealing with relatively dilute ( $10^{-6}$  mole/mole) crystals, the intermolecular interaction is a dipole-dipole interaction. Phonons cause the pentacene intermolecular separations and relative dipole orientations to fluctuate. In an impurity band, this results in energy fluctuations in the multiplet structure of the band. In the localized molecular eigenstate case, a given pentacene molecule experiences a fluctuating dipolar field arising from the sea of other pentacene molecular transition dipoles. This causes the molecular state energy to fluctuate. In either case, the effect is concentration-dependent dephasing.

The results presented below establish the nature of the concentration-dependent dephasing mechanism. Stimulated photon echo experimental data eliminates the energy transport mechanisms. The functional form of the photon echo decay data (decay of the correlation function)

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argues strongly for a two level system, i.e., an isolated molecule in a fluctuating dipolar field. Calculations based on the dipolar field picture yield the correct concentration dependence and the correct magnitude of the parameters involved. The description of an excited state which emerges is that the intermolecular term in the Hamiltonian should not be diagonalized, but rather relegated to the "environment" which acts on a guest molecule as a fluctuating perturbation.

When the guest molecule concentration is reduced below  $\sim 10^{-7}$  mole/mole, the contribution of the fluctuating guest-guest interactions to the homogeneous linewidth becomes negligible and  $T_2$  becomes concentration independent. Under the conditions of very low concentration and very low temperature (1.4 K), in mixed crystals and in similar situations, such as rare gas matrices and glasses, it is common to assume that the guest molecule's homogeneous  $S_0 \rightarrow S_1$  optical linewidth is determined by the excited state lifetime  $T_1$ , with  $T_2 = 2T_1$ . The assumption is that the linewidth reflects only dynamical processes internal to the guest molecule, interactions with the environment having been frozen out.

The photon echo data presented below demonstrate that the linewidth is not determined strictly by the lifetime for pentacene in naphthalene at very low concentration ( $< 10^{-7}$  mole/mole) and very low temperature (1.4 K). A model is proposed which explains the additional linewidth in terms of fluctuating van der Waals interactions between the guest molecule and the surrounding host molecules. When a guest molecule is placed in a host lattice, the  $S_0$  state is stabilized by intermolecular van der Waals interactions, and the  $S_1$  state, being more polarizable,<sup>7</sup> is stabilized to a greater extent. The result is a reduction in the  $S_0 \rightarrow S_1$  transition energy from that which is observed in the gas phase. This change in energy difference is the crystal shift,  $D$ .<sup>8</sup>  $D$  is very sensitive to intermolecular separation. Therefore, phonon-induced fluctuations in the intermolecular separations produce fluctuations in the  $S_0 \rightarrow S_1$  energy difference and dephase the transition. Calculations described below show that this model is consistent with the experimental data.

## II. EXPERIMENTAL

### A. Techniques

Two basic optical coherence pulse sequences were used in the experiments, i.e., the photon echo and the stimulated photon echo. These are the direct optical analogs of the magnetic resonance spin echo<sup>2</sup> and stimulated spin echo<sup>3</sup> experiments. These techniques are well documented<sup>2,3</sup> and will be only very briefly reviewed here.

The photon echo involves a two pulse sequence, shown in Fig. 1(a). The first optical pulse, tuned to the transition frequency, produces a coherent superposition of the ground and excited states. During the interval  $\tau$ , the ensemble of superposition states undergoes inhomogeneous dephasing. The second pulse initiates a rephasing process and, at the end of a second  $\tau$  interval, the ensemble is rephased, i.e., the photon echo occurs.

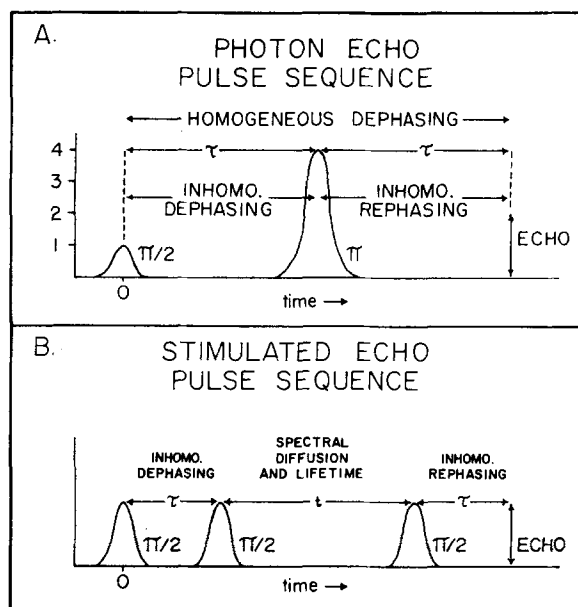


FIG. 1. (a) Photon echo pulse sequence. The echo sequence eliminates inhomogeneous dephasing. The echo amplitude depends only on the extent of homogeneous dephasing during the time  $2\tau$ . Echo decay data in which the echo intensity is measured as a function of  $\tau$  yield the homogeneous optical line shape and width. (b) Stimulated echo pulse sequence. The stimulated echo experiment measures spectral diffusion and lifetime relaxation during the time  $t$ . Decay data is obtained by scanning the time  $t$ .

The echo manifests itself as a pulse of light emitted by the sample in a direction determined by the wave vectors of the excitation pulses. As the interval  $\tau$  is increased, the echo intensity decreases. It is the change in echo intensity with  $\tau$ , i.e., the echo decay, which yields the homogeneous linewidth and line shape.

