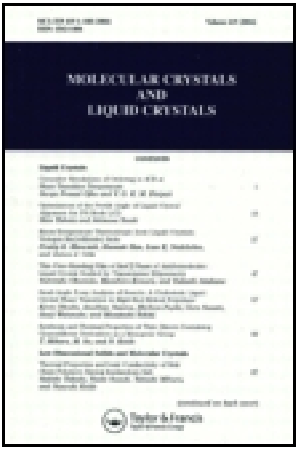

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H_2-OCTAETHYLPORPHIN IN AMORPHOUS POLYSTYRENE MATRIX: SPECTRAL HOLE BURNING AND SPECTRAL DIFFUSION

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Abstract All experimental data available on a low-temperature optical dephasing for H_2-octaethylporphin guest molecules in an amorphous polystyrene host are discussed in relation to spectral diffusion processes. Some data published earlier have once more been thoroughly studied and some corrections introduced, also some new data are presented. A notable dependence of the holewidth on a burning wavelength within the inhomogeneously broadened 0-0 absorption band at $T = 0.05$ K has been observed. The spectral diffusion is found to be actual at $T = 1.45 - 7$ K and is not at $T < 0.05$ K and at $T > 8$ K.

INTRODUCTION

At low temperatures the optical homogeneous linewidths Γ of impurity molecules in amorphous hosts and their temperature dependences $\Gamma(T)$ differ strongly from those observed for the same species in crystals.[1] Such a behaviour can qualitatively be explained in terms of so-called two-level systems (TLS) or tunneling states in a glass.[2] One of the laser spectroscopy methods widely used for measuring of Γ is the spectral hole burning (HB).[3,4] If measured under certain conditions, the holewidth δ gives the value of 2Γ. Some other methods are used to measure the optical dephasing time T_2, which gives Γ as:

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

where T_1 is the time of energetic relaxation and T_2' is the pure dephasing time.

One of the problems actively discussed in the last years' literature is whether the value of δ, obtained by HB for doped amorphous hosts at low temperatures, really yields Γ, or an additional broadening δ_D due to the spectral diffusion processes (SDP)[5] takes place during the measurement time τ_m:

$$\delta(T) = 2\Gamma(T) + \delta_D(T, \tau_m).$$

On the one hand, the dependence of δ on τ_m has been reported[6-10]; in some other studies[11-19] considerable differences have been observed in T_2 when measured using diverse techniques with different τ_m.

On the other hand, the temperature dependences of δ have been measured for a large variety of organic doped amorphous hosts between 0.3 and 20 K[20-26]; it has been found that in all cases at $T \to 0$ δ extrapolates to the fluorescence lifetime limited value $\delta_0 = 2\Gamma_0 = (\pi T_1)^{-1}$, also a universal law for temperature dependence has been observed: $\delta(T) - \delta_0 \sim T^{1.3}$. This law has been interpreted as determined by the temperature dependence of Γ, because no SDP have been observed[26]; many of the measurements by other authors, where SDP have been observed, have been found to be erroneous.[24-30]

In the present paper optical dephasing data on a specific amorphous system, H_2-octaethylporphin in polystyrene matrix (OEP-PS), will be discussed and some conclusions about SDP in OEP-PS will be made.

OPTICAL DEPHASING DATA ON H_2-OCTAETHYLPORPHIN IN POLYSTYRENE

It has already been shown[31,32] that at $T < 0.5$ K the holewidth δ, measured by HB on $S_1 - S_0$ 0-0 transition of OEP-PS, depends on a wavelength λ within the inhomogeneously broadened absorption band (see Fig. 1, left). No essential δ dependence on λ has been observed at $T > 1$ K. We have once more thoroughly studied the HB spectra measured earlier in[31,32] and the corresponding data processing used for obtaining the δ value. It has been found that the complicated temperature dependences of δ shown in Fig. 1 (left) are still valid. Also, we found that a notable dependence δ on λ occurs at $T = 0.05$ K (see Fig. 1, right) and that near the centre of the 0-0 absorption band $\delta \approx \delta_0$. Here the hole narrowing in an optically thick sample was taken into account[33], δ in Fig. 1 corresponds to the holewidth in the beginning of the burning process in an optically thin sample.

