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Hole-burning spectroscopy as a probe of guest-host interactions in amorphous materials

Cavus, Abdullah, Ph.D.

City University of New York, 1994

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HOLE-BURNING SPECTROSCOPY AS A PROBE OF GUEST-HOST INTERACTIONS IN AMORPHOUS MATERIALS

by

ABDULLAH CAVUS

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York

1994

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirements for the degree of Doctor of Philosophy.

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Chair of Examining Committee

Sept. 19, 1994

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The City University of New York

Abstract

HOLE-BURNING SPECTROSCOPY AS A PROBE OF GUEST-HOST INTERACTIONS IN AMORPHOUS MATERIALS

by
Abdullah Cavus

Advisor: Prof. John R. Lombardi

The absorption bands of organic molecules in rigid solvents are, even at low temperatures, quite broad. Typical bandwidths are of the order of several hundreds of wavenumbers. So, condensed phase spectroscopy is limited in its spectral resolution by the inhomogeneous broadening. Irradiation into these inhomogeneously broadened bands with a narrow bandwidth laser can induce resonant molecules to undergo a photochemical or photophysical transformation creating a hole in the absorption spectrum. The systems of concern to us here are those in which photochemically active molecules are present in low concentration as guests in a solid host matrix at low temperatures.

When molecules are embedded in amorphous hosts, it is found that the width of spectral lines are highly sensitive to the nature of the guest-host interaction. The advantage of hole-burning spectroscopy is that it provides the ability to obtain high resolution optical spectra in inherently low resolution situations. Measuring the dipole moment change of a guest molecule in various host matrices may shed some light on guest-host interactions involved with the homogeneous linewidth of the guest, temperature and properties of the host.

The dipole moment difference, $\Delta\mu_{eff}$, between guest molecule in the ground state and the excited state was estimated by using the spectral hole splitting or broadening that results from an applied electric field.

The fluorescence excitation spectroscopy technique was used to study the photochemical hole-burning and investigate the dipole moment change of quinazirine (1,4-dihydroxyanthraquinone) and cresylviolet perchlorate in various glass and polymer hosts such as formamide, ethanol:methanol (EM), polyvinyl alcohol (PVA), poly(2-hydroxyethyl) methacrylate (PHEMA), polyvinylbutyral (PVB), and polymethyl methacrylate (PMMA). The strong correlation between effective dipole moment change of the guest molecule and the dielectric constant of the host matrices illustrated the sensitivity of the dipole moment change as a direct measure of the guest-host interactions.

Acknowledgments

I want to acknowledge the contributions of numerous friends and colleagues who have made the completion of this thesis possible. I am grateful for the generous support, guidance, and friendship of Miss Michelle Wright, Mr. Wei Zhang, and Ms. Minfa Wang.

I would like to express my appreciation to the many colleagues in Professor Birke's and Professor Lindsay's laboratories. They were helpful beyond measure by providing necessary equipment, and various parts required for my experiments.

Mr. J. Altman, supervisor of the Physics Department Machine Shop, and his team, as well as Mr. H. Schimatz, the invaluable glassblower of CCNY, were enormously helpful and kind, spending many hours on the arduous tasks I needed for my project.

It has been my good fortune to work with Professor M. C. Tamargo. Her breadth of knowledge transcends her chosen field. Professor Tamargo's consistent support will always be remembered.

I owe a special debt of gratitude to Professor L. W. Johnson, and Professor R. Birke for their continued kindness, their insights and expert knowledge. I am thankful for their thoughtful comments and willing criticisms, for these have contributed much to whatever level of lucidity this work may be judged to have.

I am especially grateful to Professor John R. Lombardi, my esteemed friend and mentor, who deserves recognition for his vast knowledge, unyielding faith, and genuine enthusiasm for my research. Without his supervision, this work would not have been possible.

And finally, I would like to dedicate this completed thesis to my wife, Lori Jean Cavus, my parents, Ismail and Nazli Cavus, my sisters, Ayla and Leyla Cavus, and my dear friend, Mr. Horace Ainsworth. With Love.

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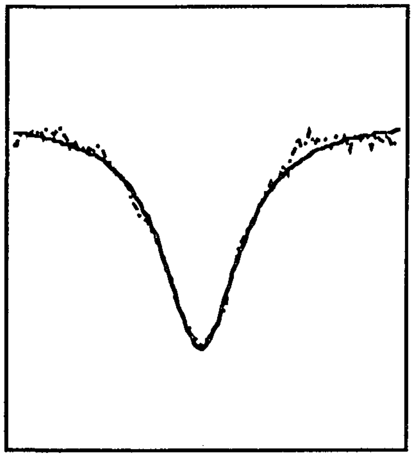

CHAPTER 1

1. INTRODUCTION

1.1 Fundamental Requirements for Persistent Spectral Hole-Burning

The study of optical relaxation processes in solids at low temperature has progressed tremendously in the last 20 years due to the development of coherent optical techniques. The latter would not have been possible without the advent of narrow-band tunable lasers, on the one hand, and lasers with very short pulses (picoseconds, femtoseconds) on the other hand. Such coherent techniques are necessary because spectral line shapes of solids doped with guest molecules are seldom determined by dynamical interactions but principally by strain or structural disorder. This causes inhomogeneous broadening, Γ_{inh}, where absorption and emission spectra usually contain several broad bands whose widths are a few wavenumbers in crystal hosts and hundreds or thousands of wavenumbers in amorphous hosts.

As is well-known, the electronic spectra of complex organic compounds in solutions and solids are characterized by an ill-resolved electron-vibrational (vibronic) structure. Inhomogeneous broadening makes these spectra of low value for analysis, characterization, science, and applications. Therefore, spectroscopists started long ago to search for means and conditions to obtain more informative fine-structured spectra of complex molecules.

Persistent spectral hole-burning (PSHB) is a process whereby normally smooth inhomogeneously broadened absorption lines in solids at low temperatures can be spectrally modified for time periods longer than the lifetime of any excited state. Given a transparent solid containing guest molecules, the basic requirements for persistent spectral hole-burning [1.1] are given as follows:

1. the optical absorption of the guest under consideration must be inhomogeneously broadened,

2. there must exist more than one ground state configuration of the total system (host + guest),

3. the optical absorption frequencies from the various ground states must differ by more than the linewidth of the tunable light source in use (which is typically a laser),

4. there must exist an optical pumping pathway that connects the ground state configurations, and

5. the relaxation among the ground states must be slower than the decay rate of any excited state.

This set of requirements may seem restrictive, but in fact the many diverse examples of PSHB described in this review show that PSHB is an universal feature of laser spectroscopy of solids at liquid helium temperatures. Some important information to be gained from PSHB experiments concerns guest-host interactions, dephasing, local microscopic environments, and photochemistry. Such experiments offer a variety of possible applications to optical data storage and optical signal processing.

The first and most essential requirement for PSHB, inhomogeneous broadening, is summarized in Fig.1.1. If an absolutely perfect crystal could be fabricated in which the guest molecules all experience identical local environments, then the absorption line due to the entire assembly would appear as in Fig.1.1.a. The width of this line is just equal to the width of the optical absorption line for a single guest molecule, Γ_{hom}, which is called the homogeneous linewidth. The word "homogeneous" is appropriate since this width is determined by excited-state dephasing interactions or lifetime effects that are identical for all guest molecules. At liquid helium temperatures where the broadening due to phonons and other excitations is minimized, homogeneous linewidths can become extremely small compared to the frequency of the transition itself. The exact value of Γ_{hom} depends heavily on the specific transition under consideration, and is usually in the range 1kHz-100MHz for zero-phonon transitions in guest molecules with weak electron-phonon coupling. This is to be compared to the 10-1000THz frequencies typical of optical and infrared transitions.

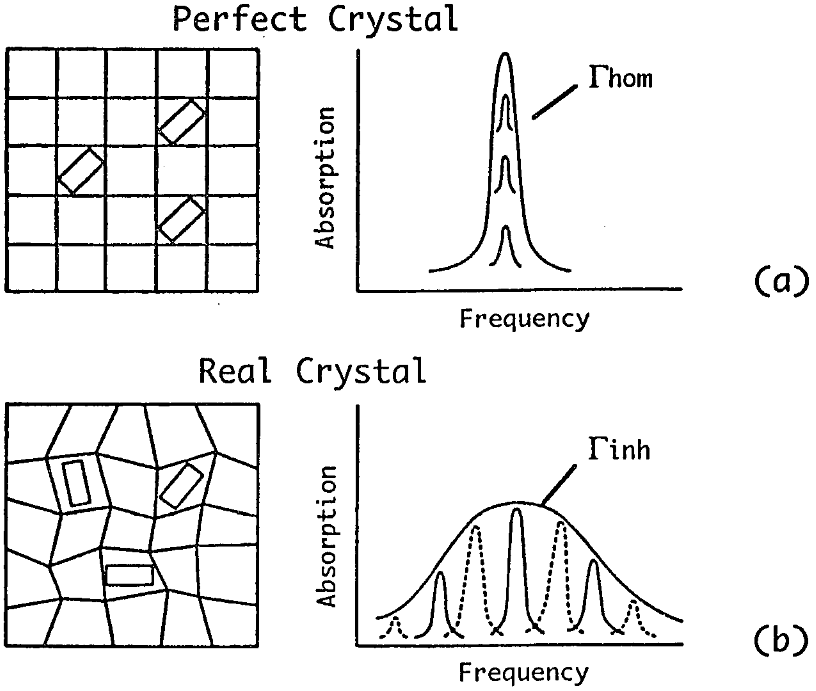

Figure 1.1. (a) Schematic of guest molecules dispersed in a perfect crystal. At low temperatures, the absorption line is homogeneously broadened with width Γ_{hom}. (b) Illustration of inhomogeneously broadened line profile in real solid matrices. The distribution of local environments leads to a distribution of center frequencies of absorption. The resulting lineshape has width Γ_{inh}. Ref.1.1.

Of course, absolutely perfect host materials do not exist, and real crystals have a distribution of local environments due to strains, other impurities, dislocations, and other imperfections. A distribution of local environments is a property of glassy or polymeric hosts by definition. In these physically realizable situations, Fig.1.1.b applies. Even though all the guest molecules are identical, the local environments around the guest molecules are not. The unavoidable distribution of local environments leads to a distribution of absorption frequencies for the various guest molecules. The resulting absorption profile is said to be inhomogeneously broadened with width Γ_{inh}, because the width is determined by interactions that vary from guest molecule to guest molecule. Depending upon the host material, the inhomogeneous linewidth may vary from a few wavenumbers to several hundreds or thousands of wavenumbers ($1cm^{-1}$=30GHz) as mentioned earlier. The critical property of inhomogeneous lines that leads to PSHB is the fact that narrowband excitation with a tunable light source at a particular frequency within the inhomogeneous line excites only those guest molecules that are in resonance with the exciting light. In most real materials, the inhomogeneous linewidth is so large that it interferes with the observation of many physical effects such as external field perturbations and certainly the value of the homogeneous linewidth. Therefore, perhaps the most useful feature of PSHB is that it allows measurements to be performed inside the inhomogeneously broadened line.

The strength of the inhomogeneous broadening may be measured by the ratio of the inhomogeneous linewidth to the homogeneous linewidth, f, where $f = \Gamma_{inh}/\Gamma_{hom}$. This factor can range from 1 to 10^4 or more, depending upon the host material. The study of PSHB is mainly concerned with optical transitions that show strong inhomogeneous broadening, i.e., $f >> 1$. Therefore, either large inhomogeneous linewidths or small homogeneous linewidths are generally required. The former requirement is easy to satisfy in amorphous hosts, although f values greater than 1000 at low temperatures can also occur in crystalline hosts with the proper guest-host combination. The latter situation of small homogeneous linewidths usually occurs for zero-phonon optical transitions of ions, aggregate color centers, or molecules with small electron-phonon coupling at liquid helium temperatures. In fact, the need for small homogeneous linewidths is the principal reason why PSHB experiments are performed at low temperatures, since at elevated temperatures, the homogeneous linewidth grows dramatically due to phonon interactions and usually becomes larger than the temperature-independent inhomogeneous linewidth. The detailed structure of homogenous lines and their temperature dependence is described in more detail in Chapt.2.

Requirements 2-5 for PSHB relate more directly to the actual mechanism for hole formation, and can be satisfied in a variety of ways. For example, the multiple ground states of requirement 2 can occur by rotation of the molecule in the host, relaxation of the two-level systems characteristic of amorphous hosts, or by direct photochemical production of new products from the original guest molecule. Requirement 3 (absorbing energies differing by more than the laser bandwidth) is quite easy to achieve due to the extremely high resolution available from modern laser sources. For example, assuming a laser bandwidth if 1-100 MHz typical of semiconductor diode and dye lasers, extremely weak differences between the ground states is sufficient to produce the required absorption shift. Requirement 4 (existence of photoinduced transformations between the various ground states) is satisfied by definition for systems that undergo photochemistry. PSHB by photophysical (non-photochemical) processes can also occur when photostable guest molecules have local configurations of the nearby host that can be altered by excitation of the guest. Examples of such photophysical processes will be briefly described below. Finally, requirement 5 (slow relaxation) basically amounts to a definition of "persistent" for the purposes of this study. Slow relaxation is often easy to achieve at liquid helium temperatures, because many reverse reactions are thermally activated.

Transient spectral holes lasting only as long as some excited state lifetime also occur, but will not be of central interest here.

When requirements 1-5 are met, persistent spectral holes form in a fashion illustrated in Fig.1.2. Part (a) of the figure shows the inhomogeneously broadened absorption line before hole-burning process. The essence of spectral hole-burning is that the transition energy of the guest molecule embedded in a crystalline or glassy solid matrix shifts after absorption of monochromatic light [1.2].

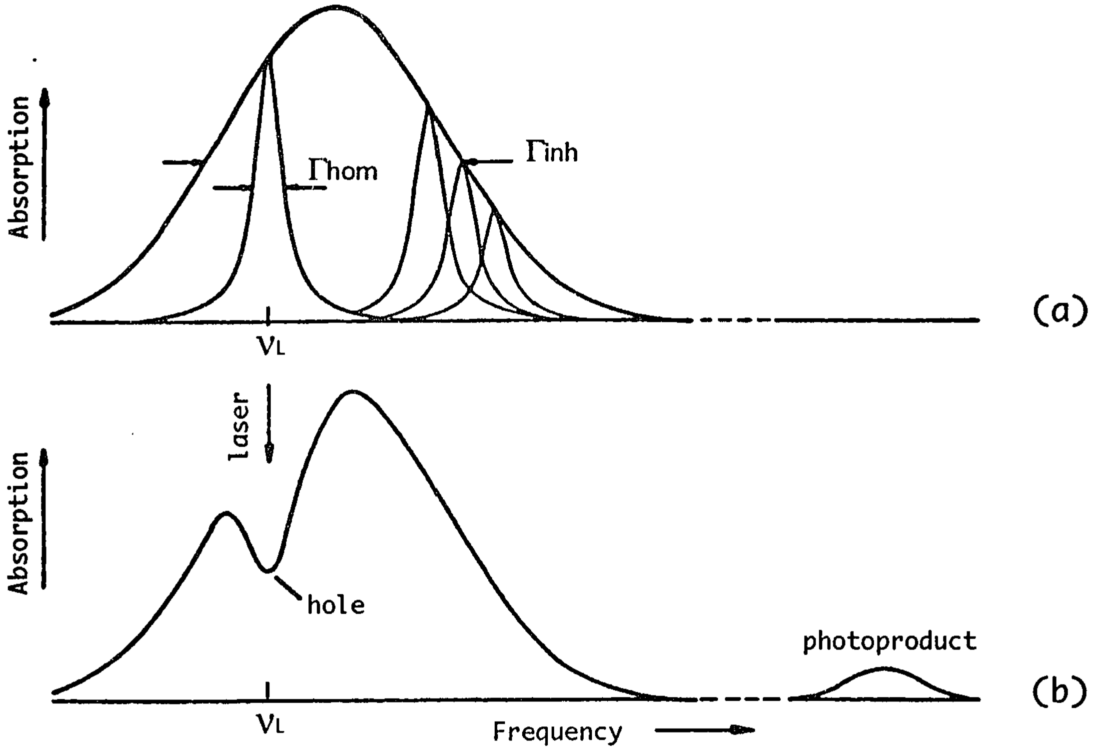

Figure 1.2. (a) Diagram of an inhomogeneously broadened absorption band of width Γ_{inh} consisting of individual electronic transitions of homogeneous linewidth Γ_{hom}. (b) Laser-induced "hole" burnt at frequency ν_L at low temperature. The photoproduct absorbs at a different frequency, which may either be inside or outside the inhomogeneous band. Ref.1.2.

Irradiation of the inhomogeneously broadened absorption band with a narrow-laser, of width Γ_L and frequency ν_L, can induce molecules that absorb resonantly with the laser to undergo a phototransformation such that the product absorbs at a different frequency. As a result of this phototransformation, the optical absorption at ν_L decreases over a narrow range as shown in Fig.1.2.b. The decrease in absorption due to photoinduced transformations between the various ground states is called a "spectral hole". The photoproduct may either be stable at low temperature, which leads to a permanent hole, or it can be a metastable state that acts as a population storage level, by which a transient hole is created. The hole is then probed in a second step by scanning a tunable laser over its spectral region with low enough intensity to avoid further burning of the absorption band. The hole represents a negative replica of the homogeneous spectral transition and the holewidth yields the unknown quantity Γ_{hom}. The optical resolution that can be obtained with hole-burning is 10^3-10^5 times higher than reached with conventional techniques [1.3-5]. This makes hole-burning spectroscopy a powerful tool for spectroscopy in the MHz-regime. It is important to realize that detection of the drop in absorption due to a spectral hole amounts to probing the ground state distribution to see which guest molecules have not been removed from the inhomogeneous profile. In the ideal case, the holewidth is equal to twice the homogeneous linewidth, because the light interacts with a spectral range equal to one homogeneous linewidth during initial excitation, transforming those guest molecules in resonance into a "product" absorbing in a different range of frequency space. Each of the guest molecules removed from the "educt" absorption line carries with it an absorption one homogeneous linewidth wide, so that detection of the remaining educt absorption yields a spectral hole with width $2\Gamma_{hom}$. In many physical systems, the actual observed holewidth may be even wider due to a variety of effects such a spectral diffusion between the hole formation and detection steps.

1.2 Significance for Science and Applications

PSHB can be used to great advantage for scientific studies of the local environments of guest molecules in solids. The advantages arise because hole-burning allows precise, high-resolution spectral measurements to be performed on essentially homogeneous groups of guest molecules without interference of resolution limitations due to the broad inhomogeneous line profile. Because spectral holes are usually narrow, the positions and widths of the holes are naturally extremely sensitive to weak perturbations caused by internal or external interactions.

Soon after the first observation of PSHB in 1974, it was quickly realized that in addition to the scientific promise, spectral holes could also be used to provide an additional dimension beyond spatial dimensions for the optical storage of digital data. The idea of using transient spectral holes for data storage was patented by Szabo [1.6], and Castro et al. extended the idea to long-term data storage using persistent spectral holes [1.7]. The presence or absence of a hole at a given frequency within the inhomogeneous line could be used to encode a digital "1" (or "0"). Due to the size of f, many thousands of bits could perhaps be stored in one diffraction-limited laser spot. This storage scheme has been called "frequency-domain optical storage", and it would offer extremely high areal densities as well as fast random access by beam deflection and laser frequency tuning. In fact, frequency-domain optical storage is the potential application of PSHB that has received the most attention in recent research.

1.3 Historical Overview

The first examples of electronic spectra of organic compounds with well-resolved vibronic structure were obtained about 40 years ago for some aromatic hydrocarbons (benzene, naphthalene, and some derivatives) in crystals at low temperature. They were described in the studies of Pesteil [1.8].

In 1952, Shpol'skii et al. [1.9] dissolved some aromatic hydrocarbons in n-paraffins (n-hexane, n-heptane, etc.). At low temperatures, they obtained fluorescence and absorption spectra consisting of several comparatively narrow bands or quasi-lines with a width of 2-20 cm^{-1} instead of broad bands. Investigations about the nature of quasi-line spectra led to the conclusion that the lines correspond to optical zero phonon transitions and that they possess all the theoretically expected features of such transitions [1.10-13]. By now, several hundred compounds are known to give quasi-line spectra in n-paraffin matrices. However, powerful as it is, the Shpol'skii method does not succeed in all cases and is not the only means to obtain fine-structured spectra. Many molecules give broad-band spectra even in n-paraffin matrices at low temperature. Taking into account the great variety of organic compounds and the wide choice of organic solvents, one can say that the majority of solutions of complex molecules possess broad-band spectra even at liquid helium temperatures.

In 1972, Personov et al. found that the low-temperature spectra of many organic solutions are broadened mainly inhomogeneously and possess concealed fine structure. The spectra consist of the sum of many zero phonon lines [1.14]. In emission spectra, this line structure can be revealed by selective laser excitation, a method called fluorescence line narrowing (FLN). In that work, it was also shown that the zero phonon line's intensity drops during laser irradiation; i.e., some photochemical or photophysical "burning out" of the selectively excited guest molecules takes place. Later, in 1974, it was shown that this process leads to the appearance of narrow persistent holes in absorption bands [1.15] (persistent spectral hole-burning, hereafter called simply hole-burning). After a few years, fluorescence line narrowing and hole-burning techniques started to be used for very fine and precise spectroscopic measurements of guest molecules in solids. Then appeared the first studies of the homogeneous linewidth [1.3,5,16] and of external field effects (Stark [1.17-19] and Zeeman [1.20,21] effects), their first application of these techniques to spectrochemical analysis [1.22] etc. Even at liquid helium temperatures, molecular lines are not fixed in the inhomogeneous spectrum but drift over many time scales, a process called spectral diffusion. Hole-burning started to be applied to the study of spectral diffusion in organic glasses [1.23-26]. Many different applications of fluorescence line narrowing and hole-burning have been discussed in reviews [1.1,2,27,28]. We will consider some of them below.

It is necessary to stress that fluorescence line narrowing and hole-burning techniques (called together site selective or energy selective spectroscopy) cannot remove all inhomogeneity. In fact, impurity molecules having the same optical transition energy may differ from each other in their guest-host interactions, their excited-state lifetime, their homogeneous linewidth, etc. Therefore, even energy selective spectroscopy at very high resolution provides average information about ensembles of molecules. An important advance in this direction was the recent discovery by two research groups of a new branch of high-resolution spectroscopy of the solid-state, single molecule spectroscopy. In 1989, Moerner and Kador published results of the first optical detection of single pentacene molecules in a p-terphenyl crystal via a sophisticated technique of doubly-modulated absorption [1.27-29]. In 1990, Orrit and Bernard [1.30] succeeded in detecting single molecules in the same system by using fluorescence excitation. They showed that this much simpler and very sensitive method provided dramatic improvement of the signal-to-noise ratio. This technique has opened a novel spectroscopy of the individual molecule in solids, in which all kinds of inhomogeneity and averaging are suppressed.

Before going to the latest results and their discussion, we shall briefly recall some general principles of the site selective (or energy selective) spectroscopy of solids.

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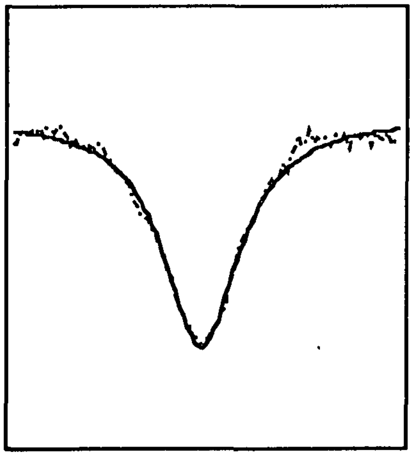
BASIC PRINCIPLES OF PERSISTENT SPECTRAL HOLE-BURNING



CHAPTER 2

2. BASIC PRINCIPLES OF PERSISTENT SPECTRAL HOLE-BURNING

2.1 Purely Electronic Lines and Phonon Sidebands

The cornerstone of persistent spectral hole-burning is the zero-phonon line (ZPL). Among ZPLs the purely electronic zero-phonon line (PEL) is of special interest. The majority of the persistent spectral hole-burning (PSHB) in investigations and all of them performed at the highest resolution have been done on PELs. PELs attain very narrow homogeneous linewidths and high peak intensities at liquid helium temperature. This holds not only for guest ions or atoms in single crystals (e.g. rare-earth guest ions in single crystals of fluorite), where the presence of narrow lines (linewidths of about 1cm^{-1}) had been well known earlier, but also for a large body of small and complex molecules in various solid matrices - polycrystals, glasses, and polymer films [2.1].

The main differences between the optical bands of a molecule in a solid matrix and those of the same molecule in the gas phase stem from the interaction with lattice vibrations, which we call phonons hereafter. The profile of vibronic bands is determined by the electron-phonon coupling. At low temperature, every vibronic band consists of a narrow zero phonon line and a relatively broad phonon sideband (PSB), (sometimes called the phonon wing), lying at the long-wave side of the zero phonon line in emission and at its short-wave side in absorption. The zero phonon line corresponds to a transition of a guest molecule without any change in the number of phonons in the matrix. Fig.2.1 depicts an inhomogeneously broadened origin of vibronic absorption band at low temperature. The sharp dashed bands are the zero-phonon lines ZPL of the "guest" molecule occupying inequivalent sites. Phonon sidebands are related to the phototransitions of the molecule in which matrix phonons are created or annihilated [2.2-4]. Today there is no doubt of the presence of PELs, vibronic ZPLs and associated phonon sidebands in the low temperature spectra of a large number of various guest atoms, ions, and molecules in different matrices. The conditions of their existence and principal properties can be reasonably well understood in the framework of a fairly simple theory [2.5,6]. The main task of the theory in understanding PSHB is to describe the spectrum of one single guest molecule in the solid matrix - the homogeneous spectrum. The presence of PELs in spectra opens new avenues for high-resolution spectroscopy and frequency-selective photochemistry.

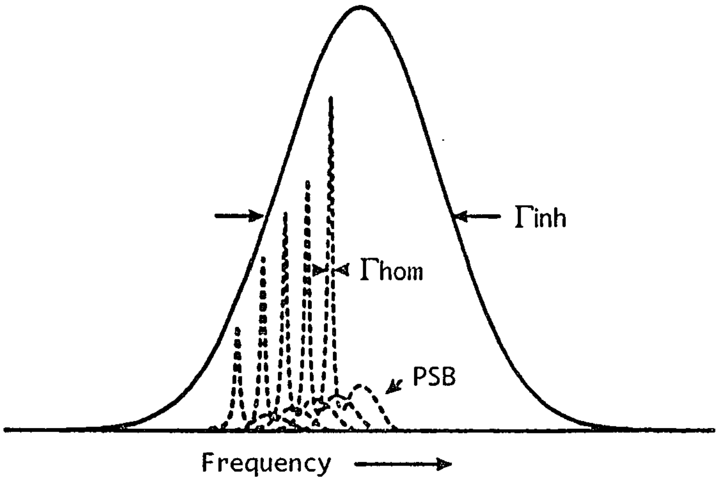


Figure 2.1. Schematic representation of homogeneous (Γ_{hom}) and inhomogeneous (Γ_{inh}) broadening and phonon sidebands (PSB). Ref.2.33.

Because of their small linewidths, ZPLs and especially PELs are extremely sensitive to inhomogeneities in the matrix structure. The inhomogeneous broadening is tremendous in comparison with the low-temperature homogeneous linewidth. In fact, inhomogeneous broadening is the reason why the PELs and vibronic ZPLs often do not show up in spectra at all. Even in luminescence spectra of small molecules in single crystal matrices with pronounced vibronic structure measured under conventional broad-band excitation, the linewidths of PELs are, because of inhomogeneous broadening, about 1 cm^{-1}, i.e., 10^3-10^4 times broader than the corresponding homogeneous linewidth. The enormous inhomogeneous broadening of PELs is the reason that for a long time the extremely small linewidths and high peak intensities of homogeneous PELs were considered to be of only purely theoretical interest.

The development of laser spectroscopy has provided two effective and relatively simple methods to overcome the problem of inhomogeneous broadening: the site-selective excitation of fluorescence or fluorescence line narrowing, and the photo-induced burning of spectral holes or dips (PSHB). These methods increase the importance of PELs in molecular and solid state spectroscopy and eliminate inhomogeneous broadening-induced disadvantages of optical PELs.

PSHB has some essential advantages over the fluorescence line narrowing method. One is the convenience of studying the homogeneous PEL itself, which is quite complicated with the method of site-selective excitation of fluorescence. Further, PSHB is not only a powerful method for performing spectroscopy without inhomogeneous broadening, but it also provides the possibility of inducing spectrally selective changes in solid matter. Actually, PSHB turns the inhomogeneous broadening of the absorption band of the guest molecule into a useful feature; owing to PSHB one can selectively excite single homogeneous PELs within a broad band of frequencies. In other words, the phenomenon of PSHB implies that an inhomogeneous broad band represents an ensemble of a large number of very sharp and intense resonances ($\Gamma_{\mathrm{hom}} \sim 10^{-3}$-$10^{-4}$ cm^{-1}) covering a broad band of frequencies ($\Gamma_{\mathrm{inh}} \sim 100$-$1000$ cm^{-1}). It is clear that such unique systems of narrow optical resonances built-in by nature provide new possibilities for novel physical phenomena. Among the possible applications are narrow-line optical filters and spectral devices for optical data processing and information storage (high-density optical memories, time-domain holography).