The optical line shape function is the Fourier transform of the normalized transition dipole correlation function. The echo decay measures directly the decay of the correlation function. Therefore, the optical line shape is the Fourier transform of the echo decay. For example, if the correlation function decays exponentially as  $as^{(a)} \Delta^2 \exp(-\gamma|t|)$  with  $\gamma/\Delta \gg 1$ , a Lorentzian will be observed with width

$$1/\pi T_2 = \Delta^2 \gamma^{-1}. \quad (1)$$

A photon echo decay experiment on the same system would yield<sup>2</sup>

$$I_{\text{echo}}(\tau) = I^0 \exp(-4\tau/T_2). \quad (2)$$

The echo exponential decay is the Fourier transform of the Lorentzian line. The rate of the decay gives the linewidth parameter  $T_2$ . For line shapes other than Lorentzian, the echo decay will be nonexponential. Therefore, photon echo decay measurements permit the homogeneous line shape and width to be extracted from an inhomogeneous optical line.

The stimulated photon echo is a three-pulse sequence illustrated in Fig. 1(b). While the photon echo examines the time evolution of the off-diagonal density matrix elements, the stimulated echo examines the diagonal ele-

ments. This pulse sequence was developed as a magnetic resonance experiment to study spectral diffusion.<sup>3</sup> In a given experiment, the interval  $\tau$  is fixed [Fig. 1(b)] and the time  $t$  is scanned. The stimulated echo decay is measured as a function of  $t$ .

In the absence of spectral diffusion, the stimulated photon echo decay (SE) will be determined by the excited state lifetime  $T_1$ , i.e.,

$$I_{SE}(t) = I^0 \exp(-2t/T_1). \quad (3)$$

If spectral diffusion occurs due to, for example, excited state transport between molecules having different positions in the inhomogeneous optical line, the stimulated echo decay will occur at a rate faster than that determined by the lifetime. The exact form of the decay depends on the nature of the spectral diffusion.<sup>3(b)</sup>

## B: Experimental procedures

The pentacene in naphthalene single crystals used in the experiments ( $\sim 10^{-9}$  to  $\sim 10^{-5}$  mole/mole) are grown by the Bridgeman technique using extensively zone-refined naphthalene and varying amounts of pentacene. The crystals are cleaved along the *ab* plane and have an average thickness of  $\sim 400 \mu\text{m}$ . Optically clear areas of the crystals are selected and mounted over  $300 \mu\text{m}$  or  $600 \mu\text{m}$  pinholes on the sample holder. In order to prevent sublimation of the naphthalene surfaces during the crystal cutting and mounting process, the crystals are cut in a cold room ( $\sim 2^\circ\text{C}$ ) and kept in a naphthalene-saturated environment whenever possible.

Crystal concentrations are calculated from the area of the pentacene absorption origin (602.6 nm) and the crystal thickness. Crystal absorption spectra are taken directly through the pinholes at pumped He temperatures immediately before or after the optical coherence experiments to ensure that the concentration of only that portion of the crystal actually used in the experiments is measured. Crystal thicknesses are measured both before and after the experiments. The two measurements agree. On strongly absorbing samples, the absorption of the pentacene first vibration (593.3 nm) is measured and used for the integrated absorption intensity.

In working with molecular systems, the fast decay times necessitate the use of high-energy, tunable picosecond light pulses. These pulses are provided by a synchronously pumped, mode-locked and cavity-dumped dye laser driven by the frequency-doubled output of a cw-pumped, acousto-optically mode-locked and *q*-switched Nd:YAG laser. This dye laser system has been described elsewhere.<sup>2(b)</sup> and provides a high repetition rate (0.4 kHz) stable source of 30 ps, 5  $\mu\text{J}$  pulses.

The dye laser output pulses pass through an attenuator and a beam splitter and are directed into a motorized optical delay line to form the desired pulse sequence (Fig. 2). The beams are recombined in the appropriate intensity ratio, made collinear and sent to the sample in the liquid He Dewar. The echo signal which emerges from the sample is crossed with a single, 80 ps IR pulse