All available data on the holewidth for OEP-PS, measured in the vicinity of a specific wavelength, $\lambda = 620.1$ nm, are presented in Fig.2. The HB data[17], measured in the fluorescence excitation spectrum at $T = 4.2 - 16$ K, have been corrected: we got better results when a constant additional contribution was added to the function which represents a Lorentzian approximation of the HB spectra. These corrected data are in a good accordance with our HB results measured in the absorption spec-

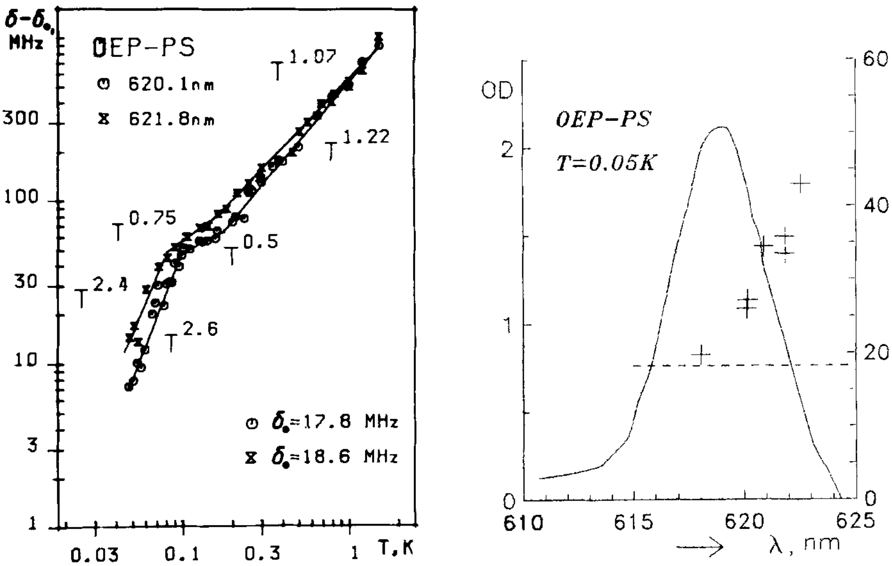

FIGURE 1 Left: Log-log plot of the holewidth (δ-δ_0) versus T, measured for two burning wavelength positions ($\lambda \approx 620.1$ nm and $\lambda \approx 621.8$ nm) within the inhomogeneously broadened 0-0 absorption band of OEP-PS.[32]
Right: δ versus λ for OEP-PS at $T = 0.05$ K. Dotted line indicates the δ_0 level; solid line - the contour of the 0-0 absorption band of OEP-PS.

trum at $T = 1.5 - 16$ K, and could be well described by the $T^{1.3}$ law. Still the values of δ from the literature[30] (dotted line in Fig. 2) are by a factor of 2 smaller than ours. Our opinion is that the OEP-PS samples were possibly not identical. In all referred studies on optical dephasing of OEP-PS except in[30] the samples were prepared by thermal polymerization (without initiator) of an OEP solution in the monomer, by using the same temperature regime (about 20 h at 120°C and then another 20 h at 160°C). So we exclude these data[30] from the further discussion. As one can see from Fig. 2, the temperature dependence of the holewidth roughly follows the "universal" law $T^{1.3}$ only at $T > 0.16$ K. Holewidths were measured with $\tau_m \approx 10$ s. The increasing of τ_m up to 600 s did not cause any additional hole broadening.

Additionally, the optical dephasing data obtained by means of different techniques with smaller τ_m are presented in Fig. 2 (see the caption). The contradiction that exists between the transient HB result[7,8] ($\tau_m = 10^{-5}$ s) and other data is possibly due to a smaller accuracy of δ values measured by the Doppler shift technique[7,8]. A slow

