

Inhomogeneous broadening of electronic transitions of chromophores in crystals and glasses: Analysis of hole burning and fluorescence line narrowing experiments

H. W. H. Lee, C. A. Walsh, and M.D. Fayer

Department of Chemistry, Stanford University, Stanford, California 94305

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A variety of nonphotochemical hole burning experiments are performed on the system pentacene (PC) in benzoic acid (BZA) crystals. These experiments and previously reported fluorescence line narrowing experiments are used to probe the nature of the inhomogeneous broadening of electronic transitions of chromophores in crystals and glasses. A microscopic model is presented which explains detailed results from both types of experiments. Two fundamental assumptions are made in formulating the model. First, there is a large degree of accidental degeneracy in the absolute energy distributions of the chromophores; i.e., molecules in different environments can have the same absolute energy. Second, this degeneracy is lifted when the electronic state is changed. Narrow band excitation of PC causes a well-defined change in the PC's local environment, producing a narrow spectral hole in the inhomogeneously broadened PC absorption origin and an antihole which is spectrally well-separated from the PC origin. The microscopic model is successful in explaining experimental results on correlations between hole widths and antihole widths, hole positions and antihole positions, and in explaining fluorescence line narrowing experiments on the correlation between the frequencies of resonant and nonresonant fluorescence and the broadening of nonresonant fluorescence. The result is a microscopic picture which demonstrates that narrow band excitation of an inhomogeneously broadened electronic transition involves molecules with a very wide distribution of absolute energies.

I. INTRODUCTION

In this paper, detailed experiments and a microscopic model are presented which elucidate the nature of inhomogeneous broadening of optical absorption spectra in crystals and glasses. The model and its associated formalism permit explication of a diverse set of experimental observables from fluorescence line narrowing¹⁻⁹ (FLN) experiments, photochemical hole burning¹⁰⁻¹² (PHB), and nonphotochemical hole burning^{2,13,14} (NPHB) experiments.

In a perfect mixed crystal, guest molecules occupying sites of a particular symmetry sit in identical environments. Since the position of the optical absorption zero phonon line (ZPL) is determined by the total crystal field of the host at the impurity site, all such guest molecules have the same transition energy. If such a situation occurred in nature, one would observe a ZPL in absorption that is broadened only by homogeneous contributions.

However, all real crystals possess imperfections such as strains, point defects, and dislocations which add inhomogeneous contributions to the broadening of the ZPL. For a chromophore in a glass, the inherent structural disorder of the glass results in extensive inhomogeneous broadening of the guest chromophore absorption spectrum. Although a common feature of virtually all spectra, inhomogeneous broadening is not well understood, qualitatively or quantitatively. Its study is both interesting and important due to the ubiquitous nature of inhomogeneous broadening in a wide variety of problems, e.g., impurity bands, time dependent fluorescence line narrowing experiments, and photon echo experiments. Inhomogeneously broadened lines are observed in a wide variety of systems ranging from electron spin resonance lines, e.g., Fe^{2+} in MgO ,¹⁵ to optical vibronic

lines, e.g., pentacene in *p*-terphenyl.¹⁶ Understanding inhomogeneous broadening is essential to the extraction of a variety of physical information from spectroscopic observations on inhomogeneously broadened systems. Sources of inhomogeneities have been studied both theoretically¹⁷ and experimentally.¹⁸

Previously it has been recognized that inhomogeneous broadening plays a central role in fluorescence line narrowing experiments² and hole burning experiments^{2,12} and that information about inhomogeneous broadening can be obtained from such experiments.^{3,7,19} The relevant experiments all have a common feature. A narrow band laser is used to couple two states, and a narrow spectral feature results. A secondary spectral feature is observed which does not involve the identical two initial states. This second feature is very broad. In experiments by Flach *et al.*¹⁹ the system $\text{LaF}_3:\text{Pr}^{3+}$ was examined. The ground state 3H_4 was coupled to the 3P_0 state by a narrow band laser. Resonant fluorescence was sharp while fluorescence from the 3P_0 excited state to a third intermediate level 3H_6 gave broad fluorescence. Griesser and Wild⁷ examined 1,3-dichloroazulene in a 3-methylpentane glass. The ground state S_0 was coupled by the laser to the S_2 state, which gave rise to narrow resonant fluorescence, but broad fluorescence from S_2 to S_1 . In a somewhat different, but analogous experiment, Al'shits *et al.*³ excited S_0 to S_1 and saw narrow resonant fluorescence from the system 1,2-benzpyrene in butyl bromide. However, phosphorescence from T_1 following intersystem crossing from S_1 and broad. Again in an analogous experiment, Voelker and Macfarlane¹² produced a narrow photochemical hole in free-base porphyrin in *n*-octane crystals, but the spectra of the resulting photoproduct antiholes were broad.

Finally, Olson *et al.* examined nonphotochemical hole burning in the mixed crystal system pentacene in benzoic acid.^{14(a)} Again a narrow hole gave rise to a broad antihole.

Yen and Selzer⁶ have put forward a model to explain the fluorescence line narrowing experiments. This model considers the distributions of absolute energies in the ground state and in the excited states. A narrow range of energies in the ground state is coupled to a narrow range of energies in an excited state by the laser. Excitation of this narrow band of absolute energies gives rise to the spectrally narrow resonant fluorescence. The spread of absolute energies in the ground and excited state inhomogeneous distributions involved in the optical excitation is determined by the laser bandwidth or homogeneous linewidth, whichever is greater. At each absolute energy there is a set of atoms or molecules which are accidentally degenerate, i.e., there are a variety of distinct physical environments which give rise to the identical energy. When this set is excited by the laser, *the accidental degeneracy is preserved* in the resonantly coupled excited state. However, when fluorescent relaxation to a third level occurs, the accidental degeneracy of the set of fluorescing molecules is broken. The distinct physical environments now manifest themselves as a broad spread of absolute energies. Thus the resonant fluorescence occurs from a narrow spread of absolute energies to a broad spread of absolute energies in the final state. This results in broad nonresonant fluorescence.

The difficulty with this model is that it is unnecessarily restrictive in its assumptions. To apply this model to a variety of systems and a variety of techniques, one must always assume that a transition between the first two levels, which are coupled by the laser, never breaks the accidental degeneracy of the set of molecules involved, but a transition to a third state always breaks the accidental degeneracy. The mathematical model presented in Sec. II demonstrates that it is unnecessary to assume preservation of accidental degeneracy between the first two levels to explain a narrow resonant spectral feature and a broad nonresonant spectral feature.

Like the Yen and Selzer model, the model presented here considers the distribution of absolute energies in each state. The ground state is described as a Gaussian distribution of absolute energies. Following Yen and Selzer, we consider each absolute energy in a distribution to be composed of a set of accidentally degenerate molecules. In the excited state (which will be coupled to the ground state by the narrow band laser) there is also a Gaussian distribution of absolute energies with each energy accidentally degenerate.

The major tenet of this model, which is the exact opposite of the Yen and Selzer assumption, is that *any state change breaks the accidental degeneracies* associated with the absolute energies of the initial state. *The set of molecules which has a single absolute energy in one state has a broad range of absolute energies in a second state.* For mathematical simplicity in the next section, we take the broad distribution to be the entire Gaussian distribution of energies of the second state. (This will be shown to be consistent with experiment, but the exact breadth of the distribution arising from a set of accidentally degenerate molecules is unimportant, as

long as the accidental degeneracy is broken.)

Consider a narrow band laser coupling the ground state to the second state. Take the laser to be tuned to the red side of the inhomogeneously broadened absorption spectrum at frequency Ω . Now consider a single absolute ground state energy E_g somewhere to the high energy side (blue) of the distribution. The accidentally degenerate set of ground state molecules with energy E_g has energies across the entire range of absolute excited state energies. Therefore, there will certainly be some molecules in the set with excited state energy E_e such that $(E_e - E_g)/\hbar$ equals the laser frequency Ω . This subset of molecules contributes to the narrow band transition. This will be true for any choice of the ground state absolute energy.