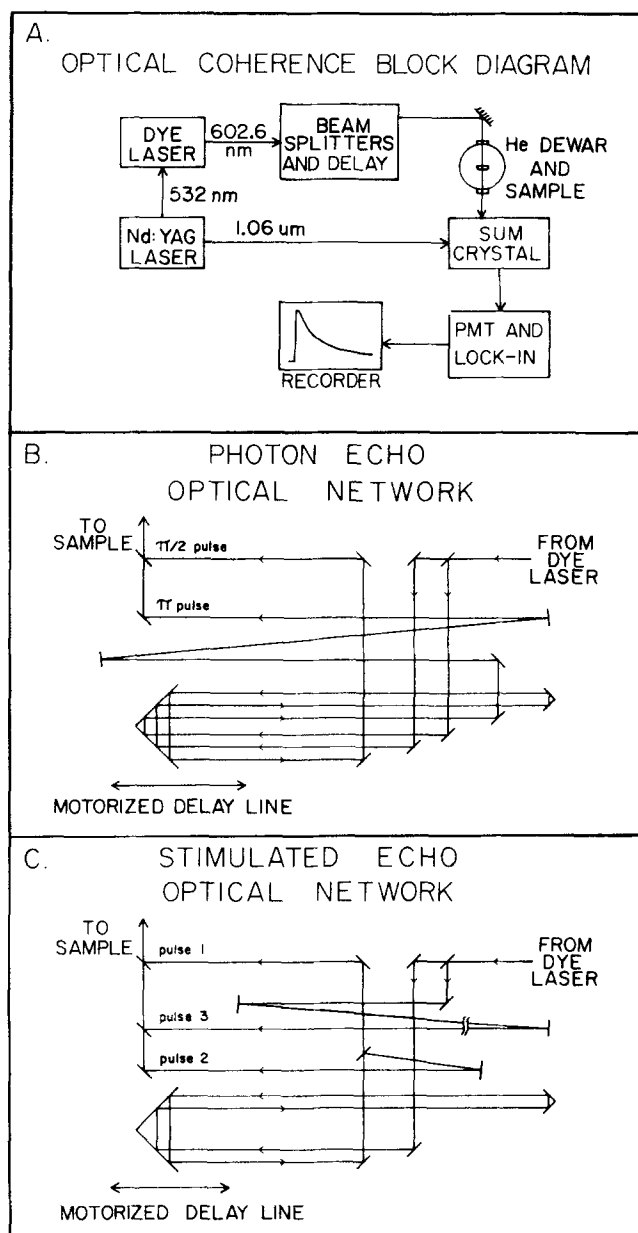


FIG. 2. (a) Block diagram of optical coherence experiments. (b) Arrangement of beam splitters and delay line to perform the photon echo decay experiment. (c) Arrangement of beam splitters and delay line to perform the stimulated echo decay experiment.

from the YAG laser in an angle-tuned, type II ammonium dihydrogen phosphate (ADP) sum generation crystal. The resulting sum pulse is wavelength and spatially filtered and detected by a cooled EMI 6256B phototube and lock-in amplifier. The signal provides the *y*-axis input to an XY recorder. The *x*-axis input is derived from a voltage proportional to the optical delay line position. This method of detection provides temporal, spatial, and frequency separation of the signal from the excitation pulses giving extremely good signal to noise (see Fig. 4).

Echo decay data is generated by running the motorized optical delay line. For the photon echo experiments, the  $\pi$  pulse traverses the round-trip delay line path once,

whereas the  $\pi/2$  pulse makes two round trips, thus ensuring that, for a given delay line travel, the  $\pi/2$  pulse receives *exactly* twice the temporal displacement of the  $\pi$  pulse [Fig. 2(b)]. For the stimulated echo experiments, one beam is double-passed down the delay line before being separated into the first two pulses of the sequence. The second beam is delayed a fixed amount external to the delay line to form the third pulse of the sequence [Fig. 2(c)].

In order to obtain accurate decays, both the position and spot size of each of the pulses must be kept constant at the sample as the delay line moves. The position is kept constant by very precise alignment of the delay line. The delay line alignment is checked during the experiments to ensure that the beams have not wandered. The spot sizes are kept constant by placing in each beam a lens exactly a focal length from the sample. The proper position is established by passing each beam through a pinhole at the sample location and observing that the transmitted intensity is constant over the entire travel of the delay line. This also serves as an additional check on the alignment of the delay line. Long term laser and alignment stability has been verified by examining the stability of the cross correlation of the IR detect pulse with an excitation pulse after each has traversed the experimental path.

Echo decay curves are obtained several times for each crystal to verify reproducibility. Often a set of echo decays is repeated after  $\sim 12$  h to ensure long term reproducibility of the results.

### III. RESULTS

#### A. Data analysis

First we will consider the photon echo data taken at 1.4 K on pentacene in naphthalene crystals in which the pentacene concentration is  $< 10^{-7}$  mole/mole. In this concentration range  $T_2$  is concentration independent. This was checked with crystals having concentrations as low as  $10^{-9}$  mole/mole. The photon echo decays are exponential. Figure 3 displays the results of  $T_2$  measurements on 28 different crystals in this very low concentration range. The figure also indicates, by the vertical line, the  $T_2$  which would result if  $T_1$ , the excited state lifetime, were the only optical dephasing process. This is based on a measured pentacene fluorescence lifetime of  $19.2 \pm 0.5$  ns in  $10^{-9}$  mole/mole samples. Hesselink and Wiersma<sup>9</sup> have reported this lifetime as  $19.5 \pm 1$  ns.

These results clearly demonstrate that  $T_2$  is not determined solely by  $T_1$  even at these very low concentrations and temperatures.  $T_2 = 30$  ns, while a  $T_2$  based solely on the lifetime would be 38.4 ns. In this situation  $T_2$  can be expressed as

$$\frac{1}{T_2} = \frac{1}{T_2^L} + \frac{1}{2T_1}, \quad (4)$$

where  $T_2^L$  is the contribution to  $T_2$  due to guest-lattice interactions. The mechanism is discussed in detail in Sec. III C. The total homogeneous linewidth,  $1/\pi T_2 = 10.6$  MHz. The contribution to the linewidth from  $T_1$  is 8.3 MHz, while the guest-lattice dephasing process

#### PENTACENE in NAPHTHALENE

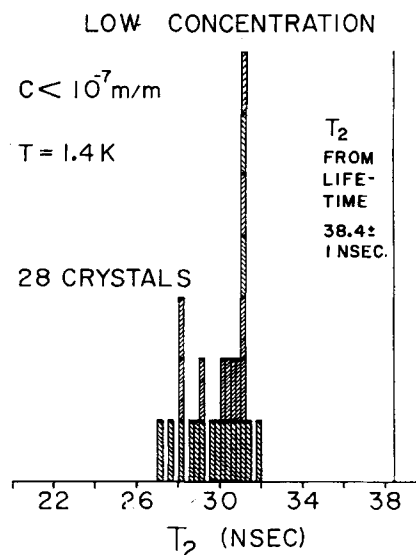


FIG. 3. Low concentration limit  $T_2$  measurements on 28 pentacene in naphthalene mixed crystals with  $< 10^{-7}$  mole/mole concentration. The line at the right is twice the  $S_1$  lifetime, i.e., the  $T_2$  value which would be observed if the lifetime were the only broadening mechanism. The average  $T_2$  value is 30 ns. This corresponds to a 10.6 MHz homogeneous linewidth, of which 8.3 MHz is due to the lifetime and 2.3 MHz arises from fluctuating guest-host interactions.

contributes 2.3 MHz, i.e.,  $T_2^L = 137$  ns. (For comparison, the Gaussian inhomogeneous linewidth is  $1 \text{ cm}^{-1} = 30 \text{ GHz}$ .)

