

PHONON SELECTIVE LOW TEMPERATURE PHOTOCHEMISTRY IN ALCOHOL GLASSES**J. FRIEDRICH and D. HAARER***IBM Research Laboratory, San Jose, California 95193, USA*

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The molecule dihydroxyanthraquinone, which exhibits reversible, light-induced proton transfer is chosen for photochemical hole burning experiments in alcohol glasses. The experiments show the novel feature of a phonon selective photochemical mechanism, which verifies experimentally that the different sites in glasses have rather large variations in electron-phonon coupling strength.

Optical site selective spectroscopy has, in the past, been successfully used to shed light on the nature of amorphous glasses [1-3]. Especially investigations of the optical linewidth of site selectivity excited guest atoms or molecules [4] have supported the notion that some low temperature properties of glasses [5] and specifically the observed optical linewidths [6] can be understood within the framework of a model which uses a double-well potential to allow for phonon-assisted tunneling processes. The main assumption of this model is a random distribution of energy barriers with a certain probability distribution which was originally suggested to be in the range between 0.1-1 eV [5].

In this paper we use the experimental tool of photochemical hole burning (PHB) [7-10] to investigate details of the electron-phonon coupling of a photo-reactive molecule in a glass environment. We will elaborate on the following observations:

(a) The novel mechanism of "phonon selective" photochemistry which allows us to discriminate experimentally between sites of different phonon coupling strength.

(b) The observation of a phonon memory effect, which entails that the observed relative phonon coupling strength of a reactive center is not affected by the tautomerization process but is determined by the local structure of the glass environment.

Fig. 1 shows a typical photochemical hole which had been produced at 2 K by irradiation into the

lowest singlet transition $S_1 \leftarrow S_0$ of 1,4-dihydroxyanthraquinone (quinizarin) doped at a 10^{-5} molar concentration into a methanol-ethanol glass (1 : 3). The laser induced (5145 Å line of argon-ion laser) photochemical change had been attributed earlier [10,11] to a configurational molecular change of one of the protons from an intramolecular hydrogen bond to an intermolecular hydrogen bond between the guest molecule and the host environment. The photophysical and photochemical aspects of this reversible, light induced reaction will not be further discussed in this paper. We will, however, use the narrow ($\approx 1 \text{ cm}^{-1}$) spectroscopic hole as a means to probe details of the electron-phonon coupling strength in the amorphous glass environment.

In fig. 1 the measured hole is approximated with both a gaussian and a lorentzian fitting procedure. The experimental results fit, within the noise margin, a lorentzian envelope thus establishing a short relaxation mechanism (T_1 or T_2), which is on the order of several picoseconds [12]. Considering the temperature of the experiment (2 K) this reflects a quite rapid relaxation mechanism and leads to a homogeneous linewidth which is one or two orders of magnitude larger than typical linewidths in inorganic glasses. Even most organic alcohol glasses show, at 2 K, narrower linewidths or gaussian line profiles [13].

The main experimental evidence for the suggested phonon selective photochemistry of the quinizarin molecule is based on the observation of a variable