At this point, it is important to discuss the concepts of ZPL, PEL, and PSB in detail. The homogeneous spectrum is the spectrum of one single guest atom or molecule as mentioned earlier. An ensemble of impurities even at low concentrations will show the same spectrum only in an ideal case when all the guest molecules are absolutely identical, and experience absolutely identical interactions with the surrounding matrix. This is never the case with the conventional solid matrices, and actual guest molecule spectra observed are always inhomogeneous. The basic properties of the inhomogeneous spectra, which we shall consider in the next section, are also determined by the homogeneous spectrum.

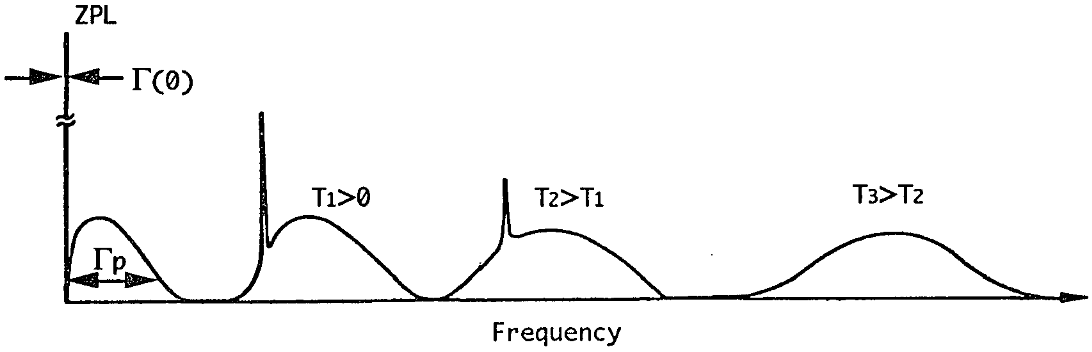


Figure 2.2. Purely electronic zero-phonon line and phonon sideband in the guest molecule homogeneous absorption spectrum and its dependence on temperature T. Ref.2.1.

Let us consider a guest molecule where no local vibrations are present and focus our attention on the electronic transition accompanied by creation-annihilation of phonons of the (matrix) lattice modes. Due to the acoustic phonons whose frequencies begin from zero, the energy spectrum of the transition covers a more or less broad-band interval; it is always continuous. Nevertheless, theory [2.1] tells us that the homogeneous spectrum of the transition is as shown in Fig. 2.2. At T=0 there is a sharp PEL of high intensity, the ZPL, which corresponds to the electronic transition without creating any phonon (there is nothing to annihilate at T=0). The PEL linewidth Γ(0) is determined by the excited electronic decay time $T_1(0)$, where

$$\Gamma(0) = (2\pi T_1(0))^{-1}. \tag{2.1}$$

For allowed optical transitions in the absence of non-radiative decay processes we have $T_1 \sim 10^{-7}$-10^{-8} s, and, correspondingly, $\Gamma(0) \sim 10^{-4}$-10^{-3} cm^{-1}. The PELs are even narrower for forbidden transitions, but in these cases more subtle details of the theory have to be taken into account when estimating the actual values of Γ [2.1].

At T>0 the PEL broadens due to dephasing processes caused by phonons excited by the thermal motion. Dephasing by phonons is due to electron-phonon interactions and may be considered as quasi-elastic scattering of a phonon at the guest molecule, resulting in a change of the phonon's direction of propagation and in a very small, if any, change in its energy. On the other hand, the phonon scattering event results in an abrupt change of the phase of the wave function of the excited electronic state. The electron is left in the excited electronic energy level L , but the time-dependent part of its wave function, exp $(iE_L t/h)$, is changed to $\exp[i(E_L t/h+\delta)]$, δ being a random phase shift. This means that the lifetime of the quantum state, i.e., the state with a fixed wave function is shortened, and the corresponding homogeneous linewidth has to broaden in comparison with the value determined by the excited-state energy decay time. On the other hand, for an ensemble of impurities this dephasing means that the coherence time of the ensemble of impurities is shortened, too. Zero-point phonons cause no dephasing. The density of thermal phonons increases with temperature, and that is the main source of the temperature broadening of PELs.

In the frame work of the adiabatic and Franck-Condon approximations, the intensity I of the optical band profile may be described in the form

$$I(\nu,T) = I_{ZPL}(\nu,T) + I_{PSB}(\nu,T) \tag{2.2}$$

where $I_{ZPL}(\nu,T)$ and $I_{PSB}(\nu,T)$ are the intensities of zero phonon line and phonon sideband, respectively. The zero phonon line has a Lorentzian shape with the width $\Gamma(T)$. The ratio of zero phonon-line and phonon sideband intensities can be characterized by the Debye-Waller factor $\alpha(T)$, which depends on temperature according to

$$\alpha(T) = I_{ZPL}/(I_{ZPL} + I_{PSB}) = \exp[-s(T)] \tag{2.3}$$

When temperature is increased, s(T) increases, so that I_{ZPL} and $\alpha(T)$ decrease rapidly. Therefore, zero-phonon lines can be observed at low temperatures only.

But spectra usually show no fine structure even at low temperature. The reason for this is the inhomogeneous broadening due to somewhat different local conditions around guest molecules, which cause a statistical distribution of their energy levels [2.7]. The microscopic sources of inhomogeneous broadening are electrostatic, polarization, and dispersion interactions, short-range repulsion, and specific interactions like hydrogen bonds. Their effect on the optical band depends strongly on matrix structure. In ordered systems, random strains and stresses due to defects and to impurities slightly shift the zero phonon lines of individual molecules. Therefore, inhomogeneous broadening is small, but significant, in crystals ($\Delta\nu \sim 1\text{-}20\ \mathrm{cm}^{-1}$), in the quasi-line spectra of molecules in n-paraffin matrices, or in specially selected guest-host couples. Glassy or amorphous matrices are characterized by their lack of long-range order and the broad variety of local environments. The spread of zero-phonon line frequencies is therefore especially large in amorphous matrices ($\Delta\nu \sim 10^2\text{-}10^3\ \mathrm{cm}^{-1}$). Since the inhomogeneous band is built from the superposition of many narrow homogeneous lines, specific experimental techniques are needed to eliminate the inhomogeneous broadening.

As mentioned earlier, the PEL is accompanied by a broad continuous band, the phonon sideband, corresponding to the transitions in which phonons are created (T=0) or both created and annihilated (T>0). The detailed structure and the width of phonon sidebands vary depending on the local lattice dynamics at the guest molecule, i.e. on the phonons in the vicinity of the guest molecule. In addition, the phonon sideband depends on the strength of the coupling of the electronic transition to the vibrations, i.e. on the changes in local dynamics caused by the change of the electronic state. Multiphonon transitions are quite often not only present, but even predominant, and so the width Γ_p of the phonon sideband is not necessarily limited by the width of the phonon spectrum. On the other hand, if the interaction takes place only with the long-wavelength phonons (which may be the case for large-radius guest molecules), the phonon sideband may be considerably narrower than the acoustic phonon spectrum. Nevertheless, the latter can serve as a starting point, and we shall use the estimate $\Gamma_p \sim$ 10-1000 cm^{-1}. Thus the purely electronic ZPL is very sharp: it is 10^4-10^7 times narrower than the phonon sideband attached to it.

When discussing the shape of the narrow structures observed in fluorescence line narrowing or hole-burning, the broad phonon sidebands should also be taken into account. They give rise to structures from "nonresonantly" excited centers (see Fig.2.3.a), which in fluorescence spectra lead to an increase of the long-wave phonon sideband (Fig.2.3.b, hatched area) and to a reduction of the observed Debye-Waller factor. In hole-burning spectra, they cause an increase of the short-wave phonon sideband of the hole and the appearance of a specific and intense long-wave sideband near the narrow zero-phonon line hole (Fig.2.3.c, hatched area). In this review, we will consider only the narrow features of the optical bands caused by zero-phonon lines.

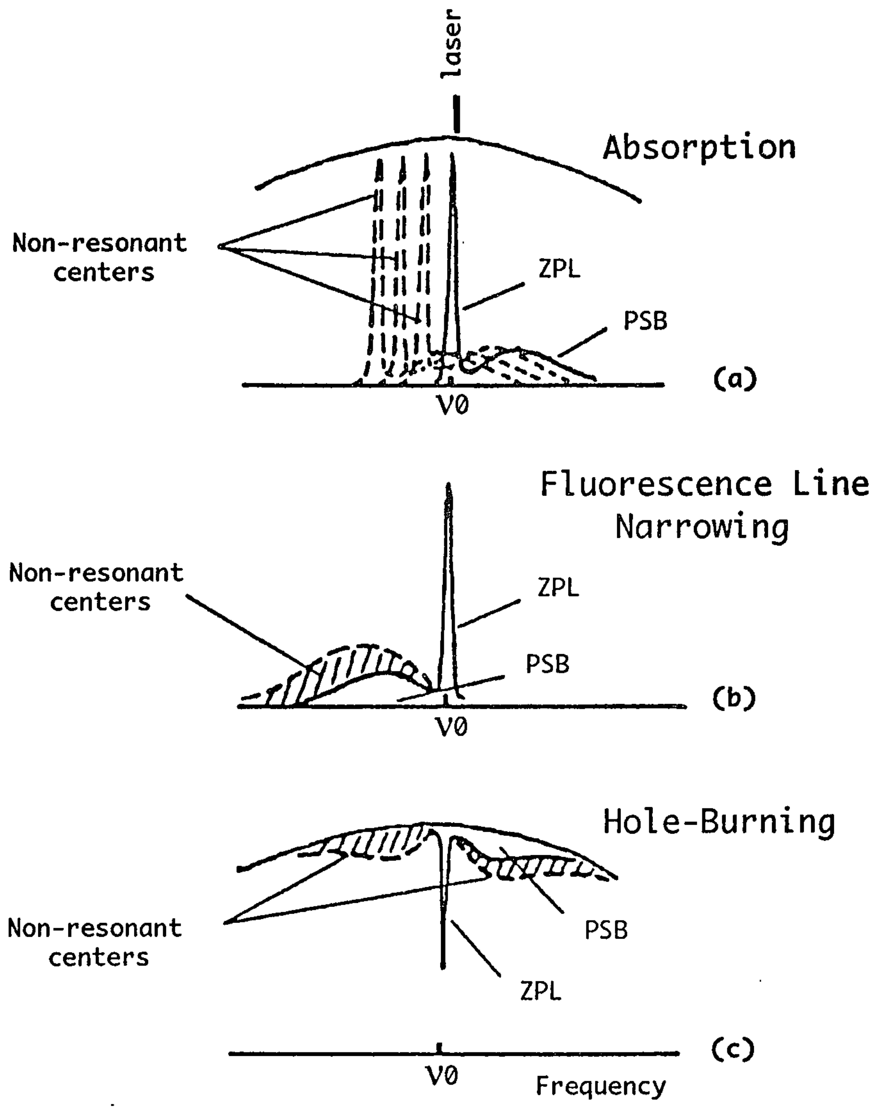


Figure 2.3. Examples of fluorescence line narrowing and persistent hole-burning diagrams explaining how zero phonon line and phonon sidebands arise. Ref.2.34.

For many applications, it is important to analyze the shape of narrow holes. For low laser intensity and short burning time, the hole profile is described by the expression

$$-\Delta D = (m \cdot n_p)^2 (m \cdot n_b)^2 \varepsilon(\nu - \nu_0)\, \varepsilon(\nu_b - \nu_0)\, d\nu_0\, d\Omega \qquad (2.4)$$

Here ΔD is the change in the optical density of a sample in the region of the narrow hole. ν_b is the burning frequency, m, n_p, and n_b are unit vectors in the directions of the transition dipole moment of the molecule and the polarization of the probing and burning light, respectively. $\varepsilon(\nu-\nu_0)$ is the homogeneous profile of the zero phonon line, and Ω is the set of Eulerian angles for molecules in the laboratory coordinate frame. If $\varepsilon(\nu-\nu_0)$ is Lorentzian, its width Γ_{hom} (or Γ_{ZPL}) is related to the holewidth Γ_{hole} by $\Gamma_{hole}=2\Gamma_{hom}$. This relationship is used for measurements of Γ_{hom} and its temperature dependence. At liquid helium temperature, for purely electronic transitions, typical values of Γ_{hom} are around 10^{-2} cm^{-1}. Many important details concerning fluorescence line narrowing and hole-burning spectroscopy and their applications can be found in reviews [2.1,2,8].

A few years ago, new experiments demonstrated the possibility of the optical detection of single molecules in solids at liquid helium temperature, either by absorption [2.9,10] or by fluorescence excitation [2.11,12]. In contrast to experiments at room temperature in liquids [2.13,14], the solid state at low temperature allows fine spectroscopic studies on single molecules, called single molecule spectroscopy. Single molecule spectroscopy opens up promising perspectives in trace detection, in the spectroscopy of localized neighborhoods, and in the optical addressing of local areas in solids.

Selective spectroscopy allows precise measurements to be performed within inhomogeneously broadened bands or lines. The spectral resolution can be improved in this way by a factor 10^3-10^5. This is now a rapidly growing field of molecular and solid-state physics. Many interesting and important results were obtained by selective spectroscopy of inorganic systems [2.1], but here we restrict ourselves to organic materials. Let us point out here some of the many different applications of these methods.

Fluorescence line narrowing and hole-burning techniques allow precise determination of molecular vibronic levels in ground and excited electronic states and investigation of the different intramolecular relaxation processes. These methods have been applied to the study of a number of aromatic hydrocarbons, heterocyclic compounds, porphyrins, phthalocyanines, and some dyes. In recent years, selective methods have also been used for some new systems: ionic forms of molecules [2.15], conjugated polymers [2.16], important biological systems such as the reaction centers of photosynthesis [2.17-20], and biopolymers [2.21-22].

Many properties of amorphous solids (for example, specific heat, thermal conductivity, etc.) at low temperatures differ drastically from those of crystals [2.23]. These differences are explained by the existence of many local minima in the complex potential energy landscape of a glass. The dynamical properties of glasses can be described by modeling the transitions from one local minimum to another by a simple two-minima model (the so-called two-level system, TLS).

The optical properties of guest molecules dissolved in glassy and crystalline matrices also differ strongly at low temperature. It was demonstrated recently that hole-burning and fluorescence line narrowing techniques are very promising tools to study the dynamics of amorphous solids.

A zero-phonon transition is one for which no net change in the number of phonons accompanies the electronic transition. Building to higher energy on each ZPL is a broad phonon sideband. Each single site ZPL carries a homogeneous linewidth, Γ_{hom}, which is determined by the total dephasing time T_2 of the optical transition. The homogeneous linewidth Γ_{hom} of the zero-phonon line is

$$\Gamma_{hom} = (\pi T_2)^{-1} = (2\pi T_1)^{-1} + (\pi T_2^*)^{-1} \tag{2.5}$$

where T_1 is the population decay time of the excited state and T_2^* is the pure dephasing time determined by fast residual thermal motion. The temperature dependence of Γ_{hom} arises from that of T_2*. In crystalline matrices, dephasing is caused by electron-phonon coupling. For Debye acoustic phonons, the dependence of Γ_{hom} on temperature T is $\Gamma_{hom} \alpha T^n$ where n=7 for $T<<\Theta$ and n=2 for $T>>\Theta$, Θ being the Debye temperature [2.3,4]. If a local or psuedolocal mode in the crystal is responsible for the dephasing process (which happens in many cases), $\Gamma_{hom}(T)$ decreases exponentially when T-->0. In amorphous matrices at liquid helium temperatures, the zero phonon linewidth is 1 or 2 orders of magnitude larger than in crystals and in most cases has a dependence $\Gamma_{hom} \alpha T^n$, with 1<n<2 [2.1,2]. The theoretical approaches to dephasing in glasses are based on the TLS model, which may also explain spectral diffusion as discussed below.

Disordered solids, or glasses, are nonequilibrium systems and evolve with time. The relaxation processes of glasses produce so-called spectral diffusion. Because of the evolution of the surrounding matrix, the resonance frequency drifts (diffuses) within the inhomogeneous spectrum. Therefore, results of a linewidth measurement will depend on the time scale of the experiment. Indeed, careful comparison of the experimental data obtained by hole-burning to those obtained by photon echoes showed that "homogeneous" linewidths are much smaller when measured by photon echoes [2.24]. These data prove that spectral diffusion processes slower than dephasing take place in glasses in the time span between hole-burning and hole-recording. Optical experiments have confirmed the broad distribution of characteristic times for spectral diffusion in organic glasses, from picoseconds [2.25,26] to hours [2.27]. Recently, the study of the long-lived stimulated photon echo at 1.5 K has proved a very convenient method for the study of spectral diffusion processes between picoseconds and milliseconds [2.28]. But the detailed mechanisms of spectral diffusion and the molecular nature of the TLS's in organic glasses are still ill-known, and much work should be done to understand them better. Single molecule spectroscopy seems very promising in this respect.

2.2 Inhomogeneous Broadening of Purely Electronic Lines

The first consequence of the high spectral resolution of PELs is that even very small differences in the influence of the matrix on the guest molecule cause frequency shifts of PELs that are much larger than their linewidth. This leads to a tremendous inhomogeneous broadening. The high spectral resolution of a homogeneous PEL disappears very easily in a real ensemble of absorbing centers.

In a reasonable approximation, small differences in guest molecule sites cause shifts of the homogeneous spectrum as a whole in frequency space without any change of the PEL lineshape. In that case, it is convenient to introduce the inhomogeneous distribution function $\rho(\nu)$. For a certain electronic transition $\rho(\nu)\Delta\nu$ gives the fraction of impurities which have their PELs in the frequency interval $\Delta\nu$ at ν [2.29]. The inhomogeneous distribution function depends not only on the inhomogeneities in the matrix (e.g., other impurities of the same and different kinds, point, linear and surface defects of the matrix, and the stress field in it) but also on the character of the transition under consideration. If both the ground and excited electronic states undergo equal energy shifts, there will be no inhomogeneous broadening and the inhomogeneous distribution function becomes a very narrow peak. This is the case for most f-f transitions in rare-earth ions.

Of course, the inhomogeneous structure of the matrix has some influence on the frequencies of local modes, on the Debye-Waller factors, and on the electronic transition probabilities as well. The inhomogeneous distribution function may be easily generalized to describe the first of these influences. The other effects may be of importance in some special cases, e.g., for electronic transitions forbidden by spatial symmetry of the guest molecule. Further, for very small samples, very low concentrations, and very high spectral selectivity the statistical fluctuations of the number of impurities have to be taken into account.

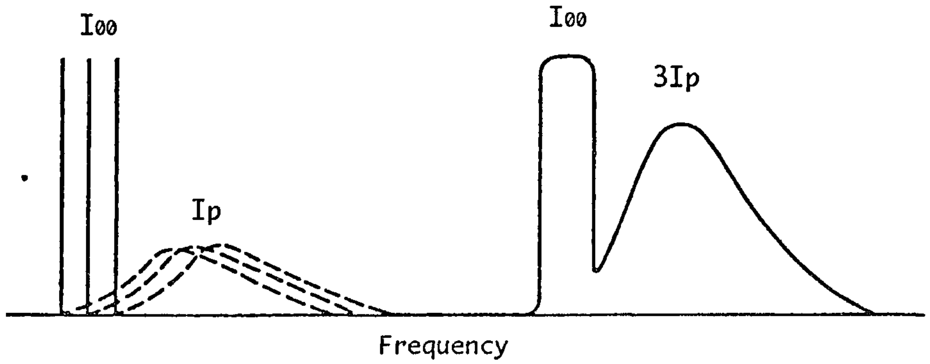


Figure 2.4. Formation of inhomogeneous zero-phonon line and phonon sideband for the case of three guest molecules. Ref.2.1.

Below we shall mainly consider smooth, single-maximum inhomogeneous distribution functions with simple bell-like shapes. The linewidth of an inhomogeneous distribution function, Δ, is always much larger than the homogeneous $\Gamma(0)$ and often narrower than the phonon sideband's Γ_p. Fig.2.4 shows an example of how the unique properties of the homogeneous PELs are destroyed by inhomogeneity. The superposition of three shifted homogeneous spectra results in summing up the phonon sideband intensities while the resultant PEL becomes only broadened. The simplest calculation shows that the peak intensity of an inhomogeneous PEL increases with the number of impurities N as $(\Gamma(0)/\Delta)N$, while the maximum intensity of a phonon sideband grows as $\Gamma_p N/(\Gamma_p + \Delta) \sim N$. Thus, the ratio of the peak intensities of the PEL and the respective phonon sideband in an inhomogeneous spectrum is reduced by a factor of $r = \Delta/\Gamma(0)$. In other words, if $\Gamma(0) << \Delta << \Gamma_p$, we will see PELs in the conventionally measured inhomogeneous spectra, whose shape is governed not by the homogeneous shape but by inhomogeneous distribution functions, as well as the phonon sidebands whose shapes are distorted to some extent by inhomogeneous distribution functions. This is the case for a number of optical transitions of rare-earth ions and O_2^--type molecules as impurities in ionic crystals and frozen gas matrices with $\Delta \sim 0.1\text{-}1\ \mathrm{cm}^{-1}$, and also for Shpol'skii systems, where $\Delta \sim 1\text{-}5\ \mathrm{cm}^{-1}$.

In these cases with relatively small inhomogeneities, rather sharp and intense PELs are present even in conventionally measured inhomogeneous spectra of absorption and luminescence. However, many solid organic guest systems, chemically analogous to the Shpol'skii systems, do not have any sharp spectral lines even at low temperatures. It is well-known that the reason lies not in strong electron-phonon coupling or other specific features of these systems, but in the strong inhomogeneous broadening. In fact, the latter may be almost completely eliminated and parts of the homogeneous spectra revealed by applying quasi-monochromatic laser excitation in the proper way. One technique for achieving this is frequency-selective excitation of fluorescence line-narrowing, another technique persistent spectral hole-burning (PSHB) spectroscopy.

Phonon sidebands are always present in guest molecule spectra, and they also appear in selectively excited inhomogeneous spectra. The inhomogeneous distribution function itself tells nothing about the phonon sidebands. Fig.2.5 represents an inhomogeneous absorption band (curve 3) composed of homogeneous spectra with a sharp PEL and a smooth phonon sideband (curve 2), where the inhomogeneous distribution function (curve 1) is several times broader than the sideband.

An inhomogeneous guest molecule absorption band is actually a superposition of two distinctly different parts: a continuous band representing the sum of overlapping phonon sidebands (curve 4), and a sum of sharp, purely electronic zero-phonon lines. Only the second part leads to spectral selectivity as a result of excitation. Under narrow-line laser illumination with frequency ν_L and bandwidth $\Delta\nu_L$, which is much narrower than that of the homogeneous PEL ($\Delta\nu_L << \Gamma_{hom}(T)$), a selected subset of impurities whose PELs lie in the frequency interval $2\Gamma_{hom}(T)$ about ν_L get excited. Strictly speaking, the homogeneous linewidth varies slightly in different parts of the inhomogeneous distribution function, but in most cases the dependence is very weak and may be neglected. Thermal broadening of PELs is the main reason for the loss of selectivity with increasing temperature.

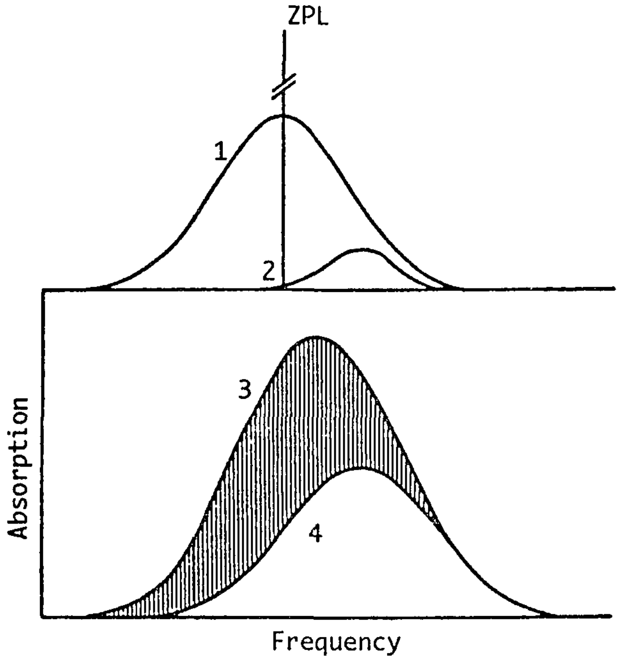


Figure 2.5. Illustrating the inhomogeneous distribution function (1), the homogeneous absorption spectrum of the guest molecule (2), and the inhomogeneous absorption band (3) as the sum of two parts: a continuous contribution (4) formed by the overlapping phonon sidebands of spectrum 2 and a particular one (between curves 3 and 4) formed by homogeneous zero-phonon lines distributed as given by curve 1. Ref.2.1.

It is clear from Fig.2.3 that the intensities of the two components of the inhomogeneous band depend strongly on the exact excitation frequency: the contribution of the PEL is more pronounced on the long-wavelength side of absorption, while the phonon sidebands prevail on the short-wavelength side. This is an obvious consequence of the shape of the homogeneous shown in Figs.2.5. If the inhomogeneous distribution function is narrow in comparison with the distance from the PEL to the maximum of the phonon sideband, the dependence on frequency becomes still more pronounced: on the short-wavelength side the inhomogeneous band consists of a sum of phonon sidebands only, whereas on the long-wavelength side the band consists of PELs. The shape of the latter is determined mostly by the inhomogeneous distribution function. Of course, if the inhomogeneous distribution function or the phonon sidebands are not smooth, the picture becomes more complicated [2.30,31].

2.3 Main Features of Persistent Spectral Hole-Burning

In site-selective spectroscopy, the guest molecules excited with near-monochromatic excitation usually luminescence or return back to the ground state via non-radiative transitions, and the initial inhomogeneous distribution function is restored. In general, however, a fraction of the selected group of molecules may be subject to phototransformations and thus not return back to the same ground state. The new ground state may have a very long lifetime if it is formed and fixed by new equilibrium positions of the same atoms of the molecule or matrix. As has been emphasized sect.2.2 even a slight change in the molecule or its surroundings is strong enough to move the PEL's frequency far away from ν_L in comparison to the PEL's low-temperature homogeneous linewidth. When this occurs, a fraction of the excited molecules is absent at ν_L after the excitation-deexcitation cycle is over, and a spectral hole (dip) is left in inhomogeneous distribution function as a long-lived label of the selectively excited body of molecules. The hole shape (depth, width, asymmetry) and its dependence on temperature, irradiation time, etc. provide a wealth of high-resolution spectral information about homogeneous PELs. The amazing fact is that the information is revealed by the molecules that are absent from the ensemble which formed the initial inhomogeneous distribution function.

Processes leading to spectral hole formation may be chemical reactions of the molecule itself or various rearrangements of the particles of the matrix. Some mechanisms have been discussed in Chapt. 1. Here we provide a list of the main features of persistent spectral hole-burning (PSHB).

1. A hole in the inhomogeneous distribution function has different manifestations in different spectra. Usually a hole is detected by recording the absorption, luminescence or excitation spectrum. But a hole in the inhomogeneous distribution function may be detected also in a vibrational band or in spectra of other kinds where inhomogeneous broadening of the transition occurs. We shall see further that excitation with one single frequency can create holes in several different overlapping inhomogeneous distribution functions and more than one hole in one inhomogeneous distribution function, if vibronic ZPLs are involved. One single hole in an inhomogeneous distribution function may give rise to several holes in the observed spectra.

2. An essential advantage of PSHB in comparison with site-selection spectroscopy is that the PELs are studied in the absence of any background of strong excitation resonant with the PELs.

3. In many cases of interest the holes are persistent, i.e. they may have extremely long lifetimes at low temperatures. For instance, in [2.32] a half-decay time of 22,000 years is reported for holes in the spectra of quinazirine molecules in deuterated alcohol glass (C_2D_5OD/CD_3OD 3:1). On the other hand, the process of PSHB itself must involve relatively brief excitation: if

the excitation lasts endlessly, all the inhomogeneous band will be burned away (i.e., transformed into an entirely different absorption spectrum) without any spectral selectivity left that is correlated with ν_L. The selectively burned holes are created as a result of the fact that PSHB develops along three different time scales. First, the molecules absorbing resonantly through their PELs at ν_L are removed from ν_L. Second, the molecules having their PELs at frequencies lower than ν_L are transformed due to absorption in phonon sidebands; third, the guest molecules having their PELs at frequencies higher than ν_L absorbed weakly through their anti-Stokes phonon sidebands. Of course, the last process actually has to be neglected at low temperatures and for PEL frequencies well above ν_L. However, the absorption via phonon sidebands is often competitive with direct PEL absorption, especially if there are vibronic ZPLs or other sharp peaks present. Thus, the hole shape is a time-varying function depending on the irradiation dose, and on the illumination time.

4. PSHB allows a piece of solid matter activated with impurities, having an inhomogeneous distribution function shown in Fig.2.5, to serve as a medium for photochemistry with high spectral selectivity. The sample may actually be regarded as a broad-band high-resolution spectral device for persistent recording and study of the spectrum of the incident light. Such spectral recording may also allow storage of the phase relations between the Fourier components of the incident light, which is equivalent to the recording of the time dependence of light pulses. In this fashion, space-time domain holography of fast processes of pico- and nanosecond duration becomes possible.