As the concentration of pentacene is increased above  $10^{-7}$  mole/mole,  $T_2$  becomes progressively faster. Figure 4(a) displays the data for a  $6 \times 10^{-6}$  mole/mole crystal. The inset shows a log plot of the data. An exponential decay accurately fits the data. Figure 4(b) shows log plots of the data for crystals having several different concentrations. In all cases, the echo decays were exponential. Including the concentration dependence,  $T_2$  can be written as

$$\frac{1}{T_2} = \frac{1}{T_2^C} + \frac{1}{T_2^L} + \frac{1}{2T_1}, \quad (5)$$

where  $T_2^C$  accounts for the concentration-dependent line broadening. Since

$$\frac{1}{T_2^L} + \frac{1}{2T_1} = \frac{1}{30 \text{ ns}},$$

$T_2^C$  is given by

$$\frac{1}{T_2^C} = \frac{1}{T_2} - \frac{1}{30 \text{ ns}}. \quad (6)$$

Equation (6) permits the concentration-dependent optical dephasing to be examined.  $1/T_2^C$  is plotted versus concentration in Fig. 5. The data exhibits a linear dependence on concentration over two orders of magnitude.

As discussed in detail in Sec. I, there are two mechanisms which could produce concentration-dependent dephasing. The first involves excited state transport,

which will be accompanied by spectral diffusion and, therefore, optical dephasing. The second mechanism involves phonon-induced fluctuations in guest-guest intermolecular interactions (dipole-dipole interactions), producing fluctuations in the state energies and, therefore, optical dephasing.

The results of the stimulated photon echo experiments permit the energy transport mechanism to be ruled out. As discussed in Sec. II, the stimulated echo pulse sequence directly examines the rate of spectral diffusion. In the absence of spectral diffusion, the stimulated echo decay is determined solely by the excited state lifetime. In every sample examined over the entire concentration range, the stimulated photon echo experiments agreed accurately with the lifetime. Even in the highest concentration crystals in which the echo decay was  $\sim 5$  times faster than the lifetime, the stimulated echo gave the lifetime.

The stimulated echo results establish that the concentration-dependent dephasing mechanism involves phonon-induced excited state energy fluctuations. The important question (discussed in detail in Sec. I) then

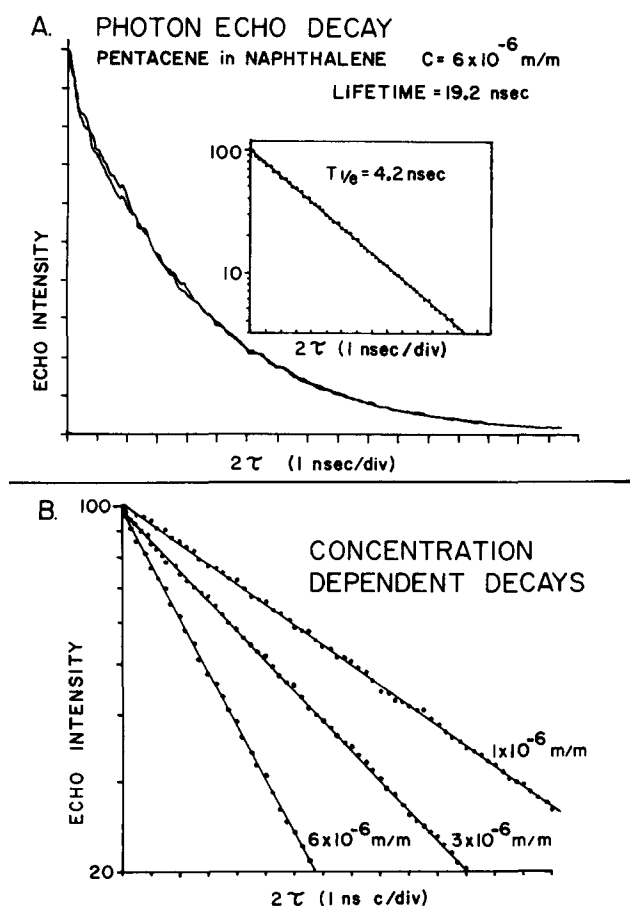


FIG. 4. Concentration dependent photon echo decays: pentacene in naphthalene. (a) Data from a  $6 \times 10^{-6}$  mole/mole sample. Two runs are shown to demonstrate the reproducibility of the data. Inset shows a log plot of the data. It is accurately exponential over many decay times. (b) Log plots of data from various concentration samples showing the change in decay rate with concentration. Each decay was run several times to verify reproducibility.

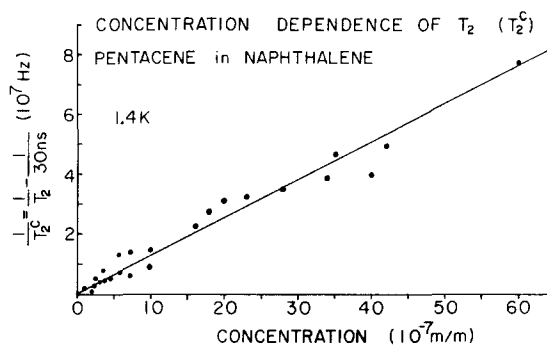


FIG. 5. Concentration dependent photon echo decay rate  $(T_2^C)^{-1}$  vs concentration. Decay rate (linewidth) is a linear function of concentration over two orders of magnitude.

arises as to whether the fluctuations are in the multiplet structure of an impurity band with delocalized eigenstates or whether the system is best described in terms of localized molecular eigenstates experiencing a fluctuating dipolar field.