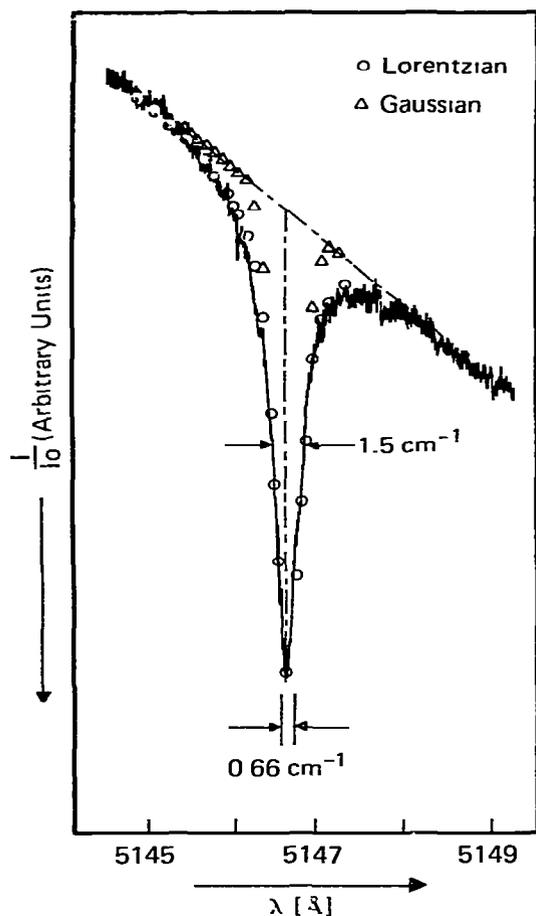


Fig. 1. Photochemical hole in the first singlet absorption of quinizarin in a 3 : 1 mixture of EtOH and MeOH (2 K), produced by 15 min irradiation, with an Ar-ion laser (3 mW). The bandpass of the spectrometer was 0.66 cm^{-1} .

Debye–Waller factor α which reflects the photochemical history of the sample. α is defined as:

$$I_{\text{zph}}/I_{\text{tot}} \equiv \alpha_{\eta} \quad (1)$$

$$= \exp \left[- \int_0^{\infty} D(\omega) S(\eta, \omega) \coth(\hbar\omega/2kT) d\omega \right].$$

I_{zph} is the area under the zero-phonon line and I_{tot} is the integrated area of the zero-phonon line and its corresponding phonon wing. S is the Huang–Rhys factor which characterizes the electron–phonon coupling strength. The parameter η accounts for the variations of S as a function of the glass environment. η

may be a random variable or may be related to the position of the zero-phonon line within the inhomogeneous profile. T is the temperature, and $D(\omega)$ is the density of phonon states as a function of the frequency ω .

The ratio $I_{\text{zph}}/I_{\text{tot}}$ gives the exact Debye–Waller factor for the case of negligible inhomogeneous broadening. For the real experimental conditions of a large inhomogeneous width, however, one has to consider the fact that a multitude of zero-phonon lines and phonon wings contribute to the absorption at the laser frequency. In this case, the ratio between the zero-phonon hole and the phonon side hole is subject to minor numerical corrections[‡]. Nevertheless, eq. (1) can be applied to the measured spectra for a rough estimate of the electron phonon coupling strength.

Fig. 2b shows a photochemical zero-phonon line and its corresponding phonon wing after about 20% of the photoactive molecules which have their zero-phonon origin at the laser frequency have been transformed into the photoproduct (see top scheme of fig. 3). From the areas of the two peaks we estimate $\alpha \leq 1/20$. If, in a subsequent experiment, one irradiates with a broadband light source (xenon lamp with filters) into the blue-shifted photoproduct (2000 cm^{-1} ; not shown in the figure [12]), one can reverse the photochemistry and refill the photochemical hole. Fig. 2c shows the result after an incomplete reverse reaction (90%). The remarkable feature of this reverse process is that it *selectively* reverses photochemical centers with strong electron–phonon coupling, leaving only the “weakly coupled” reaction centers unchanged, i.e., leaving them in the originally produced photochemical hole. From fig. 2c we get a new and much larger value of $\alpha \geq 2/5$. This value is about an order of magnitude larger than the one obtained after a completed forward reaction (see fig. 2b).

It is known from fluorescence line narrowing experiments in glasses that the coupling strength between guest and host can exhibit variations from site to site [15]. However, it is a quite novel aspect of the presented PHB experiments that different electron–phonon coupling strength can lead to selective photochemical processes which allow one to scan experi-

[‡] For the exact numerical value a mathematical convolution technique has to be applied [14].

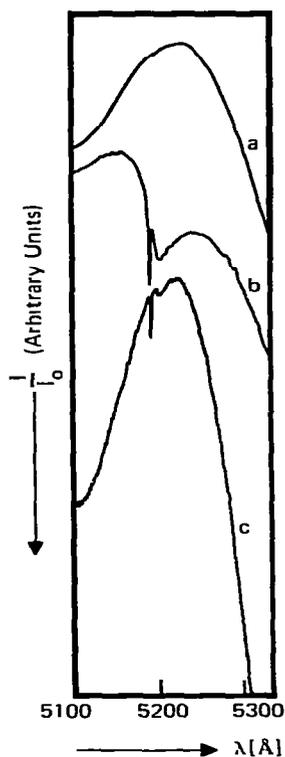


Fig. 2. (a) First singlet absorption band of quinizarin in an EtOH-MeOH glass (3 : 1). (b) After 20 min exposure to the radiation of an Ar ion laser. (c) After 5 min exposure to the radiation of a Xe high-pressure lamp (75 W, trace c is on a different scale).

mentally the dimension of coupling strength and thus discriminate the various centers. In this case the performed reverse photochemistry provides an efficient way of achieving selection which favors the strongly phonon coupled fraction of the photoreactive species.