5. All methods of PSHB involve the preparation of persistent spectral filters and the study or utilization of their properties. The accuracy of the method in high-resolution spectroscopy depends fundamentally upon the

understanding of the relation of the hole shape to the characteristics of the homogeneous spectral line. To achieve narrow holes, the holes should not be "overburned", i.e. the irradiation doses must be rather modest. The same applies to the fluence used for reading. Further, the characteristic time τ_{HB}, i.e. the hole formation time plus the measurement time, must not be too long. The dependence of the hole shape on τ_{HB} is usually weak, but for some materials τ_{HB} plays a central role in determining the hole shape. This may be the case for glassy matrices even at very low temperatures, where the process of spectral diffusion still seem to be present (Chapt.4).

6. PSHB may be performed for modestly photosensitive guest molecules. In fact, holes can almost always be observed if one waits long enough: because of their usually large absorption cross-section the molecules whose PELs are in resonance with the laser frequency ν_L are being excited so frequently (in comparison with the molecules absorbing via their phonon sidebands) that something must happen to them in the end. The portion of exciting energy absorbed at ν_L in various phonon sidebands and the microscopic events leading to PSHB are distributed over a large number of guest molecules covering an interval of the inhomogeneous distribution function which is much broader than $\Gamma_{hom}(T)$. Of course, the quantum efficiency of PSHB is important in considering the time and laser power needed to burn a given hole and the actual observed parameters of holes - width, depth, stability. High photosensitivity results in a decrease of the excited state lifetime, as compared to optical or energy-transfer-limited values, and leads to broad energy levels, preventing the creation of narrow holes.

7. The dose of energy delivered to the sample to create a detectable hole may be small even if the hole-burning efficiency is very low. First, only a small fraction β of the guest molecules has to be transformed to create even a deep hole. For $\Delta = 100$ cm^{-1} and $\Gamma_0 = 0.001$ cm^{-1} we have $\beta = 10^{-5}$. For a guest

molecule concentration of 10^{-4} moles/mole, only one molecule out of 10^{9} in the sample has to be phototransformed to produce a narrow, 100% deep hole. Second, with sensitive techniques such as holographic detection even very shallow holes having a relative depth of 10^{-6} may be detected. In that case only one out 10^{15} molecules need to be transformed. Regarding further minimization of the number of phototransformations, we must not forget about the limits set by the fluctuations of the number of the impurities in the frequency interval of one hole, especially when we want to create and detect narrow holes in small spatial spots.

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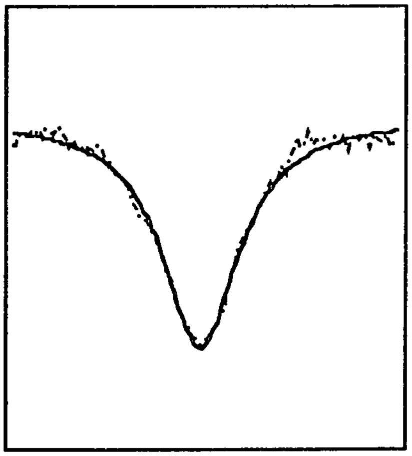
HOLE-BURNING MECHANISMS AND TECHNIQUES



CHAPTER 3

3. HOLE-BURNING MECHANISMS AND TECHNIQUES

3.1 Mechanisms

Hole-burning can be divided into two categories: permanent hole-burning and transient hole-burning. Within the first category, one may distinguish between photochemical hole-burning and photophysical hole-burning. The time scale on which photochemical and photophysical hole-burning experiments are performed is usually seconds to minutes, whereas transient hole-burning often occurs in micro- or milliseconds.

Table 3.1. Mechanisms for persistent spectral hole-burning. Ref.3.113.

Mechanism	Examples
Photochemical	
Proton tautomerization	Free base phthalocynines and porphyrins in n-alkanes, polymers
Photoionization and trapping	Color centers, rare earth and transition metal ions, trapped electrons in organic glasses, donor-acceptor systems
Hydrogen bond rearrangements	Quinazirine in hydrogen bonding glasses and polymers
Photodecomposition	s-tetrazine, dimethyl-s-tetrazine in crystals and polymers
Conformer interconversion	1,2-difluoroethane in rare gas matrices
Photophysical	
Host TLS transitions	Many photostable molecules and ions in glasses and polymers
Host H-bond rearrangements	Pentacene, thioindigo in hydrogen-bonded organic crystals
Photoinduced reorientation of guest	ReO_4^-, CN^- in alkali halides

After these pioneering observations, many researchers sought to establish the broadest class of mechanisms and materials that undergo persistent spectral hole-burning (PSHB). To date, upwards of hundreds of materials have shown the effect, in organic and inorganic crystals, glasses, and polymers. Here the various classes of mechanisms leading to PSHB will be briefly surveyed. On a general level, microscopic mechanisms leading to PSHB can be roughly classified into two categories: photochemical and photophysical. Photochemical mechanisms usually involve some internal change in the guest center itself, such as bond-breaking, ionization, isomerization, tautomerization, and so forth. Photophysical mechanisms arise from a change in the environment around the center, or perhaps a reorientation of the center itself with respect to the local environment. Although this classification scheme is not completely rigorous, it does provide a good starting point for a discussion of the mechanisms. In the remainder of this section, a selection of mechanisms for PSHB will be presented using Table 3.1. The reference list presented here is by no means exhaustive; it should provide a good starting point for a study of the literature.

3.1.1 Photochemical Hole-Burning

Two types of photochemical reactions lead to hole-burning: intramolecular reactions within the guest molecule, and intermolecular reactions between the guest and the host. Intramolecular photochemistry may be reversible (e.g. phototautomerism in free-base porphyrins [3.1,2,3-7], or irreversible (e.g. photodissociation of dimethyl-s-tetrazine [3.8] and s-tetrazine [3.9]). Further, the photochemical process can be the result of the absorption of one photon (e.g. porphyrins [3.1], quinazirine [3.10-12], ionic dyes [3.13,14]), or two photons (e.g. dimethyl-s-tetrazine [3.15] and carbazole in boric acid glass [3.16]). In all these cases, absorption band of the photoproduct is usually well separated from the original absorption band. Photochemical holes are persistent for hours or days, as long as the sample is kept at low temperature.

Starting at the top of Table 3.1, the reversible proton tautomerization process of free-base phthalocyanines and porphyrins was studied as early as 1971 using broad band spectroscopy [3.17,18]. The mechanism is light-induced tautomerization of the pair of central imino protons in the molecule. It was later recognized that this photochemical mechanism is a route to PSHB that can operate in virtually any kind of matrix [3.19,20]. In a sense, free-base porphyrins and phthalocyanines can be viewed as bistable devices, in that either of the two tautomers can be stable at low temperatures and light (or heat) can induce transformations between the two forms. This mechanism has provided many materials for the study of dephasing and temperature dependence of holewidths [3.21,22] and a variety of other effects, such as spectral diffusion [3.23], and Stark effects [3.24].

A second fairly general mechanism for PSHB is photoionization of the defect and subsequent trapping of the ejected electron. The basic process is thought to involve photoinduced tunneling of the optically excited electron from the center to a nearby trap, because usually the optical excitation energy is less than the actual ionization threshold. The ionized center often has quite different energy levels, which generally yields a drop in absorption at the excitation wavelength. Aggregate color centers in inorganic crystals provide a number of examples of this mechanism [3.25,26]. Photoionization has also been observed for rare-earth and transition metal ions in crystals [3.27-29], trapped electrons in organic glasses [3.30], J-band aggregates [3.31], and recently for donor-acceptor systems in polymers [3.32].

Hydrogen bond rearrangements form another photochemical mechanism for PSHB. (Here rearrangements within the molecule or between the molecule and the host are of interest; spectral holes caused by host hydrogen bond rearrangements alone are mentioned below as photophysical mechanisms.) This process usually requires a molecule with an adjacent pair of carbonyl-hydroxide substituents in which a hydrogen atom can form a hydrogen bond to one or the other of two oxygen atoms. 1,4-dihydroxy-anthraquinone (quinazirine) serves as the principal example of this class of mechanisms. This molecule and its derivatives have been extensively studied in alcohol and boric acid glasses [3.33,34], polymers [3.35], and even in amorphous silica [3.36].

Photochemical hole-burning can also occur when the absorbing center simply decomposes upon photoexcitation. The first example of PSHB by this process was provided by s-tetrazine in crystals and polymers [3.37-39]. Recently, two-color photodecomposition has been reported for a tetracene-anthracene adduct [3.40].

The preceding mechanisms for PSHB have all involved excitation of electronic transitions. In fact, spectral holes can also form in some systems if vibrational modes of the electronic ground state are excited. For example, infrared-induced conformer interconversion has been shown to lead to spectral hole formation for 1,2-difluoroethane in rare gas matrices [3.41]. Using CO_2 or lead salt diode lasers, molecules were transformed between trans and gauche conformations at low temperatures, yielding spectral holes. Because the molecular changes in this case are fairly subtle compared to photodissociation or photoionization, this mechanism is one in which it is not so easy to clearly classify as photochemical or photophysical.

3.1.2 Photophysical Hole-Burning

Photophysical hole-burning process is characteristic for amorphous systems. After excitation with a narrow-band laser, a slight structural rearrangement of the local environment of the guest molecule seems to take place [3.42-48]. Small and co-workers [3.43,49,50] have proposed a mechanism to explain the phenomenon. They assumed that the guest molecule in its ground and excited states is coupled to very low frequency excitations of the glass, the so-called two-level systems (TLS) (see below), and that tunneling occurs in the electronically excited state followed by relaxation to a different ground state configuration. As a consequence, the optical transition is shifted, and a photophysical hole appears in the absorption band. The spectral position of the "photoproduct" is expected to be very close (<2 cm^{-1}) to the original molecule [3.43], usually within the inhomogeneously broadened absorption band. Photostable organic molecules that undergo photophysical hole-burning in glassy matrices are, for example, perylene [3.42], tetracene [3.43,49,50], and pentacene [3.47,48]. A similar type or photophysical hole-burning has also been observed in inorganic glasses doped with rare earth ions [3.45].

Whereas in photochemical hole-burning holes are produced due to photochemistry involving the guest molecules in the matrix, in photophysical hole-burning holes are produced through rearrangements of the matrix itself. Although this distinction between photochemical and photophysical hole-burning appears straight forward, it is better, perhaps, to think in terms of a continuum of hole-burning mechanisms rather than clearly distinct mechanisms. Thus PSHB mechanisms may be visualized as proceeding from the intramolecular photochemical hole-burning, in which bonds in the absorber may be rearranged; through intermolecular photochemical hole-burning, in which bonds between the absorber and solvent are rearranged; to photophysical hole-burning in which only matrix bond rearrangement is operative. We will return to the matter of categorizing and distinguishing between hole-burning mechanisms in a moment, but first we will elaborate a bit further on the nature of glasses and the mechanisms of photophysical hole-burning.

The nature of disordered solids, e.g. glasses and polymers is fundamental to understanding how photophysical hole-burning occurs. That disordered solids are basically different from crystalline media was first noted in measurements of the specific heat and thermal conductivity of glasses at very low temperatures [3.51]. The specific heat was found to contain a linearly temperature-dependent part and the thermal conductivity a quadratic temperature dependence in contrast to the cubic dependence expected for both quantities which is observed in crystals. These observations indicated that while the low-temperature properties of crystals are determined by phonons, a different type of low-energy excitation dominates the low-temperature behavior of disordered media. It was proposed by Anderson et al. [3.52] and by Phillips [3.53] that glasses are characterized by atoms or groups of atoms, which can occupy nearly isoenergetic configurations, the so-called two-level systems, or TLS.

Finally, the simulations clearly illustrate the difficulties attendant upon a glass system at low temperatures attempting to attain thermal equilibrium. Fig.3.1 presents a transition mapping for an amorphous packing. Each filled circle represents a potential-energy minimum, and lines connecting minima represent feasible localized transitions of the system. The figure shows that there is a sparse and widely separated set of minima at the low-potential limit. The minima labeled A and B are two such minima. As the system is cooled to low temperatures the system will tend to be trapped along one of the downward-hanging tendrils, such as that ending at A. To remain in thermal equilibrium the system must have kinetic access to lower minima such as B. However, such access requires substantial backing up to higher potential configurations. Thus, thermal equilibrium is frustrated by deadends. This explains why photophysical hole-burning cannot be a driving force for the system to reach thermal equilibrium.

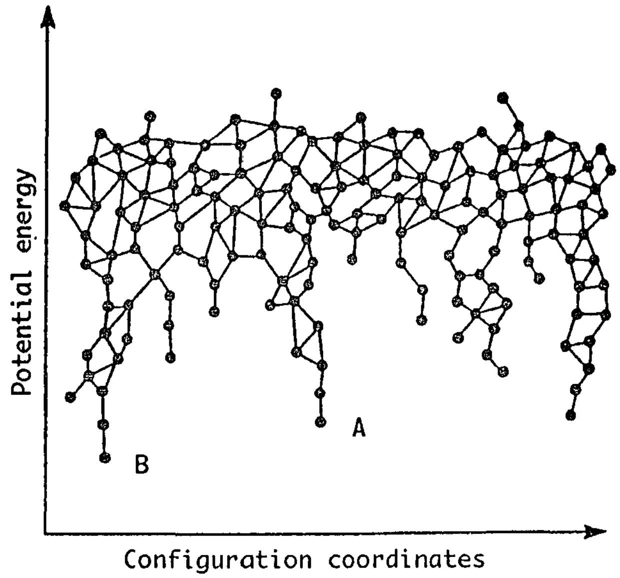


Figure 3.1. Schematic representation of the transition network for amorphous packings. Ref.3.113.

Although the originally proposed TLS model was meant to explain phenomena that only occur at temperatures in the vicinity of 1 K, the model has subsequently been extended to a variety of phenomena in which there is anomaly in either magnitude or temperature dependence in glasses relative to the same quality in crystalline media. Table 3.2 summarizes some of the anomalous glass properties which have been observed. Photophysical hole-burning is one of the basic tools for determining homogeneous optical linewidths in disordered media. An understanding of the observed temperature dependence for optical absorption and emission linewidths is one of the more active and challenging areas of photophysical hole-burning research.

The absorption spectra of materials dissolved in a disordered matrix are generally very broad due to site inhomogeneous broadening, i.e. the energy of electronic transitions of molecules is influenced by the disordered environment. This results in a distribution of absorption energies rather than a sharp absorption line. For any single guest molecule the absorption energy is thus sensitive to the arrangement of solvent molecules around it . If the solvent cage rearranges, then there is a shift of the absorption energy for that molecule. A driving force for inducing such a shift is the absorption process itself. If, as described above, there is a distribution of low-energy solvent rearrangements and if as is evident from the large absorption linewidths, there is a coupling between the solute and the solvent, then it is not difficult to imagine that during the excited-state lifetime or during nonradiative decay to the ground state, through this coupling a transition between the minima of a TLS can be induced. The effect of this TLS transition is that the microenvironment around the excited molecule has changed, and following deexcitation the absorption energy has changed. The coupling mechanism between the TLS and the absorbing species is, of course, the familiar electron-phonon coupling, and as the coupling strength varies, this is manifested in the nature of the hole.

Table 3.2. Comparison of glass and crystal properties. Ref.3.113.

Property	Crystal	Glass	Rel.Magnitude*
Specific heat	T^3	$cT + cT^3$	larger
Thermal conduct.	T^3	$\sim T^2$	smaller
Ultrasound atten.		saturates	larger
Sound velocity	T independent	ln T	10-100
Dielectric constant	T independent	ln T	10-100
Optical linewidth	T^7	T-T^2	10-100

* glass value relative to crystal value

To make the proceeding discussion less abstract, Fig.3.2 depicts schematically the photophysical hole-burning mechanism. TLS_α represents a particular TLS coupled to an impurity molecule in its electronic ground state α. The TLS potential energy is characterized by a barrier height v, a zero-point energy splitting Δ, and a well separation d. For all of these parameters there is a distribution within the glass. In addition, there may be a variety of TLS coordinates q. Photophysical hole-burning occurs because, for a subset of the TLS distribution, the rate W of phonon-assisted tunneling while the impurity is in its ground state, is slow on the time scale of the experiment, while for the impurity in its excited state interconversions between tunnel states can occur in a time scale competitive with the excited state lifetimes. In the figure the excited state is represented by TLS_β, and the dramatic rise in the interconversion rate is depicted as being due to a decrease in the potential barrier. In photophysical hole-burning, an impurity is coupled to a TLS which is trapped in one of the wells of TLS_α but which converts to the other well in TLS_β during electronic excitation and remains in that well during deexcitation. The net result is that the absorption energy of the impurity has been shifted by an amount dependent on the zero-point splittings of TLS_α and TLS_β.

With only slight modification essentially the same figure has also been used to explain PHB. The major difference in the case of a photoreactive species is that it is not necessary to invoke TLS to produce a double-well potential. Rather, the two wells are merely the reactant and product. This may alter the energy scales but serves to unify the mechanisms.

A somewhat less rigorous approach to the mechanism identification is the hole filling experiments first described by Hayes and Small [3.54] in the tetracene in alcoholic glass system. In this case it was shown that a major portion of the photoproduct (antihole) lay within a few wave numbers of the initially burnt hole. This implied that if photochemistry were responsible for the hole, the absorption spectrum of the photoproduct was essentially identical to that of the starting material. The known, ambient temperature photochemical reactions of tetracene all yield products with substantially shifted absorptions. Rather than postulating a new, low-temperature photochemical reaction it was concluded the tetracene molecule remained intact but that its absorption energy had been shifted a few wave numbers due to a solvent rearrangement.

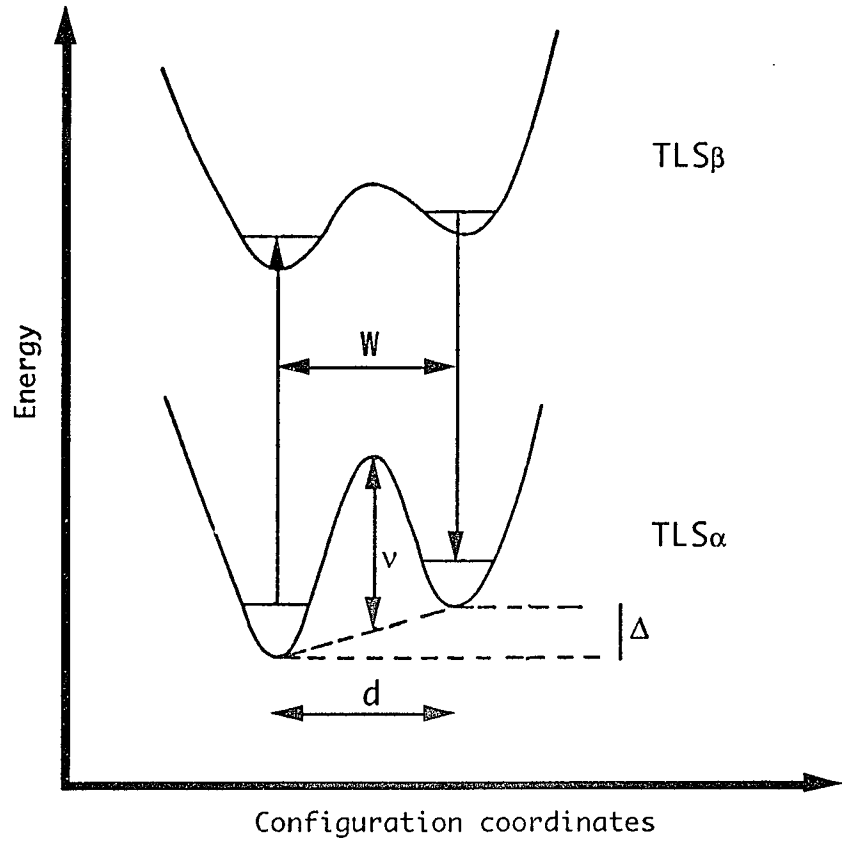


Figure 3.2. Potential energy curves for a TLS coupled to a guest molecule in its ground state, α, or excited state, β. The tunneling rate between potential wells is given by W. Ref.3.113.

Those mechanisms for photophysical hole-burning listed in the second half of Table 3.1 that do not result in an intrinsic chemical change of the absorbing center itself are called photophysical mechanisms. Photophysical hole-burning [3.55] usually requires a change in the local environment around the guest or perhaps a reorientation of the guest with respect to the host. In most cases, the absorption of the product for photophysical hole-burning processes is not very far removed in frequency space from the original educt absorption. In fact, in some materials the absorption of the product appears as regions of increased absorption immediately adjacent to the hole [3.56]. In addition, the energy barriers preventing reverse reactions may not be very high, so that photophysical holes often irreversibly disappear upon warming above liquid helium temperatures, whereas the changes caused by photochemical hole-burning either require even higher temperatures for reversal, or are irreversible.

A quite general mechanism for photophysical hole-burning occurs when photostable molecules are incorporated into amorphous host molecules and excitation of the guest molecules induces transitions among the TLSs of the host. In fact, this mechanism for perylene and 9-aminoacridine in ethanol glasses provided one of the very first examples of PSHB [3.10], although its generality and theoretical interpretation were not fully recognized until the work of Small et al. [3.57,58]. The effect appears to be quite widespread, and had been studied for perylene in glasses and polymers [3.10,59], tetracene in glasses [3.60,61], resorufin in polymers [3.62], and dye molecules in hydrogen-bonded polymers [3.63,64], to give a partial list. For certain hosts, the rich vibronic structure hidden within the inhomogeneous line can be conveniently probed using photophysical hole-burning techniques [3.63].

A similar mechanism exists for photophysical hole-burning of ions in glasses and polymers. Here again, the absorbing center itself undergoes no intrinsic change, and transitions among the TLS's of the amorphous matrix or rearrangements of the nearby host structure are responsible for the hole formation. The effect has been observed Eu^{3+}, Pr^{3+}, and Nd^{3+} in silicate glasses

[3.65-67] and even for Pr^{3+} and Nd^{3+} in polymer films [3.68]. These holes can persist for times much longer than the spin-lattice relaxation times because the relevant back reaction involves TLS tunneling times of the nearby host.

Photophysical hole-burning can also occur for photostable guest molecules in crystalline host matrices, if the host crystal has hydrogen bonds that can be altered during excitation of the guest. This novel form of photophysical hole-burning has been studied for pentacene in benzoic acid crystals [3.69,70] as well as for thioindigo in benzoic acid [3.71].

An interesting question is whether or not photophysical hole-burning can occur for stable absorbing centers in rigid crystalline hosts. For the case of tetrahedral ReO_4^- ions in alkali halides, hole-burning does occur due to light-induced reorientations of the molecule in the host [3.56,72]. This mechanism also provides an example of photophysical hole-burning in which electronic transitions are not involved - the excitation leading to hole-burning is an internal vibrational mode of ReO_4^- molecule. For certain choices of secondary dopant, antiholes are also observed for this interesting system [3.73]. In recent measurements, infrared hole-burning has been observed for CN^- in alkali halide hosts, again due to molecular reorientation [3.74].

3.1.3 Transient Hole-Burning

In this process, population is transferred from the ground state through the excited state of interest to a metastable state [3.75-78]. The latter may either be the same excited state, a long-living triplet state, or a hyperfine level of the ground state. The lifetime of the hole (usually microseconds to seconds) is determined by the decay time of the metastable state.

To conclude this brief summary of mechanisms for PSHB, it is clear that hole formation is a fairly general process for zero-phonon excitations in solids at low temperatures, and that it gives information about multiple stable ground states of the coupled guest-host system that may not be observable at elevated temperatures. Even though a wide variety of mechanisms and guest-host combinations have been considerate in recent research, much remains to be done. Through further study, additional information can be obtained about spectral properties and dynamics within the inhomogeneous line that cannot be obtained using other techniques. The fact that small, persistent, localized changes can be made at will in inhomogeneously broadened lines using PSHB, is an intriguing process that deserves continued attention in the research community.

3.2 Techniques

Persistent holes are usually burnt with narrow-band dye lasers (width, Γ_L) at a given temperature, and probed either at the same temperature [3.1,2,4-8,42,43,47,48,75,78-87], or at a different one [3.12,46,88-90]. The most common probing schemes are transmission spectroscopy [3.12,42,44,47,86-92] and excitation spectroscopy [3.1,2,7,8,45,79,83,85]. In the latter, the spectrum is generally scanned with the same laser as used for burning, but at 10^{-3}-10^{-1} of its original intensity. In many transmission experiments, a lamp in combination with a monochromator have been used for the hole-burning step, but this introduces significant errors in the determination of the holewidth. The excitation method is more convenient, because samples of low optical quality and density can be measured with high sensitivity at very low laser burning powers [3.48,93]. The only prerequisite is a luminescent sample. If one wants to get information on the homogeneous linewidth, Γ_{hom}, an additional condition is that $\Gamma_L << \Gamma_{hom}$.

The detailed experimental aspects of hole-burning have been discussed in the literature [3.94,95] and are not repeated here. The holes are probed either by fluorescence excitation spectroscopy or simultaneously by the latter and in transmission through the sample [3.48]. In the absence of emission from the sample, a special type of low temperature photoacoustic spectroscopy had been used, which is based on resonant detection of second sound in superfluid ^{4}He [3.96].

Other hole probing techniques that yield signals against zero background are laser frequency modulation (FM) spectroscopy [3.97-99], ultrasonic modulation of holes [3.100], polarization spectroscopy [3.101-102], and holographic detection [3.103-104].

Transient hole-burning may either be performed with one or two single-frequency cw dye lasers, depending on the lifetime of the metastable level [3.75-78]. If two lasers are used, the first one burns the hole at a fixed frequency, whereas the second, at lower intensity, scans the excitation spectrum of the hole either during burning or after a delay time. If one laser is used, the beam is divided in two, and one part is delayed with respect to the other by acoustic-optic modulators. For a discussion on cryostats used between 0.3K and 20K, see [3.105-107].

In order to get an accurate determination of Γ_{hom}, under the assumption that the time scale of the experiment plays no role, a series of holes should be burnt as a function of laser power, P, and burning time, t, and the holewidths extrapolated to P-->0 to t-->0. Since the hole shape is the result of a convolution of a burning step and a probing step, the relation $\Gamma_{hole} = 2\Gamma_{hom}$ is valid for holes burnt and probed at the same temperature [3.2,108].

Systematic studies of the influence of laser power and burning time on the holewidths [3.48,105,109] have suggested that many of the holewidths previously reported in the literature [3.12,43,44,46,47,81,110] may suffer from saturation and/or heating effects. It should be noticed that the holewidths become saturated at longer burning times and/or higher burning powers. It follows that the "true value of Γ_{hom} " is discussed below in relation to spectral diffusion processes in glasses.

Local heating of the sample may also be a reason for artifacts in the evaluation of holewidths in amorphous material, since the latter have poor thermal conductivity [3.111]. It is improbable that in many hole-burning experiments performed at rather high burning powers in flow cryostats, where the sample was only in contact with helium gas [3.12,43,44,47,81,86,112] and the holes were probed in transmission, the temperature in the bulk of the sample was higher than assumed.

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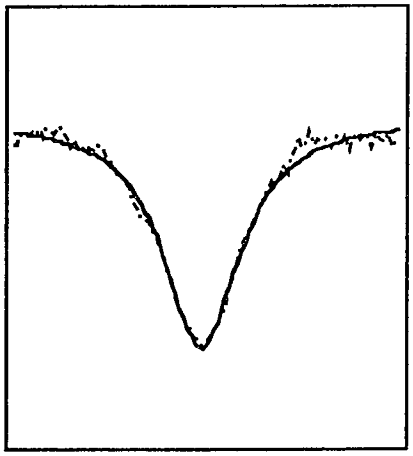
RELAXATION PROCESSES IN ELECTRONIC TRANSITIONS



CHAPTER 4

4. RELAXATION PROCESSES IN ELECTRONIC TRANSITIONS

The high spectral resolution, on the order of MHz, attainable with hole-burning makes this technique attractive for many applications. In particular, since permanent holes at liquid helium temperature represent sharp frequency markers in the absorption spectrum, it is possible to detect frequency shifts, in addition to hole broadening, as a function of temperature, that are many orders of magnitude smaller than the width of the inhomogeneous absorption band. Thus, optical dephasing and relaxation processes of electronically excited states of molecules and ions incorporated in either crystalline or amorphous hosts at low temperature can be studied with high accuracy by spectral hole-burning spectroscopy (PSHB).

The optical properties and hole-burning characteristics of many of the organic systems to be discussed have been described in detail in [4.1] and thus are not repeated here.