In contrast to the Yen and Selzer model, the net result is that a wide spread of energies in the ground state and a wide spread of energies in the excited state contribute to the transition at Ω . At each absolute ground state energy, *the laser selects* from the set of accidentally degenerate molecules the subset with the appropriate excited state energy. The laser-selected distribution of absolute ground state energies involved in the transition at Ω is different from the full ground state distribution. It is narrower, and it is shifted to the blue side of the full ground state absolute energy distribution for a laser frequency on the red side of the inhomogeneous absorption line. The laser-selected distribution of absolute excited state energies is shifted to the red rather than to the blue.

The model specifies that all states have broad distributions of absolute energies involved in the transitions. The initial two states coupled by the narrow band laser have a laser-selected subset of molecules with a single transition energy, giving rise to narrow resonant fluorescence or narrow holes. Spectroscopic observables involving other states or other mechanical situations (antiholes) do not have the laser selection, and thus the broad distributions of absolute energies manifest themselves as broad spectral features.

In the following sections we give a simple mathematical formulation of this model and compare to experiments. The weight of the experimental evidence confirms this basic model.

II. MATHEMATICAL FORMULATIONS

The observables in the experiments to be discussed in this paper are the distributions of transition energies of guest chromophores in crystals and glasses. To obtain a mathematical model which describes the experimental results, it is necessary to consider the distribution of absolute ground state energies and absolute excited state energies of the chromophores. In the following discussion, $E_g = \hbar\omega_g$ and $E_e = \hbar\omega_e$ will denote, respectively, the absolute ground state energy of a guest molecule. All transition frequencies will be written as Ω . In the NPHB experiments, the photoproduct, or antihole will have its own set of absolute ground and excited state energies and transition frequencies, which will be represented by the analogous variables with a bar over the top: $\bar{E}_g = \hbar\bar{\omega}_g$, $\bar{E}_e = \hbar\bar{\omega}_e$, and $\bar{\Omega}$.

The absolute ground state energy of a molecule is determined by many different parameters describing intermolecular interactions and various fields present in the solid.²⁰

Therefore, it is reasonable to describe the distribution of ground state energies for a large number of molecules with a Gaussian distribution centered at some $\omega_g^0: G(\omega_g) = g \{ \exp [a^2(\omega_g - \omega_g^0)^2] \}$. The coefficient a is related to the width δ_G (FWHM) of the Gaussian by $a = 2\sqrt{\ln 2}/\delta_G$. The number of molecules with the same ground state energy $E_g = \hbar\omega_g$ is $G(\omega_g)$.

As was discussed in the Introduction, the degeneracy at each E_g is accidental. Molecules belonging to the set with energy E_g have many different local environments, but the interplay of interactions results in a single energy. When the electronic state is changed from the ground state to an excited state, the accidental degeneracy can be broken. The first assumption to be made in this model is that a set of molecules which has a single ground state frequency ω_g will have a broad distribution of excited state frequencies given by $f(\omega_g, \omega_e)$. The total distribution of excited energies will be the sum of all these distributions:

$$F(\omega_e) = \int_{-\infty}^{+\infty} f(\omega_g, \omega_e) d\omega_g. \quad (1)$$

For mathematical simplicity, it will be assumed that each set of molecules degenerate in the ground state will have a Gaussian distribution of excited state energies spanning all of $F(\omega_e)$, i.e., it will be assumed that molecules having lower or higher energy than average in the ground state will not have this relationship in the excited state, so that each $f(\omega_g, \omega_e)$ is centered at the same frequency ω_e^0 . It must be emphasized that the specific assumptions that each $f(\omega_g, \omega_e)$ is a Gaussian of the same width as $F(\omega_e)$ and is centered at the same frequency as $F(\omega_e)$ are not necessary for the success of this model. The only essential assumption is that each set of degenerate molecules in the ground state will have a broad distribution of excited state energies, with width on the same order as the width of $F(\omega_e)$. The particular choice we have made simplifies the mathematics, reduces the number of parameters in the model, and is consistent with experiment.

Since the total number of molecules must be conserved, for a particular ω_g the area under each Gaussian $f(\omega_g, \omega_e)$ must be equal to $G(\omega_g)$. $f(\omega_g, \omega_e)$ can be written

$$f(\omega_g, \omega_e) = B(\omega_g) \exp [- b^2(\omega_e - \omega_e^0)^2]. \quad (2)$$

Therefore,

$$\int_{-\infty}^{+\infty} f(\omega_g, \omega_e) d\omega_e = B(\omega_g) \times \int_{-\infty}^{+\infty} \exp [- b^2(\omega_e - \omega_e^0)^2] d\omega_e = G(\omega_g), \quad (3)$$

so that $B(\omega_g) = G(\omega_g) b / \sqrt{\pi}$. The parameter b is related to the width of the excited state absolute energy distribution δ_F by $b = 2\sqrt{\ln 2}/\delta_F$. Summarizing, the breaking of accidental degeneracy in going from the ground state to the excited state is described by

$$G(\omega_g) \rightarrow [G(\omega_g) b / \sqrt{\pi}] \exp [- b^2(\omega_e - \omega_e^0)^2] = N(\omega_g, \omega_e). \quad (4)$$

$N(\omega_g, \omega_e)$ is the number of molecules with ground state energy $\hbar\omega_g$ and excited state energy $\hbar\omega_e$.

The observables in all experiments involve the transition energies between states, not the absolute energies of

molecules in a given state. In the following discussion, Ω will denote transition frequencies, whereas ω will represent absolute frequencies. Also, the widths of transition energy distributions will be represented as Δ , while widths of absolute energy distributions will be written δ .

Molecules which absorb with a transition frequency Ω must necessarily have $\omega_e - \omega_g = \Omega$. As described in the Introduction and by Eq. (4), a wide spread of energies in the ground state and a wide spread of energies in the excited state will contribute to the transition at Ω , since our model says that for each set of molecules with ground state energy $\hbar\omega_g$, there will be $N(\omega_g, \omega_e)$ of these molecules that have excited state energy $\hbar\omega_e$ such that $\omega_e - \omega_g = \Omega$. Therefore,

$$N(\omega_g, \omega_e) = N(\omega_g, \Omega + \omega_g) = [G(\omega_g) b / \sqrt{\pi}] \exp [- b^2(\Omega + \omega_g - \omega_e^0)^2]. \quad (5)$$

The absorption spectrum of the entire inhomogeneously broadened line $A(\Omega)$ will involve all molecules that absorb at Ω , so that Eq. (5) must be integrated over ω_g to obtain the expression for $A(\Omega)$:

$$A(\Omega) = \int_{-\infty}^{+\infty} N(\omega_g, \Omega + \omega_g) d\omega_g = (b / \sqrt{\pi}) \int_{-\infty}^{+\infty} G(\omega_g) \times \exp [- b^2(\Omega + \omega_g - \omega_e^0)^2] d\omega_g. \quad (6)$$

Carrying out the integration gives

$$A(\Omega) = [gb / (a^2 + b^2)^{1/2}] \exp \{ - [a^2 b^2 / (a^2 + b^2)] \times [\Omega - (\omega_e^0 - \omega_g^0)]^2 \}. \quad (7)$$

The absorption spectrum is described by a Gaussian centered at $\Omega^0 = \omega_e^0 - \omega_g^0$. As expected, Ω^0 is simply the difference between the center frequencies of the excited state and ground state distributions. The width Δ_A (FWHM) of the absorption Gaussian can be related to the width δ_F of the excited state Gaussian and the width δ_G of the ground state Gaussian:

$$\Delta_A = (\delta_G^2 + \delta_F^2)^{1/2}. \quad (8)$$

Now suppose that a laser with a negligible bandwidth is tuned to a frequency Ω which is on the red side of the absorption curve with $\Omega = \Omega^0 - R$ (see Fig. 1). (Note: for excitation on the blue side of the absorption band, R is a negative number.) The distribution of absolute ground state energies contributing to the transition at Ω is not the same as the entire distribution of absolute ground state energies $G(\omega_g)$, and will be called the laser-selected distribution of ground state energies, denoted by $G(\omega_g, \Omega^0 - R)$. As discussed in the Introduction, $G(\omega_g, \Omega^0 - R)$ will be narrower than $G(\omega_g)$ and will be shifted to the blue of $G(\omega_g)$ if the excitation is to the red of Ω^0 . Similarly, there will be a laser-selected distribution of excited state energies represented as $F(\omega_e, \Omega^0 - R)$. $F(\omega_e, \Omega^0 - R)$ will be narrower than $F(\omega_e)$ shifted to the red of $F(\omega_e)$.