The functional form of the photon echo decay argues strongly in favor of the isolated molecule description. The isolated molecule picture implies a system with two levels,  $S_0$  and  $S_1$ . Rapid, random fluctuations in the energy among a Gaussian distribution of energies produces an exponential decay of the correlation function and thus an exponential decay of the photon echo signal, i.e., a Lorentzian homogeneous line.<sup>1(a)</sup> (See Sec. II.) On the other hand, the impurity band<sup>4</sup> has a multiplet structure with oscillator strength distributed among the levels in a manner determined by the band structure. Although this is a complex problem, it is possible to say that in general a fluctuating multiplet structure will not give rise to a Lorentzian line,<sup>1</sup> i.e., the photon echo decay would not be exponential.

In Sec. IIIB we consider a detailed model for  $T_2^C$  based upon the fluctuating dipolar field picture. The model predicts the correct (linear) concentration dependence and is quantitatively consistent with the physical parameters associated with the pentacene in naphthalene system.

### B. $T_2^C$ calculation: Fluctuating dipolar field model

In this section an expression will be derived which relates  $T_2^C$  (concentration-dependent line broadening) to the physical properties of the pentacene in naphthalene mixed crystal system. The calculation is based on the model that each guest molecule is a two-level system ( $S_0$  and  $S_1$ ) which experiences a fluctuating dipolar field arising from dipole-dipole interactions with the other guest molecules in the sample. The pairwise interaction is

$$E = \frac{\mu_1 \cdot \mu_2}{r^3} - \frac{3(\mu_1 \cdot \mathbf{r})(\mu_2 \cdot \mathbf{r})}{r^5}, \quad (7)$$

where  $\mu = \langle S_0 | \mu | S_1 \rangle$  is the  $S_0$  to  $S_1$  electronic transition dipole and  $\mathbf{r}$  is a vector from molecule 1 to molecule 2. The fluctuations in  $E$  are produced by phonon-induced fluctuations in the separation  $r$  and in the relative orientation of  $\mu_1$  and  $\mu_2$ .

Pentacene enters the naphthalene lattice in a single well-defined site as evidenced by the single and relatively narrow ( $1 \text{ cm}^{-1}$ )  $S_0 \rightarrow S_1$  absorption origin. In the absence of other information, we will assume that all of the pentacene transition dipoles are parallel. This will not change the form of the results, but may make small changes in the quantitative calculations. (Detailed orientation measurements on pentacene in naphthalene using ESR are currently being performed in the Netherlands.<sup>10</sup>) For  $\mu_1$  and  $\mu_2$  parallel and equal,

$$E = (1 - 3 \cos^2 \theta) \mu^2 / r^3, \quad (8)$$

where  $\theta$  is the angle between  $\mathbf{r}$  and  $\boldsymbol{\mu}$ .

For a two-level system with exponential decay of the photon echo signal (Lorentzian homogeneous line),  $T_2$  is given by Eq. (1).  $\Delta$  characterizes the spread in frequencies "sampled" by the system. As mentioned above,  $\Delta$  will have contributions from both changes in  $r$  and in  $\theta$ . First, consider changes in  $r$ . The change in  $E$  with  $r$  for a pair of guest molecules separated by  $r$  is

$$\frac{dE}{dr} = (1 - 3 \cos^2 \theta) \left( -\frac{3\mu^2}{r^4} \right). \quad (9)$$

For the wide separations of guest molecules in the  $\sim 10^{-6}$  mole/mole samples studied, it is reasonable to assume that position fluctuations of two molecules are uncorrelated. Then the fluctuation in intermolecular separation is approximately the root-mean-square fluctuation in position of a single molecule. This parameter is labeled  $\delta_r$ . Thus, for a pair of molecules separated by  $r$ , the frequency fluctuation  $\Delta(r)$  is

$$\Delta(r) = \frac{1}{\hbar} |\Delta E| = \frac{\delta_r}{\hbar} \left| \frac{dE}{dr} \right| = \frac{3\delta_r}{\hbar} (1 - 3 \cos^2 \theta) \frac{\mu^2}{r^4}. \quad (10)$$

To obtain the total dephasing, the contributions from all guest molecules are needed, i.e.,

$$\frac{1}{\pi T_2^C} = \iint \frac{\Delta^2(r)}{\gamma} P(r, \theta) dr d\theta, \quad (11)$$

where  $P(r, \theta)$  is the probability of finding another guest at  $r, \theta$  given that molecule 1 is at the origin.

$$P(r, \theta) = \frac{2\pi\chi r^2}{a^3} \sin \theta, \quad (12)$$

where  $\chi$  is the concentration in molecules/unit cell and  $a^3$  is the volume of the unit cell.  $\gamma$ , the rate of frequency fluctuations, is taken to be independent of  $r$  since the fluctuations arise from the uncorrelated positional fluctuations of the individual guest molecules.