4.1 Optical Dephasing in Crystalline Hosts

The first MHz-resolution hole-burning (HB) experiment performed on an organic system with a holewidth close to the true value of Γ_{hom} was reported in 1976 [4.2]. The system was dimethyl-s-tetrazine (DMST) in a durene crystal. The holewidth at 2K (120 MHz), however, was still significantly broader than the width that corresponds to the decay time of DMST (~25MHz), and was attributed to low temperature electron-phonon coupling [4.2]. In a crystalline system at the lowest temperatures, one would expect, however, that the population decay time T_1 is ultimately the factor limiting the holewidth, because phonon processes are frozen out. This was, indeed, observed for the $S_1 \leftarrow S_0$ 0-0 transition of free-base porphin (H_2P) in an n-octane (n-C_8) crystal, where the holewidth for T<2K was entirely determined by the fluorescence lifetime of H_2P, T_1=17ns. Thus, $\Gamma_{hom} = (2\pi T_1)^{-1}$

when T-->0 [4.3,4]. The same result was found by HB for other porphin molecules in n-alkane hosts: ZnP in n-C_8 [4.5], chlorin in n-C_6, n-C_8, and n-C_{10} [4.6], H_2P in n-C_{10} [4.7], and MgP in n-C_8 [4.8]. By contrast, photon echo decay times, $1/2T_2$, obtained for the S_1-S_0 0-0 transitions of tetracene and pentacene in p-terphenyl [4.9], naphthalene in durene and perdeuteronaphthalene [4.10], and pentacene in naphthalene [4.11] at 1.4K were claimed not to be determined by T_1. It was suggested that not all relaxation processes in these organic crystals were frozen out at the lowest temperature [4.9]. Energy transfer [4.10] and quadratic electron-phonon coupling [4.11] processes were held responsible for these discrepancies. Subsequent hole-burning experiments carried out with a better-stabilized laser [4.12] and more accurately measured photon echoes [4.13-16], confirmed that homogeneous linewidths in crystals at 2K are entirely determined by T_1.

As the temperature increases, thermally induced dephasing processes rapidly set in. As mentioned above, PSHB has the unique advantage, with respect to coherent transient techniques, to be able to measure not only the homogenous linewidth but also its frequency shift as a function of temperature.

The holewidth and frequency shift of the S_1-S_0 0-0 transition of H_2P in n-octane were found to depend exponentially on temperature as exp $(-E/kT)$, with activation energies E between 10 and 35 cm^{-1}, depending on the site [4.3,4,17]. Such low activation energies have been interpreted [4.3,4] in terms of pseudo-local phonon modes [4.9,18,19], which arise from a distortion of the host crystal due to the presence of the guest molecule [4.20]. In the case of porphin molecules in n-alkane crystals, they correspond to librational motions of the guest in the host [4.3,4,21]. Localized modes have been observed as phonon sidebands in excitation and fluorescence spectra of mixed molecular crystals, like pentacene in naphthalene [4.22] and benzoic acid [4.23], and of various porphin molecules and their derivatives (MgP [4.8], ZnP [4.21], H_2-chlorin [4.6], H_2-bacteriochlorin [4.24], H_2-tetra-ter-butylphthalocyanine [4.25]) in n-alkane crystals. The frequencies of these phonon sidebands coincide with the activation energies found from the temperature dependent hole dynamics [4.26]. The frequencies and lifetimes of psuedo-local phonon modes are related to the tightness of the fit of the guest in the host [4.4,7,27]. Very similar dephasing behavior as for H_2P was observed for H_2-chlorin in n-alkane hosts (n-C_6, n-C_8, and n-C_{10}). From the very small increase of the holewidth with temperature between 1.6 and 4.2K, and from Zeeman [4.28-30] and Stark [4.31] effect measurements, the type of site that H_2-chlorin occupies in the n-alkanes studied was inferred [4.6].

Optical dephasing of S_1-S_0 0-0 transitions of metal porphins was initially interpreted differently from free-base porphin and its derivatives. Only ZnP [4.5] an MgP [4.8] in n-C_8 have been studied by transient hole-burning so far. Transient hole-burning occurs here by selective depletion of the ground state population and storage in the metastable triplet state. The temperature dependence of the homogeneous linewidth of ZnP in n-C_8 was attributed to a resonant one-phonon absorption between the S_{1x} and S_{1y} components [4.5] rather than to coupling to a low-frequency local mode. Subsequent transient hole-burning experiments on four sites of MgP in n-C_8 proved that optical dephasing is in fact caused by thermal excitation and de-excitation of local phonon modes [4.8], just as for H_2P in n-alkanes. The one-phonon scattering mechanism [4.5] could be disregarded, because the crystal-field splittings for the various sites of MgP in n-C_8 differ markedly from the activation energies measured [4.8].

As we discussed above (Chapt.2), homogeneous ZPLs (especially PELs) are very narrow at the liquid helium temperature and therefore extremely sensitive to various impurity-matrix interactions. In particular, the measurements of the homogeneous broadening of ZPLs with increasing temperature give information about relaxation processes of electronic and vibrational excitations in impurity molecules. In addition to radiative and nonradiative decay of the excited electronic level, homogeneous linewidths are controlled by pure dephasing of the excited electronic state and the decay and dephasing of the excited molecular vibrations.

To a reasonable approximation, the theoretical PEL shape is Lorentzian with the total homogeneous linewidth Γ_{hom} depending on the excited state population decay time T_1, and on the pure dephasing time T_2*[4.32]. For a dipole-allowed purely electronic transition the depopulation time T_1 may be considered as temperature-independent at the liquid helium temperature, whereas the dephasing time T_2* increases with decreasing temperature due to the disappearance of thermally excited lattice modes. As the temperature approached zero, Γ_{hom} approaches its limiting value determined by T_1: $\Gamma(0) = (2\pi T_1)^{-1}$. By studying the temperature dependent-component of the linewidth, $\Gamma(T)$-$\Gamma(0)$, one can study the pure dephasing processes. Measurements of the temperature dependence of linewidth may serve as a useful probe of the low-frequency dynamics of matrices in the vicinity of the impurity center.

The most accurate measurements of PEL homogeneous linewidth have been made by burning narrow, non-saturated zero-phonon holes in the inhomogeneous band of the corresponding transition. The low-temperature broadening process of the PEL homogeneous linewidth was first studied in 1977 [2.33-35] for the S_1-S_0 transition in H_2-tetra-4-tert-butylphthalocyanine molecules in tetradecane at temperatures of 1.8-30 K. A 692.947 nm Ne-discharge line and scanning with a Fabry-Perot interferometer were used to burn and measure holes, respectively, in the Shpol'skii component at 693.0 nm. The Γ_{hom} was determined as the zero-burning-time limit of the holewidths δ_t produced at different irradiation times t. Making a correction for the instrumental width yields the limiting holewidth of the $\Gamma_{hole} = 2\Gamma_{hom}(T)$. Data for $\Gamma_{hom}(T)$ are presented in Fig.4.1a. At 1.8 K the Γ_{hom} was found to be $\Gamma = 0.002\text{cm}^{-1}$. The lifetime-limited value, calculated from the fluorescence decay time ($T_1 = 5.2\text{ns}$), was $\Gamma(0) = 0.001\text{cm}^{-1}$. The dephasing component at 1.8 K is 0.001cm^{-1} and the corresponding pure dephasing time, $T_2^* = 10\text{ns}$. The pure dephasing broadening $\Gamma(T)$-$\Gamma(0)$ is shown in Fig.4.1b on a double logarithmic scale. Curve 1 represents the theoretical dephasing rate caused by Raman scattering of Debye phonons . The characteristic Debye temperature T_D is taken to be 50 K. Curve 1 fits the experimental data well not only at high temperatures $T>T_D$, where theory [4.37] tells us that a simple T^2 dependence should be expected, but the T^2 law approximates the experimental data fairly well also at lower temperatures $10K<T<T_D$. However, for T<10K the behavior of the experimental data is entirely different from the predicted considering only the Debye phonons: instead of $\Gamma_{hom}(T) \sim T^7$ the experiment shows that $\Gamma_{hom}(T)$ decreases exponentially when T --> 0. All experimental data in this regime can be described by curve 2 taken into account one kind of phonon only, presumable pseudolocalized phonons of frequency ν_0. For this single-mode model $\Gamma_{hom}(T)$ is expressed as [4.38]

$$\Gamma_{hom}(T) = bn(\nu_0)\,[n(\nu_0) + 1], \qquad n(\nu_0) = (e^{h\nu_0/kT} - 1)^{-1} \qquad (4.1)$$

The fitting parameters for curve 2 are: the pseudo-local mode frequency $\nu_0 = 8\text{-}12\text{cm}^{-1}$ and the quadratic electron-phonon coupling constant $b = 0.06\text{-}0.19\text{cm}^{-1}$. Therefore in this case, the perturbation of the lattice modes by the impurity molecule is strong enough to create a peak in the density of the low-frequency vibrational states at the impurity-pseudolocal mode. This mode is responsible for the better part of the dephasing process at low temperatures. The calculated total $\Gamma_{hom}(T)$ is presented in Fig.4.1a (dashed line). Its extrapolated limit at T=0 coincides, within the experimental accuracy, with the independently measured decay-limited Γ(0). This was a result of basic importance for the theoretical understanding, because it proved that the PEL homogeneous linewidth is actually limited by the radiative lifetime at the lowest temperatures. At the same time, the resolution of PSHB spectroscopy approached here the Γ(0) limit. This result was confirmed later [4.39], with more accurate measurements, by using single-mode tunable cw dye laser with frequency stability better than 10MHz.

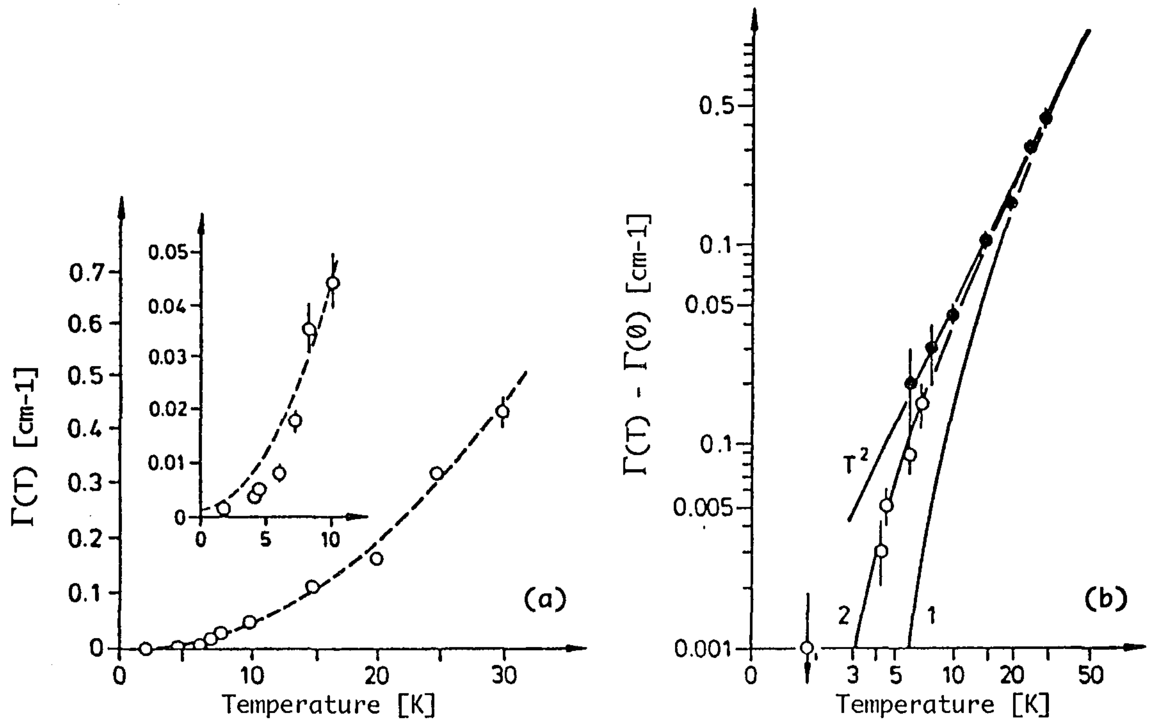


Figure 4.1. Temperature dependence of the linewidth for the purely electronic S_1-S_0 transition in H_2Pc^*-C_{14} in an ordinary (a) and a double-logarithmic (b) plot. Ref.4.125.

In the time period since these early measurements, PEL broadening in crystals has been studied by PSHB [4.39-41] as well as by photon echo experiments [4.42-45] for a number of impurity molecules; the crucial role of psuedolocal modes in optical dephasing at low temperatures has been confirmed. For example, for the S_1-S_0 PEL of free-base porphin in n-decane, $\Gamma_{hom}(T)$ was measured by PSHB at temperatures 1.2-4.2 K, which yielded an exponential dependence on temperature [4.41]. The data were analyzed assuming optical dephasing due to exchange interactions with a psuedolocal mode of frequency ν_0. In the slow exchange limit,

$$\Gamma_{hom}(T) - \Gamma(0) = \pi\tau[e^{-h\nu_0/kT}] \tag{4.2}$$

and the psuedolocal mode frequency was determined independently by measurements of phonon sidebands (ν_0 = 7.0 and 5.6cm^{-1} in S_0 and S_1 states, respectively). The homogeneous linewidth of the psuedolocal mode in the S_1 state was obtained by hole-burning in the phonon sideband, from which the corresponding lifetime was estimated to be τ = 115ps. These parameters fit rather well the broadening caused by the exchange interaction. Recently, the data of [4.41] were reconsidered [4.46] on the basis of the newly developed nonperturbative theory of ZPL width of impurities in crystals [4.47], but no satisfactory agreement with the theory was obtained.

The temperature-dependent optical dephasing (measured by picosecond photon echoes) for tetracene and pentacene monomer and dimer molecules in a p-terphenyl crystal shows exponential dependence over many orders of magnitude of T_2 [4.44]. The activation energies (psuedolocal mode frequencies) obtained from the exponential fit varied (from 10 to 30cm^{-1}) for different impurity molecules in the same crystal host, excluding the coupling to regular acoustic host phonons as a relevant dephasing process. An exponential dependence of dephasing at low temperatures with an activation energy of 13.8cm^{-1} has also been detected (using the photon echo) for a spin-forbidden T_1-S_0 transition of dibrombenzophenone in dibromdiphenylether

[4.45]. In this case, the situation is more complicated because the molecules excited to T_{1x}, T_{1y}, and T_{1z} states all participate in the echo signal.

These experiments have underscored the dominant role of psuedolocal vibrations for the guest molecule dephasing in crystal hosts at low temperatures. It seems reasonable that a well-pronounced psuedolocal peak will arise in the phonon density of states when a large molecule is imbedded in the crystal and strong perturbations are created. In the frequency region of such local modes, the acoustic phonon density of states is relatively low, and therefore at temperatures $kT < h\nu_0$ the psuedolocal mode predominates over acoustic phonons in dephasing processes. At higher temperatures acoustic phonons will dominate because the higher-frequency phonons with higher density of states become thermally populated. However, experimental studies of the Γ_{hom} are difficult at temperatures above 40 K because of the broadening and damping (decreasing Debye-Waller factors with increasing temperature) of the PELs. From this point of view the observations of homogeneous broadening of purely vibrational transitions are important because sometimes they allow one to follow $\Gamma_{hom}(T)$ up to higher temperatures. Interesting results were obtained by burning holes in the infrared absorption band of the molecular vibration ν_3 of the ReO_4^- impurity molecule in alkali halide crystals [4.48,49]. The temperature dependence of the homogeneous linewidth, measured over 4 orders of magnitude using transient and persistent hole-burning, indicates the dominant role of acoustic lattice phonons in the dephasing of the vibrational excitation in the ground electronic state. At T < 10 K the Γ_{hom} was independent of temperature, showing the limiting value determined by the decay time T_1 of the vibrational excited state. In this simple case, the molecule is in a site of cubic symmetry in the crystal and the formation of persistent holes is probably caused by the reorientation of the molecule during vibrational de-excitation [4.49].

4.2 Optical Dephasing in Amorphous Hosts

The first experiments on the homogeneous linewidths in glasses were performed with rare earth ions in silicate glasses [4.50-54]. some of the transitions investigated were: Eu^{3+}, $^5D_0$ --> $^7F_0$; Pr^{3+}, $^3P_0$ --> $^3H_4$ and Yb^{3+}, $^2F_{5/2}$ --> $^2F_{7/2}$. The experiments were performed in a temperature range between 1.6 and 300 K. Two observed phenomena were particularly surprising. First, the linewidth in glasses is typically one to two orders of magnitude larger than in compatible crystalline systems. Second, the temperature variation of $\Gamma_{hom}(T)$ is proportional to T^{α} with α values between 1 and 2 (as compared to $\alpha = 7$; see above).

The first experiments with organic glasses to investigate the lowest singlet transition S_1<--S_0 of organic molecules yielded similar results [4.55,56], namely comparatively large homogeneous linewidths and algebraic temperature dependencies with $\Gamma_{hom}(T) \sim T^{\alpha}$.

The experimental studies of homogeneous linewidths in glasses were stimulated by the theoretical interest in the subject of low-lying excitations in glasses. These excitations have a constant density of states which, at low energies, is larger than the Debye phonon density of states (which increases as v^2dv). The low-energy excitations were introduced to interpret the anomalous specific heat data of glasses [4.57]. The model of low lying two-level systems (TLS) was originally proposed by Anderson et al. [4.58] and Phillips et al. [4.59]; it was subsequently adapted to interpret the anomalous homogeneous linewidths observed in rare earth ion systems [4.50].

The origin of the dephasing of molecules or ions in amorphous media stimulated many theoretical papers dealing with the general theme of dephasing in amorphous hosts [4.55,56,60-68]. All these theoretical approaches utilize the concept of TLS with a density of states which is approximately constant (on the energy scale). The theoretical models vary with respect to the coupling of the TLS to other degrees of freedom like phonons, fractons or librational excitations. The difficulty at the present time is, in our opinion, the fact that a multitude of experimental data is available yielding T^{α} dependencies with $1<\alpha<2$ and at least three to four different theoretical approaches can be used to interpret the optical data.

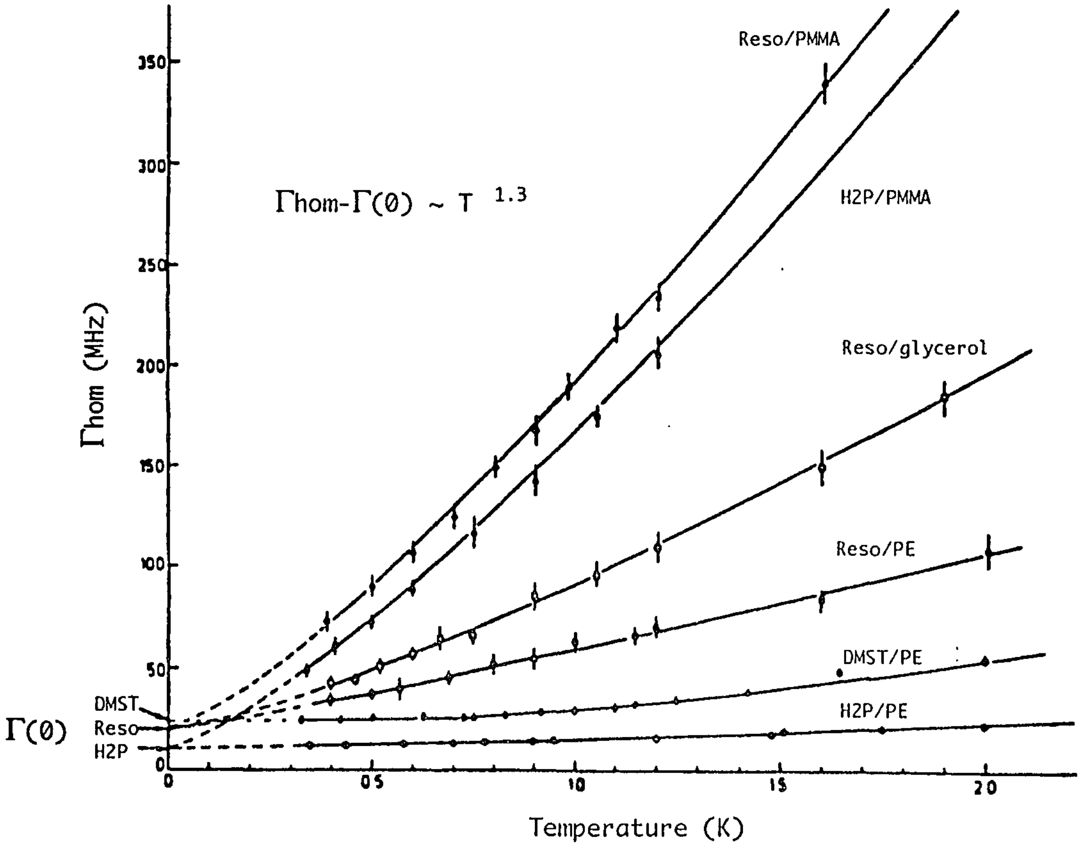


Figure 4.2. Homogeneous line width (Γ_{hom}) as a function of temperature for various guest-host systems. Ref.4.126.

In recent years quite a few review articles have appeared on the subject of linewidths in amorphous glasses [4.66,69-72]. In order to highlight the main features of the subject rather than discussing the details, which the reader will find in the above review articles, we will select some aspects of current research and also discuss some of the controversies.

One of the most frequently discussed issues is the question of whether the algebraic exponent α allows one to draw conclusions about the dephasing mechanisms of optical centers in amorphous media. Several groups have recently found an α-value of 1.3; the group of Volker et al. was able to measure a $T^{1.3}$ law for practically all PHB experiments using (H_2P) [4.73-78]; the group found the same α-law for other molecules such as DMST, resorufin and cresylviolet. These results, together with those found for H_2P, suggested that the $T^{1.3}$ law is independent of the chemical structure of the guest. In fact, many organic amorphous systems subsequently showed that Γ_{hom}-$\Gamma_0 \sim T^{1.3}$, at least between 0.3 and 20K, independent of their hole-burning mechanism [4.79-82]. In addition, it was verified that Γ_{hom} extrapolates smoothly to $\Gamma_0=(2\pi T_1)^{-1}$ when T-->0 [4.79,81,83-85], which is summarized in Fig.4.2. Volker et al. promote the idea that the exponent of 1.3 reflects a fundamental property of the amorphous state. The T^1 dependence that Volker et al. have found for small linewidths (<50 MHz) complicates the pictures somewhat. Lyo et al. [4.68] speculated that this may indicate a transition from a quadrupolar process to a dipolar process. They found for a dipole, TLS-quadruple interaction a theoretical $T^{4/3}$ dependency as experimentally measured by the Volker-group. The Lyo-Orbach exponent is given by

$$\Gamma(T) \sim T^{1+d/4} \tag{4.3}$$

where d is the spatial dimensionality, as defined by Alexander and Orbach [4.86]. The latter model hinges on the fact that the density of states of fractals is different from the density of states of phonon-like excitations. Without the elegant conjecture of Orbach et al. [4.86], one can also explain a $T^{1.3}$ dependency by assuming a dipolar interaction and a density of states function which has the following form:

$$\rho(E) = \rho_0 E^{\mu} \tag{4.4}$$

For this case Lyo [3.70] obtained a linewidth of

$$\Gamma(T) \sim T^{1+\mu} \tag{4.5}$$

Inserting a μ value of 0.3 one obtains the above 1.3 dependency. The issue of temperature exponents is further complicated by the fact that other very plausible theories, like the one of Jackson and Silbey [4.67] can also yield α exponents of 1.3-1.5 by assuming a dephasing process which is initiated by both TLS processes as well as by localized librational modes. This model seems especially realistic, since Jankowiak et al. [4.87] have recently found both a $T^{1.4}$ dependence and evidence for a librational mode of low frequency (7-11cm^{-1}). There photophysical hole-burning system was 9,10-diphenylanthracene in 2,3-dimethylanthracene.

To make the situation regarding the $T^{1.3}$ dependence even more puzzling, the Bell-Laboratory/Wisconsin groups [4.64,88,89] have found a $T^{1.3}$ dependence for Nd^{3+}-doped silica (as detected by echo experiments). Their data interpretation, however, is based on a model of spectral diffusion as formulated by Black and Halperin [4.89] based on previous theories for spin systems of Klauder and Anderson [4.90], and Mims [4.91]. It should be noted a spectral diffusion model describes the frequency change of the optical system (A-spins) due to a spin flip of a more abundant species characterizing the amorphous lattice (B-spins). Hence, the transition will "wander away from

v_0", i.e. from the resonance frequency of the site-selected transition. This process of diffusion drift of the resonance frequency is different from a simple T_2 and can carry the frequency over an interval which is larger than that defined by the width of a conventional "spin packet". The $\alpha = 1.3$ exponent observed for the Nd^{3+} system, was attributed to a density of states of the TLS system following an $E^{0.3}$ dependence. If one were to assume a constant density of states in energy space, the Black and Halperin model would yield a linear temperature dependence.

An independent interpretation of the $T^{1.3}$ dependence based on a spectral-diffusion picture was presented by Hunklinger et al. [4.92]. The researchers pointed out that the time and temperature dependence of the linewidth as derived by Black and Halperin [4.89] is of the form

$$\Gamma(t,T) = C_1 T[C_2 + \ln(C_3 T^3)] \tag{4.6}$$

if one considers direct processes. Here the constants C_1, C_2 and C_3 are determined by the sound velocity, the deformation potential and the TLS density of states [4.89]. The authors show numerically that the above dependence can be numerically approximated by a $T^{1.3}$ law assuming reasonable values for the various potentials and density of states. It should also be noted that (4.6) contains a time dependence which is, for the long time limit, logarithmic. This had already been pointed out by Reinecke [4.60] who also discussed the short-time limit, $t \ll T_1$, where the linewidth increases linearly with time. In the next section we will discuss the phenomenon of slow spectral diffusion processes from a different point of view.

So far we have focused on the $T^{1.3}$ class of hole-burning systems. There are, however, a significant number of experiments that do not fit into this picture of a generalized exponent. In inorganic glasses the exponents seem to vary between 1 and 2.2 [4.51-54,93-95]. In organic glasses, too, exponents between 1 and 2 are being reported [4.96-102] and thus contribute to a colorful picture. It is firmly believed that the question of temperature exponents will be of further importance; however, the question of spectral diffusion deserves serious discussion. Only if the optical data can be linked to other relevant material's parameters such as the specific heat, the thermal expansion, and dielectric losses will it be possible to finally establish the physical processes that are responsible for the dephasing of excited optical states in glasses.

4.3 Spectral Diffusion Process

Whereas crystals are characterized by periodic potentials with well-defined and identical potential wells (Fig.4.3a), glasses are characterized by potentials with variable minimum energies and with variable barrier heights. This randomness, as shown in Fig.4.3b, is due to the local disorder of the amorphous state, and reflects the non-periodic nature of the potential curve.

Following the model of Anderson et al. [4.58] and Phillips [4.59], instead of working with a complex coordinate, as shown in Fig.4.3b, one can chose a double-well potential, as shown in Fig.4.3c. In this simplified representation, one considers only two minima of the multivalley potential of Fig.4.3b. The amorphous nature of the material is taken into account by allowing the main parameters Δ and V_0 of the two-level systems to have broad distributions rather than well-defined values. This assumption has far reaching consequences: the glassy system will be characterized by dynamical parameters whose distribution is so wide that the slow components characterizing the ensemble of TLS will, within finite times, not reach their equilibrium configurations or energies. In other words, the glassy state is a non-equilibrium state, and if we are able to make our optical experiments sensitive enough and observe the system over long enough periods of time, we should be able to observe changes which are indicative of the non-equilibrium nature of the system.

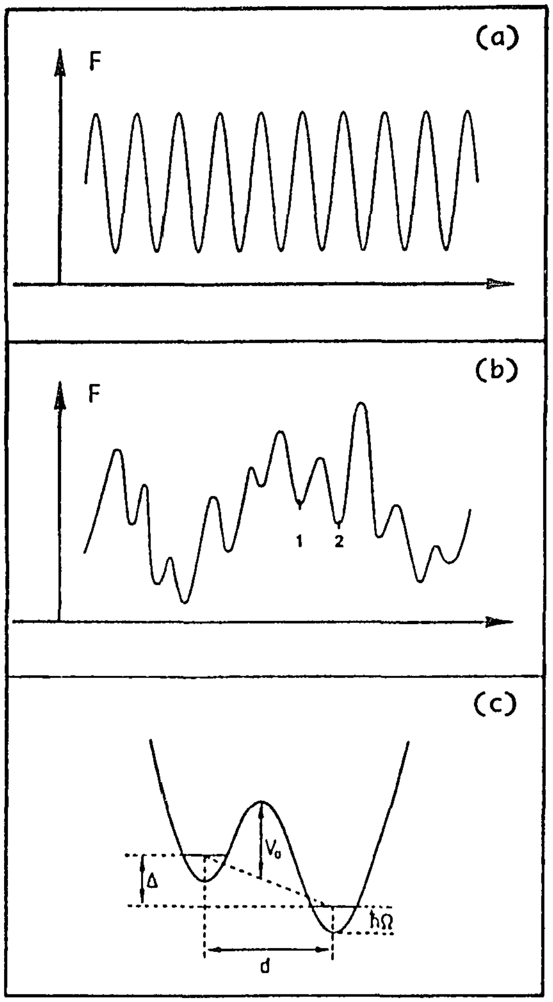


Figure 4.3. (a) Periodic potential of a crystalline solid. (b) Potential along a fictitious coordinate q of a glass: Note the lack of periodicity. (c) Idealized two level scheme with the two parameters Δ and V_0 (see text). The oscillators in the two wells are separated by the distance d and have a zero-point frequency on the order of Ω. Ref.4.125.

It has been suggested that the extra broadening of the hole-burning with respect to the photon-echo data arises form spectral diffusion, and that it follows a power law dependence T^{α} with $\alpha<1$ [4.103]. It is obvious from

Fig.4.4 that the difference between the linewidths determined by hole-burning [4.79] and by photon echoes [4.103] for resorufin in glycerol does not obey such a power law, because the data cross each other at T~12K and probably at T<1.1K.

