HOLE-BURNING SPECTROSCOPY OF GLASSES

This two-photon spectroscopy technique yields quantitative measures of the distribution functions for local variables such as the dipole moment and the compressibility. It may also provide a means to enhance the capacity of optical memories.

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The history of man-made glass dates back to ancient Egypt, where the first glass containers were created around 1500 BC. Later, in classical Rome, glass objects of unparalleled beauty were made. Glassy materials and the artifacts and objects made from them have fascinated mankind since those early times.

Two properties of glasses underlie their fascinating properties. First, glasses are very forgiving in their chemistry, in the sense that the melting point of pure sand (or silicon dioxide), which is above 1400 °C, can be lowered to about 600–700 °C by the addition of a variety of metal oxides. Potash, which contains large amounts of the metal potassium, is an example. Glass is not an equilibrium state of matter; it is an undercooled liquid. With some additives, the undercooled liquid solidifies into a transparent and beautiful material—the glass—which when cut and polished looks like quartz crystals. The second unique feature of glass is that it acquires beautiful colors when certain metal oxides are added to the melt. For example, the color is purple with nickel oxide, blue with cobalt oxide, and blue–green or yellow with iron oxide, depending on the oxidation state of iron. In fact, cheap, inexpensive glass has a greenish tint due to iron impurities, which are present in the raw material unless it is extensively purified. As an example of the beauty of glass, we show in figure 1 a window panel created around 1485 by Wohlgemuth, who was a teacher of Albrecht Dürer.

Glasses are homogeneous on the length scale of the wavelength of light (a fraction of a micron). They therefore do not scatter light and are transparent at optical frequencies if, of course, there is no absorption at those frequencies. On a finer scale—that is, on the atomic or molecular scale of several tens of nanometers—however, glasses are very inhomogeneous. For example, unlike in a crystalline solid, in which each atom or molecule has a fixed number of nearest neighbors at a fixed distance that is the same for all nearest-neighbor pairs, in a glass we know only the statistical distribution of the nearest-neighbor distances.[1] Given an atom or molecule in glass, therefore, the positions of its nearest neighbors are known only probabilistically. As we will discuss, this randomness, which is inherent to the glassy structure, poses formidable obstacles in our attempts to understand the properties of glasses.

High-resolution optical spectroscopy has long played an important role in the study of solid non-opaque materials.[2] High-resolution optical spectra have been used to investigate the energy levels, intermolecular interactions and energy transport in those materials as a function of temperature, impurity concentration, pressure

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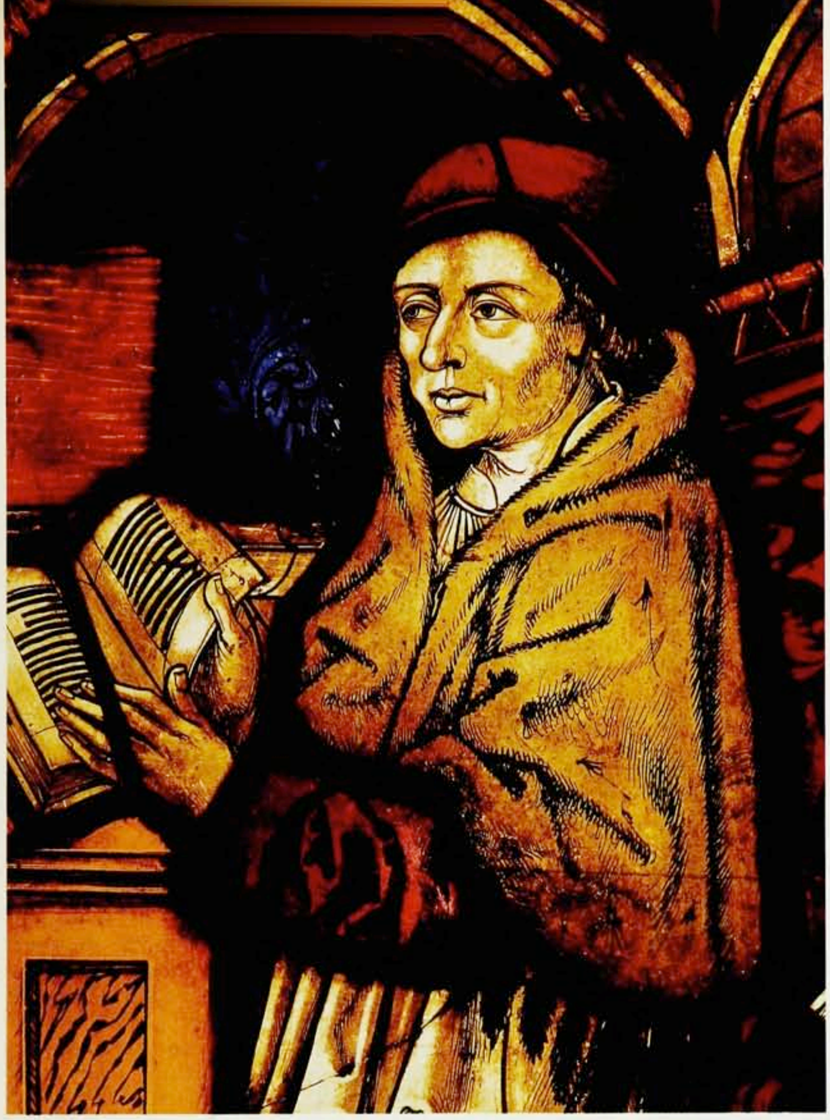