Using the mathematical formulation developed thus far, analytical expressions for the laser-selected distributions $G(\omega_g, \Omega^0 - R)$ and $F(\omega_e, \Omega^0 - R)$ can be obtained. Since $\omega_e = \Omega^0 - R + \omega_g$, then

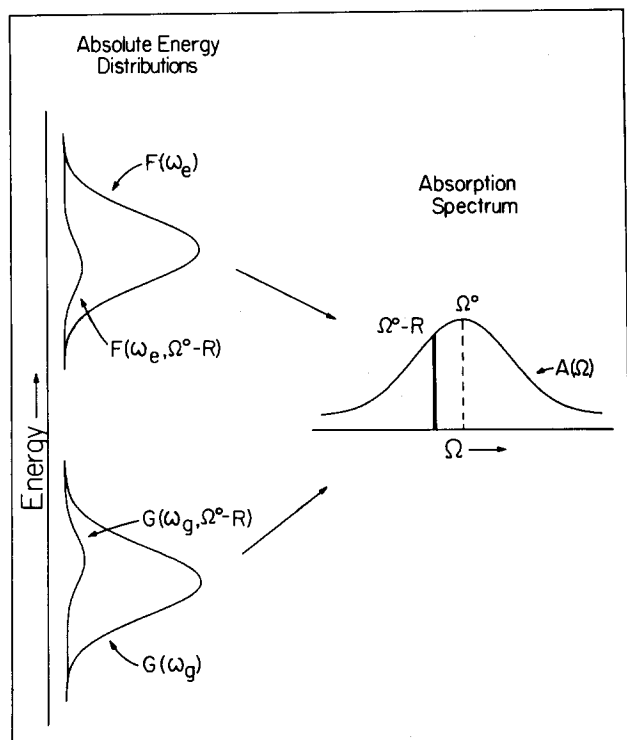


FIG. 1. The absolute ground state energy distribution $G(\omega_g)$ centered at ω_g^0 and the absolute excited state energy distribution $F(\omega_e)$ centered at ω_e^0 for an inhomogeneously broadened electronic transition are shown on the left. Due to accidental degeneracy, molecules from many different environments can have the same absolute energy in a given state. $G(\omega_g)$ and $F(\omega_e)$ are convolved to form the absorption spectrum $A(\Omega)$ centered at Ω^0 for the ground state-excited state transitions $|g\rangle \rightarrow |e\rangle$. Narrow band excitation of the absorption spectrum at $\Omega^0 - R$ (represented by the dark line) creates the laser-selected distribution of absolute ground and excited state energies, $G(\omega_g, \Omega^0 - R)$ and $F(\omega_e, \Omega^0 - R)$. Note that monochromatic excitation on the red side of the absorption spectrum selects out a set of molecules with a wide, blue-shifted distribution of ground state energies and a wide, red-shifted distribution of excited state energies.

$$N(\omega_g, \omega_e) = N(\omega_g, \Omega^0 - R + \omega_g).$$

Therefore,

$$G(\omega_g, \Omega^0 - R) = N(\omega_g, \Omega^0 - R + \omega_g) = [G(\omega_g)b/\sqrt{\pi}] \times \exp[-b^2(\omega_e^0 - \omega_g^0 - R + \omega_g - \omega_e^0)^2] \quad (9a)$$

or

$$G(\omega_g, \Omega^0 - R) = (gb/\sqrt{\pi}) \exp[-a^2(\omega_g - \omega_g^0)^2] \times \exp[-b^2(\omega_g - \omega_g^0 - R)^2]. \quad (9b)$$

Combining terms and completing the square in the exponent gives the final expression for $G(\omega_g, \Omega^0 - R)$:

$$G(\omega_g, \Omega^0 - R) = (gb/\sqrt{\pi}) \exp\{-b^2R^2[a^2/(a^2 + b^2)]\} \times \exp\{-(a^2 + b^2)\{\omega_g - [\omega_g^0 + Rb^2/(a^2 + b^2)]\}^2\}. \quad (9c)$$

The laser-selected distribution of ground state energies is characterized by width δ_{GR} and center frequency ω_{gR}^0 :

$$\delta_{GR} = \delta_G \delta_F / (\delta_G^2 + \delta_F^2)^{1/2}, \quad (10a)$$

$$\omega_{gR}^0 = \omega_g^0 + Rb^2/(a^2 + b^2). \quad (10b)$$

The laser-selected distribution of excited state energies is obtained in an analogous manner:

$$F(\omega_e, \Omega^0 - R) = (gb/\sqrt{\pi}) \exp\{-a^2R^2[b^2/(a^2 + b^2)]\} \times \exp\{-(a^2 + b^2)\{\omega_e - [\omega_e^0 - Ra^2/(a^2 + b^2)]\}^2\}. \quad (11)$$

$F(\omega_e, \Omega^0 - R)$ has width δ_{FR} and center frequency ω_{eR}^0 :

$$\delta_{FR} = \delta_G \delta_F / (\delta_G^2 + \delta_F^2)^{1/2}, \quad (12a)$$

$$\omega_{eR}^0 = \omega_e^0 - Ra^2/(a^2 + b^2). \quad (12b)$$

Figure 1 depicts these laser-selected distributions and their relationship to the total ground and excited state distributions.

The equations obtained so far are applicable to the initial excitation step in both the fluorescence line narrowing experiments and hole burning experiments that will be discussed in subsequent sections of this paper. Only two major assumptions have been made up to this point: (1) There is a distribution of absolute energies, and each absolute energy has a large degree of accidental degeneracy; (2) the accidental degeneracy is broken when the electronic state is changed so that a set of molecules with a single ground state energy will have a broad distribution of excited state energies.