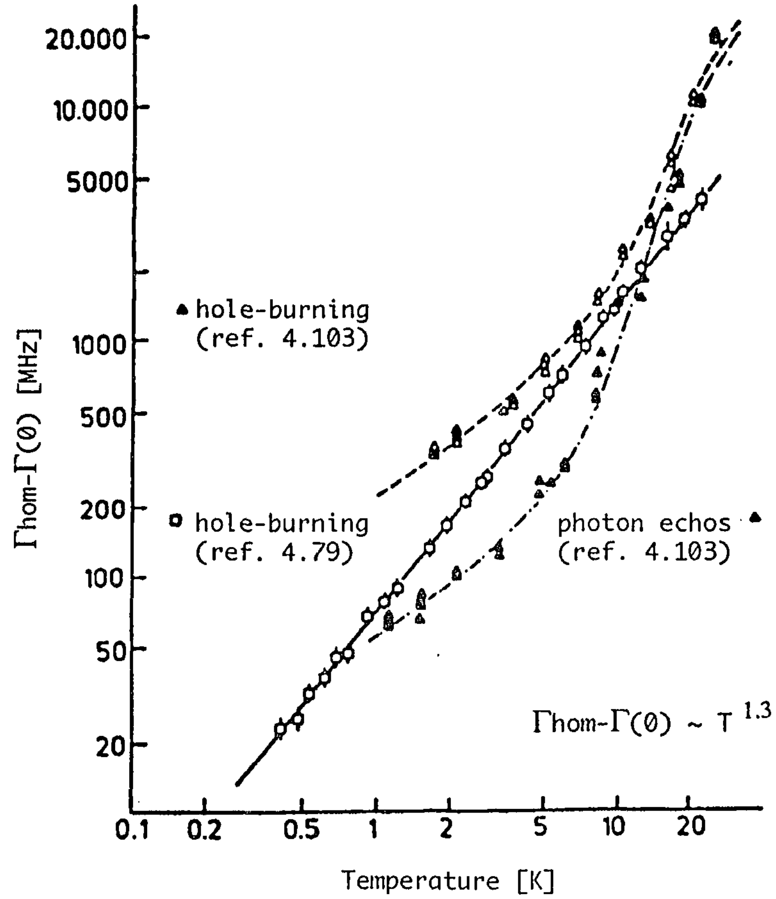


Figure 4.4. Log (Γ_{hom}-$\Gamma(0)$) versus logT between 0.3 and 25K for resorufin in glycerol. Ref.4.126.

Spectral diffusion processes on a time scale between that of photon echoes (picoseconds to milliseconds) and that of conventional hole-burning experiments (seconds to milliseconds) have not been unambiguously demonstrated for organic amorphous systems yet. Transient hole-burning experiments on H_2P in PE between 1.2 and 4.2K performed on a time scale of milliseconds have yielded results identical to those obtained by conventional

HB on a time scale of minutes [4.79,104]. Furthermore, holes burnt in H_2P in PE at 1.2K probed in fluorescence did not broaden as a function of time after burning, not even after many hours, a result that suggests that spectral diffusion does not take place in a time span of seven orders of magnitude (from 10^{-3} to 10^4 s), at least for this system at low temperature. In contrast, hole-burning experiments at 1.5K on a time scale of 10^{-5}s [4.105-106], and resonance fluorescence experiments between 5 and 11K [4.107], both on OEP in PS, yielded linewidths that were a factor 7 and 2, respectively, smaller than those obtained by conventional hole-burning in the same group [4.108].

It is worth comment that accumulated photon echo and hole-burning experiments on Pr^{+3} in silicate glass between 1.6 and 20K yielded identical linewidths, despite the very different time scales of these two experiments of $\sim 10^{-4}$ and 10^2 s, respectively [4.109]. Thus, no slow rearrangement of the glass network seems to contribute to the holewidth in this experiments on Nd^{3+} doped-silica at $T<0.1K$ [4.110] suggesting the presence of short-time spectral diffusion processes.

Slow relaxation processes in organic glasses, occurring on time scales of hours and even days, have been observed by hole-burning [4.111-115]. This spectral diffusion effect, however, only occurs under special experimental conditions, as has been demonstrated in [4.116]. Holewidths probed simultaneously by fluorescence excitation and in transmission through a sample of pentacene in poly-methylmethacrylic acid (PMMA) at 1.2K were measured as a function of time after burning. The holes detected in fluorescence did not broaden on a time scale of hours, even at large burning fluences, a finding that indicates that, as long as the molecules are in thermal contact with liquid helium, no spectral diffusion occurs, at least not on a time scale between a few seconds and 10^4 s [4.79,116]. Similar results have been obtained for resorufin in glycerol [4.79]. However, when holes are probed in transmission through a rather thick amorphous sample [4.116], they do broaden on a time scale of minutes to hours [4.111-116], the effect being more pronounced for higher burning fluences. The conclusion from these experiments was that in the bulk of the glass, which has poor thermal conductivity, the heat of the laser probably induces strain that causes slow structural relaxation of the host. During this process the inhomogeneous linewidth is affected and, as a consequence, broadening of the hole is observed.

Long-time, spectral diffusion in hole-burning experiments on organic glasses have been interpreted by Friedrich & Haarer in terms of a model based on the concept of spectral diffusion of a dilute spin system. The expression for the holewidth then becomes time dependent [4.113-115]. From reversible and irreversible hole broadening contributions obtained by thermal cycling experiments, the same group concluded that temperature-induced spectral diffusion is small compared to pure dephasing processes at temperatures between 4 and 25K [4.117].

We must not forget that the holewidth in glasses contains some inhomogeneous part which was shown to depend on the time τ_{HB} spent on the burning and detecting of the hole, i.e. spectral diffusion is present. The full holewidth may be given as follows

$$\Gamma_{hole}(T) = 2\Gamma_{hom}(T) + \Gamma_D(T,\tau_{HB}) \tag{4.7}$$

where Γ_D is the contribution by the spectral diffusion.

The TLS may take part in both processes of hole broadening: in dephasing [4.118] and in spectral diffusion [4.119]. To fit the experimental data Gorokhovskii et al. [4.120] have used the form for $2\Gamma_{hom}(T)$ proposed by Lyo [4.121], see also [4.122], for the dipole-quadruple interaction between impurity and TLS in the form

$$2\Gamma_{hom} = Ae^{h\nu_0/kT} (e^{h\nu_0/kT} + 1)^{-1.75} (e^{h\nu_0/kT} - 1)^{-0.25} \qquad (4.8)$$

and the form for $\Gamma_D(T,\tau_{HB}) \sim T^{\alpha}$ proposed in [4.119,123]. Curve 1 in Fig.4.5 represents the homogeneous part of $\Gamma_{hole}(T)$ with the psuedolocal mode frequency n_0 = 0.08cm-1. Curve 2 exhibits the contribution of spectral diffusion with the exponent α = 1.66. The spectral diffusion contribution becomes negligible below 0.1K. It is interesting to compare curve 1 with the holewidth measured with the Doppler spectrometer. The experimental point at T = 1.45 K with the measurement time τ_{HB} = 10^{-5}s is shown in Fig.4.5; and it is in agreement with the homogenous holewidth predicted by curve 1.

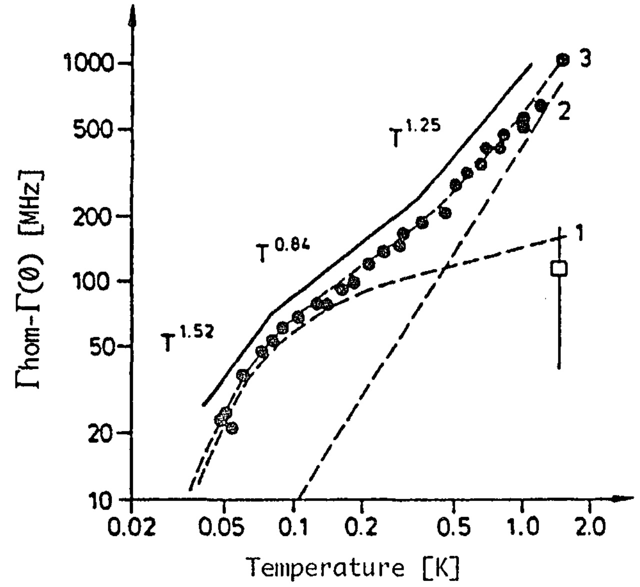


Figure 4.5. Temperature broadening of spectral holes in the region 0.05-1.5K for OEP-PS. Ref.4.125.

Form the experimental data available for spectral hole broadening in glasses at low temperatures one can conclude that holewidths measured slowly (i.e., at $\tau_{HB} >> T_1$) are affected by a substantial inhomogeneous broadening, caused by a diffusion-like process of rearrangement in the matrix resulting in spectral diffusion. Diffusional broadening of the hole was also observed when holes were burned in a T_1-T_0 transition of pyrene in butylbromide [4.124]. The inhomogeneous contribution may be decreased by shortening the measurement time τ_{HB}. The processes of spectral diffusion become inactive at very low temperatures (for OEP-PS below 0.1 K), where inhomogeneous broadening of the holewidth caused by spectral diffusion becomes negligible. Therefore, it seems reasonable to suppose that a crossover from the law $\Gamma_{hole}(T) \sim T^{1.3}$ to an approximately linear T dependence takes place because of a competition between inhomogeneous and homogeneous affects on the holewidth.

The behavior $\Gamma_{hole}(T)$ at very low temperatures (at T<0.1K for OEP-PS) is due to the homogeneous broadening $\Gamma_{hom}(T)$ of the purely electronic zero-phonon line of the impurity molecule. Holewidths close to the electronic lifetime-limited value $\Gamma(0) = (2\pi T_1)^{-1}$ are possible at still lower temperatures (for OEP-PS at T<0.01K). The difference $\Gamma_{hole}(T)$-$2\Gamma(0)$ at higher temperatures is due to dephasing processes. For OEP-PS, $\Gamma_{hole}(0.05)=4\Gamma(0)$.

The results for OEP-PS also show that dephasing in glasses at very low temperatures is sensitive to the details of the local structure of the matrix in the vicinity of impurity. The same microscopic processes are, to some extent, responsible for the position of ZPLs in the inhomogeneously broadened band and, therefore, a correlation arises between the parameters of $\Gamma(T)$ and the hole-burning frequency. On the other hand, at some higher temperature the $\Gamma_{hom}(T)$ dependence on the hole-burning frequency vanishes. This indicates that the processes causing spectral diffusion are relatively insensitive to the local structure of the impurity centers.

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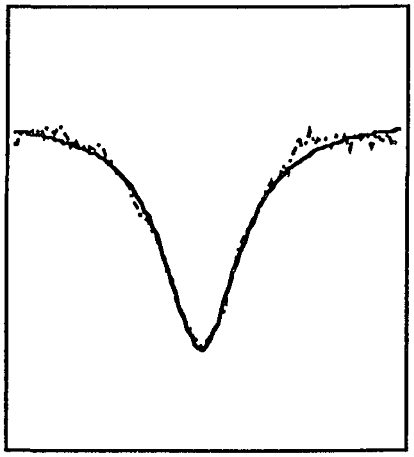
HOLE-BURNING IN EXTERNAL FIELDS



CHAPTER 5

5. HOLE-BURNING IN EXTERNAL FIELDS

In this section we briefly discuss how the marriage of spectral hole-burning with external electric (Stark) or magnetic (Zeeman) fields, hydrostatic pressure, ultrasound, and high frequency acoustic phonons can provide important information on the properties of the probe molecule, microscopic compressibility, and new approaches for detection of the spectral holes. Very narrow holewidths attainable at low temperatures enhance the effects of external fields by several orders of magnitude.

5.1 Electric Field Effects

The principles of Stark hole-burning spectroscopy of optical transitions of impurity centers were recently reviewed by Maier [5.1]. Detailed descriptions of experimental data and model calculations of electric field effects on persistent spectral holes have been presented for a variety of dye molecules in amorphous polymers [5.1-14]. In general, an electric field induces a frequency shift, $\Delta\nu$, of a line (Stark effect [5.1,9,15,16]) in the electronic spectrum of a molecule due to its interaction with the dipole moments and polarizabilities of the ground and excited states. The frequency shift is given by [5.1,9,11,15].

$$\Delta\nu = (1/h)(L\Delta\mu_{eff}\cdot E + 1/2\, L^2 E\cdot\Delta\alpha\cdot E) \tag{5.1}$$

where $\Delta\mu_{eff} = \mu_e - \mu_g$ is the difference of the permanent dipole moment vectors of the excited (e) and ground (g) states and $\Delta\alpha$ is the difference of the polarizability tensors of the two states. The external field is given by E. In eq. (5.1) L is the Lorentz local field correction given by $L = (\varepsilon + 2)/3$, where ε is the dielectric constant in an amorphous host with isotropic orientation of the impurity molecules, the Stark effect depends on the dipole moments and polarizabilities averaged over all possible molecular orientations [5.1,4]. Filling, broadening, and/or splitting of the spectral holes may be observed experimentally, depending, in part, on the senses of the vectors associated with the external field and polarizations of the burn and read beams [5.1,3].

In all measurements in amorphous solids reported to date, a linear dependence of the electronic level shifts of the molecules on the electric field strength has been found. Thus, the second term in eq. (5.1) is not considered. In this case, the relationship between $|\Delta\mu_{eff}|$ and $\Delta\nu$ can be expressed as follows:

$$|\Delta\mu_{eff}| = 59.6\,\Delta\nu\;/\;(2EL) \tag{5.2}$$

where $\Delta\nu$ is the spectral splitting or broadening (in cm^{-1}), E is the applied field (in kV/cm), and L is the Lorentz local field correction mentioned earlier.

For molecules with inversion symmetry the Stark effect has been attributed to the influence of the host matrix [5.8]. In this case, since the dipole moment can be described as matrix induced dipole moment ($\Delta\mu_{ind}$) which is a measure of dipolar coupling, it is assumed that the transition dipole μ_{ge} and the change in the dipole moment $\Delta\mu_{ind}$ are not correlated. However, correlation has to be considered for noncentrosymmetric molecules. Different types of correlation have been considered [5.11,13,17]. Changes of spectral holes of amorphous guest-host have been calculated for various combinations of senses for E and the wave vectors and polarization vectors of the burn and read light of the hole-burning laser light field, the probing laser light field, and the external electric beams [5.13]. When $|\Delta\mu_{eff}|$ dominates $|\Delta\mu_{ind}|$, the spectral hole broadens or splits into two holes in the electric field, depending on the angle γ between $|\Delta\mu_{eff}|$ and the transition dipole moment μ_{ge} and the just mentioned field, wave vector, and polarization senses [5.1,4,13]. When $|\Delta\mu_{ind}|$ dominates, the spectral hole broadens in the electric field and reduces in depth. In this case, the spectral hole shape and width are independent of the polarizations directions of the light fields [5.7,13]. From an analysis of the dependence of the Γ_{hole} profile on the external electric field strength $|\Delta\mu_{eff}|$, the angle γ, as well as matrix-induced contribution $|\Delta\mu_{ind}|$ can be determined [5.4]. Values of these three quantities determined from Stark hole-burning profiles and theoretical simulations for several systems are presented in Table 5.1.

Table 5.1. Examples of experimental results for Stark effect measurements

Guest mole.	Host matrix	$\|\Delta\mu_{eff}\|$ (D)	γ (degrees)	$\|\Delta\mu_{ind}\|$ (D)
resorufin		0.42 0.2	90	0.13 Ref.5.4,5 Ref.5.50
oxazine-4	PVB	0.66	90	0.28 Ref.5.4
cresylviolet	PVB	2.1	28	0.90 Ref.5.4
chlorin	PVB	0.28		0.10 Ref.5.6
perylene	PVB			0.27 Ref.5.4,7
perylene	PVB			0.31 Ref.5.7
perylene	cellulose nitrate			0.46 Ref.5.7
tetracene	benzophenone			0.35 Ref.5.16
isobacteriochlorin	n-octane	1.62		Ref.5.16
chlorophyll a	PVB			0.22 Ref.5.50

Kanaan et al. [5.7] demonstrated that the electric field effect for centrosymmetric dye molecules, like perylene, embedded in a complex matrix, e.g. in Langmuir-Blodgett films, can be used as a sensitive probe to obtain information on the effective matrix-induced electric dipole moment differences for different host matrices.

Electric field effects have also found applications in optical storage [5.10,18]. It is also believed that the molecular systems with large Stark shifts and narrow holewidths are interesting candidates for frequency- and field-sensitive holographic storage devices [5.2,14]. Recently, Maier et al. [5.1] and Schwoerer et al. [5.19] have demonstrated a hybrid optical bistable device which is based on voltage-controlled changes of the absorption in the center of a persistent spectral hole. Finally, voltage-induced changes of spectral holes have already been used for pulse forming [5.10] and modulation of the laser light [5.10,20].

5.2 Hydrostatic Pressure Effects

Spectroscopy at high pressures has also proven to be a very useful tool for the study of intermolecular interactions in the condensed phase [5.21,22]. Pioneering work by Drickamer and coworkers [5.22] showed that the investigation of electronic transitions a function of pressure provides, e.g., information about the relative stabilization/destabilization of electronic states by intermolecular interactions, and the pressure dependence of vibrational transitions can reveal the perturbation of the vibrational potential of the electronic ground state by intermolecular interactions.

In the past, experimental and theoretical efforts have been directed to study the pressure-induced red shifts (of the order of 0.2-0.6 $\mathrm{cm}^{-1}/\mathrm{MPa}$) of electronic transitions of the entire absorption band [5.21-23]. More recently, using high resolution hole-burning spectroscopy, inhomogeneous solvent effects may be studied in a more sensitive way [5.24-28].

Inhomogeneous broadening is an indicator of the degree of structural disorder present in the system under study. PSHB and FLN spectroscopies belong to the most sensitive techniques for clarifying the influence of the environment on electronic transitions in impurities [5.29-31]. In high-pressure hole-burning spectroscopy two types of experiments are, in general, performed. In the first type, after the hole is burned the external hydrostatic pressure is changed [5.24,32,33]; the second involves burning and recording the spectral holes under the same fixed physical conditions [5.25]. In the first case, spectral holes exposed to hydrostatic pressures experience a line shift and a broadening [5.27-29,33]. In the second case, narrowing of spectral holes by nearly a factor of 2 at 510 MPa (for chlorin molecules embedded in PS matrix) and an incomplete restoration of the widths of the holes burned at normal pressure after pressure cycling was observed [5.25].

The above hole-burning experiments provide more sensitive probes of the pressure dependence of inhomogeneous solvent effects than studies which focused on the pressure dependence of the entire band, for several reasons [5.32,34,35]. First, because of the narrow holewidths (~ 0.01 cm^{-1}), the pressure necessary to produce detectable changes may be orders of magnitude smaller [5.32] than the pressure necessary to shift detectably the entire inhomogeneously broadened absorption band [5.28,30]. Second, the degree to which the holes are broadened is a good indication of the degree of microscopic disorder in the amorphous structure and provides information that is not obtainable from the previous studies [5.34]. A simple theory, which predicted a pressure dependence of the frequency shift of the spectral holes and their broadening in reasonable agreement with the experimental data was described by Haarer and coworkers [5.24,32]. A fully statistical microscopic theory of pressure effects on spectral holes and of the inhomogeneous line shape itself, was recently developed by Laird and Skinner [5.36,37]. Their theory predicted that the pressure-induced holewidth is frequency dependent, i.e., that it depends on where in the inhomogeneous line the hole is burned [5.36,37]. In addition, the theory [5.36] predicts that both the inhomogeneous line shape and the hole shape after a pressure change will be Gaussian, in qualitative agreement with experiment. Experimental data for the pressure broadening parameter δ for H_2Pc molecule in PS and PE matrices [5.32], which are 2.43 and 3.67 respectively and the theoretical values which are 1.97 and 4 respectively [5.36]. In addition, Table 5.2 provides pressure shift (s) and pressure broadening (δ) of the Γ_{hom} with increasing pressure for H_2Pc in several host matrices (e.g. PS, PE and PMMA). Comparison of the experimental results with theoretical calculations for s and δ demonstrates that the theory of Laird and Skinner is general enough to predict the results of the pressure-tuning experiments, as well as the inhomogeneous line shape itself [5.32,36]. The theory of Laird-Skinner has been recently extended by Kador [5.38] beyond the Gaussian approximation. In his model, Kador calculated pressure effects on hole-burning spectra in glasses in a semianalytical fashion without using this approximation. It turned out that not only the pressure shift but also the pressure broadening of hole-burning spectra increases from the blue to the red of the absorption band. Moreover, hole-burning spectra are predicted to become asymmetric when the sample is exposed to hydrostatic pressure. Although experimental studies are in good agreement with the Gaussian approximation, more experimental data is required to test these predictions.

Table 5.2. Pressure broadening (δ) and pressure shifts (s) of the zero-phonon linewidth with increasing pressure in amorphous solids.

Guest molecule	Host matrix	δ (cm^{-1}/MPa)	s (cm^{-1}/MPa)
H_2Pc	PS	-0.22	0.12 Ref.5.24
H_2Pc	PMMA	-0.17	0.09 Ref.5.24
H_2Pc	PE	-0.18	0.06 Ref.5.32

However, for sufficiently high pressures (> 500 MPa) depending on the pressure, i.e., the pressure applied to the polymer sample before hole-burning, the changes in holewidth may be irreversible [5.25]. This could indicate that in soft polymeric matrices irreversible or post-pressure effects may be present. Possible mechanism(s) of recently observed line narrowing of the spectral holes burned at high pressure as compared with the results obtained at normal pressure have been discussed [5.25]. Very recently, nonlinear color effects in the pressure-induced broadening of a spectral hole burned into resorufin-doped alcohol glasses were also observed [5.27,28]. These observations were explained in terms of correlation between dispersive and electrostatic forces.

Although more studies on different host/guest molecule systems are necessary to establish the physical mechanisms of the pressure effects reported so far, it has been already established that pressure tuning of spectral holes can provide a more detailed insight into the microscopic interactions between a probe and its surroundings and can yield information on structural disorder [5.24,25,27-29,32-35,36-38]. The study of a physical property as a function of pressure and temperature, rather than temperature alone, should provide the data required for a better understanding of the molecular dynamics in disordered solids. It is also believed that application of high-pressure hole-burning spectroscopy to proteins and/macromolecules will become a very valuable method for investigation of many biochemical problems at the molecular level. For example, very recently, the compressibilty and volume fluctuations in proteins (e.g. horseradish peroxidase and myoglobin) were measured by hole-burning spectroscopy [5.34,35].

5.3 Other Field Effects

Magnetic effects, utilizing hole-burning spectroscopy, have been studied in various crystalline [5.39] and organic amorphous systems [5.1,18]. From the shift of spectral holes due to the quadratic Zeeman effect, the matrix element of the angular momentum operator L_Z between the excited singlet states can be derived. In organic glasses where the orientation of the molecules with respect to the magnetic fields is random, in addition to shift a broadening phenomenon is observed [5.40,41]. The small sifts are visible, due to the high resolution of hole-burning, where a sharp holes serves as a frequency marker in the broad absorption band. From the hole shape in magnetic fields, the change in magnetic field on excitation to its lowest excited singlet state, and the matrix element $\Lambda = |\langle S_1 | L_z | S_2 \rangle|$ of the effective orbital angular momentum between two lowest excited singlet states S_1 and S_2, could be determined [5.42,43]. In general, Zeeman shifts of the order of 10^{-4} to 10^{-3} of Γ_{inh} are not observed. It has been shown, for example, that the change of magnetic susceptibility $1/2\ \chi^{z'z'}$ of H_2P in PE is 60.6 MHz/T^2 [5.44], in good agreement with the value previously found for the same molecule in a crystalline host [5.44]. From

$$\chi^{z'z'} = 2\beta^2\Lambda^2/(E_2 - E_1) + \chi_D \tag{5.3}$$

where β is the Bohr magneton and χ_D = -17 MHz/T^2 [5.44] is the diamagnetic effect resulting from the Larmor precession of the electrons in the field, one can easily obtain the value of Λ=5.64 [5.43]. It has been shown that magnetooptical properties, and the interaction between the lowest excited singlet states of complex molecules not only in single crystal hosts but also in disordered materials [5.40]. For example, Ulitskii et al. [5.45] have analyzed the hole profile and its dependence on an external magnetic field for molecules with a doubly degenerate S_1 level. From these measurements the static magnetic moment in the degenerate S_1 state (for zinc phthalocyanine in PVB) at T= 4.2 K was obtained. Magnetic field hole-burning experiments also allow determination of an average value of the relatively small Jahn-Teller splitting [5.45] which otherwise cannot be observed in disordered systems due to the large inhomogeneous broadening.

Spectral holes can be also detected using phase-sensitive ultrasonic modulation [5.46]. This method developed by Moerner and Huston, offers zero background and the potential for high-speed detection with sensitivity near the quantum limit. It also has been demonstrated that prolonged exposure to ultrasound causes erasing and modulation of holes. Thus, an optical measurement of the hole depth provided a method of monitoring the ultrasound in solids [5.47].

Investigations of the influence of phonons on spectral holes were also carried out, by either heating the sample or generating phonons with a heat-pulse technique [5.48]. Two types of phonon detection have been demonstrated, real-time phonon detection [5.48] and phonon memory [5.49]. In the first type, the filling of the persistent spectral holes is by heat-pulse phonons which are radiated to the sample simultaneously with the detecting laser light. The phonons give rise to changes of the spectral hole depth which follow instantaneously the changes of the phonon pulses with time. This method is used for real-time broad band phonon detection which is compatible to phonon detection by a bolometer [5.44]. In the second type of experiment, a heat pulse generates phonons in the dark pause between laser pulses causing a partial filling of the spectral holes. Since, after phonon radiation, the hole does not recover to its original value, information on the effect of the phonons can be stored and detected later by switching on the laser and measuring the hole depth. Phonon-induced filling of the spectral holes has been explained by phonon processes in which barriers of the double-well potential are crossed [5.49].

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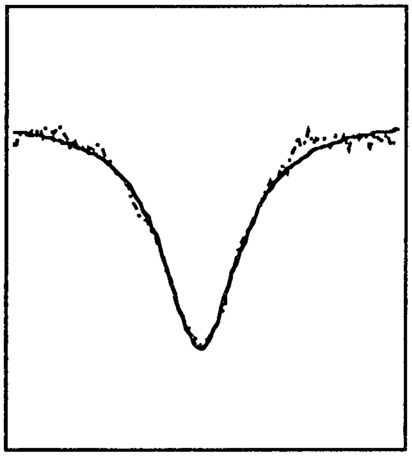
QUINAZIRINE (1,4-DIHYDROXYANTHRAQUINONE)



CHAPTER 6

6. QUINAZIRINE (1,4-DIHYDROXYANTHRAQUINONE)

6.1 Introduction

In recent years there have been a number of experiments in which the interaction between an amorphous host and dilute guest molecule at low temperatures have been explored [6.1]. Studies utilizing the technique of hole-burning spectroscopy have been of considerable value to this endeavor [6.2,3]. For example, a series of careful studies [6.4-9] has shown that the homogeneous linewidth (Γ_{hom}), measured in the limit of zero laser fluence, is a sensitive measure of relaxation processes in the excited state. If T_1 represents the population decay time of the excited state, and T_2^* is the pure dephasing time corresponding to thermally induced fluctuations in the spectroscopic transition frequency, then the homogeneous linewidth can be written:

$$\Gamma_{hom} = (2\pi T_1)^{-1} + (\pi T_2^*)^{-1} \tag{6.1}$$

Extensive measurements of the dephasing time in varied hosts and at differing temperatures have yielded a variety of information concerning the nature of the guest-host interaction. Unlike crystals, where low temperature properties are dominated by phonon interactions, glasses are characterized by atoms or atomic groupings which can attain several nearly isoenergetic configurations, or two-level systems (TLS). The absorption spectra of molecules embedded in disordered matrices are generally very broad due to site inhomogeneities. A given molecule has an absorption frequency which is quite sensitive to the arrangement of solvent molecules surrounding it. The most interesting results of such studies show that the optical dephasing (T_2^*) properties of impurities in amorphous solids are quite different from those in crystals. Namely, it is found that the dephasing times at low temperatures are several orders of magnitude shorter in amorphous matrices. Furthermore, the temperature dependence of the holewidth is found to be T^n where the exponent n varies between 1 and 2. For a large number of systems, this parameter is near 1.3. These results have been the subject of a large number of theoretical studies (for a review see ref.1) most of which involve phonon assisted tunneling in the two level system. If the density of two-level system states varies as $E^{0.3}$ (where E is the energy) and the impurity-two level system interactions are assumed to be dominated by dipole-dipole terms, a $T^{1.3}$ dependence may be predicted. Huber et al. [6.10] have examined the nature of dipole-dipole interactions responsible for such a dependence and indicate that the strain field resulting from the orbit-lattice interaction is considerably larger than that expected from the dipole interaction with the two-level tunneling system.