Stained-glass window panel, created by Wohlgemuth in the 1480s, illustrates the beauty of glassy materials. (Courtesy of Gottfried Frenzel.) **Figure 1**

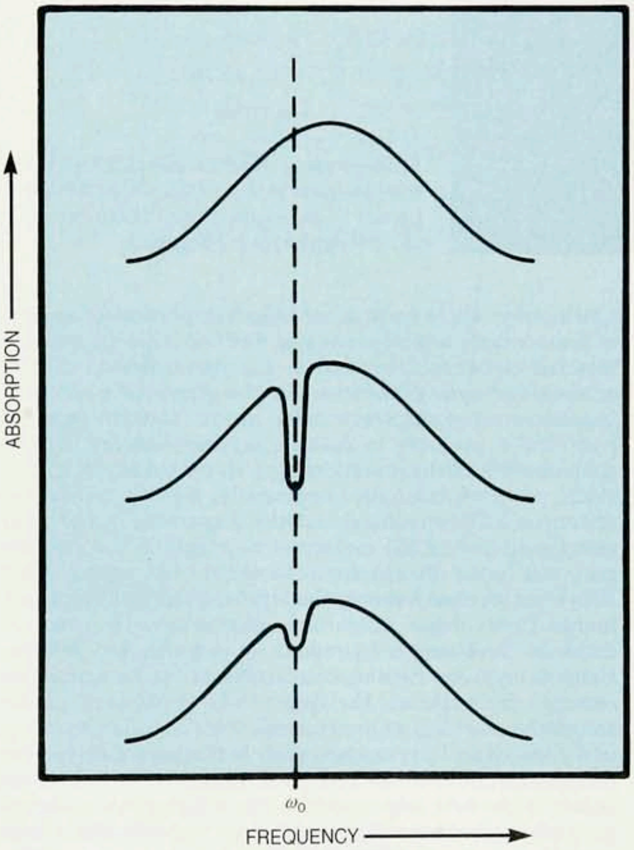
and external fields. In the case of crystalline solids, the underlying translational symmetry allows a simplification in the theoretical description and provides the key to unraveling the spectra. Furthermore, because each site in the crystal is to a high degree of approximation equivalent to some other site, there is only a little "inhomogeneous" broadening of the spectral features. The optical spectroscopy of molecules and ions in glasses is, by contrast, quite different. Glasses have no long-range order and only poorly understood short-range order. Each site in the glass, and therefore the energy spectrum of the molecule or ion occupying that site, is unique. This lack of uniformity, or homogeneity, broadens the lines in the optical spectra of glasses: The lines are said to be inhomogeneously broadened. Furthermore, because the glass is an undercooled liquid, the optical properties are affected by a variety of processes that occur on a wide distribution of time scales.

In this article we will discuss recent and ongoing experiments in the optical spectroscopy of glasses. We will focus on methods used to unravel the site distribution of the energy, the dipole moment and the homogeneous line shape. The methods involve a special kind of two-photon spectroscopy, called the hole-burning spectroscopy. The first photon selects a group of molecules or ions in the glass that absorb a particular wavelength, and the next photon probes the properties of that group. The tandem two-photon nature of the experiment can be exploited in a special way: Once one has used the first photon for energy or wavelength selection, one is dealing with an energy-selected subensemble, called the isochromat, of the ensemble of optical absorbers in the glass. One can now use external parameters such as an electric field or hydrostatic pressure to make a further selection in the subensemble of the given energy. If, for example, hydrostatic pressure is applied externally, all intermolecular distances will be reduced and the dispersion in the local compressibility of the molecules or atoms in the isochromat will cause its spectrum to spread out again. This simple experiment shows clearly that the local environments in a glass, which are determined by sums of distance- and angle-dependent intermolecular interactions, cannot be uniquely characterized by the excitation energy. By contrast, the degree of "spreading" of the selected subset is a unique measure of the inhomogeneity in a glass of local parameters such as compressibility. This double selection, whose technical details we will describe below, is the first step toward a two-dimensional spectroscopy of glasses that allows an energy variable and a local variable to be interrogated separately by successive photons. The double selection also allows us to probe distribution functions in glassy environments.

Photochemical hole burning

The term "hole burning" was coined by N. Bloembergen, E. M. Purcell and R. V. Pound in the early days of magnetic resonance spectroscopy.[3] In the initial hole-burning experiment, one of the many inequivalent spin packets of the inhomogeneous absorption band was saturated selectively. The two levels of each of these spins being thus equally populated, the total nmr absorption band showed a *hole* corresponding to the lack of net absorption by the selected spin packet. The width of the hole was on the order of the homogeneous linewidth (see figure 2). The experiment therefore showed, for the first time, that the spectroscopic resolution could be increased by local saturation beyond the limit set by the inhomogeneous linewidth.