To discuss the FLN experiments of Griesser and Wild⁷ and Flach *et al.*,¹⁹ no further assumptions need to be made. To briefly summarize the FLN experiments, a certain $|g\rangle \rightarrow |e\rangle$ transition is pumped with a narrow band laser. The resonant $|e\rangle \rightarrow |g\rangle$ fluorescence is narrow, but nonresonant fluorescence to an intermediate level $|i\rangle$, $|e\rangle \rightarrow |i\rangle$ is broad. The model described above will predict this effect. To use the example already discussed, suppose the $|g\rangle \rightarrow |e\rangle$ transition is excited with frequency Ω which is on the red side of the absorption spectrum. A distribution $F(\omega_e, \Omega^0 - R)$ of excited state energies is selected by this process. Each set of degenerate molecules in state $|e\rangle$ will have a broad distribution $h(\omega_e, \omega_i)$ of state $|i\rangle$ energies, which is analogous to $f(\omega_g, \omega_e)$ in Eq. (2). Again for simplicity, it will be assumed that each $h(\omega_e, \omega_i)$ spans the total distribution of state $|i\rangle$ absolute energies $H(\omega_i) = (D) \exp[-c^2(\omega_i - \omega_i^0)^2]$. An equation exactly analogous to Eq. (4) can be written to describe the process of going from level $|e\rangle$ to level $|i\rangle$:

$$F(\omega_e, \Omega^0 - R) \rightarrow [F(\omega_e, \Omega^0 - R)c/\sqrt{\pi}] \times \exp[-c^2(\omega_i - \omega_i^0)^2] = N(\omega_e, \omega_i). \quad (13)$$

$N(\omega_e, \omega_i)$ is the number of molecules excited by irradiation at $\Omega^0 - R$ that have level $|e\rangle$ energy $\hbar\omega_e$ and level $|i\rangle$ energy $\hbar\omega_i$. For emission from level $|e\rangle$ to level $|i\rangle$, the transition frequency is given by $\Omega_{ei} = \omega_e - \omega_i$. The fluorescence spectrum $L(\Omega_{ei})$ due to $|e\rangle \rightarrow |i\rangle$ transitions will be Eq. (13) integrated over all ω_e :

$$L(\Omega_{ei}) = (cgb/\sqrt{\pi}) \exp\{-a^2R^2[b^2/(a^2 + b^2)]\} \times \int_{-\infty}^{+\infty} \exp\{-(a^2 + b^2)\{\omega_e - [\omega_e^0 - Ra^2/(a^2 + b^2)]\}^2\} \times \exp[-c^2(\omega_i - \omega_i^0)^2] d\omega_e. \quad (14)$$

Carrying out this integral gives the final expression for the

nonresonant $|e\rangle \rightarrow |i\rangle$ fluorescence after narrow band excitation of the $|g\rangle \rightarrow |e\rangle$ transition to the red side of the absorption spectrum,

$$L(\Omega_{ei}) = [cgb/(a^2 + b^2 + c^2)^{1/2}] \\ \times \exp\{-a^2 R^2 [b^2/(a^2 + b^2)]\} \\ \times \exp\{-[(a^2 + b^2)c^2/(a^2 + b^2 + c^2)] \\ \times \{\Omega_{ei} - [\Omega_{ei}^0 - Ra^2/(a^2 + b^2)]\}^2\}, \quad (15)$$

where $\Omega_{ei}^0 = \omega_e^0 - \omega_i^0$. It can already be seen that this nonresonant fluorescence will be broad. This result will be discussed in detail in Sec. IV.

The NPHB and PHB experiments to be discussed are somewhat different from the FLN experiments. After narrow band excitation at $\Omega = \Omega^0 - R$ creates the laser-selected distributions of ground state energies $G(\omega_g, \Omega^0 - R)$, the molecules making up this distribution undergo a mechanical perturbation. The perturbed molecules absorb in a different range of frequencies and form the broad antihole spectrum. To calculate the antihole absorption spectrum, it is necessary to make assumptions about what the mechanical perturbation does to the energy distribution $G(\omega_g, \Omega^0 - R)$. The second type of FLN experiments mentioned in the Introduction is directly analogous to this. In these experiments, the $S_0 \rightarrow S_1$ transition is excited with a narrow band source forming the laser-selected distribution of excited state energies. The excited molecules undergo intersystem crossing to T_1 , giving broad $T_1 \rightarrow S_0$ phosphorescence. In this case, it is necessary to make assumptions about what the intersystem crossing does to the laser-selected distribution of excited state energies.

The NPHB experiment involving a mechanical perturbation will be dealt with in detail here, and then discussed in context with the experimental results in Sec. IV. In the following discussion, all quantities with a bar over the top refer to molecules that have undergone mechanical perturbation and have formed the antihole. Otherwise, they are completely analogous to their unbarred counterparts. There are several choices that could be made in addressing the question of what happens to $G(\omega_g, \Omega^0 - R)$ when the molecules making up this distribution are mechanically perturbed. One limiting case is that $G(\omega_g, \Omega^0 - R)$ could be completely destroyed upon mechanical perturbation so that the molecules have a ground state energy distribution which spans all of $\bar{G}(\bar{\omega}_g)$. In the opposite limit, $G(\omega_g, \Omega^0 - R)$ could remain essentially intact so that the perturbed set of molecules will have a distribution of ground state energies $\bar{G}(\bar{\omega}_g, \Omega^0 - R)$

which bears the same relationship to $\bar{G}(\bar{\omega}_g)$ as did $G(\omega_g, \Omega^0 - R)$ to $G(\omega_g)$; i.e., $\bar{G}(\bar{\omega}_g, \Omega^0 - R)$ will be shifted to the blue and narrower than $\bar{G}(\bar{\omega}_g)$. For now, it will simply be stated that the best choice is the latter. The reasons for this choice will be discussed in Sec. IV in terms of the experimental results.

Burning away the entire inhomogeneously broadened absorption spectrum $A(\Omega)$ creates the entire inhomogeneously broadened antihole absorption spectrum $\bar{A}(\bar{\Omega})$ centered at $\bar{\Omega}^0$ and of width $\bar{\Delta}_A$. Since we are assuming that the fundamental nature of the laser-selected distribution of ground state energies is preserved upon hole burning although shifted in energy by the mechanical perturbation, then $\bar{G}(\bar{\omega}_g, \Omega^0 - R)$ will be centered at

$$\bar{\omega}_{gR}^0 = \bar{\omega}_g^0 + R\bar{b}^2/(\bar{a}^2 + \bar{b}^2) \quad (16)$$

with width

$$\bar{\delta}_{GR} = \bar{\delta}_G \bar{\delta}_F / (\bar{\delta}_G^2 + \bar{\delta}_F^2)^{1/2}. \quad (17)$$

It must be emphasized that these specific assumptions are not necessary for the success of the model. The only essential features of $\bar{G}(\bar{\omega}_g, \Omega^0 - R)$ are that it is shifted to the blue of $\bar{\omega}_g^0$ and that it has a width somewhat narrower than $\bar{\delta}_G$:

$$\bar{G}(\bar{\omega}_g, \Omega^0 - R) = (K) \exp\{-[\bar{a}^2 + \bar{b}^2] \\ \times [\bar{\omega}_g - (\bar{\omega}_g^0 + R\bar{b}^2/(\bar{a}^2 + \bar{b}^2))]^2\}. \quad (18)$$

The constant K includes the preexponential factors analogous to those in Eq. (9c), plus the hole burning efficiency, which is a measure of how many of the molecules excited by the narrow band laser actually undergo a mechanical perturbation to form the antihole.

One of the two basic assumptions of the model is that a set of degenerate ground state molecules will contain subsets with excited state energies distributed over a wide range of excited state energies. Therefore, the analysis of the antihole absorption spectrum will parallel that of the unperturbed molecules, except that the set of ground state molecules is the laser-selected distribution $\bar{G}(\bar{\omega}_g, \Omega^0 - R)$ instead of the entire distribution $\bar{G}(\bar{\omega}_g)$. The equation analogous to Eq. (4) is

$$\bar{G}(\bar{\omega}_g, \Omega^0 - R) \rightarrow [\bar{G}(\bar{\omega}_g, \Omega^0 - R) \bar{b} / \sqrt{\pi}] \\ \times \exp[-\bar{b}^2(\bar{\omega}_e - \bar{\omega}_e^0)^2] = \bar{N}(\bar{\omega}_g, \bar{\omega}_e). \quad (19)$$