Substituting Eqs. (10) and (12) into (11) and performing the integral over  $\theta$  yields

$$\frac{1}{\pi T_2^C} = \frac{144\delta_r^2 \mu^4 \chi \pi}{5\hbar^2 a^3 \gamma} \int \frac{1}{r^6} dr. \quad (13)$$

The upper limit of the integral should be the radius of the crystal but can be extended to  $\infty$  without affecting the results. The lower limit should not be zero, but rather the smallest possible intermolecular spacing between two guest molecules. To be consistent with the isotropic model of the crystal implied by the form of the integrals, we choose the lower limit on  $r$  as  $a(3/4\pi)^{1/3}$ . This excludes one unit cell volume from the integral. Using

these limits of integration, the contribution to the concentration-dependent line broadening from fluctuations in the dipolar field due to guest-guest intermolecular separation variations is

$$\frac{1}{\pi T_2^C} = \frac{192\delta_r^2 \mu^4 \chi \pi^2}{25\hbar^2 a^3 \gamma} \left( \frac{4\pi}{3} \right)^{2/3}. \quad (14)$$

In an analogous treatment for the contribution to  $T_2$  from fluctuations in dipole directions, the variations in dipole directions are assumed to be uncorrelated. Then

$$E = (\mu^2 / r^3) (1 - 3 \cos \theta_1 \cos \theta_2), \quad (15)$$

which leads to

$$\Delta(\theta) = (3\delta_\theta \mu^2 / \hbar r^3) \cos \theta \sin \theta. \quad (16)$$

$\delta_\theta$  characterizes the fluctuation in dipole direction for a single guest molecule. The total dipole direction dependent dephasing is

$$\frac{1}{\pi T_2^C} = \iint \frac{\Delta^2(\theta)}{\gamma} P(r, \theta) dr d\theta, \quad (17)$$

and using the limits of integration discussed above yields

$$\frac{1}{\pi T_2^C} = \frac{32\pi^2 \chi \delta_\theta^2 \mu^4}{15\gamma a^3 \hbar^2}. \quad (18)$$

Then the total concentration-dependent dephasing is the sum of Eqs. (14) and (18), i.e.,

$$\frac{1}{\pi T_2^C} = \frac{1}{\pi T_2^C} + \frac{1}{\pi T_2^C}. \quad (19)$$

The results of the model calculation, Eq. (19), predict that the concentration-dependent contribution to the homogeneous linewidth will increase linearly with concentration. This is precisely what is observed experimentally (Fig. 5) over the two orders of magnitude concentration range studied.

The angular fluctuations in the dipole-dipole interaction will be caused primarily by optical phonons while the positional fluctuations will arise from acoustic phonons. At the experimental temperature of 1.4 K ( $kT \approx 1 \text{ cm}^{-1}$ ), optical phonons ( $E > 50 \text{ cm}^{-1}$ ) will be frozen out. Wiersma has reported the observation of a  $16.5 \text{ cm}^{-1}$  pseudolocal phonon in the pentacene in naphthalene system.<sup>11</sup> This phonon will also be unimportant at 1.4 K.

In light of these considerations it is plausible to postulate that low frequency acoustic phonons, which are highly populated at 1.4 K, are solely responsible for the observed concentration-dependent dephasing. In this case, Eq. (14) should describe the system. We can test the acoustic phonon postulate quantitatively by substituting known values into Eq. (14). The pentacene transition dipole moment  $\mu = 1 \text{ D} = 10^{-18} \text{ esu cm}$ .<sup>12</sup> For  $a$ , we will use the average naphthalene lattice constant which gives  $a = 7 \times 10^{-8} \text{ cm}$ .  $\delta_r$  is reported for naphthalene at 1.4 K, i.e.,  $\delta_r = 0.05 \times 10^{-8} \text{ cm}$ .<sup>13</sup> In the absence of other information, this should be a reasonable number to use here. For a given concentration  $\chi$ ,  $1/\pi T_2^C$  is given in Fig. 5. Therefore the only unknown parameter is  $\gamma$ , the rate of frequency fluctuations. For  $\chi = 10^{-6}$ ,  $1/\pi T_2^C = 3.8 \times 10^6 \text{ Hz}$ , and substituting into Eq. (14) yields

$$\gamma = 2.2 \times 10^{10} \text{ Hz}. \quad (20)$$

This number should be compared to the frequency of a phonon with energy  $kT$ , i. e.,  $2.9 \times 10^{10}$  Hz, and to the 1.4 K thermal average acoustic phonon frequency,  $\sim 6 \times 10^9$  Hz. Thus, the rate of frequency fluctuations,  $\gamma$ , is entirely consistent with the frequencies associated with the thermally populated acoustic phonons. This strongly supports the postulate that acoustic-phonon-induced fluctuations in position produce the fluctuating dipolar interactions responsible for the concentration-dependent line broadening in this system. In addition, the correct prediction of the observed linear concentration dependence also provides strong support for the basic model.

### C. $T_2^L$ calculation: Fluctuating crystal shift model

Below  $10^{-7}$  mole/mole, the pentacene homogeneous linewidth becomes independent of concentration. In this section we will present a model which accounts for the nonlifetime component of the linewidth. The model was described in Sec. I in detail. Briefly, phonon-induced fluctuations in nearest neighbor guest-host separations produce fluctuations in the  $S_0-S_1$  energy difference through the distance dependent crystal shift,  $D$ .

