

Ground state tunneling and optical spectral diffusion in organic glasses

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Glasses are characterized by low frequency tunneling modes, the so-called two level systems (TLS), which determine the thermal and dielectric properties of amorphous solids at low temperatures. For a review see Ref. 1. In the last few years, it has been well established by several experiments that the TLS do not only determine the thermal and dielectric properties but also the optical properties of impurity molecules, such as their optical linewidth, the time scale of their dephasing in the excited state,²⁻⁷ and their photoreactivity at low temperatures (photophysical hole burning).⁸ In general, there is a change in the optical energy of an impurity molecule whenever a tunneling transition occurs within the TLS system interacting with the molecular energy levels. This is due to the fact that the interaction between a given TLS and an optical center is different in the two possible TLS states. The difference in optical energies is not directly observable since the tunneling dynamics do not change the overall site distribution function, i.e., the relative number of molecules absorbing in a certain frequency interval of the inhomogeneous band. This distribution function can be viewed as stationary in the sense that the same number of molecules diffuse into and out of a certain frequency packet. However, if the initial distribution is perturbed, e.g., by optical hole burning, a population gradient in the frequency domain is created, and the system is no longer stationary, but tends to restore the original distribution by tunneling processes thereby smearing out the photochemically produced

sharp spectral hole. We have shown in a recent paper that there are irreversible contributions to the linewidth when a photochemical hole is subjected to a closed temperature cycle.⁹ The driving force of these irreversible contributions was assumed to originate from the perturbation of the site distribution function due to the hole burning process.¹⁰ In this communication, we want to demonstrate that spectral diffusion due to ground state tunneling provides, indeed, an important contribution to the optical width, even at very low burning temperatures, and that the driving force for the diffusion processes is related to the magnitude of the population gradient established by the photochemical hole. To this end, we burned a photochemical hole in a solution of 1,4-dihydroxyanthraquinone in perdeuterated alcoholic glass (Fig. 1) (EtOD/MeOD 3:1) using a N₂ pumped dye laser with a width of 0.02 cm⁻¹ and observed its recovery dynamics. The temperature during the whole experiment was kept at 1.3 K and the observation time was about 9 h. (Experimental limit under pumped He conditions.) The hole burning time was about 6 min. The recovery dynamics is governed by two different processes: (1) The back reaction from the product state to the reactant and (2) the redistribution of the ensemble of molecules, within the inhomogeneous band, which were not affected by the laser photochemistry. While the first process definitely fills up the burned hole and thus affects the area of the hole, the second redistribution process just changes its shape. In order to distinguish between both

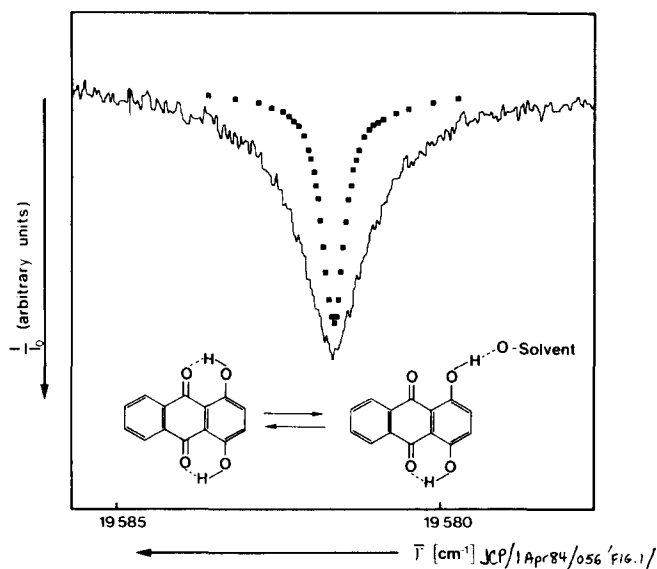


FIG. 1. A narrow and a power broadened photochemical hole of the same depth. The insert shows schematically the proposed photochemical reaction scheme.

Narrow hole: Laser power 5 kW/cm², burning time: 6 min.

Broad hole: Laser power 20 kW/cm², burning time: 6 min.

Resolution: 0.15 cm⁻¹, temperature: 1.35 K.

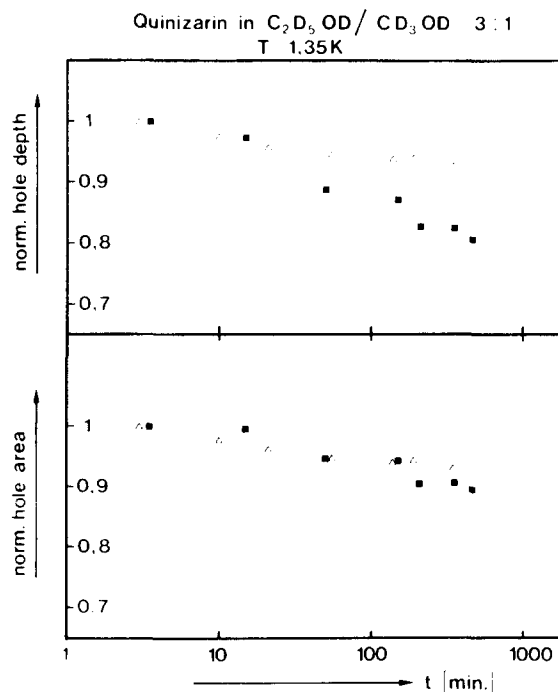


FIG. 2. The recovery data for both the hole depth and hole area.