Clearly, the saturation hole in the absorption spectrum will exist as long as the saturating rf power is on. This, however, poses an experimental difficulty. As long as the high-power saturating radio source at the hole frequency ω_0 is on, an absorption experiment in the neighborhood of ω_0 is impossible, since any sensitive detector would be destroyed by the high rf power. Therefore one has to switch off the saturation source (photon 1) and use a second, variable source of lower intensity (photon 2) to investigate the saturation hole. During this gating process the hole decays with a time constant T_1, the spin–lattice relaxation time, which can be quite long, on the order of seconds. This decay brings the spins back to thermal equilibrium.



Nmr line shape shows the hole that forms when water is irradiated by an rf source at frequency ω_0 (middle) and the gradual disappearance of the hole (bottom) after the rf source is turned off. (Adapted from ref. 2.) **Figure 2**

An optical analog of the nmr hole-burning experiment is difficult, since in optical transitions T_1 corresponds to the lifetime of molecular states, which is on the order of 10^{-8} seconds. To observe the hole, therefore, the absorption experiment must be performed within this time interval after the saturating source is switched of. This makes more complicated gating techniques necessary. A. Szabo performed the first optical hole-burning experiment.[4] He used the R_1 band of ruby, which has a moderately long lifetime (on the order of a millisecond). But the real breakthrough in extending hole-burning spectroscopy to optical frequencies was made by two Soviet groups. The groups, which were led by R. Personov[5] and L. Rebane,[6] discovered that if atoms or ions with an energy level intermediate between the levels probed by optical absorption were doped into the material, the hole spectrum might have a very long, and even infinite, lifetime if the lifetime for the deacy of the intermediate state into the ground state was very large. This so-called photochemical hole burning is shown schematically in figure 3. Unlike the nmr hole-burning experiment, which involves only two levels, the photochemical hole-burning experiment involves at least three levels. Furthermore, in the optical spectrum the hole is a permanent feature of the spectrum—or at least it persists for as long as the third level does not decay back to the original level and any other processes do not broaden the hole.

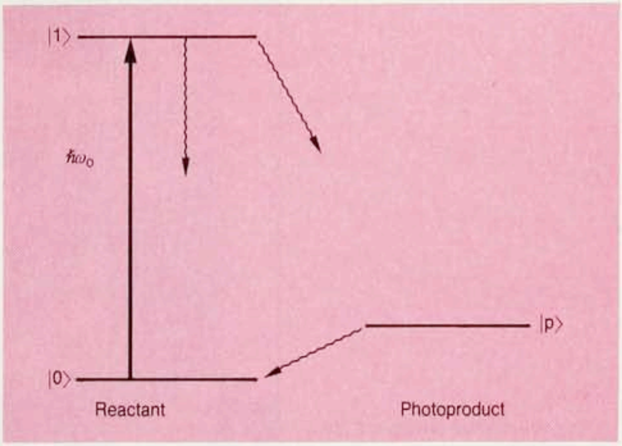
Since it was introduced in 1974, many researchers have used the photochemical hole-burning scheme (PHB) to obtain a gain in resolution in optical absorption experiments at low temperatures. The gain is given by the multiplexing factor

$$\gamma = \frac{\Gamma_{\text{inh}}}{\Gamma_{\text{hole}}} \tag{1}$$

where Γ_{inh} is the width of the inhomogeneous band and Γ_{hole} is the hole width. The hole width depends on temperature and may be narrower than 10^{-3} cm^{-1} at low temperatures. The inhomogeneous width, on the other hand, has a negligible temperature dependence. It is typically on the order of 10^2 cm^{-1}. Thus the total optical resolution R of a typical hole-burning experiment, defined as

$$R = \frac{\bar{\nu}}{\Gamma_{\text{hole}}} \tag{2}$$

where $\bar{\nu}$ is the photon energy in wavenumbers, can be on the order of 10^7–10^8. Once we had this powerful technique in hand, it was natural to apply it in a field where the gain in resolution was much needed, namely, the spectroscopy of glasses of all kinds, including polymers, which often solidify in glassy form.



Three-level system with reactant levels |0⟩ and |1⟩ and dopant level level |p⟩. If the excited state |1⟩ decays into the dopant, or photoproduced, state |p⟩ and the lifetime of the photoproduced state's decay into the state |0⟩ is large, such a system may be used to obtain a hole-burned spectrum at the frequency ω_0. **Figure 3**

Figure 4 shows a photochemical hole-burning spectrum of the dye phthalocyanine in a polystyrene host at 4 K. The narrow hole is on the order of 10^{-2} cm^{-1} wide. Figure 5 shows a typical experimental setup. In the foreground one sees the laser beam with mirrors and etalons to measure the exact wavelength. The tall vessel at left in the background is a superfluid helium cryostat. The sample, typically having dimensions of 5 mm × 5 mm × 1 mm, is immersed in the cryostat. Varying the gas pressure above the helium level allows one to apply hydrostatic pressure to the sample; the pressure can range from millibars to several atmospheres.