$\bar{N}(\bar{\omega}_g, \bar{\omega}_e)$ is the number of antihole molecules with excited state energy $\hbar\bar{\omega}_e$ and ground state energy $\hbar\bar{\omega}_g$. Therefore, the antihole absorption spectrum is written

$$\bar{A}(\bar{\Omega}, \Omega^0 - R) = \int_{-\infty}^{+\infty} \bar{N}(\bar{\omega}_g, \bar{\Omega}^0 + \bar{\omega}_g) d\bar{\omega}_g \\ = K \int_{-\infty}^{+\infty} \exp(-(\bar{a}^2 + \bar{b}^2)\{\bar{\omega}_g - [\bar{\omega}_g^0 + R\bar{b}^2/(\bar{a}^2 + \bar{b}^2)]\}^2) \exp[-\bar{b}^2(\bar{\omega}_e - \bar{\omega}_e^0)^2] d\bar{\omega}_g \\ = [K(\bar{a}^2 + 2\bar{b}^2)^{1/2}/\sqrt{\pi}] \exp(-[(\bar{a}^2 + \bar{b}^2)\bar{b}^2/(\bar{a}^2 + 2\bar{b}^2)]\{\bar{\Omega} - [\bar{\Omega}^0 - R\bar{b}^2/(\bar{a}^2 + \bar{b}^2)]\}^2). \quad (20)$$

The width of this antihole absorption is

$$\bar{\Delta}_{AR} = (\bar{\delta}_{GR}^2 + \bar{\delta}_F^2)^{1/2} = \bar{\delta}_F [(2\bar{\delta}_G^2 + \bar{\delta}_F^2)/(\bar{\delta}_G^2 + \bar{\delta}_F^2)]^{1/2}. \quad (21)$$

The width $\bar{\Delta}(\bar{\Omega})$ of the entire inhomogeneously broadened antihole absorption is

$$\bar{\Delta}_A = (\bar{\delta}_G^2 + \bar{\delta}_F^2)^{1/2}. \quad (22)$$

The center frequency of the antihole absorption produced by narrow band hole burning of the origin at $\Omega^0 - R$, $\bar{A}(\bar{\Omega}, \Omega^0 - R)$, is $R\bar{b}^2/(\bar{a}^2 + \bar{b}^2)$ to the red of $\bar{\Omega}^0$, the center frequency of $\bar{A}(\bar{\Omega})$.

III. EXPERIMENTAL SYSTEM AND PROCEDURES

The experimental results were obtained by using non-photochemical hole burning techniques on the system pentacene in benzoic acid (PC/BZA).¹⁴ Optical electronic excitation of a pentacene molecule induces a physical rearrangement of a neighboring host benzoic acid dimer via an acidic proton tautomerization. The resulting change in the pentacene local mechanical environment shifts its electronic transition and gives rise to optical NPHB.¹³ This NPHB creates four new distinct pentacene sites in the crystal as is evidenced by the appearance of four sharp new spectral features outside of the original pentacene inhomogeneous line. These photoproducts or antiholes (sites I–IV)^{14(a),14(b),14(d)} are spectrally narrow and well separated from the origin and exhibit pentacene vibrational structures. The antiholes are pentacene molecules in four well-defined new environments^{14(a),14(c)} having different crystal shifts.

The antihole experiments were conducted on the site I antihole exclusively, as it is the principal antihole. Approximately 70% of the molecules which leave the origin upon hole burning are found in the site I antihole ($\sim 135 \text{ cm}^{-1}$ to the red of the PC origin). The sites II through IV antiholes and a series of slightly populated sites contain the remaining 30% of the molecules.

NPHB thus provides a way to effect a well-defined mechanical rearrangement of the system. Line shape studies of the nonphotochemical hole and antihole, in addition to studies of the spontaneous reversion (SR) and laser-induced reversion (LIR) of an antihole (hole-filling) are presented.

The NPHB experiments were performed with the experimental setup shown in Fig. 2. The system consists of a Coherent model CR-599-21 single mode scanning cw dye laser pumped by 2.5–3.0 W of the 514 nm line of a Coherent Innova 90-5 argon ion laser. Maximum dye laser power used

was $\sim 40 \text{ mW}$ with $\sim 1 \text{ MHz}$ bandwidth. The commercially available CR-599-21 was modified to increase the frequency sweep from 30 to 120 GHz.

There were four basic experimental procedures used in these NPHB experiments. The first involved burning a hole with the narrow band dye laser and recording its excitation spectrum. The fluorescence was collected at 90° with an EMI 9658B photomultiplier tube (PMT) filtered with Hoya R625 and R645 cutoff filters. The second procedure involved burning a hole and recording the resultant excitation spectrum of the antihole. The third procedure involved burning a hole, burning away the entire resultant antihole by scanning the dye laser multiple times slowly across the antihole, and finally recording the spectral region of the original hole. The fourth procedure involved burning away the entire unburned inhomogeneously broadened PC origin and recording the total width of the inhomogeneously broadened antihole. The entire PC origin was burned away by scanning the unattenuated dye laser repeatedly across the 16 cm^{-1} pseudolocal phonon peak in the phonon sideband of the PC absorption spectrum. Variations in the dye laser output were normalized out of the excitation spectra by digitizing the signal intensity and a reference beam intensity and dividing the two. The resulting normalized signal was stored on disk. Several scans were usually averaged (typically 10) to improve signal to noise.

Absolute frequency calibration of a spectrum was obtained using I_2 gas as a standard. Part of the dye laser beam was directed into an I_2 cell. The excitation spectrum of the I_2 was recorded with the same laser sweep used to record the hole burning spectra. The method permits the absolute position of various spectral features recorded in different experiments to be compared.

The PC/BZA crystals were grown from the melt by the Bridgman technique. The pentacene was obtained from Aldrich and used after vacuum sublimation. Benzoic acid (Baker analyzed reagent 0076) was recrystallized from deionized water and extensively zone refined (~ 800 passes). Crystals were mounted such that the \hat{a} axis polarized PC transition was parallel to the laser polarization. All experiments were performed at 1.4 K.

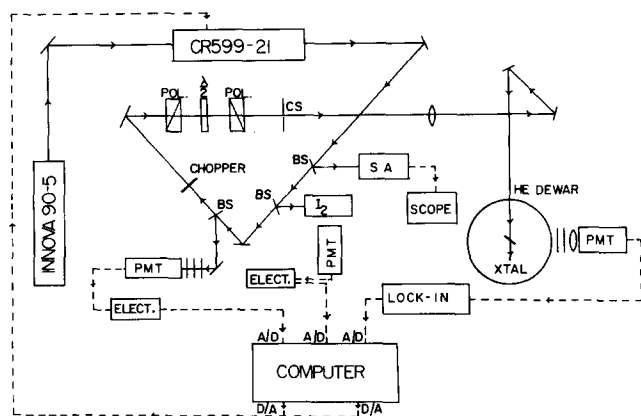


FIG. 2. Experimental setup for nonphotochemical hole burning. This system utilizes a single model scanning cw dye laser pumped by 2.5–3.0 W of the 514 nm line of an Ar^+ laser. BS = beam splitter; CS = camera shutter; SA = Tropel 240 spectrum analyzer; Elect. = electrometer; $\lambda/2$ = half-wave plate; Pol. = cube polarizer; I_2 = gaseous I_2 cell. See the text.

IV. RESULTS AND DISCUSSION

In this section, the results of various hole burning experiments on the pentacene origin and the site I antihole are described and discussed in terms of the mathematical model presented in Sec. II. Fluorescence line narrowing experiments are also analyzed. First, the entire inhomogeneously broadened PC origin was burned away by laser irradiation into the 16 cm^{-1} pseudolocal phonon peak in the phonon sideband. In all crystals studied after burning away the PC origin of width Δ_A , the resultant inhomogeneously broadened total antihole width $\bar{\Delta}_A$ was similar in width to Δ_A . The results are shown in Table I.

Equations (8) and (22) give Δ_A and $\bar{\Delta}_A$ in terms of the absolute ground and excited state energy distributions of perturbed and unperturbed molecules, respectively. The fact that Δ_A is similar to $\bar{\Delta}_A$ indicates that the mechanical perturbation does not basically change the manner in which the

TABLE I. Correlation between widths (FWHM) of total inhomogeneously broadened PC/BZA unburned origins and total inhomogeneously broadened site I antihole resulting from burning away entire PC origin at 1.4 K.