If the interaction between the guest molecule and the two-level system of the host can indeed be described in terms of dipolar interactions, then it is likely that examination of molecular dipole moments of the guest molecules in various hosts might also shed some light on this problem. For example, it has been noted that the dipole moment change $|\Delta\mu|$ in chlorin varies between 0.25D in poly(vinylbutyral) [6.11,12] and 0.4D in poly(styrene) [6.13]. Even more remarkable has been the observation of linear Stark effects in intrinsically nonpolar molecules, such as octaethylporphyrin [6.14,15] perylene [6.16,17] and (Zn)-tetrabenzo-porphin [6.18]. These electric field effects are also attributed to the influence of the two-level system fluctuations on the guest excitation. In this work, we present a systematic study of the effective dipole moment change in quinazirine (1,4-dihydroxyanthraquinone) in a series of glassy and polymeric hosts. This molecule was chosen partly because of the vast difference between the effect of host structure on dipolar interaction observed in a non-polar crystal [6.19] in comparison with polymers [6.20] and glasses [6.21]. This suggests that the guest-host interaction will be quite strong and easily measurable. Our results indicate a strong correlation between the effective dipole moment change and the zero-fluence holewidth. We utilize the observed relationship to extract several parameters which we believe measure directly the distribution of dipole-dipole interactions between the two-level system and the guest molecule.

6.2 Previous Studies

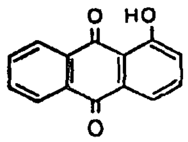
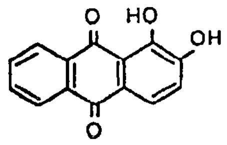
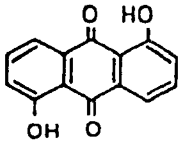
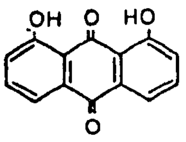
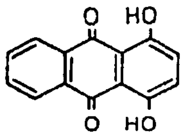
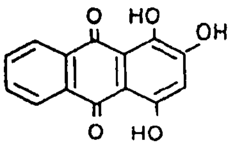
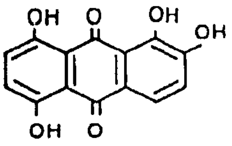
A basic prerequisite for the understanding of the various photochemical hole-burning (PHB) phenomena is a detailed knowledge of the photochemical reaction scheme and its relation to the host material.

Quinazirine is one of the most extensively studied dye molecules in PHB-reactions [6.1]. It has been suggested that the PHB reaction of this molecule is strongly dependent on the host matrix as opposed to porphyrin- and phthalocyanine-like molecules, and is due to a breakage of an internal hydrogen bond and a subsequent formation of an external bond to the solvent [6.22]. Tani et al. have looked into some details of the phototransformation process in quinazirine by preparing a series of quinazirine derivatives with different functional groups: hydroxy, amino and stearylamino groups [6.21]. They had already noticed that only the two hydroxy or other electron-donating groups located at 1 and 4 positions give rise to effective intramolecular charge transfer. Their goal was to find out how these functional groups of quinazirine (1,4-DAQ) are involved in the hole-burning photochemistry.

Table 6.1 summarizes the results of the burning ability of seven molecules in which the number and position of OH group(s) are changed in anthraquinone (AQ) framework [6.21]. They clearly fall into two groups, one showing photochemical holes with a hole-burning efficiency of the order of

10^{-4} and the other with no detectable hole-burning efficiency. One can conclude as follows: the occupation of the 1 and 4 positions by two OH groups seems essential for the appearance of the persistent holes in quinazirine and related molecules.

Table 6.1. Photochemical burning efficiencies (η) in the zero phonon line of seven anthraquinone derivatives at each burning wavelength (λ_B). Ref.6.21.

Derivatives		λ_B(nm)	η
	1-HAQ	420.0	-
	1,2-DAQ	476.5	-
	1,5-DAQ	457.9	-
	1,8-DAQ	457.9	-
	1,4-DAQ	520.8	1.8×10^{-4}
	1,2,4-TAQ	520.8	1.6×10^{-4}
	1,2,5,8-TAQ	530.9	1.4×10^{-4}

Tani et al. [6.21] also substituted OH group(s) of the quinazirine molecule with amino and stearylamino functional groups, Fig.6.1. The efficiencies of the molecules (II), (III) and (IV) are smaller by two orders of magnitude as compared to (I). Obviously, the capability of undergoing light induced changes decreases as the hydroxyl group in the anthraquinones is changed to an amino or stearylamino group. In the molecules (V) and (VI), they could not detect any hole-burning photochemistry.

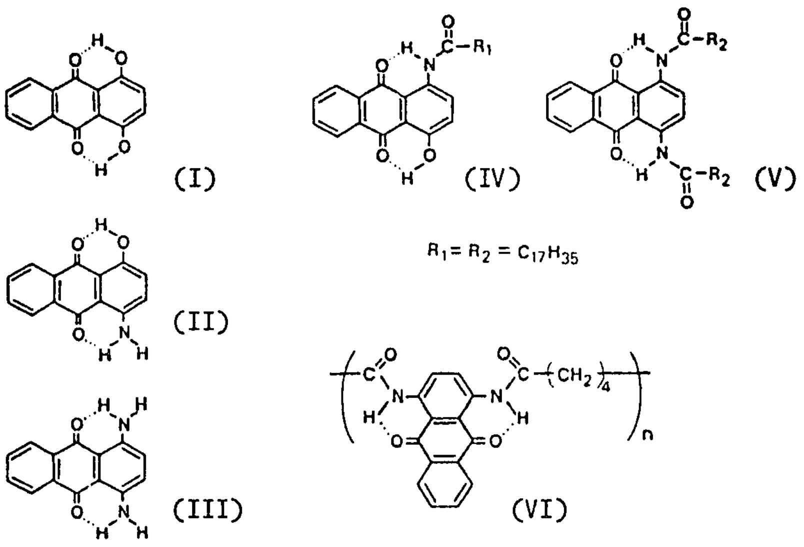


Figure 6.1. Structures of the molecules investigated in some previous studies. (I) 1,4-dihydroxyanthraquinone, (II) 1-amino-4-hydroxyanthraquinone, (III) 1,4-diaminoanthraquinone, (IV) 1-hydroxy-4-stearylaminoanthraquinone, (V) 1,4-bis(stearylamino)-anthraquinone, (VI) poly(iminoadipoyl-imino(1,4-anthrylene-9,10-dione)). Ref.6.21.

Two possible mechanisms for the PHB reaction of quinazirine could be considered to be: (a) the intramolecular proton transfer (tautomeric change), and (b) the formation of an intermolecular hydrogen bond to the matrix (conformational change). It has been argued that the photochemical process could involve both intramolecular and intermolecular bonds [6.1]. The results Tani et al. have reported seem to support the idea that the electron donating power (i.e. the amount of charge transfer character) of the two functional groups at 1 and 4 positions to create intramolecular charge transfer is essential to PHB and the present observations strongly support the process (b) [6.21].

As to process (b), there are two possibilities, namely that only one of the two functional groups participates in the process or that both of them do. Let us assume, for the moment, that both functional groups act independently in the photoreaction and that the final product would be characterized by a proton rearrangement reaction of just one group. Then, since both functional groups on the same molecule should take part in the photochemistry with the same probability, the reaction efficiency (i.e. the probability of finding a suitable configuration for external hydrogen bonding with the microscopic neighborhood) per one functional group should be only half the value as for two functional groups. But the efficiencies given for molecules in Table 6.1 show that no stable photoproduct can be formed with only one functional group taking part in the PHB process.

From this difference we could draw the conclusion that a stable photoproduct is only formed in the case where two hydrogen bonds in 1,4-position take part in the photoreaction as illustrated in Fig.6.2. It seems that the final photoproduct in quinazirine is explained by the structure in which both hydroxy groups are involved in solvent hydrogen bonds. This reasoning is also supported by the fact that quinazirine in the presence of a small amount of KOH, which removes one of the active protons, does not show PHB as reported by Drissler et al. [6.22].

Experimental results seem to support the idea that the intramolecular hydrogen bond is broken and an intermolecular hydrogen bond is formed in the presence of a hydrogen acceptor (A) in the host structure [6.22,23]. Stable photoproducts are formed only when two hydrogen bonds in the 1 and 4 positions are involved in the photoreaction resulting in a solvent induced conversion shown in Fig.6.2.

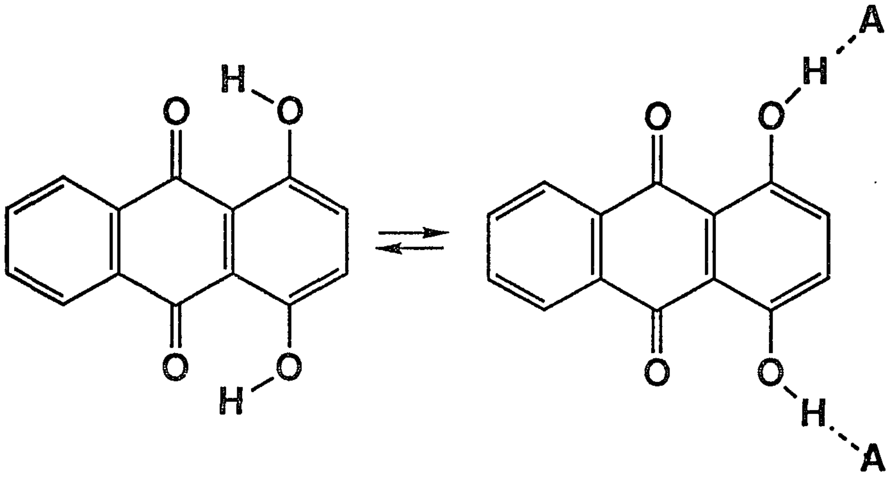


Figure 6.2. Suggested isomerization for quinazirine immersed in polar hosts. A represents an electron acceptor.

Studies of quinazirine in non-hydrogen bonding matrices, such as n-alkanes, methyl-tetrahydrofuran show no photoinduced net proton transfer with detectable yield ($>10^{-4}$/photon) [6.23]. Similar effects were discussed in a review by Klopfer [6.24]. Further experiments in 3-methyl pentane strongly corroborate this model. Since 3-methyl pentane cannot form hydrogen bonds, it is not suprising that no photochemical transformation occurs [6.25].

Brienl, Freidrich and Haarer [6.26] studied the temperature dependence of the homogeneous linewidth in amorphous alcohol glasses from 0.4K to 4K and showed that the linewidth obeyed the T^n (with n varying between 1.0 and 1.3) dependence. This was interpreted as indicating several mechanisms to be operative in this region, but that the two-level system dephasing is likely the dominant mechanism. Tani et al. [6.20] studied the linewidth as a function of polymer structure. They systematically varied the polarity of the host using poly(ethylene), poly(methacrylic acid) and poly(ethylene-co-methacrylic acid) and found the holewidth at 4.5K to decrease from 1.4 cm^{-1}

to 0.05 cm^{-1} as the polarity of the polymer decreases. This dramatic decrease of several orders of magnitude illustrates the sensitivity of this molecule to interactions with its surroundings. The authors interpret these results to be due to dipole-dipole interactions.

Previously, the Stark effect was used on quinazirine in a single crystal n-octane hosts [6.19]. Hole-burning was not observed, as expected for non-hydrogen bonding hosts. This is consistent with the above interpretation of the hole-burning mechanism in this molecule. However, in crystalline media the spectral lines of the S_1-S_0 (0-0) band are sufficiently sharp and narrow, and the fact that the transition is charge transfer in nature allows for a large spectral splitting on application of an external field. It was determined that $|\Delta\mu| = 1.64 \pm 0.03$ D; also the direction cosines of the orientation of the molecular axes with respect to the crystal axes were found.

6.3 Experimental Results

Stark hole-burning experiments were carried out in a manner previously described [6.27]. Excitation spectra were obtained by using a Molectron DLII scanning, pulsed dye laser (bandwidth 0.3 cm^{-1}) pumped with a Molectron UV14 nitrogen laser. Total emission was monitored with a R818 photomultiplier tube. An average power of 20-30 mW/cm^2 was obtained by using Coumarin 500 laser dye. The spectra were scanned with the same dye laser as used for burning, but 10^{-3}-10^{-4} of its original intensity. In our experiments, the electric field (d.c) could be applied either parallel or perpendicular to the light polarization by positioning the polarizer placed on the front face of the Stark cell. The cell consists of a thin polymer film (1 mm) placed between a copper plate and a glass plate coated with SnO_2 (Metavac, Inc.). We were able to apply electric fields as large as 60-70 kV/cm without electrical breakdown. Laser excitation was brought in by a single fiber optic with the core diameter of 200μm (Newport, Inc.) and repolarized on the front face of the Stark cell. Total emission was collected through the glass electrode by a fiber optic bundle (Edmund Sci.,Inc.) with a diameter of 6mm. All measurements were made with the sample immersed in liquid He.

Quinazirine was obtained from the Aldrich Corp. and used without purification. The following hosts were utilized in the experiments: 1) ethanol:methanol (EtOH:MeOH, 3:1); 2) poly(methyl methacrylate) (PMMA); 3) poly(methacrylic acid) (PMAA); and 4) poly(2-hydroxyethyl methacrylate) (PHEMA). For the polymers, the solution blend method was used and the solvent was allowed to evaporate on a flat glass plate to form a thin transparent film which could be cut to fit our Stark cell. The concentration of guest in the EtOH:MeOH mixture was 10^{-5} to 10^{-6} M, and in polymers, was 10^{-3} mole/kg.

The effects of an applied electric field on the hole burned in the spectrum of quinazirine are shown in Fig.6.3. The host used to obtain the data in Fig.6.3a was EtOH:MeOH; fields up to 60 kV/cm were applied without electrical breakdown. In Fig.6.3b, we show typical Stark spectra of quinazirine in PMAA. From the broadened spectra, full-widths at half maxima ($\Delta\nu$ in cm^{-1}) could be measured, and after subtracting out the zero field holewidth, the broadening versus applied field was plotted. Typical plots are shown in Fig.6.4, where ,in each graph, data is collected from several samples in separate experiments. Fig.6.4a shows results for quinazirine in EtOH:MeOH host while 4b is for PMAA as host. A linear Stark effect is clearly indicated in both cases, and the effective dipole moment change may be determined (in Debye) from the slope of the best fit straight line through the data after correction for the Lorentz approximation to the local field as follows:

$$|\Delta\mu| = 59.6\ \Delta\nu / (2EL) \tag{6.2}$$

where E is the applied field (in kV/cm) and L is the Lorentz correction due to the polarizability of the host structure. L is a function of the dielectric constant (ε) of the media { $L = (\varepsilon+2)/3$ }.

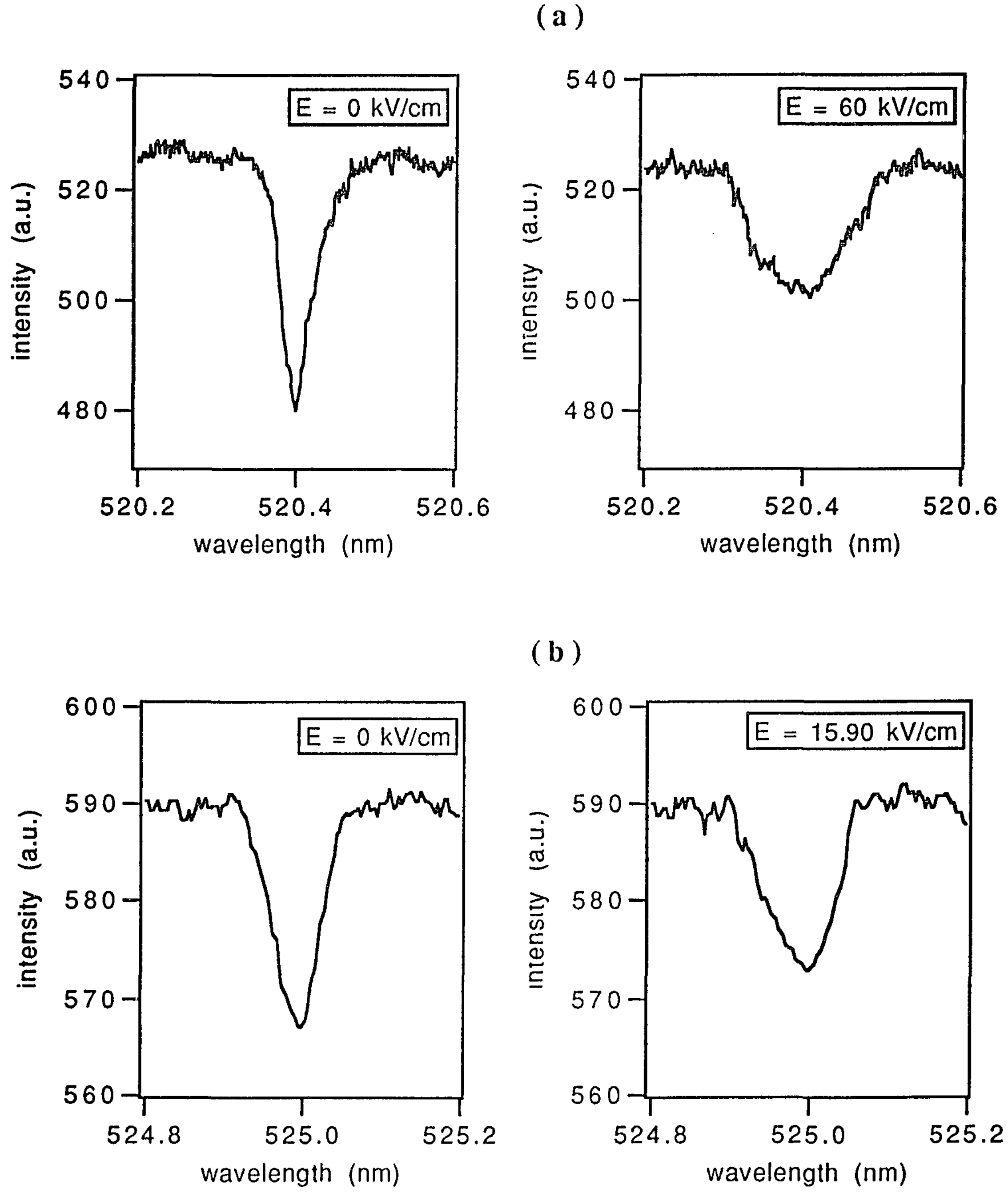


Figure 6.3. The effect of an external electric field on the spectral hole profile of quinazirine at 4.2K in (a) EtOH/MeOH and (b) PMAA.

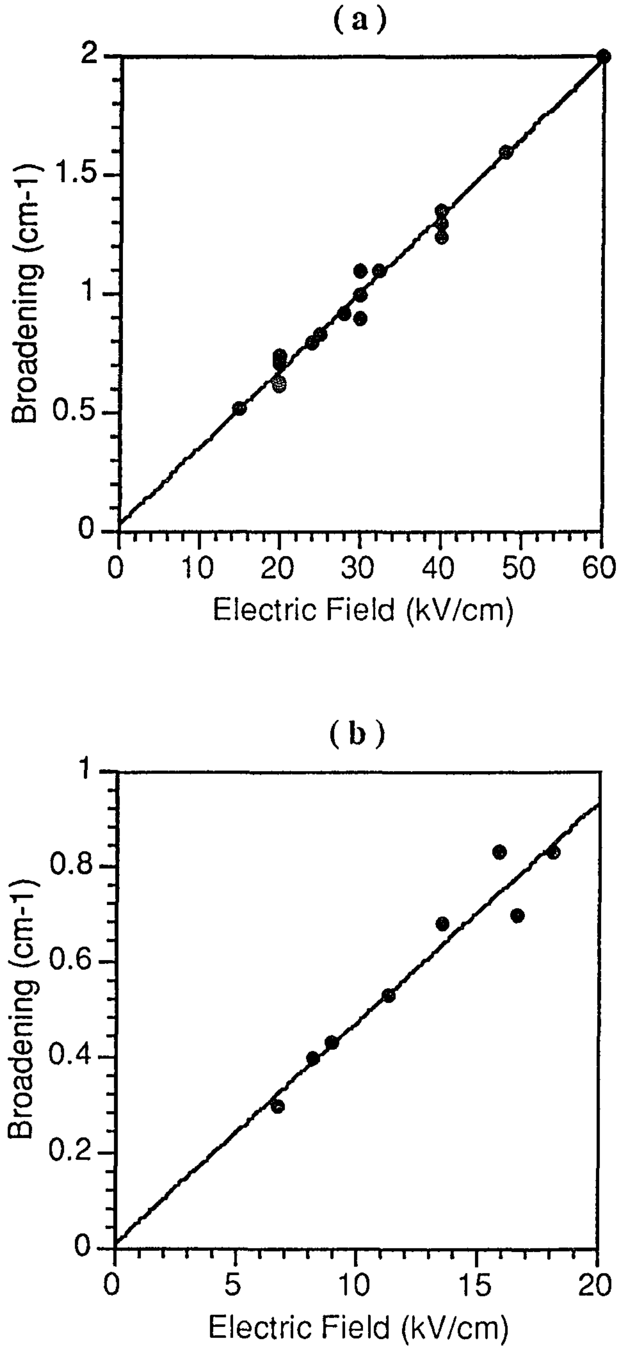


Figure 6.4. Plot of the spectral hole broadening as a function of applied electric field for quinazirine at 4.2K in (a) EtOH/MeOH and (b) PMAA. Linear least-squares fits to data is indicated by a solid line.

In the EtOH:MeOH host as well as in the polymeric PHEMA and PMAA it was possible to burn observable holes in a relatively short period of time (in some cases, seconds). This is consistent with the interpretation of Tani et al. given in Section 6.2 that the hole-burning is photochemical in nature and involves a hydrogen bonding mechanism. The zero-fluence holewidths measured in these hosts thus represent the effects of photochemical burning. However, in PMMA, which does not hydrogen bond, observable holes were much more difficult to burn, in our case. The resulting low signal-to-noise ratio made it impossible to obtain a reliable value for the zero-fluence holewidth. However, we were able to measure an effective dipole moment change although the signal-to-noise ratio was such that the data were of considerably lower quality.

Table 6.2 Zero-fluence holewidths (Γ_{hole}) for photochemical hole-burning in the lowest optical transition in quinazirine at 4.2K, effective and induced dipole moment changes ($|\Delta\mu_{eff}|$ and $|\Delta\mu_{ind}|$, respectively) in various hosts. ε represents the dielectric constant of the host.

Host	ε	$\Gamma_{hole}(cm^{-1})$	$\lvert\Delta\mu_{eff}\rvert$ (D)	$\lvert\Delta\mu_{ind}\rvert$ (D)
n-octane	2.0	-	1.64±0.03	-
PMMA	3.45[a]	see text	0.5 ±0.1	-
PHEMA	4.0	0.25	0.38[b]	0.07
PMAA	12.1	0.64[c]	0.30±0.02	0.15
EtOH/MeOH	26.6	1.37[d]	0.11±0.01	0.34

a) From ref. 6.14 b) From ref. 6.28 c) From ref.6.20 d) From ref. 6.29

In Table 6.2, we summarize the dipole moment data for quinazirine obtained in this work along with that mentioned from previous work in n-octane, as well as the dipole moment change in PHEMA obtained by Nishimura et al. [6.28]. Since they did not report a holewidth extrapolated to zero burning fluence, we report our own measurement of that parameter in Table 6.2.

Experimentally observed holes are convolutions of burning and detection steps and consequently $\Gamma_{hole} = 2\Gamma_{hom}$. Additional broadening due to the processes of spectral diffusion has been observed in some cases (see ref.6.1, pp.43-53). However, at short burning times this broadening is often negligible [6.4-9]. As a check, we measured zero-field holewidth at the end of our experiments and no broadening was observed due to spectral diffusion.

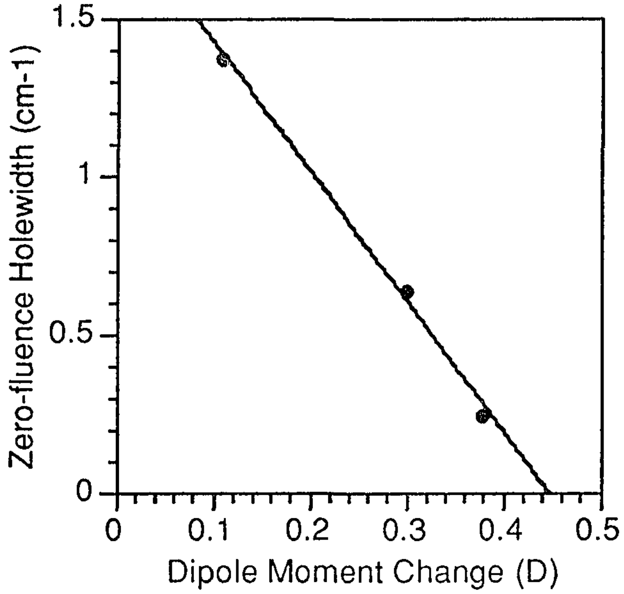


Figure 6.5. Plot of the dipole moment change in the first excited state of quinazirine as a function of zero-fluence holewidth obtained in several hosts at 4.2K. The solid line represents a linear best fit to the observed data. The intercept on the abscissa is 0.45 D.

The first thing we notice about the data is the large difference between the measured dipole moment change in the crystalline n-octane and in the amorphous hosts. This is attributable to the fact that n-octane is a non-polar solvent thus we may take the measurement as the dipole moment change for the relatively undisturbed molecule. The rather large value of dipole moment change, too large for a π-π^* transition, has been attributed to the intramolecular charge transfer nature of the optical transition [6.19]. Apparently, immersion in a polar amorphous solvent drastically effects the molecule, most likely producing the rotamer suggested by Drissler et al. [6.22] and Tani et al. [6.20]. This rotamer might be expected to have a very different electron distribution from the parent compound, possibly destroying the charge transfer character of the transition. The much smaller dipole moment changes in the amorphous hosts are much more consistent with those normally associated with π-π^* transitions. Thus a large effect on dipole moment change is not so surprising. This effect cannot be attributed to hydrogen bonding alone since it is seen in PMMA in which hydrogen bonding is nonexistent. We must conclude that the polarity of the solvent causes isomerization.

Among the polar amorphous hosts, there is still considerable variation of the effective dipole moment change. In Fig.6.5, we plot the effective dipole moment change against the holewidth measured at zero laser fluence for the three hosts in which good values for the holewidth could be obtained (This procedure is only valid to the extent that the thermal exponent, n, does not deviate much from host to host in this study). Note that the dependence is nearly linear, and we may infer a strong correlation between the two parameters. We may thus conclude that the variation in dipole moment change is related to the dipolar interactions with the two level system of the solvent. Measurements of the temperature dependence of the homogeneous linewidth for quinazirine in EtOH:MeOH mixtures in the limit of very low temperatures indicate that the linewidth is dominated by the dephasing time at 4.2K [6.18]. (Similar results have been obtained for other molecules by Renn et al. [6.30] in which the ratio of homogeneous linewidth to the natural linewidth (T_1) at 1.7K is on the order of 1000:1). Thus, if we extrapolate our results to the presumed limit of zero dephasing contribution (effectively

Γ_{hom} = 0), the dipole moment change obtained should represent the intrinsic dipole moment change in the limit in which interactions with the two level system are minimal. The value for this parameter is $|\Delta\mu_0|$=0.45D. Presumably this would be the value obtained in the limit of zero Kelvin. The deviations observed from this intrinsic dipole moment change may thus be interpreted as the result of the effects of dephasing on the intrinsic dipole moment change in the (isomerized) molecule.

Silbey and Kassner [6.31] have published an invaluable review of the various theories of homogeneous linewidths in glasses in which they interpret the broadening of optical linewidths as optical dephasing caused by interaction of the chromophore with the two level system. Phonons cause transitions between the two level system states, whose rates are modified by differences in the ground and excited guest states. The linewidths are shown to be strongly dependent on the parameter δ which is proportional to the difference in two-level system splittings when the guest is in each of two separate states. They state that δ in turn is proportional to the strength of the dipolar coupling and goes as R^{-s} (where R is the distance to the two level system and s is determined by the detailed nature of the interaction). We suggest that our observed correlation between effective dipole moment change between the two electronic states and the zero-fluence holewidths for photochemical hole-burning is clear evidence that such a mechanism is operative. One interpretation of the results is that there is a pure dephasing contribution to the measured dipole moment change. In order to account for the distribution of interactions between the two-level systems and the guest molecule, several authors [6.12,14,18] have postulated that the Stark lineshape is modulated by a Gaussian distribution of effective dipole moments. Resulting lineshape convolutions have been invoked to obtain an average value for the induced dipole moment change $|\Delta\mu_{ind}|$ as a measure of the magnitude of dipolar coupling. Meixner et al. [6.12] indicate that the effective dipole moment change can be written:

$$|\Delta\mu_{eff}| = \{|\Delta\mu_0|^2 + |\Delta\mu_{ind}|^2 + 2|\Delta\mu_0|\,|\Delta\mu_{ind}|\cos\Omega\}^{1/2} \tag{6.3}$$

where Ω is the angle between the induced dipole moment change and the intrinsic dipole moment change. It is intended that this be averaged over the assumed distribution of two-level systems. Note that our measurements show a decrease in effective dipole moment change with increasing guest-host interaction. This implies that the average value of $\cos\Omega$ is negative. Rather than carrying out the extensive calculations required by such a model, we choose instead a crude measure of the magnitude of the induced dipole moment change; simply that $\cos\Omega = -1$, i.e. that all interactions with the two-level system result in the same direction of decrease, which is antiparallel to the intrinsic dipole moment change. Note a similar result was obtained by C. De Caro and co-workers [6.32] for isobacteriochlorin where $|\Delta\mu_{eff}| = 1.2$D and $|\Delta\mu_{ind}| = 0.4$D since in n-octane host [6.19] $|\Delta\mu_0| = 1.64$; this leads as to a value of $\cos\Omega = -1$. Although our results probably represent only an upper limit to the induced dipole moment change, they do provide a test of the magnitude of the effect, as well as an indication of the trend as a function of host structure. These approximate values for $|\Delta\mu_{ind}|$ are listed in the last column of Table 6.2. As seen, these are of the same order of magnitude as those values obtained in other systems. Furthermore, notice that they scale as the dielectric constant, similar to an observation of Meixner et al. [6.14] for octaethylporphrin.