In the following we shall describe only a few of the directions that have proven fruitful in the use of hole-burning spectroscopy. Interested readers may find it useful to consult a book W. E. Moerner has edited,[7] a special issue of *Journal of Luminescence*,[8] or the review articles by J. Friedrich and Haarer[9] or by Volker.[10] We will focus mainly on organic glasses; in inorganic glasses, the favored experimental techniques for resolution enhancement are fluorescence line narrowing[11] and use of optical echoes.[12] A mixture of ethanol and methanol in the ratio 3:1 at low temperatures is an example of an organic glass. Some of the first extensive discussions of the mechanisms of photophysical[13] and photochemical[14] hole burning and of the line broadening in these systems appeared in 1978.

Hole linewidth

A number of powerful experimental techniques, including hole burning, have been used to uncover the homogeneous line shape of an inhomogeneously broadened optical transition of a molecule in a glassy host. Surprisingly, the homogeneous linewidth, as well as its temperature dependence, is qualitatively different in a glassy host from that in crystalline hosts. The difference can be understood in terms of the structural and dynamical properties of the glassy state.

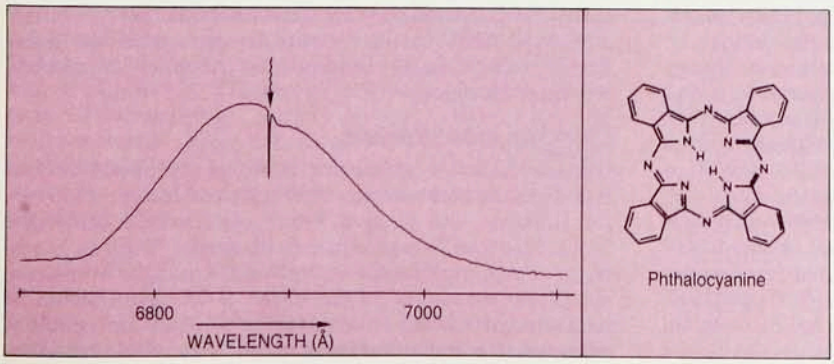
The homogeneous linewidth Γ of an optical transition is usually written as

$$\Gamma = (2\pi T_1)^{-1} + (\pi T_2)^{-1} \qquad (3)$$

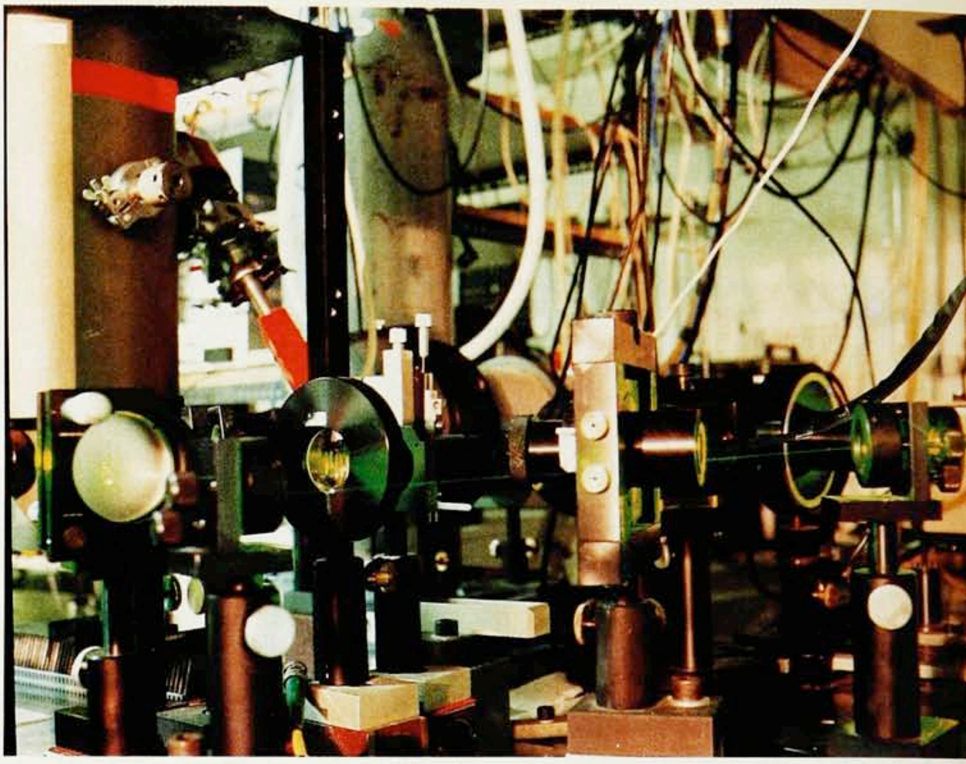
where T_1 is the population decay, or longitudinal, relaxation time and T_2 is the pure dephasing time. (See chapter 3 in the book by Moerner.[7]) The dephasing time is determined by fluctuations in the frequency of the optical line and depends on temperature (see below for further discussion). But the population decay time is usually temperature independent, so that the temperature dependence of the optical line is contained in the dephasing term alone.