An explanation of the observed large changes in Debye-Waller factor would be quite difficult, if based on schemes which do not allow for phonon selectivity. One would have to postulate fairly complex back-reaction schemes in which the photoproduct does not return to its original position within the inhomogeneous line profile. Processes of this kind could change the Debye-Waller factor to some extent but, in our opinion, not to the large extent which is observed experimentally. Therefore we propose a conceptually simpler scheme which is based on a phonon selective mechanism and which explains the experimental data in a straightforward fashion.

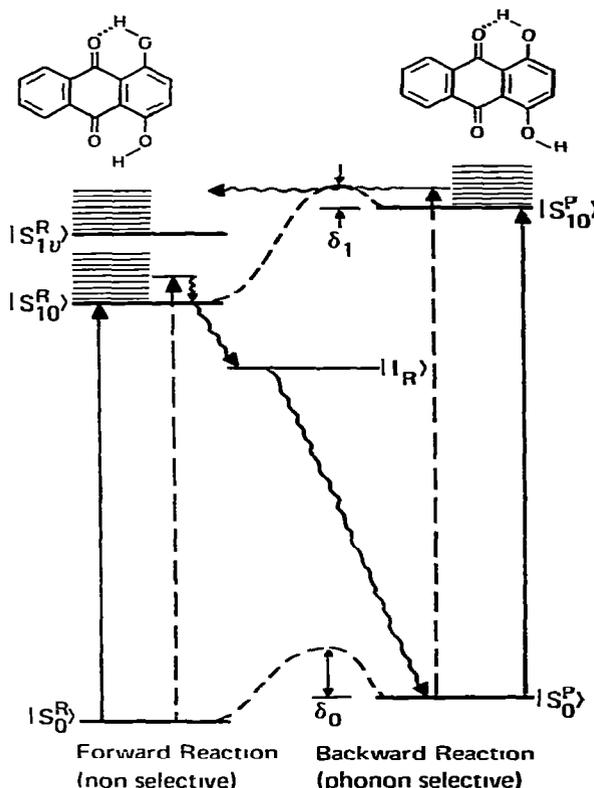


Fig. 3. The energy level scheme for quinizarin (R) and its photoproduct (P). Superimposed on the electronic and vibrational states (ν) are the phonon states of the glass. $|I_R\rangle$ represents an intermediate state in the photochemical reaction scheme. δ_0 and δ_1 are reaction barriers in the ground and excited state energy surface.

The proposed scheme is depicted in fig. 3. The forward reaction (i.e. the chelate ring opening) occurs in a nonselective fashion and involves an intermediate photochemical state (most likely a triplet state). The forward reaction therefore transforms both low- and high- α centers according to their absorption strength at the laser frequency. The reverse reaction is performed with "white light" irradiation into the spectral absorption of the photoproduct. This reaction is highly selective and transforms mostly centers with small α values, i.e., large electron-phonon coupling. Thus rather unusual phenomenon allows us to select photochemical centers according to their phonon coupling strength and, in our case, leaves only the weakly coupled centers in the original photochemical

hole (fig. 2c). This phenomenon can be understood if we assume a backward reaction (most likely singlet-singlet) which has an activation barrier whose height is on the order of the phonon sideband energy ($\approx 50 \text{ cm}^{-1}$). Assuming this scheme (fig. 3) one would expect no or little reverse photochemistry in the purely electronic 0-0 transition, depending on the magnitude of δ_1 , and one would expect efficient photochemical transformation from excited phonon states via the depicted tunneling process.

An interesting aspect of the proposed scheme is the occurrence of a "static" phonon memory (as opposed to a suggested dynamical phonon modulation effect in nonphotochemical systems [16]). Our scheme requires that the original molecule and its photoproduct have similar phonon coupling strength thus allowing the detection of the selective back reaction in the original photochemical hole which had been produced via forward reaction. This observation links the phonon coupling strength clearly to the amorphous glass environment rather than to the molecular properties of the two involved modifications of the quinzarin molecule.

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