More recently, Renge [6.33] has pointed out a relationship between the Debye-Waller factors and matrix-induced part of the zero-phonon linewidths and dipole moment changes for a collection of numerous guest-host systems.

However, the ability to draw quantitative conclusions was hampered by the difficulty in comparing results from a wide range of sources of varying quality. Renge's results in conjunction with ours are highly suggestive of more systematic experiments which should be carried out.

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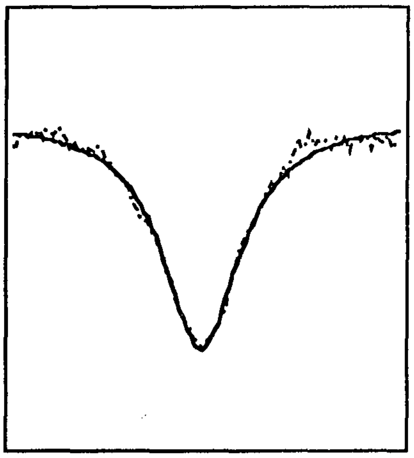
CRESYLVIOLET PERCHLORATE



CHAPTER 7

7. CRESYLVIOLET PERCHLORATE

7.1 Introduction

When incorporated in alcoholic glasses and polymers, a phenoxazine dye, cresylviolet perchlorate (henceforth referred to as cresylviolet or CV) shows a broad (~ 300-1000 cm^{-1}) and structureless absorption band in the visible region, even at liquid helium temperature [7.1-3]. The reason is probably its sizable guest-host interaction strength. Because the inhomogeneously broadened S_1<--S_0 0-0 transitions and vibronic bands are strongly overlapped, it is difficult to get information on the vibrational structure and dynamics of this system by conventional techniques. The 0-0 band of cresylviolet in polyvinylbutyral (PVB) was determined to be about 625 nm with a width of 600 cm^{-1} as shown in Fig.7.1 [7.4].

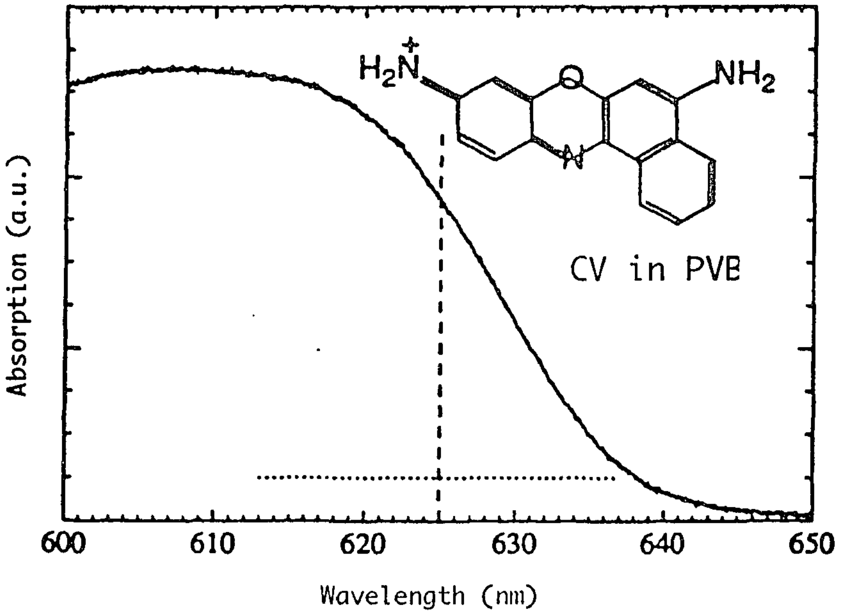


Figure 7.1. Absorption spectrum of CV in PVB at 4.2K. The vertical dashed lines correspond to the center of the 0-0 transition and the horizontal dotted lines to its inhomogeneous linewidth (FWHM). Ref.7.4.

In spite of the broad inhomogeneous absorption band, very narrow homogeneous linewidths, Γ_{hom}, in the MHz regime, have been observed for this amorphous ionic dye system at liquid helium temperature [7.2,5-8]. In fact, values of Γ_{hom} as small as for uncharged molecules in organic glasses [7.2,8-10] have been measured, which extrapolate to $\Gamma_0 = (2\pi T_1)^{-1}$ for zero Kelvin, where T_1 represents the fluorescence lifetime of each molecule. The temperature dependence of Γ_{hom}-Γ_0 between ~0.3 and ~20 K obtained by hole-burning follows a $T^{1.3}$ law [7.8].

In most of the subsequent hole-burning studies on cresylviolet [7.1,11-17] in organic amorphous hosts, the mechanism has been attributed to a photophysical reaction, although it had not been properly justified. Photophysical hole-burning is a process by which, after laser excitation, a reorientation occurs of the photostable (neutral) guest molecule in its glassy host [7.18]. A criterion has been suggested by Hayes and Small [7.18] to distinguish between photochemical and photophysical processes. If the absorption frequency of the photoproduct is very close (<2 cm^{-1}) to that of the originally burnt hole, a photophysical mechanism takes place. Furthermore, it has been observed that photophysical processes have very low hole-burning efficiencies (~10^{-6}) [7.18,19] as compared to photochemical processes (~10^{-4}) [7.20]. By means of "hole-filling" [7.13,18] experiments at spectral distances of ~ 1 cm^{-1} to higher and lower energies from the original hole it was shown that, for example, the amorphous systems tetracene in ethanol/methanol glass [7.18] and pentacene in polymethylmethacrylic acid (PMMA) [7.21] undergo photophysical reactions. In contrast, a hole burnt in the ionic dye cresylviolet in polyvinylalcohol (PVA) was efficiently filled when a new hole was burnt at 100 cm^{-1} higher energy indicating the position of the photoproduct even though the hole-burning mechanism was suggested as photophysical [7.14-17]. As mentioned above, not only the spectral distance at which a hole is filled in, but also the hole-burning efficiency is a parameter to judge whether a system undergoes photochemical or photophysical hole-burning process. The following section will hopefully shed some light on the proposal that the hole-burning mechanism of cresylviolet should not be described as conventional photophysical hole-burning process.

7.2 Previous Studies

The hole-burning mechanism of cresylviolet has been investigated by Van Den Berg and Volker [7.22] in various alcoholic glasses, non-hydroxylic polar solvents and polymers at liquid helium temperature. Preliminary results of that study have already been reported [7.2,23], which suggest that an intermolecular photochemical reaction takes place in this charged dye system. The results are compared with those of the neutral free-base porphin (H_2P) molecule in amorphous hosts, and an energy level diagram is presented which reflects the intermolecular guest-host interactions occurring in cresylviolet system.

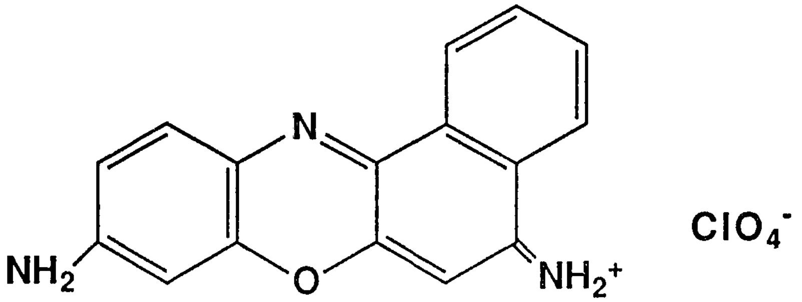


Figure 7.2. The ionic dye molecule cresylviolet.

The ionic dye molecule cresylviolet with its counter ion ClO_4^- is represented in Fig.7.2. The method that was used to determine the spectral position of the photoproduct absorption band is the following [7.1,11,13,18]: first, a hole was burnt in the absorption band and its relative depth measured, then a second hole was burnt on either its blue of red side, and the depth of the original hole was measured again. The percentage of hole-filling was a measure of the absorption intensity of the photoproduct at the wavelength of the second hole. The experiment was then repeated by varying the spectral distance of the second hole with respect to the original hole, and the percentage plotted as a function of the distance between the two holes. A fresh sample was used for each experiment. It has been observed that burning for only 30-60 s on the blue side of the original hole induced a considerable percentage of hole-filling for cresylviolet [7.22]. By contrast, burning with a similar power and length of time on the red side of the original hole had little or no effect on the latter. If the interpretation of the experiment is correct, it seems that the photoproducts of this ionic dye in most of the hosts studied absorb at a higher energy than the original ion.

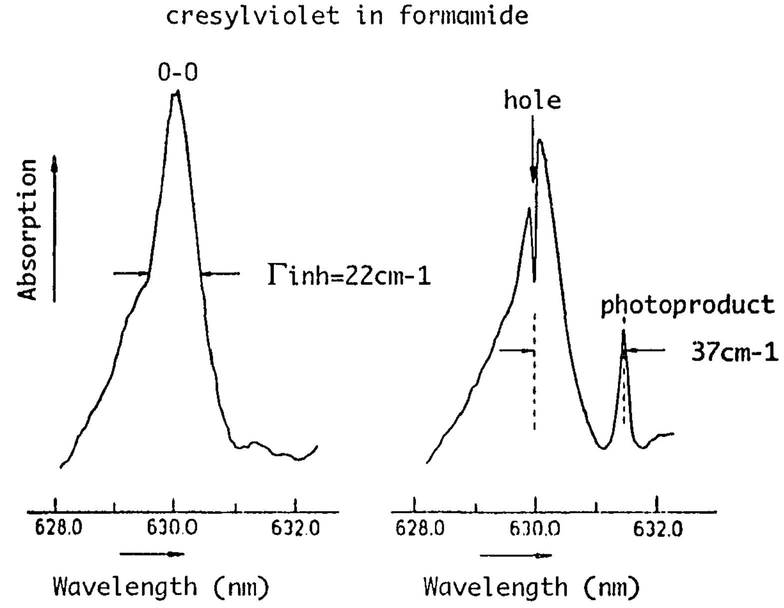


Figure 7.3. Fluorescence excitation spectra of the S_1<--S_2 0-0 band of cresylviolet at 4.2K. Notice the small inhomogeneous linewidth of 22 cm^{-1} as compared to other hosts. A hole burnt in the 0-0 absorption band creates a photoproduct at ~37 cm^{-1} lower energy. By burning a hole in the photoproduct absorption band, the originally burnt hole is filled in. Ref.7.22.

An exception to this trend is cresylviolet in formamide, the spectrum of which shows a photoproduct absorbing on the low-energy side of the original molecule as seen in Fig.7.3. Contrary to the other hosts studied, the absorption band is very narrow Γ_{inh} ~ 22 cm^{-1}. After hole-burning, a narrow photoproduct appears at ~ 37 cm^{-1} lower energy for cresylviolet. The process is reversible: by burning in the photoproduct, the original hole is filled in. The narrow inhomogeneous linewidths suggest that formamide provides a rather ordered environment for the ionic dye.

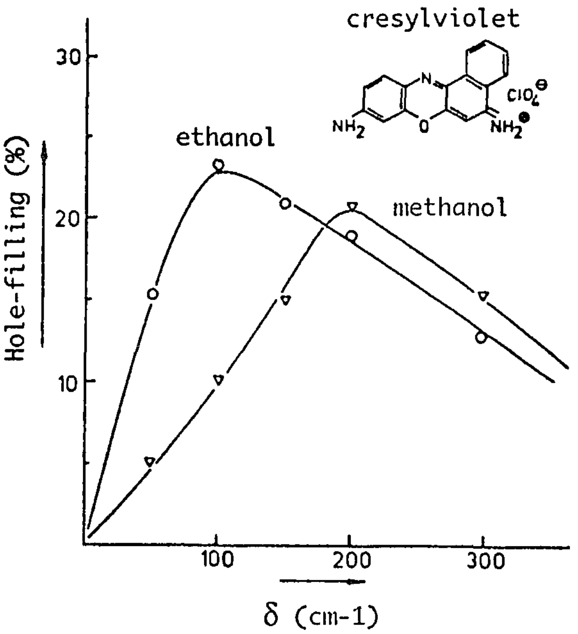


Figure 7.4. Percentage of hole-filling as a function of the spectral distance from the originally burnt hole, δ, for cresylviolet in ethanol (circles) and methanol (triangles) at 4.2K. The maximum of the curve is observed at δ_{max} ~ 100 cm^{-1} for ethanol, and ~ 200 cm^{-1} for methanol. The original hole was burnt for 2 min, the second hole (on the high-energy side) for 45 s. Ref.7.22.

Fig.7.4 is a plot of the percentage of hole-filling as a function of spectral distance between the first and second hole, δ for cresylviolet in ethanol and methanol at 4.2 K. The maxima of the curves are at δ_{max} ~ 100 and 200 cm^{-1}, respectively. Similar plots were obtained for cresylviolet in other glasses. In general, the original hole was burnt for about 2 min, whereas the second hole on the high energy side was burnt for about 45 s. The maximum percentage of hole-filling obtained in this way was ~ 20-30%. If a second hole was burnt on the red side of the original hole for about 4 min, hole-filling of only 5-8% was measured, the percentage being independent on the spectral distance. We have observed that the first hole had the same width, limited by the laser bandwidth, before and after having burnt the second hole. The reconstructed photoproduct absorption bands are ~ 200-300 cm^{-1} broad; this width is of the same order as that of the original 0-0 absorption bands. For comparison, we have also studied a neutral molecule, free-base porphin (H_2P), which yields widths of only 80-100 cm^{-1} when incorporated in the same glasses.

The large change of δ_{max} with host polarity indicates a strong guest-host interaction. Most probably the charge redistribution in the ionic dye, which results from laser excitation, strongly affects its interaction with the hydroxylic polar host [7.22].

Let us now turn to a discussion on the nature of the hole-burning mechanism. It has been observed from absorption spectra at room temperature that the neutral form of cresylviolet absorbs at ~ 4000 cm^{-1} higher energy then the positive cresylviolet. This spectral distance is approximately an order of magnitude larger than those found by hole-filling experiments at low temperature indicating that the hole-burning mechanism of cresylviolet could not be an acid-base reaction [7.22]. It has been checked whether hydrogen bonds between guest and host are essential for a hole-burning reaction to occur. It was suggested that hydrogen bonds influence the hole-burning efficiency, but are not necessary for the hole-burning reaction. In fact, it has been found that hole-burning also takes place for cresylviolet in aprotic polar solvents such as acetonitrile, pyridine and dimethylformamide. On the other hand, no one has observed hole-burning for neutral cresylviolet in ethanol (absorption maximum at 490 nm). These results strongly suggest that it is the charge redistribution in the excited state that plays an important role in the hole-burning mechanism of this dye.

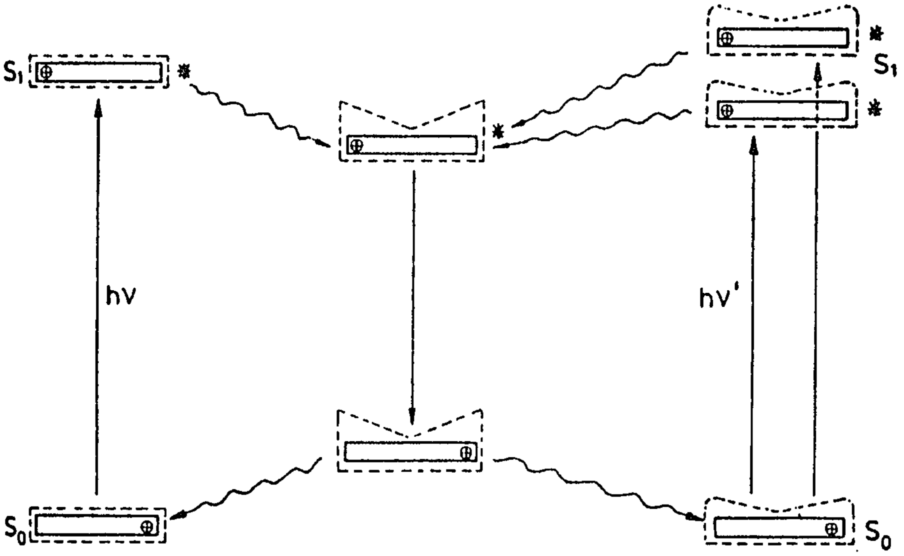


Figure 7.5. Schematic energy level diagram for the intermolecular photochemical reaction of cresylviolet in amorphous hosts at liquid helium temperatures. Ref.7.22.

From the absorption spectra at room temperature of a large number of phenoxazine dyes, with similar chemical structures to cresylviolet, dissolved in many organic solvent, Stuzka and Sindelarova [7.24] concluded that an intramolecular electron transfer probably takes place upon excitation by light. Such a charge shift will cause a considerable change in electric dipole moment, and thereby a reorganization of the electric dipoles of the host surrounding the guest molecules [7.25-30]. On return to the ground state, the guest molecule will find itself in a different, energetically less stable configuration with the photoproduct identified in the hole-filling experiments. It is clear from this picture that the absorption frequency of this photoproduct will be strongly dependent on the polarity of the host.

The hole-burning mechanism of cresylviolet suggested by Van Der Berg and Volker is illustrated in the energy level diagram of Fig.7.5. On the left-hand side, the 0-0 transition of the original dye molecule, assumed to be positive (like cresylviolet), had arbitrarily been drawn at the extreme right in the ground state S_0. It is known, however, that this molecule has a resonance structure in which the charge is only partially localized [7.28]. The surrounding solvent cage is represented by the larger dashed rectangle. On laser irradiation, hv, the ionic dye is excited and its charge redistributed. The excited state configuration, on the upper left side, is unstable and will reach equilibrium after the solvent cage has adapted itself to the shift of charges in the ion [7.25-30] (upper middle part of the diagram). Upon decay to the ground state, a new charge redistribution will occur in the dye, leading to an unstable situation (lower middle part). The system may now return to its original stable form, or reach a metastable conformation which we have associated with the photoproduct (lower right part of the diagram). The transition energy, hv', of the photoproduct may lie either to the blue or to the red side of that of stable original molecule, hv. This energy will depend on the sign of the change of electric dipole moment on excitation of the ion, and on the polarity of the surrounding host. The back reaction will further proceed as on the diagram, with the same arguments as used above for the forward reaction. The process responsible for the hole-burning in this ionic dye might thus be called an intermolecular photochemical reaction. Whether is should be considered photochemical or photophysical is a question of semantics, since the essential part of the photoreaction is a charge redistribution accompanied by a strong solvent cage reorganization. This process, however, should be distinguished from a conventional photophysical hole-burning reaction [7.18], which occurs in neutral molecules embedded in a glass and is characterized by a nearby absorbing photoproduct (< 2cm^{-1}) [7.18,21] and a very low hole-burning efficiency [7.18,19] that is orders of magnitude smaller than that observed for cresylviolet. So, even if we would like to call the hole-burning mechanism of cresylviolet in amorphous hosts as photophysical reaction, we should not overlook the fact that this is not a conventional photophysical hole-burning process in terms of the spectral distance between the hole and the photoproduct.

It is clear based on the previous studies that cresylviolet is very sensitive to its surrounding. Dipole moment change measurement is an effective way to probe guest-host interactions. That is the reason we thought cresylviolet was a good candidate for our project.

7.3 Experimental Results

Excitation spectra were obtained by using a Molectron DLII scanning, pulsed dye laser (bandwidth 0.3 cm^{-1}) pumped with a Molectron UV14 nitrogen laser. Total emission was monitored with a R818 photomultiplier tube. An average power of 20-30 mW/cm^2 was obtained from the dye laser by using the mixture of Rhodamine 610 and Rhodamine 640 laser dyes. The spectra were scanned with the same dye laser as used for burning, but 10^{-3}-10^{-4} of its original intensity. In our experiments, the electric field (d.c) could be applied either parallel or perpendicular to the light polarization by positioning the polarizer placed on the front face of the Stark cell. Fig.7.6 illustrates the geometry of the Stark cell that was used. The cell consists of a thin polymer film (1 mm) placed between a copper plate and a glass plate coated with SnO_2 (Metavac, Inc.). We were able to apply electric fields as large as 60-70 kV/cm without electrical breakdown. Laser excitation was brought in by a single fiber optic with the core diameter of 200μm (Newport, Inc.) and repolarized on the front face of the Stark cell. Total emission was collected through the glass electrode by a fiber optic bundle (Edmund Sci.,Inc.) with a diameter of 6mm. All measurements were made with the sample immersed in liquid He.

Cresylviolet Perchlorate (CV) was obtained from Exciton, Inc. and used without purification. The following hosts were utilized in our experiments: formamide, ethanol:methanol (EM, 3:1), polyvinyl alcohol (PVA), 2-hydroxyethyl methacrylate (PHEMA), polyvinylbutyral (PVB), and polymethyl methacrylate (PMMA). For the polymers, the solution blend method was used and the solvent was allowed to evaporate in a glass petri dish to form a thin film (1 mm). The concentration of CV in formamide and EM was 10^{-5}-10^{-6}M, and in polymers, was 10^{-3} mole/kg.

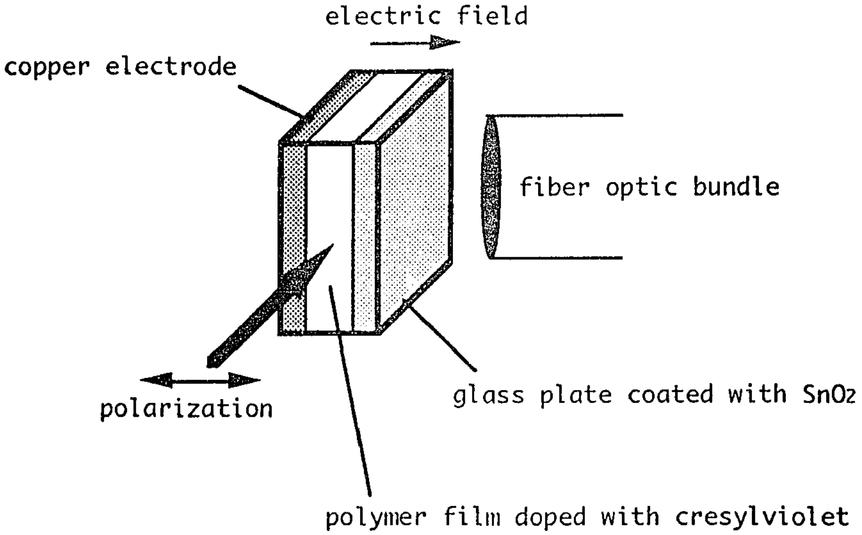


Figure 7.6. Geometrical configurations and Stark cell used in the experiments.

The effects of an applied field on the spectral hole burned in the spectrum of cresylviolet are shown in Figs.7.7-7.15. All these spectra were fitted to Lorentzian. From the broadened spectra, full-widths at half maxima ($\Delta\nu$ in cm^{-1}) could be measured, and after subtracting out the original holewidth (the holewidth in the absence of the electric field), the broadening versus applied electric field was plotted. These plots are given in Figs.7.16-7.20. Data in each plot were collected from several samples in separate experiments. A linear Stark effect is clearly indicated in each case, and the effective dipole moment change may be determined (in Debye) from the slope of the best fit straight line through the data after correction for the Lorentz approximation to the local field. Please see Chapter 6 for details regarding the formula we used to calculate the effective dipole moment change.

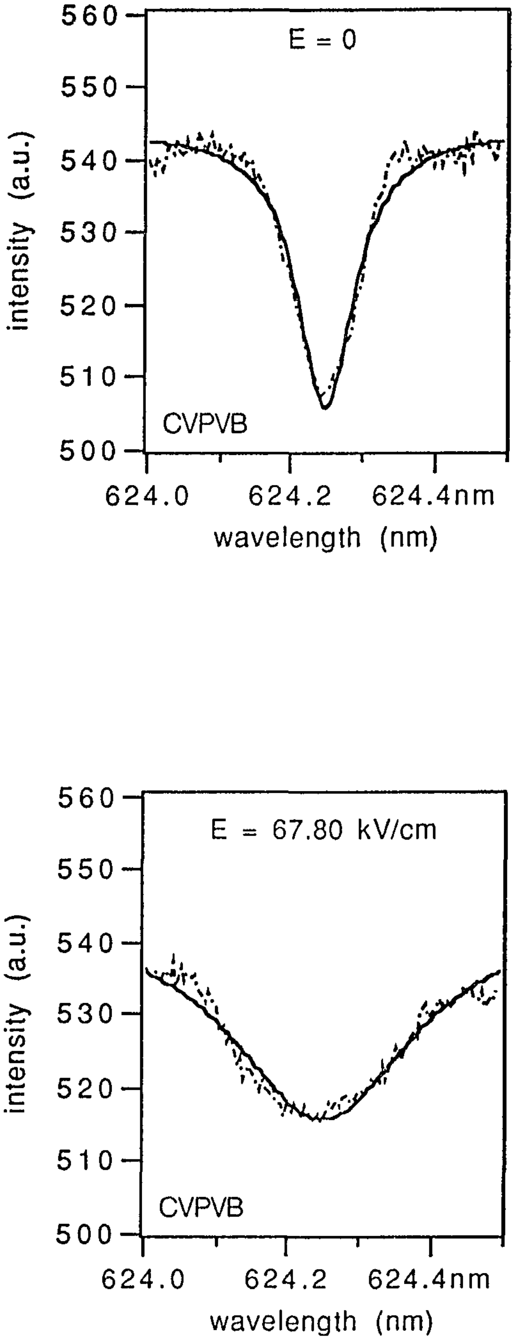


Figure 7.7. Effect of an external electric field on the spectral hole profile of CV in PVB.

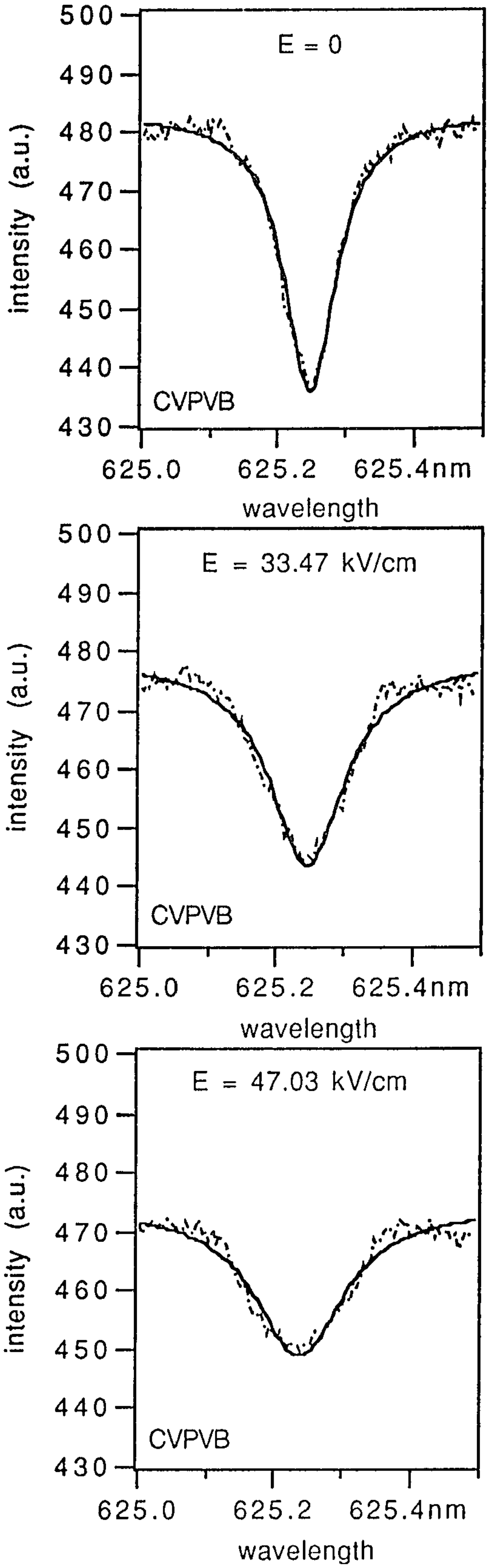


Figure 7.8. Effect of an external electric field on the spectral hole profile of CV in PVB.