At low temperatures in a crystalline host, an optical transition will be broadened by the lattice vibrations: The thermal motion of a molecule and its neighbors will cause the interaction energy between molecules to fluctuate. This implies that the energy difference between the two states involved in the optical transition will also fluctuate. These fluctuations cause a dephasing that broadens the optical line. The temperature dependence of Γ (which is entirely given by that of T_2^{-1}) due to a typical two-phonon Raman-scattering process is T^n, with the exponent n equal to 7 at low temperature and to 2 at higher temperatures. The large value of the exponent at low temperatures is due largely to the frequency dependence of the phonon density of states, which varies as the second power of the frequency at temperatures well below the Debye temperature.

In a glassy host, by contrast, the width of the *same* optical transition varies at low temperatures—in the range of 0.3 K to about 10 K in some cases—as T^α, with α between 1 and 2. The explanation for this striking change in the value of the exponent must lie in the amorphous nature of the host. A number of theoretical treatments have been developed to explain these observations.[7,8] Almost all of these treatments start from the idea, first pointed out by G. J. Small,[7,13] that the dephasing in glasses is due, at least in part, to the interaction between the "probe" molecule and the low-frequency two-level tunneling modes (usually referred to as TLS, or two-level systems) in the glass. The tunneling modes were originally suggested by P. W. Anderson, B. I. Halperin and C. M. Varma and by



Hole spectrum of phthalocyanine in polystyrene host at 4 K. The wavy arrow marks the pseudophonon wing. The structure of phthalocyanine is shown in the inset. **Figure 4**



Experimental setup used in photochemical hole-burning experiments at superfluid helium temperatures. In the foreground one sees the laser beam and the mirrors and etalons used for wavelength measurements. The sample, typically of dimensions 5 mm × 5 mm × 1 mm, is immersed in the cryostat, the tall vessel in the background at left. **Figure 5**

W. A. Phillips in their explanations of the anomalous specific heat and thermal conductivity of glasses.[15] For example, the specific heat of glasses varies as T^{γ} below 1 K, with γ between 1 and 1.3. This behavior of the specific heat is explained by assuming that the density of states of the TLS, $\rho_{\text{TLS}}(\omega)$, where ω is the energy splitting between the two levels of the TLS, varies as ω^{ϵ} near $\omega = 0$, with ϵ between 0 and 0.3. A physical picture explaining the origin or source of the TLS has yet to be agreed on. But these tunneling modes continue to be a theoretical construct that allows us to describe the results of a number of low-temperature experiments.

The basic model for the dephasing of optical transitions in glasses says that the optical center interacts with many TLS. The optical transition frequency depends on the quantum states of the various TLS. The interaction of the phonons with the TLS causes the latter to "flip" and thus makes the optical transition frequency fluctuate, leading to dephasing. The predicted temperature dependence of the dephasing is a function of the forms assumed for the phonon–TLS interaction (for example, whether the interaction is linear or quadratic in phonon coordinate) and for the the TLS–probe molecule interaction (whether or not it is a dipole–dipole interaction.) The temperature dependence is a function also of the distribution of TLS energies (or splittings). Since very little is known about the TLS distributions and interactions, a variety of theoretical models can be made to fit experiment by an appropriate choice of the details in the interactions and distributions.[8] But almost all of the models assume that the density of the TLS states that interact with the optical center varies as ω^{ϵ} for small ω, with $\epsilon = 0$–0.3, just as in the model developed to explain the specific heat. R. Jankowiak and Small, however, using Gaussian distribution functions for the TLS parameters, have shown how ϵ can be determined by a combination of the dephasing, specific heat and thermal conductivity data.[16] Recently C. Yu and A. Leggett have proposed that the TLS are so strongly interacting that a multilevel picture should be considered.[17] This interesting and potentially important idea has not yet been worked through in detail.

The assumptions usually employed in the study of TLS models lead to the prediction that the flip rates (or relaxation rates) of the TLS vary strongly with temperature and the energy splitting and that there is a very broad distribution of rates. Therefore some of the TLS flip very quickly compared with the optical time scale (the inverse optical linewidth), while others flip very slowly on this time scale, contributing to spectral diffusion processes. Experimental evidence for slow spectral diffusion comes from thermal cycling measurements and photon echo measurements. In a thermal cycling experiment,[18] a hole is burned at temperature T_0; the sample is then warmed to a temperature $T_0 + \Delta T$ for a few minutes and finally returned to the initial temperature T_0. Since the frequency excursions in the line position due to spectral diffusion increase with temperature as $T^{1+\epsilon}$, the linewidth will be larger at the higher temperature. When the sample is returned to T_0, some of the TLS will be "caught" outside the frequency excursion allowed at T_0. As a result the hole will have broadened slightly from its original width. It is found experimentally that the excess broadening is approximately linear in ΔT, suggesting that spectral diffusion processes are responsible. Photon echo measurements with variable delay time between the two pulses also show that the decay rate changes with the delay time,[19] which again implies the existence of spectral diffusion processes.