Crystal	Origin FWHM (GHz)	Site I antihole FWHM (GHz)
1	48.4	52.2
2	62.3	50.7
3	28.0	42.9
4	47.3	66.1

disorder in the environments of the guest chromophores manifests itself in the energy, and suggests that the widths of the absolute energy distributions associated with the origin and the antihole are similar.

Burning a narrow hole in the PC origin always produces a broad antihole which is not quite as broad as Δ_A . The antihole width is independent of the hole width for narrow to moderate holes burned in the same crystal. Antihole widths will vary somewhat from crystal to crystal as does the origin width. Holes of various widths and their corresponding antihole widths are listed in Table II for several samples. Figure 3 shows typical excitation spectra of a hole and its corresponding site I antihole, which in this sample is a 482 MHz (FWHM) hole and a 25.4 GHz antihole.

It follows directly from the model, independent of the assumption made concerning the effect of the mechanical perturbation on the ground state laser-selected distribution, that a narrow hole will give rise to a broad antihole. Burning a narrow hole involves molecules with ground state energies spanning $G(\omega_g)$. Molecules in the laser-selected distribution have the same $S_0 \rightarrow S_1$ pentacene origin transition energies. When these molecules undergo a mechanical perturbation, the laser-selected transition energy degeneracy is not preserved. The broad range of laser-selected ground state molecular energies is manifested when there is no longer a particular relationship between ground and excited state energies

TABLE II. Correlation between widths (FWHM) of holes burned in PC/BZA origin and their corresponding site I antihole widths (FWHM) in various crystals at 1.4 K.

Crystal	Origin FWHM (GHz)	Hole FWHM (MHz)	Site I antihole FWHM (GHz)
1	63.1	25	33
		28	26
		34	31
		428	26
		448	27
		482	25
2	57.3	421	15
		470	19
		948	15
		408	20
3	66.0	32	26
		81	24
		580	22
		500	15
		486	21
4	54.3	484	10
		807	12
5	28.0		

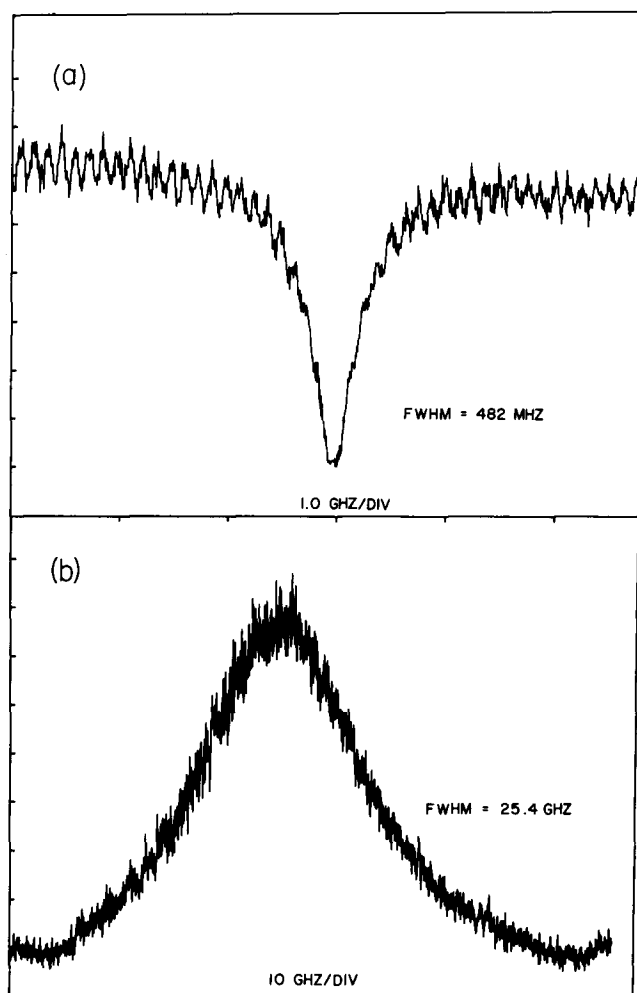


FIG. 3. (a) Typical excitation spectrum of hole burned near center of the pentacene in benzoic acid optical absorption origin at 1.4 K. The pentacene origin is located at 5879.6 Å and typically has an inhomogeneous linewidth of 50 GHz. The hole shown corresponds to a hole depth of 40%. (b) Excitation spectrum at 1.4 K of site I antihole produced by the hole shown in (a). The antihole appears $\sim 135 \text{ cm}^{-1}$ to the red of the hole. Vertical axes of both spectra are in arbitrary units.

produced by the laser. The antihole width will be discussed below.

There is a strong correlation between the frequency of the hole burned in the PC origin and the frequency of the resulting antihole. That is, burning a hole on the red (blue) side of the PC origin results in an antihole shifted to the red (blue) of the center of the inhomogeneously broadened antihole. Figure 4 shows two holes, labeled A and B, and their corresponding antiholes, labeled A' and B', respectively. It can be seen that burning B to the blue of A results in B' shifted to the blue of A'. This is observed in all cases, independent of the hole position in the inhomogeneous PC origin and independent of the particular sample crystal of PC/BZA.

This correlation between hole and antihole frequency permits insights into the effect of the mechanical change on the ground state laser-selected distribution which accompanies hole burning. Burning a hole at $\Omega = \Omega^0 - R$ creates a laser-selected distribution of ground state energies $G(\omega_g, \Omega^0 - R)$. Suppose, upon burning, that the energies

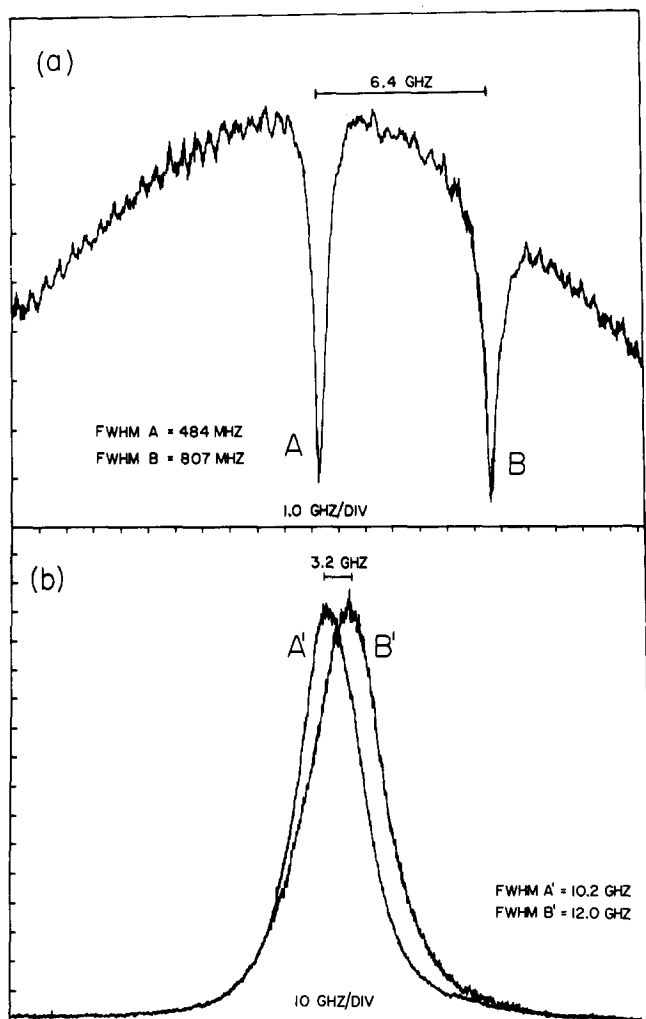


FIG. 4. (a) Excitation spectra at 1.4 K showing relative positions and sizes of holes A and B burned in the pentacene origin. Hole A was burned first, then recorded. The spectrum and position of its antihole A' [see (b)] was also recorded. Laser-induced reversion (LIR) of A' was observed to completely fill hole A. Hole B was then burned 6.4 GHz to the blue of hole A, giving rise to antihole B'. LIR of B' completely filled hole B. The spectra in (a) and (b) are a superposition of the two independently recorded spectra. (b) Excitation spectra at 1.4 K of site I antiholes A' and B', corresponding to holes A and B of (a), respectively. B' appears 3.2 GHz to the blue of A'. The area of the overlap region of antiholes A' and B' is 74% of the area of antihole A'. Although the holes are well separated, the antiholes overlap substantially. See the text for discussion.