Consider a guest molecule located between two host molecules, 1 and 2. Assuming the guest interaction with each host is a Lennard-Jones potential, then the ground state guest-lattice interaction energy is

$$E^{S_0}(r_1, r_2) = \left( \frac{A_0}{r_1^{12}} - \frac{B_0}{r_1^6} \right) + \left( \frac{A_0}{r_2^{12}} - \frac{B_0}{r_2^6} \right). \quad (21)$$

$r_1$  and  $r_2$  are the separations between the guest molecule located at the origin and molecules 1 and 2, respectively.  $A$  and  $B$  are constants determining the well depth,  $-B^2/4A$ , and the position of the well minimum,

$$r_0 = (2A/B)^{1/6}. \quad (22)$$

In the excited state, the potential surface is different. The repulsive constant  $A$ , the attractive constant  $B$ , and the equilibrium separation  $r_0$  change. The excited state is stabilized relative to the ground state. Here we will assume that  $r_0$  is the same in  $S_0$  and  $S_1$ . The crystal shift is accounted for by changes in  $A$  and  $B$  only. For pentacene in naphthalene this is not an unreasonable assumption since the origin Stoke's shift is very small and the origin has by far the greatest oscillator strength. Then the excited state guest-lattice interaction energy is

$$E^{S_1}(r_1, r_2) = \left( \frac{A_1}{r_1^{12}} - \frac{B_1}{r_1^6} \right) + \left( \frac{A_1}{r_2^{12}} - \frac{B_1}{r_2^6} \right). \quad (23)$$

The difference in the ground and excited state interaction energies is

$$\begin{aligned} \Delta E(r_1, r_2) &= E^{S_1}(r_1, r_2) - E^{S_0}(r_1, r_2) \\ &= (A_1 - A_0) \left( \frac{1}{r_1^{12}} + \frac{1}{r_2^{12}} \right) - (B_1 - B_0) \left( \frac{1}{r_1^6} + \frac{1}{r_2^6} \right). \end{aligned} \quad (24)$$

Changes in  $\Delta E(r_1, r_2)$  with  $r_1$  and  $r_2$  are responsible for the optical dephasing. Note that in  $S_0$  and  $S_1$  the equilibrium separations are the same, so

$$r_0^6 = \frac{2A_0}{B_0} = \frac{2A_1}{B_1} \quad (25)$$

and, consequently,

$$(A_1 - A_0) = \frac{1}{2} r_0^6 (B_1 - B_0). \quad (26)$$

To obtain the change in  $\Delta E(r_1, r_2)$ , we note that for small shifts in  $r_1$  and  $r_2$  from equilibrium, the two potential wells look like harmonic oscillator potentials. Hence, a shift of  $\delta$  in  $r$  gives a transition energy change of  $\frac{1}{2} K \delta^2$  where

$$K \equiv \left. \frac{\partial^2 \Delta E}{\partial r^2} \right|_{r_0}.$$

The total energy change for shifts of  $\delta_1$  in  $r_1$  and  $\delta_2$  in  $r_2$  is

$$\Delta D = \frac{1}{2} \delta_1^2 \left. \frac{\partial^2 \Delta E(r_1, r_2)}{\partial r_1^2} \right|_{r_0} + \frac{1}{2} \delta_2^2 \left. \frac{\partial^2 \Delta E(r_1, r_2)}{\partial r_2^2} \right|_{r_0}. \quad (27)$$

Performing the operations and using Eq. (26) gives

$$\Delta D = \frac{18(B_1 - B_0)}{r_0^6} \left( \frac{\delta_1^2 + \delta_2^2}{r_0^2} \right). \quad (28)$$

Substituting the root-mean-square fluctuation in nearest neighbor separation  $\delta_n$  for  $\delta_1$  and  $\delta_2$  and dividing by  $\hbar$  gives the frequency fluctuation parameter

$$\Delta = \frac{36}{\hbar} \frac{(B_1 - B_0)}{r_0^6} \frac{\delta_n^2}{r_0^2}. \quad (29)$$

In Eq. (29), the quantity  $(B_1 - B_0)/r_0^6$  can be evaluated from the crystal shift  $D$ .

$$D = \Delta E(r_0, r_0) = 2 \left( \frac{A_1 - A_0}{r_0^{12}} - \frac{B_1 - B_0}{r_0^6} \right). \quad (30)$$

$D$  is experimentally determined to be  $1400 \text{ cm}^{-1}$ .<sup>14</sup> Using this and Eq. (26) gives

$$\left| \frac{B_1 - B_0}{r_0^6} \right| = 1400 \text{ cm}^{-1}$$

and therefore Eq. (29) becomes

$$\Delta = 5 \times 10^4 (2\pi) c (\delta_n^2 / r_0^2). \quad (31)$$

The contribution from the fluctuation in the crystal shift to the homogeneous line is

$$1/\pi T_2^L = \Delta^2 \gamma^{-1}, \quad (32)$$

where  $\Delta$  is given by Eq. (29) in general and Eq. (31) for pentacene in naphthalene. From Fig. 3, we know that  $1/\pi T_2^L = 2 \times 10^6$  Hz. Therefore,

$$\gamma = \Delta^2 / (2 \times 10^6).$$

Using Eq. (31) with  $r_0 = 7 \text{ \AA}$  and a reasonable estimate of  $\delta_n$  as  $0.001 \text{ \AA}$  gives

$$\gamma = 1.9 \times 10^{10} \text{ Hz}. \quad (33)$$

As in Sec. IIIB, the  $\gamma$  obtained corresponds to the frequencies of acoustic phonons populated at the experimental temperature of 1.4 K. The fact that the  $\gamma$ 's given in Eqs. (20) and (33) are virtually identical is probably a fortuitous coincidence. However, the same phonon population plays the central role in both the concentration-dependent and concentration-independent dephasing processes. In the dipolar field model, we were concerned with guest-guest fluctuations in separation. Since the positions were taken to be uncorrelated, the net displacement of a single guest was considered. This is a much larger displacement than the nearest neighbor

changes in separation, but one might expect the time scale of the fluctuations to be similar.

#### IV. CONCLUDING REMARKS

The experimental data and theoretical models provide an accurate description of the nature of a guest molecule in a very dilute mixed crystal. At the lowest concentrations, dynamical guest-lattice interactions contribute to the homogeneous linewidth. As the concentration is increased, guest-guest interactions become important. Above  $10^{-6}$  mole/mole concentration, the dynamics of guest-guest interactions dominate the homogeneous linewidth in the pentacene in naphthalene system.