processes, we burned two holes of approximately equal depth, but one was artificially broadened by using high laser power (see Fig. 1). As far as the integrated hole area is concerned, the recovery dynamics is the same for both holes, as can be seen from Fig. 2. Obviously, the photochemical back reaction rate does not depend on the shape of the hole. However, the situation is quite different for the parameter of the hole depth. The latter depends on both the rate of the back reaction and the redistribution processes. As is clearly seen, the depth of the sharp hole decreases much faster than that of the broad hole, indicating that spectral diffusion via ground state tunneling is much more pronounced in the case of the sharp hole as compared to the broad hole. This confirms one of the basic assumptions of our recent model,¹⁰ which was developed for describing spectral diffusion processes due to temperature variations. Since this model does not include the dynamical aspects of the spectral diffusion, it cannot be applied to fit the time dependent data as shown in Fig. 2. For a quantitative comparison, a major extension of the theory of Ref. 10 would be necessary.

In summary we report first data on spectral diffusion due to ground state tunneling. The experiments show that the driving force of the spectral diffusion is the frequency gradient produced by the narrow band laser photochemistry.

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¹*Amorphous Solids*, edited by W. A. Philips (Springer, Berlin, 1981).

²P. M. Selzer, D. L. Huber, D. S. Hamilton, W. M. Yen, and M. J. Weber, *Phys. Rev. Lett.* **36**, 813 (1976).

³J. Hegarty and W. M. Yen, *Phys. Rev. Lett.* **43**, 1126 (1979).

⁴S. K. Lyo and R. Orbach, *Phys. Rev. B* **22**, 4223 (1980).

⁵S. K. Lyo, *Phys. Rev. Lett.* **48**, 688 (1982).

⁶H. P. H. Thijssen, S. Voelker, M. Schmidt, and H. Port, *Chem. Phys. Lett.* **94**, 537 (1983).

⁷P. Reineker and H. Morawitz, *Chem. Phys. Lett.* **86**, 359 (1982).

⁸G. J. Small, in *Spectroscopy and Excitation Dynamics of Condensed Molecular Systems*, edited by V. M. Agranovich and R. M. Hochstrasser (North-Holland, Amsterdam, 1983).

⁹J. Friedrich, H. Wolfrum, and D. Haarer, *J. Chem. Phys.* **77**, 2309 (1982).

¹⁰J. Friedrich, D. Haarer, and R. Silbey, *Chem. Phys. Lett.* **95**, 119 (1983).

A large deuterium isotope effect on molecular dipole moments

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It generally is believed that the variation of a molecular charge distribution with vibrational level is small and that little variation of a dipole moment with isotopic substitution is expected. For example, in HCl the dipole moment of the fundamental vibrational level is about 3% larger than the moment of the zero point level, and substitution of deuterium for hydrogen changes these moments by 1% or less.¹ For the case of excited electronic states, no such isotope effects have been reported, and only in a few cases has a variation of dipole moment with vibrational level been found.²

In this Communication we report the first observation of a large (60%) isotope effect on a molecular dipole moment. The isotope effect appears to have its origins in the proximity of two states with different electronic configurations and vibronically induced coupling between them. The system we have investigated is 2,4,5-trimethylbenzaldehyde- $1d_1$ and $-1h_1$ (TMB) isolated in durene single crystals at 4 K. As described below, the projections of the dipole moment difference vectors onto the *a*, *b*, and *c*' crystal axes for $T-S_0$ transitions were determined by using the techniques of laser emission excitation Stark spectroscopy.³ The results are reported in Table I. The dipole moment difference vector is the difference between the dipole moments of the upper and lower levels in a spectroscopic transition.

The possibility of a large vibronic contribution to excited state dipole moments with a consequent very large deuterium isotope effect on dipole moment difference vectors was

first discussed in detail in the literature by Goodman and Özkan.⁴ The likelihood of a large isotope effect with the triplet states of substituted benzaldehydes was suspected from our previous studies. Observations of abnormally small⁵ dipole moment difference vectors for the $T_1(n\pi^*)$ states of *p*-methylbenzaldehyde and *p*-chlorobenzaldehyde and the anomalous^{6,7} dipole moment difference vector for the $T_2(n\pi^*)$ state of TMB- $1h_1$ were considered to be a consequence of a large mixing of the $^3n\pi^*$ states with nearby $^3\pi\pi^*$ states. In view of the proposed role of vibrational modes involving the aldehydic hydrogen in coupling these states,⁸ it was of interest to determine whether altering the vibronic coupling by deuterium substitution of this hydrogen would result in a significant effect on the dipole moments.

Single crystals of durene doped with the TMB compounds (0.01% by weight) were prepared by the Bridgman technique. Low temperature (4 K) phosphorescence excitation spectra were obtained by monitoring the most intense vibration in the phosphorescence spectra through a monochromator (Spex 1704X) while scanning a nitrogen pumped dye laser (Molelectron UV 400/DL 200). The Stark measurements were made on oriented single crystals held between highly polished stainless steel electrodes immersed in liquid helium. Details of such experiments have been published previously.^{3,7}

The data in Table I for the T_1 states were calculated from the Stark splittings of the $T_1(0,0)$ bands observed in the