External parameters

One of the most attractive features of photochemical hole-burning spectroscopy is its high resolution. It allows, for example, the study of small electric-field shifts (the Stark effect) and small strain-field effects. The first Stark-effect experiments showed that small changes in molecular dipole moments, on the order of 0.1 debye, could be measured in glassy environments.[20] More importantly, however, the experiments showed that even molecules with an inversion center show changes in the dipole moment and thus are characterized by a *linear* Stark effect. This phenomenon is again a typical feature of glass-like configuration. The intrinsic lack of inversion symmetry of the *local* configuration produces a large local field, which in turn induces a dipole moment in molecules that may have inversion symmetry in the gas phase or even in crystalline hosts. Figure 6 shows a Stark spectrum for Zn-TBP, a zinc porphyrin whose molecular structure has a four-fold symmetry axis, in a polyvinylbutyral host.[20] The spectrum yields an average induced dipole moment on the order of 0.2 debye. In a simple minded electrostatic theory, such a value of the dipole moment would require[21] local electric fields on the order of 10^7 V/cm. Clearly the simpleminded theory must break down and the interactions and local electric fields that arise from the disordered environment in the host must be treated with a more elaborate model.

The effects due to external strain fields, although equally small and subtle, are more obvious and easier to interpret. The method of hole burning is so sensitive that a pressure change of only 1 atmosphere (about 0.1 megapascal) is sufficient to shift and broaden a photochemical hole considerably. Figure 7 shows the shifts of a photochemical hole-burning line of phthalocyanine in a polyethylene host.[22] The top panel shows the shifts obtained when the hydrostatic pressure is applied after hole burning; the bottom panel shows the spectrum obtained when the pressure is *released* after hole burning. The two panels illustrate the nature of the tandem two-photon experiment: The labeling photon is applied before the pressure is varied, and the new hole profile is measured by a second photon. The experiment's two-photon nature makes it possible to measure hydrostatic *expansion* as easily as hydrostatic compression.

It came as somewhat of a surprise to us that we could determine the bulk compressibility κ without adjustable parameters simply by assuming a Lennard–Jones potential for the interaction between the dye molecules and the host. The determination needs two experimental quantities, namely, the pressure shift $\Delta\bar{\nu}(p)$ and the solvent shift $\Delta\bar{\nu}_s$, which is the shift from the gas phase value due to interactions with the surroundings at zero pressure. The connection between the pressure shift and the compressibility may be written as[22]

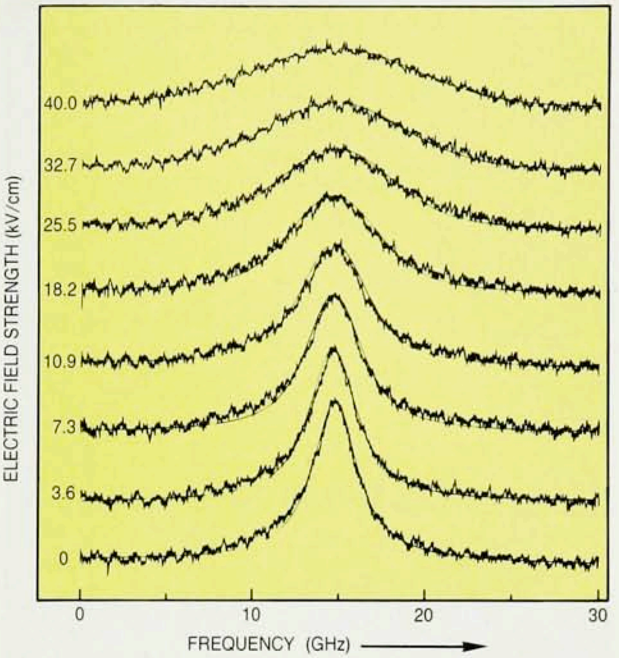
$$\Delta\bar{\nu}(p) = \Delta\bar{\nu}_s + 2\Delta\bar{\nu}_s\,\kappa\Delta p \qquad (4)$$

It is remarkable that the *local* compressibility values obtained optically from the shifts in hole-burned lines agree, within about 15%, with those obtained from a mechanical measurement.[22]

A beautiful theory of the pressure-induced shifts and the broadening of hole-burned lines in an inhomogeneously broadened spectrum has been worked out by B. Laird and J. Skinner.[23] The theory has been extended to the case of an external electric field by Kador and his collaborators.[24] If the inhomogeneous broadening is due to the variation in the intermolecular interactions at the various sites in the glass, then the hole line shape can be written as

$$I(\omega) = V^{-N}\int \mathrm{d}\mathbf{R}^N \delta(\omega - \omega_0 - \sum_i^N \omega(\mathbf{R}_i))\,\mathscr{P}(\mathbf{R}^N) \qquad (5)$$

where $\mathscr{P}(\mathbf{R}^N)$ is the probability distribution for the positions of the N host molecules in the glass volume V and $\omega(\mathbf{R}_i)$ is the shift of the spectral line from ω_0 due to the interaction of the optical center with the host molecule at $\mathbf{R}_i$. If we assume that $\mathscr{P}(\mathbf{R}^N)$ factors into a product of N two-particle solute–solvent distribution functions, $\mathscr{G}(\mathbf{R})$, then we can write $I(\omega)$ as[23]



Width of the hole-burned line of the porphyrin Zn–TBP in a polyvinylbutyral host increases as the applied electric field increases. **Figure 6**