spread out in such a way that the mechanically perturbed set of laser-selected energies, which make up the antihole ground state, has the same width and center as the total distribution of antihole ground state energies $\bar{G}(\bar{\omega}_g)$. In this case, the position of the antihole will be the same regardless of where the hole is burned. Furthermore, this supposition would predict that all antiholes will have the same width $\bar{\Delta}_A$ as the total antihole. These results directly contradict experiment. Clearly there is some correlation between the laser-selected distribution $G(\omega_g, \Omega^0 - R)$ and its corresponding antihole distribution $\bar{G}(\bar{\omega}_g, \Omega^0 - R)$.

Now suppose that $G(\omega_g, \Omega^0 - R)$ is essentially preserved so that $\bar{G}(\bar{\omega}_g, \Omega^0 - R)$ has the same characteristics as $G(\omega_g, \Omega^0 - R)$. $\bar{G}(\bar{\omega}_g, \Omega^0 - R)$ will be shifted to the blue by $R\bar{b}^2/(\bar{a}^2 + \bar{b}^2)$, and it is somewhat narrower than $\bar{G}(\bar{\omega}_g)$, hav-

ing width $\bar{\delta}_{GR} = \bar{\delta}_G \bar{\delta}_F / (\bar{\delta}_F^2 + \bar{\delta}_G^2)^{1/2}$. The antihole absorption spectrum obtained after making this assumption is given by Eq. (20). The width of the absorption $\bar{\Delta}_{AR} = (\bar{\delta}_{GR}^2 + \bar{\delta}_F^2)^{1/2}$ is narrower than $\bar{\Delta}_A = (\bar{\delta}_G^2 + \bar{\delta}_F^2)^{1/2}$ since $\bar{\delta}_{GR}$ is smaller than $\bar{\delta}_G$. This expression for the width of the antihole also shows why the antihole width is essentially independent of hole width for reasonably small holes. $\bar{\delta}_{GR}$ is the only factor that will change with hole width. Since $\bar{\delta}_{GR}$ is quite large even for an infinitely narrow hole (if $\bar{\delta}_G = \bar{\delta}_F$, $\bar{\delta}_{GR} = 0.7\bar{\delta}_G$ for an infinitely narrow hole), then $\bar{\delta}_{GR}$ will not be a sensitive function of hole width as long as the hole width is small relative to the $\bar{\delta}_{GR}$ produced by an infinitely narrow hole. Thus the antihole width $\bar{\Delta}_{AR}$ will not depend on hole width as long as the holes are narrow to moderate in width.

Under the assumption that the mechanical perturbation which generates the antihole leaves the laser-selected ground state distribution essentially the same but shifted in energy, i.e., $\bar{G}(\bar{\omega}_g, \Omega^0 - R)$ has the same characteristics as $G(\omega_g, \Omega^0 - R)$, the antihole spectrum is shifted to the red of the center of the total antihole absorption spectrum by an amount $R\bar{b}^2/(\bar{a}^2 + \bar{b}^2)$ after burning a hole shifted R to the red of the center of the origin absorption spectrum.

Burning two holes in the inhomogeneous line gives rise to two antiholes which are separated in frequency by less than the two holes. This is illustrated in Fig. 4. The antiholes are, within experimental error, a factor of 2 closer together than the holes. This occurs in all PC/BZA samples examined. If the two holes are burned at Ω^0 and $\Omega^0 - R$, then the corresponding antiholes will be positioned at $\bar{\Omega}^0$ and $\bar{\Omega}^0 - R\bar{b}^2/(\bar{a}^2 + \bar{b}^2)$. For distributions of ground and excited state antihole energies having the same width, i.e., $\bar{a} = \bar{b}$, two holes separated by R will have two antiholes separated by $R/2$, as observed. These observations support the basic validity of the overall model and demonstrate that the ground and excited state absolute energy distributions of the PC/BZA site I antihole have nearly identical widths.

The model presented in Sec. II is successful in describing a variety of NPHB results. It can also describe the results of the FLN experiments of Flach *et al.* Equation (15) gives the form of the nonresonant fluorescence from the excited state $|e\rangle$ to a third intermediate level $|i\rangle$ after the resonant $|g\rangle \rightarrow |e\rangle$ transition is pumped with a narrow band laser at frequency $\Omega = \Omega^0 - R$. The fluorescence to $|i\rangle$ arises from the set of excited molecules in $|e\rangle$ having the laser-selected distribution of excited state energies, $F(\omega_e, \Omega^0 - R)$. This narrowed and red-shifted distribution of energies is coupled to the entire range of level $|i\rangle$ energies, giving rise to the red-shifted broad fluorescence band described by Eq. (15).

If the $|g\rangle \rightarrow |e\rangle$ transition is pumped with a broadband source so that all energies are excited, the nonresonant $|e\rangle \rightarrow |i\rangle$ fluorescence will have a total inhomogeneous width $\Delta_L = (\delta_F^2 + \delta_H^2)^{1/2}$, where δ_F and δ_H are the widths of the distribution of level $|e\rangle$ and $|i\rangle$, respectively. Equation (15) shows that exciting only at $\Omega = \Omega^0 - R$ gives fluorescence with width $\Delta_{LR} = (\delta_{FR}^2 + \delta_H^2)^{1/2}$, where δ_{FR} is the width of the laser-selected distribution of level $|e\rangle$ energies and δ_H is the width of the total distribution of level $|i\rangle$ energies. Since δ_{FR} is smaller than δ_F , Δ_{LR} will be smaller than Δ_L . Therefore, the nonresonant fluorescence from $|e\rangle$ to $|i\rangle$ following

narrow band excitation of $|g\rangle$ to $|e\rangle$, while very broad, is predicted not to be as broad as the total inhomogeneous width of the $|e\rangle$ to $|i\rangle$ fluorescence.

Earlier in this section, in connection with the NPHB experiments, the reason for the insensitivity of δ_{GR} (hence, δ_{FR}) to the bandwidth of the exciting source was described. This explains why antihole widths are independent of hole widths. The analogous reasoning applies to FLN experiments and predicts that the width of the nonresonant $|e\rangle \rightarrow |i\rangle$ fluorescence should not be critically dependent upon the width of the pumping of the $|g\rangle \rightarrow |e\rangle$ transition. In fact, this is observed by Griesser and Wild in their experiments on 1,3-dichloroazulene in glasses.⁷