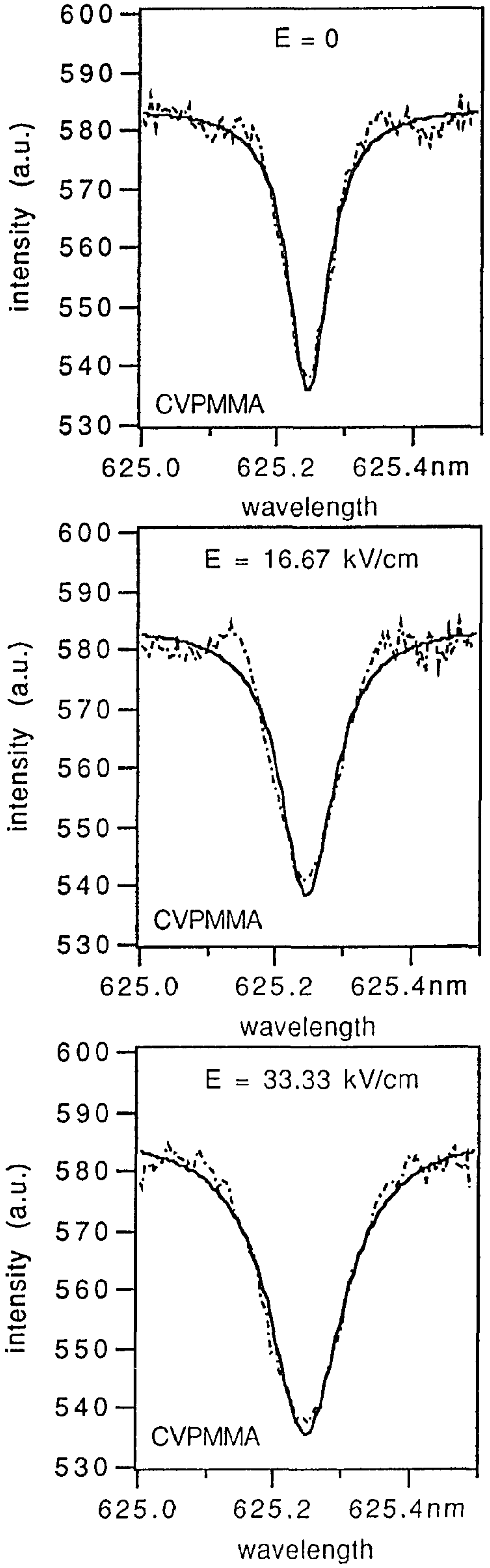


Figure 7.9. Effect of an external electric field on the spectral hole profile of CV in PMMA.

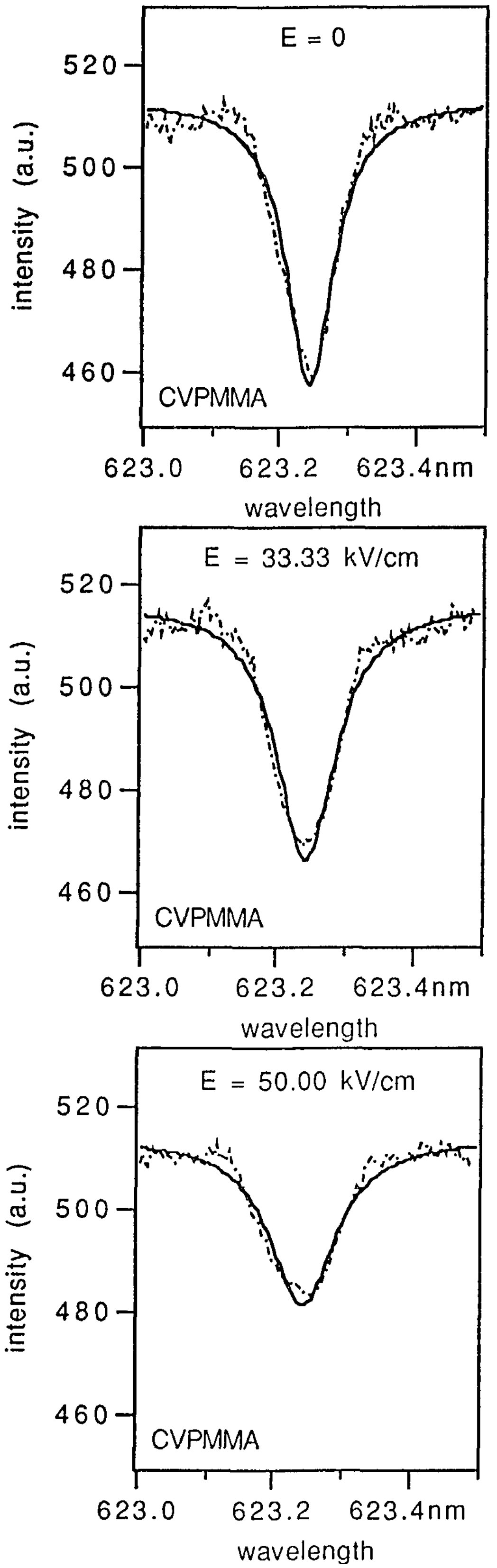


Figure 7.10. Effect of an external electric field on the spectral hole profile of CV in PMMA.

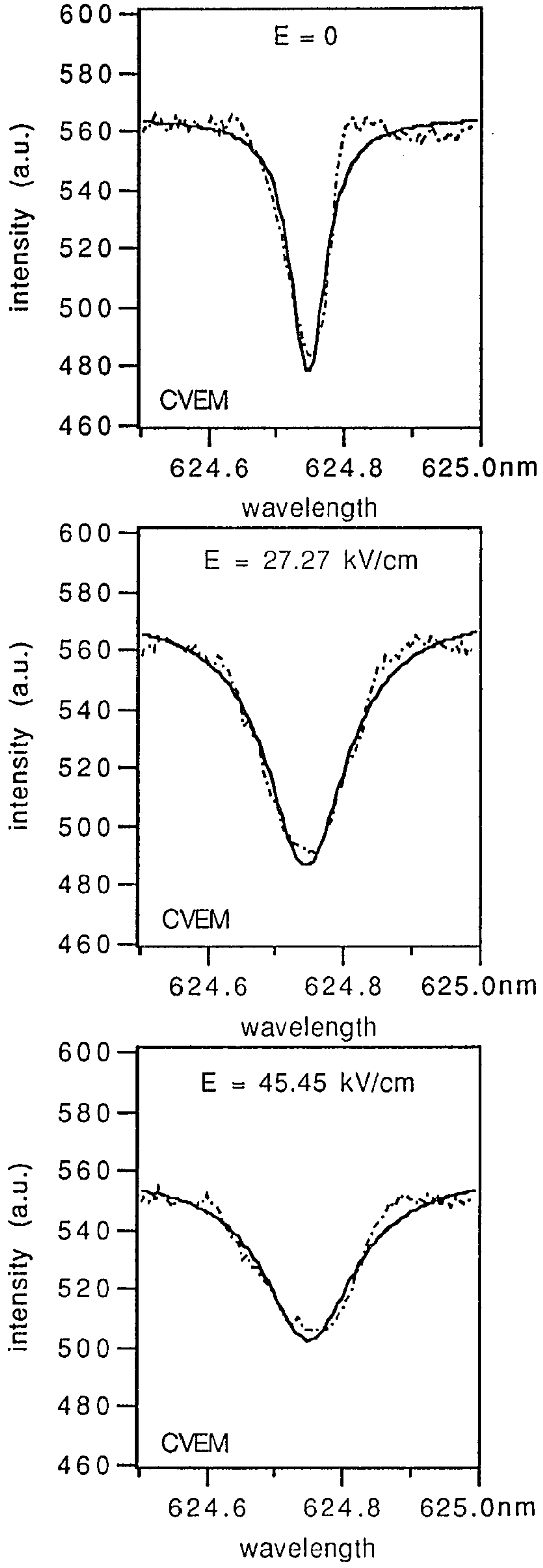


Figure 7.11. Effect of an external electric field on the spectral hole profile of CV in EM.

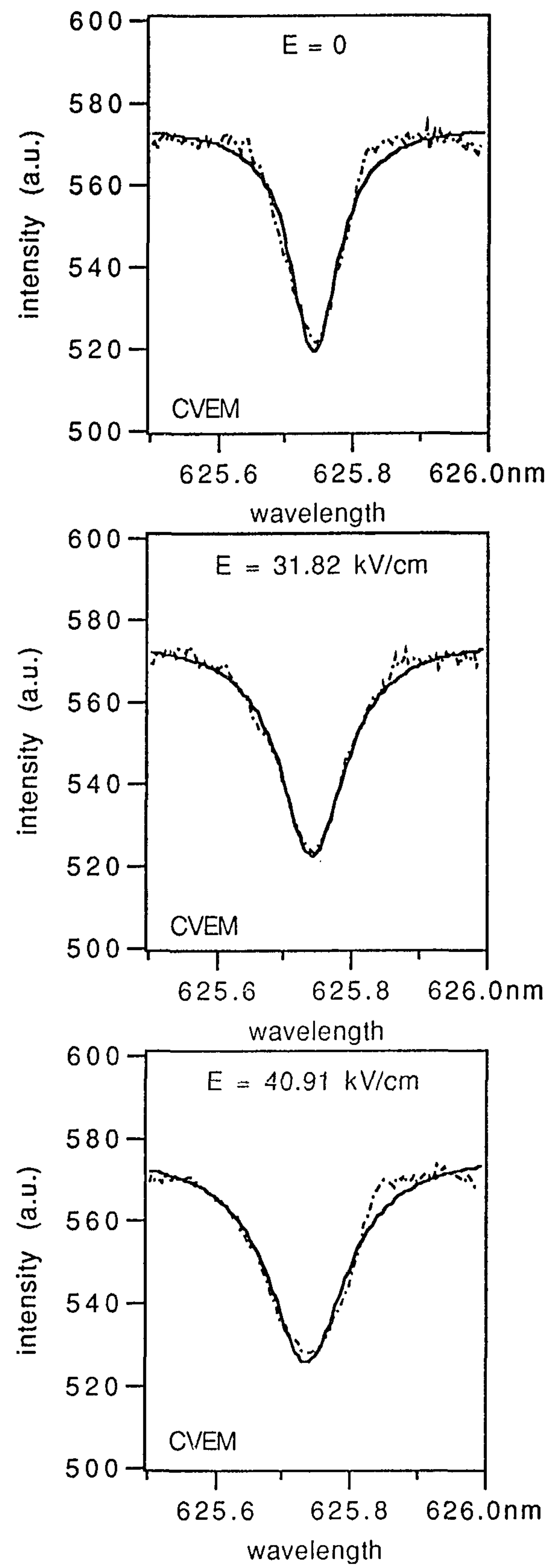


Figure 7.12. Effect of an external electric field on the spectral hole profile of CV in EM.

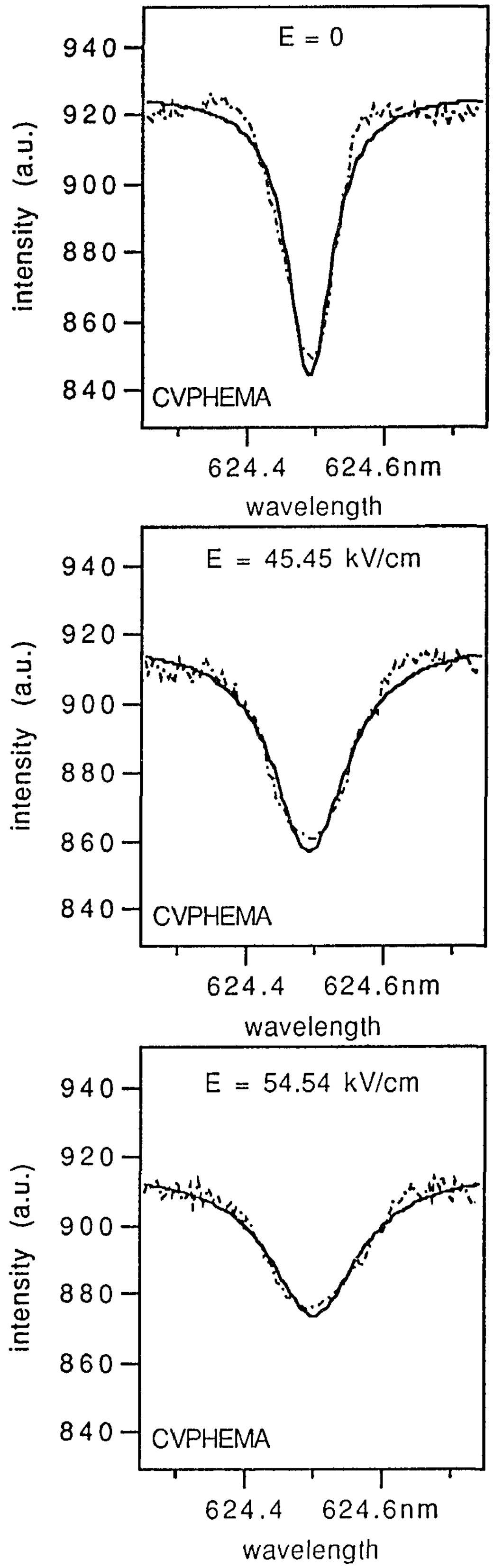


Figure 7.13. Effect of an external electric field on the spectral hole profile of CV in PHEMA.

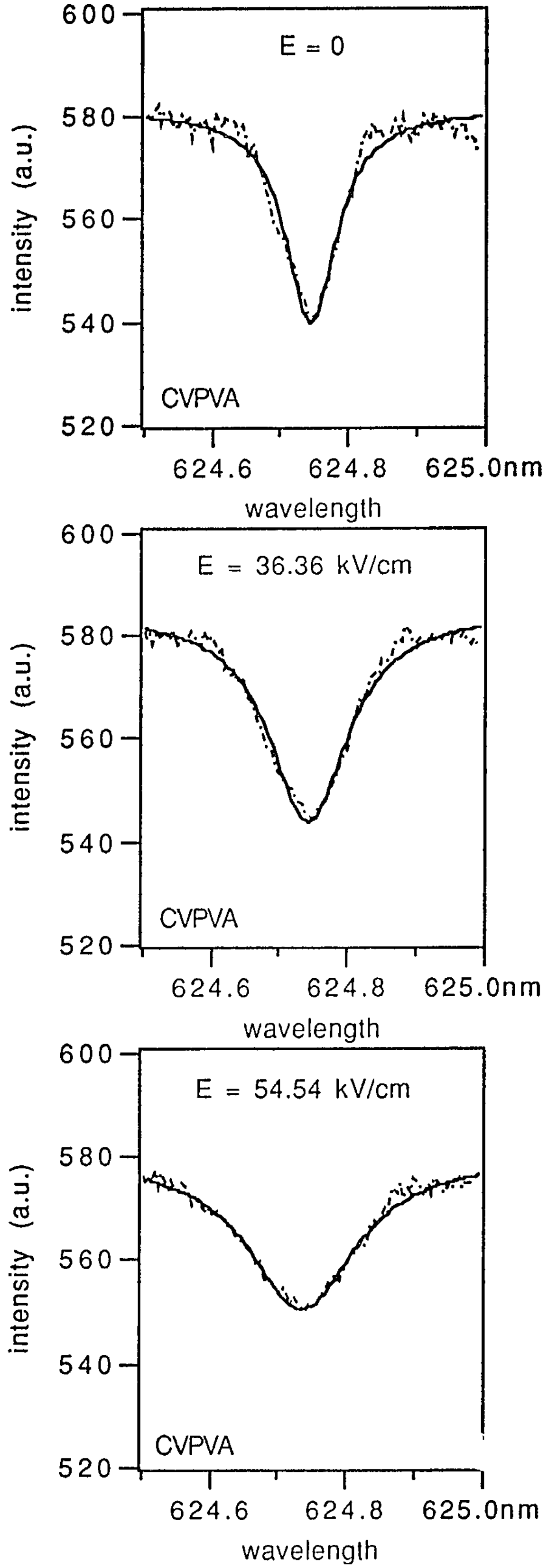


Figure 7.14. Effect of an external electric field on the spectral hole profile of CV in PVA.

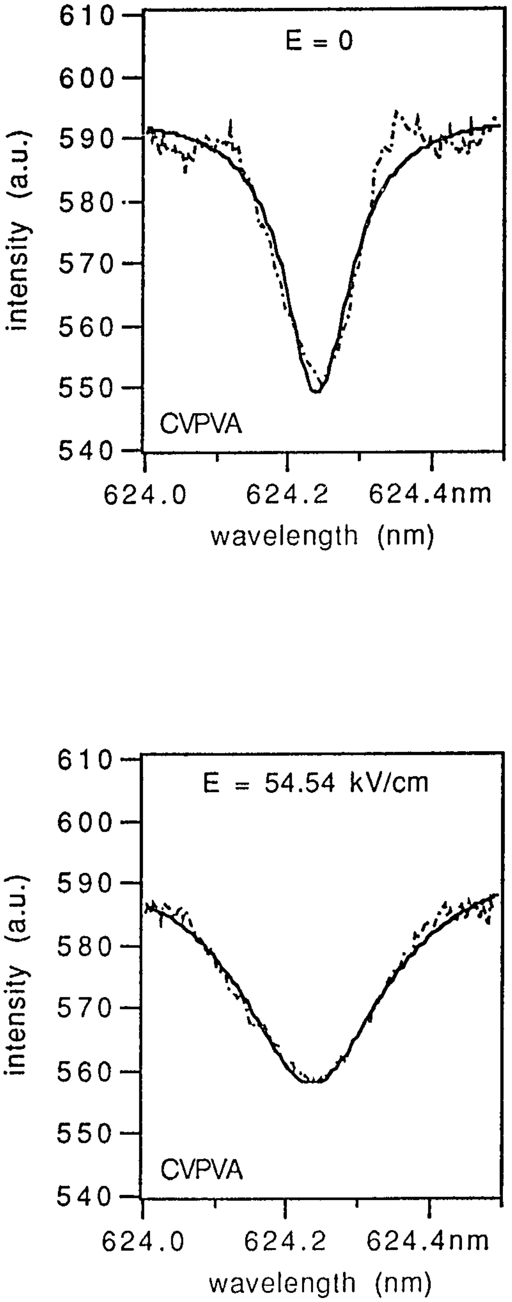


Figure 7.15. Effect of an external electric field on the spectral hole profile of CV in PVA.

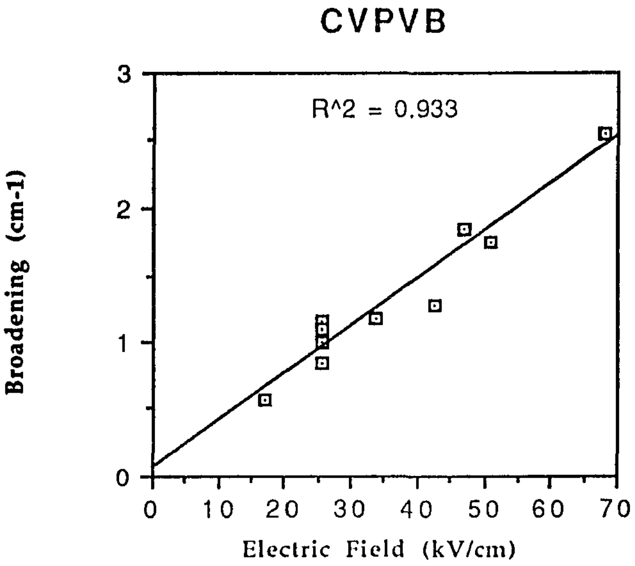


Figure 7.16. Plot of the spectral hole broadening (cm^{-1}) as a function of applied electric field (kV/cm) for CV in PVB.

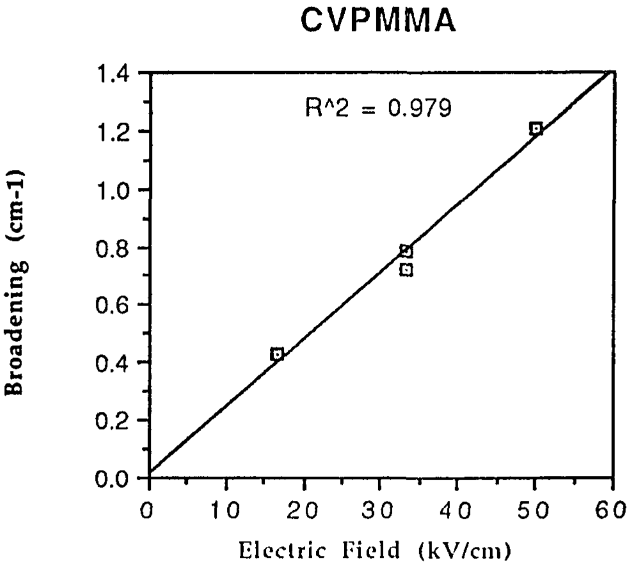


Figure 7.17. Plot of the spectral hole broadening (cm^{-1}) as a function of applied electric field (kV/cm) for CV in PMMA.

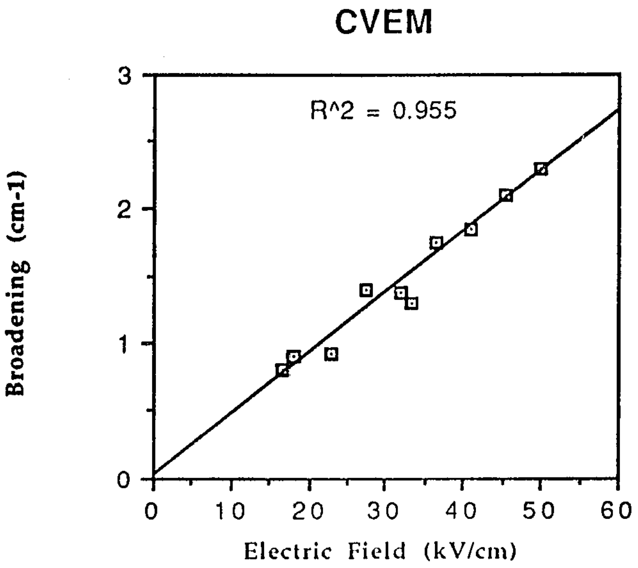


Figure 7.18. Plot of the spectral hole broadening (cm^{-1}) as a function of applied electric field (kV/cm) for CV in EM.

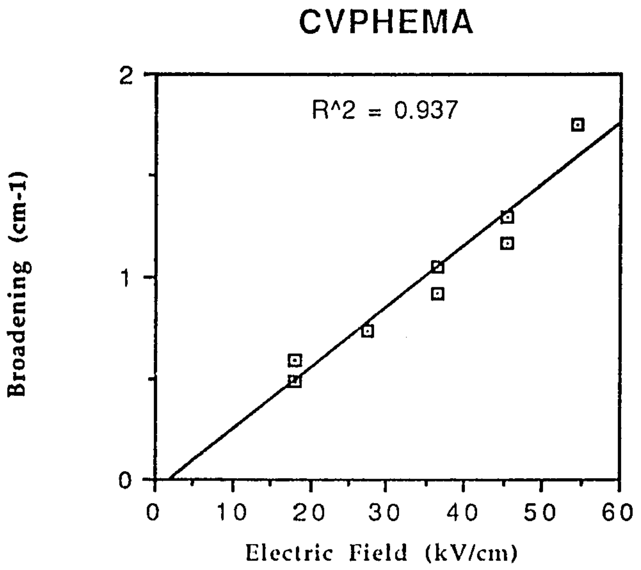


Figure 7.19. Plot of the spectral hole broadening (cm^{-1}) as a function of applied electric field (kV/cm) for CV in PHEMA.

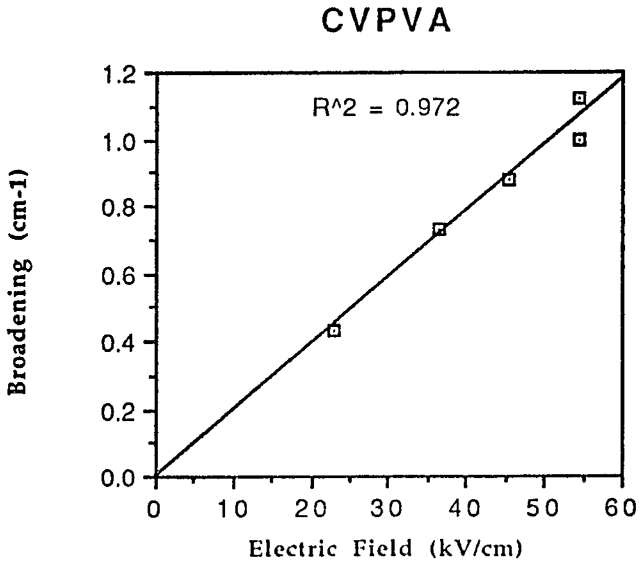


Figure 7.20. Plot of the spectral hole broadening (cm^{-1}) as a function of applied electric field (kV/cm) for CV in PVA.

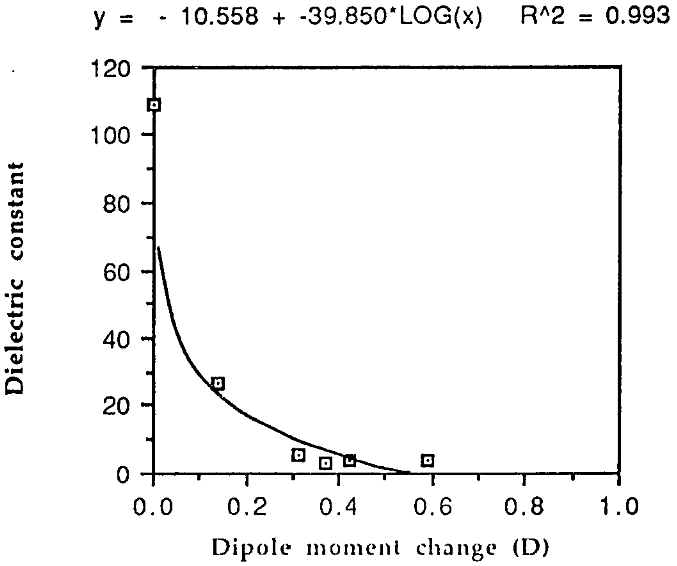


Figure 7.21. Plot of the dipole moment change in the first excited state of CV as a function of dielectric constant in several hosts.

Table 7.1. The effective dipole moment change ,$\Delta\mu_{eff}(D)$, of cresylviolet in various host matrices. ε represents the dielectric constant of the host.

Guest	Host	ε	$\Delta\mu_{eff}$ (D)
Cresylviolet	Formamide	109	0
	EM	26.6	0.14 ± 0.02
	PVA	5.2	0.31 ± 0.04
	PHEMA	4.0	0.42 ± 0.04
	PVB	3.6	0.59 ± 0.10
	PMMA	3.4	0.37 ± 0.03

The influence of externally applied electric fields on spectral holes has been investigated in a several publications[7.31-33]. Since spectral holes can be three to five orders of magnitude narrower than inhomogeneously broadened absorption bands, moderate electric field strengths are sufficient to affect the Lorentzian hole contours significantly. In amorphous hosts often a broadening and decrease of the hole contours is observed as the applied field strength is increased. With sensitive detection techniques [7.34] precise measurements of the electric field effect indicates that the hole shapes do not only depend on the applied field strength but in addition on the orientation of the electric field with respect to polarization of the light [7.35-37]. Spectral holes, in the inhomogeneously broadened S_1<--S_0 absorption band of cresylviolet perchlorate in a poly(vinylbutyral) matrix split when the electric field is applied parallel to the polarization of the light and broaden when the field is applied perpendicular to the polarization of the light [7.38]. A detailed analysis which includes the dichroism of spectral holes and the geometry of the experiment, revealed that the experimental data can be best described by assuming that the difference between the electric dipole moments in the ground and the excited state is given by effective dipole moment change $\Delta\mu_{eff}$ = 2.1D that contains a matrix-induced part, $\Delta\mu_{ind}$ = 0.9D [7.38]. $\Delta\mu_{ind}$ is fairly large and results from the polarization of the guest molecules. Molecules such as cresylviolet may be very sensitive to the guest-host interaction because of its polarizability. Also for centrosymmetric molecules like perylene, octaethylporphyrin, Zn-tetrabenzoporphin, and phthalocyanine [7.35,36,39-43] a linear Stark effect has been observed. Within the range of applied field strengths, which reached tens of kV/cm, the hole broadening was fully reversible and the original holewidths were recovered when the initial field strength was restored. In all examples the center frequencies of the holes were not affected by the applied electric field indicating that a second-order Stark effect can be neglected at these strengths.

The magnitude of the matrix-induced dipole moments being on the order of intrinsic dipole moments suggest that the distortion of the guest molecules by the surrounding host molecules is rather large. This reflects the fact that an amorphous solid is highly anisotropic on a molecular scale and that a set of dye molecules with identical transition frequencies is not uniform with respect to the strengths of interactions between the guest and the host molecules. The matrix-induced Stark effect was interpreted by Bogner et al. [7.39] as polarization of guest molecules by local electric fields built up by the surrounding host molecules [7.35,39,41,43] and by dispersion interactions [7.44]. The same mechanisms play an important role in the discussion of inhomogeneous line broadening and solvent shifts [7.45,46]. In a recent publication a variation of the matrix-induced dipole moment difference and the optical zero-phonon linewidth over the inhomogeneously broadened absorption band has been found for octaethylporphyrine in polystyrene [7.42]. As a consequence, one expects that the matrix-induced dipole moments depend on the strength of the local matrix and thus are linked to the dielectric properties of the host. It has been suggested that the matrix-induced dipole moment, $\Delta\mu_{ind}$, decreases as the dielectric constant of the host decreases [7.47]. Vauthey and coworkers have found out another interesting property of cresylviolet: effective dipole moment varies between 2.6 and 0.8 D as a function of spectral position of the hole in the absorption band [7.4].

In the previous chapter on the quinazirine molecule, we have suggested the correlation between effective dipole moment change, induced dipole moment change and the polarity of the host matrices. Accordingly, we were expecting the same dependency of the dipole moment change for cresylviolet. The effective dipole moment change of cresylviolet ranges from 0.14 to 0.59 D as we varied the host matrix with different dielectric constants. These measurements are summarized in Fig.7.20 and Table 7.1 showing the enormous effect of the polarity of the host matrix on the effective dipole moment change of the guest molecule.

The conclusion of this study warrants further investigation. The review provided thus far satisfies a fundamental inquiry only; the theoretical component necessary to explain the logarithmic correlation between effective dipole moment change of the guest molecule and the dielectric constant of the host matrix has yet to be determined.

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