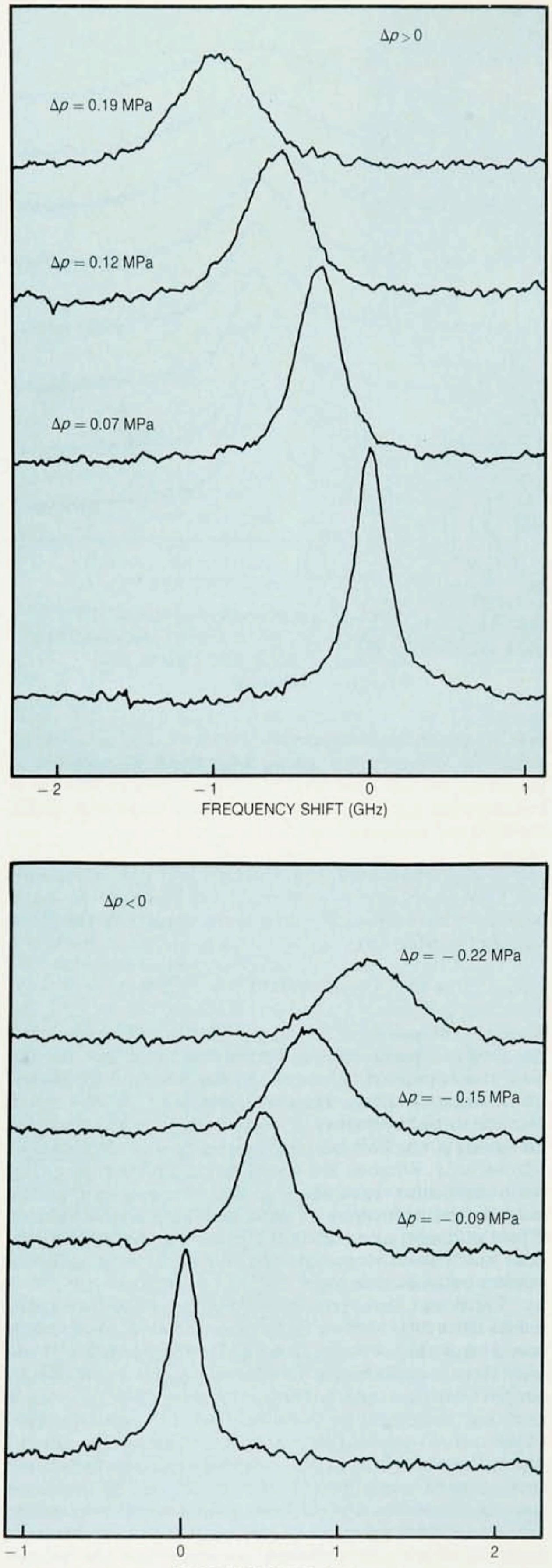
$$I(\omega) = (2\pi)^{-1}\int_{-\infty}^{\infty} \mathrm{d}x\, \mathrm{e}^{\mathrm{i}\omega x - \rho J(x)} \qquad (6)$$

where we have taken $N \to \infty$, ρ is the density in the glass, and $J(x)$ is given by

$$J(x) = \int \mathrm{d}\mathbf{R}\,\mathscr{G}(\mathbf{R})(1 - \mathrm{e}^{-i\omega(\mathbf{R})x}) \qquad (7)$$

If we are interested in the change in the hole shape when an external parameter is varied, we must ask for the conditional probability $f(\omega, \omega', X)$ that the final frequency, after variation of the external parameter X, is ω' given that the initial frequency, which may have been chosen by, for example, the hole-burning process was ω. Or we might like to ask: What is the distribution function $p(\omega,\mu)$ of some molecular parameter μ that is contained in the intermolecular interaction potential, such as the induced dipole moment, as a function of ω across the inhomogeneous line? The theory outlined above can be modified to answer both of these questions.

Laird and Skinner showed that the pressure experiments described above can be understood by assuming a specific but simple form for $\partial\omega(\mathbf{R})/\partial p$, the variation in the local frequency shift as a function of pressure, and using a simple Gaussian approximation for the integrals. Kador and his collaborators showed that the electric field experiments—specifically, the distribution of the induced dipole moments across the inhomogeneously broadened line—can be explained by the model, using the same parameters to describe the intermolecular interactions as Laird and Skinner used. In principle, if the experiments could be done with sufficient accuracy and the solute–solvent distribution function $\mathscr{G}(\mathbf{R})$ were known, then $\omega(\mathbf{R})$,