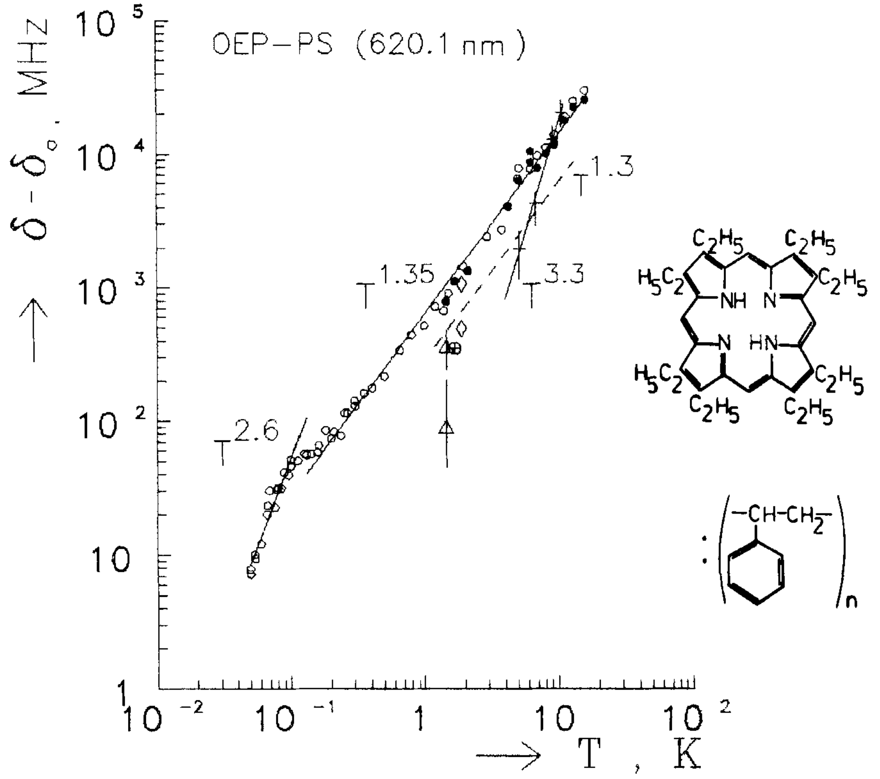

FIGURE 2 Log-log plot of the holewidth (δ-δ_o) versus T, measured in the absorption spectrum (empty circles, data for $T \leq 1.5$ K from ref.[32]) and in the fluorescence excitation spectrum (filled circles, data[17] corrected) for OEP-PS at $\lambda \approx 620.1$ nm; $\tau_m \approx 10$ s. Dotted line - HB data[30] for OEP-PS (sample not identical), $\tau_m \approx 10^2$ s. For the other optical dephasing data, measured by different techniques, δ indicates 2Γ: Δ - transient HB[7,8], $\tau_m = 10^{-4}$ s (upper point), $\tau_m = 10^{-5}$ s (lower point); ⊕ - photon echo[18], $\tau_m \approx 10^{-8}$ s; ◇ - photon echo[19], $\tau_m = 20$ s (upper point), $\tau_m \approx 10^{-10}$ s (lower point); + - resonance fluorescence, $\tau_m \approx 10^{-8}$ s (data[17] corrected).

temperature dependence of Γ (between $T^{0.5}$ and $T^{0.9}$), observed by photon echo technique[18] ($\tau_m \approx 10^{-8}$ s) at $T = 1.6 - 2.15$ K, is represented in Fig. 2 by only one point ($T = 1.7$ K).

The resonance fluorescence data[17], measured at $T = 5 - 11$ K, have been corrected: the spectral curves[17] have been processed by using an improved procedure. We applied the general non-linear least-square procedure[34] to approximate these spectral curves with modified function.

This function includes as an additional part the convolution of a Lorentzian (for the homogeneously broadened spectral line) with a spectral shape of the HB-filter, which was used as a spectral device.[17]

CONCLUSIONS

Some conclusions about SDP in OEP-PS could be derived from the analysis of the optical dephasing data referred to (Fig. 2). The contribution of SDP to δ is rather small ($\delta_D \ll 2\Gamma$) at $T > 8$ K and at $T \leq 0.05$ K (at least near the centre of the 0-0 band, see Fig. 1). There is a considerable contribution ($\delta_D \approx 2\Gamma$) of SDP with characteristic times $\tau_D < 10$ s at $T = 1.45 - 7$ K; at $T \approx 1.5$ K it seems most probable that $\tau_D > 10^{-4}$ s. So in the case of OEP-PS the "universal" law $T^{1.3}$ for the temperature broadening of the holewidth, which is nearly valid in the range $T = 0.16 - 16$ K, is determined not only by the temperature broadening of Γ as assumed[28], but the temperature dependence of δ_D must be taken into account as well.

The dependence of δ on λ, observed at very low temperatures (Fig. 1), is evidently caused by a corresponding dependence of Γ (freezing of SDP is assumed). Lowering of T makes the interaction of the guest molecule with TLS states to be more local. TLS, which are localized near the impurity, obviously cause changes in the transition energy, which are correlated with the dynamic line broadening effect.[31]

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