At the highest concentrations investigated in this study ( $6 \times 10^{-6}$  mole/mole), an excited state of the guest system is well described as a localized guest molecular excitation experiencing a fluctuating dipolar field arising from the sea of other guest molecules. Following Klafter and Jortner's work on impurity bands for triplet excited states of mixed molecular crystals,<sup>4</sup> we obtained an estimate of the concentration range in which the pentacene in naphthalene Anderson transition should occur. This estimate was made using a dipole-dipole interaction and finding the median intermolecular guest-guest interaction as a function of concentration. If the criterion for the transition is comparison of  $\langle J \rangle$  to the total inhomogeneous linewidth,<sup>15</sup> the low end at the concentration range is  $4 \times 10^{-4}$  mole/mole. This is nearly two orders of magnitude greater concentration than the samples examined in this study. Pentacene in naphthalene reaches its maximum solubility at  $< 10^{-5}$  mole/mole. However, we are currently examining other mixed systems with substantially greater guest solubilities. These will permit examination of the concentration range containing the isolated molecule-impurity band transition.

#### ACKNOWLEDGMENT

We would like to acknowledge the support of the National Science Foundation, Division of Materials Research Grant No. DMR 76-22019.

<sup>1</sup>(a) R. Kubo, *Adv. Chem. Phys.* **15**, 101 (1969); (b) Y. Toyozawa, *Prog. Theor. Phys.* **20**, 53 (1958); H. Sumi and

Y. Toyozawa, *J. Phys. Soc. Jpn.* **31**, 342 (1971); D. M. Burland, U. Konzelmann, R. M. Macfarlane, *J. Chem. Phys.* **67**, 1926 (1977); D. M. Burland, D. E. Cooper, M. D. Fayer, and C. R. Gochanour, *Chem. Phys. Lett.* **52**, 279 (1977).

<sup>2</sup>(a) I. D. Abella, N. A. Kurnit, and S. R. Hartmann, *Phys. Rev.* **141**, 391 (1966); R. G. Brewer, in *Frontiers in Laser Spectroscopy, Les Houches*, edited by R. Balian *et al.* (North-Holland, New York, 1977), Vol. 1; W. H. Hesselink and D. A. Wiersma, *Chem. Phys. Lett.* **56**, 227 (1978); T. C. Farrar and E. D. Becker, *Pulse and Fourier Transform NMR* (Academic, New York, 1971); E. L. Hahn, *Phys. Rev.* **80**, 580 (1950); J. S. Waugh, C. H. Wang, L. M. Huber, and R. L. Vold, *J. Chem. Phys.* **48**, 662 (1968); (b) D. E. Cooper, R. D. Wieting, R. W. Olson, and M. D. Fayer, *Chem. Phys. Lett.* **67**, 41 (1979).

<sup>3</sup>(a) W. B. Mims, *Electron Paramagnetic Resonance*, edited by S. Geschwind (Plenum, New York, 1972), Chap. 4; (b) W. B. Mims, *Phys. Rev.* **168**, 370 (1968); P. Hu and S. R. Hartmann, *Phys. Rev. B* **9**, 1 (1974); J. P. Klauder and P. W. Anderson, *Phys. Rev.* **125**, 912 (1962).

<sup>4</sup>N. F. Mott and E. A. Davis, *Electric Processes in Non-crystalline Materials* (Oxford University, London, 1971); J. Klafter and J. Jortner, *J. Chem. Phys.* **71**, 1961 (1979).

<sup>5</sup>P. W. Anderson, *Phys. Rev.* **109**, 1492 (1958).

<sup>6</sup>C. R. Gochanour, Hans C. Andersen, and M. D. Fayer, *J. Chem. Phys.* **70**, 4254 (1979); H. Port, D. Vogel, and H. C. Wolf, *Chem. Phys. Lett.* **34**, 23 (1975); R. Kopelman, E. M. Monberg, F. W. Ochs, and P. N. Prasad, *J. Chem. Phys.* **62**, 292 (1975).

<sup>7</sup>B. Y. Okamoto and H. G. Drickamer, *J. Chem. Phys.* **61**, 2870 (1974).

<sup>8</sup>A. S. Davydov, *Theory of Molecular Excitons* (Plenum, New York, 1971).

<sup>9</sup>W. H. Hesselink and D. A. Wiersma (private communication; to be published).

<sup>10</sup>J. Schmidt, work in progress (1979).

<sup>11</sup>D. A. Wiersma, *Adv. Chem. Phys.* in press (1979).

<sup>12</sup>H. deVries, P. DeBree, and D. A. Wiersma, *Chem. Phys. Lett.* **52**, 399 (1977); H. deVries and D. A. Wiersma, *J. Chem. Phys.* **69**, 879 (1978); T. E. Orlowski, K. E. Jones, and A. H. Zewail, *Chem. Phys. Lett.* **54**, 197 (1978); T. E. Orlowski and A. H. Zewail, *J. Chem. Phys.* **70**, 1390 (1979).

<sup>13</sup>D. W. J. Cruickshank, *Acta Crystallogr.* **9**, 1005 (1956).

<sup>14</sup>S. Okajima and E. C. Lim, *Chem. Phys. Lett.* **37**, 403 (1976).

<sup>15</sup>Kopelman has argued that comparison of the inhomogeneous linewidth to  $\langle J \rangle$  is not the appropriate criterion for the Anderson transition. He suggests a more spatially local measure of the potential fluctuations may be in order. This could lower the transition concentration. R. Kopelman (private communication).