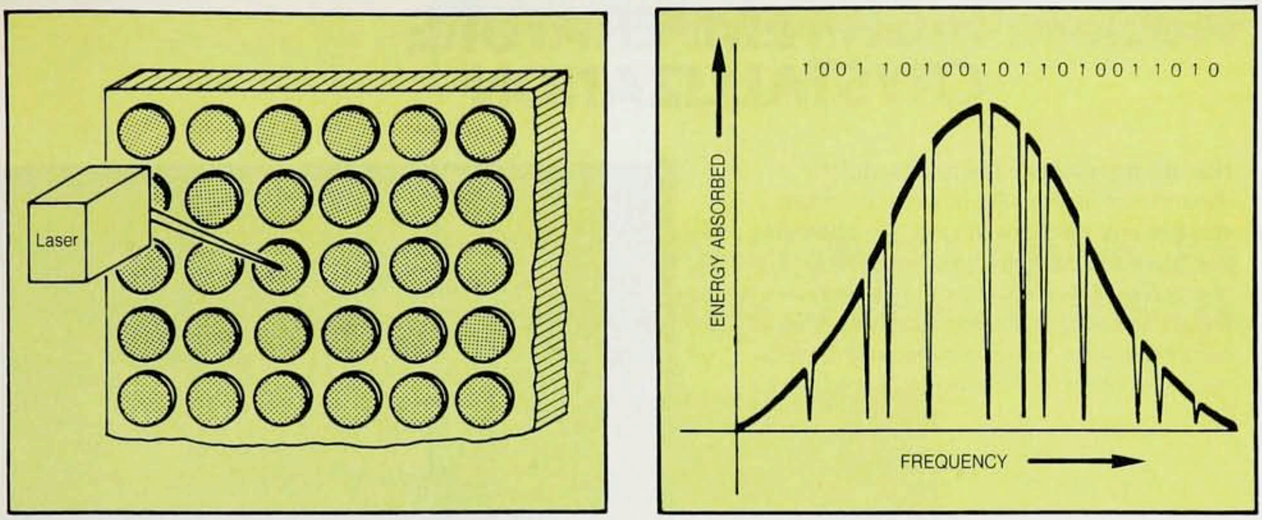
Hole-burned line of phthalocyanine in polyethylene becomes broader and shifts to smaller frequencies when pressure is applied after hole burning (top). When pressure applied *before* hole burning is released afterward, the shift is to higher frequencies (bottom). **Figure 7**

as well as another function $\zeta(\mathbf{R})$, which determines the change in some molecular parameter μ due to the presence of the solvent molecule at $\mathbf{R}$, could be determined from the experimental data. Thus experiments of the type described above, in which one first selects an energy subensemble (optical labeling) and then makes a second selection using an external field, can examine the microscopic interactions between the molecules in the glass, using as probes simple solute molecules. When enough accurate experimental data of this kind become available, it might become possible to determine intermolecular potentials in glassy environments.

Applications

The high resolution photochemical hole-burning allows may be exploited to increase the capacity of an optical storage device by the multiplexing factor γ defined by equation (1). The storage density of present-day optical memories can thus be increased from 10^8 bits/cm^2 to $\gamma \times 10^8$ bits/cm^2. At low temperatures, therefore, the density can be increased[25] to 10^{11} to 10^{12} bits/cm^2. A storage scheme that uses photochemical hole burning is shown in figure 8. In this scheme, a pattern in the frequency domain, obtained by hole burning, is superimposed on each optical storage device in the spatial domain (x–y if the device array is planar).[26]

This novel optical storage scheme offers, as already pointed out, an improvement of many orders of magnitude in the storage density, which is an important critical parameter of storage devices. But the new technique would force us to use the memory device at cryogenic temperatures, becuase spectral diffusion processes will become important at higher temperatures and lead to the broadening and even erasures of the holes. Moerner in his review has extensively discussed some of the technical aspects of the new devices, as well as some new photochemical schemes for enhancing the storage density of optical memories.[7] These schemes may find application in workable memory systems someday. What is even more important, however, is the possibility of storing and retrieving information at the molecular level in a glassy material. Each molecule embedded in a glass has its own specific environment. Let us assume that we have on the order of 10^8 "guest" molecules in a volume of 1 micron diameter, that we can select these molecules on an energy scale of 10^{-2} cm^{-1}, and that we have an inhomogeneous linewidth of 100 cm^{-1}, all of which are easily accomplished. We could then subdivide and label the molecules in packets of approximately 1000–10 000 each. This is the best we can do with the present schemes of photodetection



Bit pattern in the frequency domain, obtained by photochemical hole burning, may allow, depending on the resolution of the hole-burned lines, up to several thousand bits to be stored and retrieved from each element of an optical storage device. This scheme can enhance the storage density of the device by the multiplexing factor γ, defined in equation 1. **Figure 8**

without destroying the molecules photochemically. These considerations show that the implementation of storage devices using photochemical hole burning rests on efficient reading and writing of information at the molecular level. They also show that the sophistication we have achieved in the use of hole burning is quite low compared with that of the molecular-recognition schemes used by large biological molecules where, for example, a substrate molecule recognizes a *unique* site on an enzyme.

Hole-burning spectroscopies have also been used to study excited-state electronic structure and—what is even more important—energy and electron transfer in the protein–pigment complex that is the site of photosynthesis. The 1988 Nobel Prize in Chemistry was awarded for the elucidation of the structure of the photosynthesis reaction center in the purple bacterium *Rhodopseudomonas viridis* (see PHYSICS TODAY, February 1989, page 17). But spectral-hole burning was used to unravel the structure of the primary electron donor in the reaction center.[27]

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