Equation (15) also shows another important characteristic of the broad fluorescence that is verified experimentally. The $|e\rangle \rightarrow |i\rangle$ fluorescence obtained after exciting R to the red side of the $|g\rangle \rightarrow |e\rangle$ transition at $\Omega = \Omega^0 - R$ is centered at $\Omega_{ei}^0 - Ra^2/(a^2 + b^2)$. Ω_{ei}^0 is the center frequency of the total $|e\rangle \rightarrow |i\rangle$ nonresonant fluorescence obtained by exciting the $|g\rangle \rightarrow |e\rangle$ transition with a broadband source. In the NPHB experiments, it was found that for a hole R to the red, the corresponding antihole was $0.5R$ to the red. The coefficient 0.5 arises when the widths of the ground state and excited state antihole absolute energy distributions are the same, i.e., $\bar{\delta}_G = \bar{\delta}_F$. Flach *et al.* have examined the center frequency of the broad nonresonant $|e\rangle \rightarrow |i\rangle$ fluorescence as a function of the frequency of the $|g\rangle \rightarrow |e\rangle$ pumping in the ionic crystal system discussed in the Introduction.¹⁹ The important qualitative features are, as predicted, the same as in the NPHB experiments. For red excitation, the broad fluorescence is also red shifted. The red shift of the broad fluorescence is not as good as the red shift of laser excitation. In the NPHB experiments, the coefficient is 0.5. In the fluorescence experiments of Flach *et al.*, the coefficient is 0.7. The 0.7 coefficient will occur if the fluorescing state $|e\rangle$ has absolute energy distribution 60% wider than that of the ground state $|g\rangle$, i.e., $\delta_F = 1.6\delta_G$. Since the two states involved in the narrow pumping 3P_0 and 3H_4 , are of significantly different nature, it is not unreasonable to believe that they will interact differently with the various environments in the inhomogeneous crystal, and therefore have absolute energy distributions with different widths.

The model for the effect of inhomogeneous broadening on spectroscopic observables can be applied to the experiments involving intersystem crossing as well as the FLN experiments discussed above. As in the NPHB experiments, consideration must be given to the effect intersystem crossing has on the S_1 laser-selected distribution. A study of the correlation between the position of the narrow band $S_0 \rightarrow S_1$ excitation and the position of the corresponding phosphorescence $T_1 \rightarrow S_0$ would provide information on this effect.

It is worthwhile to experimentally address two important points which are implicit in this model. The first is, hole burning does not physically scramble the local molecular environments by thermal or other processes. The second is, accidental transition energy degeneracy exists in inhomogeneously broadened systems.

To address the first point, a time-resolved study of the spontaneous filling of a hole and disappearance of the corre-

sponding site I antihole was performed by recording their excitation spectra at various time intervals after hole burning. The line shape and linewidth of the hole and the antihole remained constant. The hole has a $1/e$ spontaneous recovery time of ~ 40 min and the site I antihole has a $1/e$ spontaneous reversion (SR) time of ~ 47 min. The hole filling time is approximately the same as the site I antihole spontaneous reversion time, but differs somewhat because a fraction of the hole filling results from the SR of the other antihole sites. More importantly, the hole is completely filled; the antihole reverts completely back to the hole. It was noted in Ref. 14 that hole filling can be induced by irradiating the antihole with a laser, i.e., laser-induced reversion (LIR). Excitation spectra of the origin were taken before hole burning, after hole burning, and after LIR of the site I antihole. It was again seen that the population in the antihole reverts completely back to the hole. This demonstrates that the hole burning process cannot involve a randomization of mechanical configurations. Such a randomization would explain why a narrow hole produces a wide antihole, but it would preclude complete filling of the hole upon reversion. If configuration scrambling occurred, molecules in the wide antihole would correspond to a wide variety of configurations which are uncorrelated with the initial origin configurations. When they revert to the origin they would have a much wider spread of energies than the hole and consequently not fill the hole.

Turning to the second point, a natural consequence of the model presented here is that monochromatic excitation at a particular frequency in an inhomogeneously broadened absorption line selects molecules with accidental degeneracy in *transition energy*. These molecules come from a wide variety of physical environments and have a large distribution of absolute energies in the ground state and excited state, but have identical transition energies. The following experiment, illustrated in Fig. 4, conclusively demonstrated this important point.

A 484 MHz wide, 50% deep hole was burned near the peak of the unburned PC origin and its excitation spectrum recorded. The resulting 10.2 GHz wide antihole was also recorded and its position was accurately determined by recording a gaseous iodine excitation spectrum with the same laser sweep. LIR as then performed on the antihole and the population was seen to revert completely back to the hole. A similar hole was then burned 6.4 GHz to the blue of the first hole. Using iodine excitation spectra as frequency markers, it was determined that the peak of the resulting antihole was 3.2 GHz to the blue of the antihole corresponding to the first hole. Again, LIR was performed on this antihole and again the entire population was observed to revert back to its corresponding hole. The important observation to be made from this experiment is that the areas of the two antihole overlap substantially, in this particular case, 74%. Similar experiments performed on other crystals give qualitatively the same results, although the percent overlap of the antihole varies somewhat from crystal to crystal.

When two holes are burned at well-separated frequencies, they must correspond to different mechanical configurations because they have different transition energies. How-

ever, the antiholes overlap. Consider the overlap region of the antihole. If there is only a single mechanical configuration at a particular transition energy, there is no way for the system to "remember" which hole the molecules in the overlap region of the antiholes came from. Upon reversion, such a model would predict that the antihole population would not revert uniquely to the hole from which it came. This is contrary to observation. On the other hand, the model presented in this paper, which has accidental transition energy degeneracy as a natural consequence, can explain the observed results. At a single transition energy in the overlap region, there can be many mechanical configurations. The memory of which hole contributed molecules at a particular transition energy in the antihole spectrum is stored in the configuration differences at that transition energy, not in the energy itself. At a particular transition energy in the antihole overlap region, the configurations which came from hole A are different from those which came from hole B, and therefore return to their respective holes upon reversion. This experiment graphically demonstrates that molecules with identical transition energies nonetheless have differences which are not manifested in their transition energies.

V. CONCLUDING REMARKS

We have presented a simple model of inhomogeneous broadening which involves two basic assumptions. The first assumption is that there exists a large degree of accidental degeneracy in the absolute energies of guest chromophores in a crystal or glass. The guest–host interactions in a molecular solid are dominated by van der Waals forces which are characterized by the dipolar tensor.²⁰ Since the absolute energy is given by a sum of terms containing various tensor elements, there can be many different combinations of tensor elements (reflecting different mechanical configurations) which give rise to the same energy, i.e., accidental degeneracy. In ionic solids, longer range electrostatic guest–host interactions are important. These are also tensor interactions which can give rise to accidental degeneracy. The second assumption is that this accidental degeneracy is broken upon a change of electronic state, so that a set of molecules with the same energy in one state will have a broad distribution of energies in another state. This is also a reasonable assumption since the balancing of influences which give molecules in different environments the same energy will be destroyed by the change in the guest chromophore's electron distribution which accompanies change of electronic state. Fluorescence line narrowing experiments^{7,19} are described in considerable detail by the mathematical model which is based on these two assumptions.

Applying the model to nonphotochemical hole burning experiments on the system pentacene in benzoic acid host crystals,¹⁴ it is found that the mechanical perturbation which accompanies hole burning preserves the laser-selected ground state absolute energy distribution. The relationships between hole width and antihole width and hole frequency and antihole frequency were explained.

A natural consequence of this model is that accidental transition energy degeneracy exists and that nonphotochemical hole burning does not result in a scrambling of the

local environment around a chromophore. Both of these points were demonstrated experimentally for the pentacene in benzoic acid system.

The picture of inhomogeneous broadening presented here is able to explain diverse experiments in a variety of crystal and glass systems. The model views the narrow band excitation of an inhomogeneous absorption line as causing transitions between a very wide distribution of ground state and excited state energies. The laser selects molecules with excited state–ground state energy differences which fall in the narrow range of the laser bandwidth, but the absolute energies of these molecules vary greatly. Therefore, molecules involved in a narrow band pumping experiment come from a wide variety of local environments. It has been suggested previously that narrow band experiments do not provide site selectivity.⁷ The success of the model presented here confirms this idea and provides an experimental tool for the investigation of inhomogeneous absolute energy distributions and how they are affected by state changes, intersystem crossing, and nonphotochemical hole burning mechanical perturbations.

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