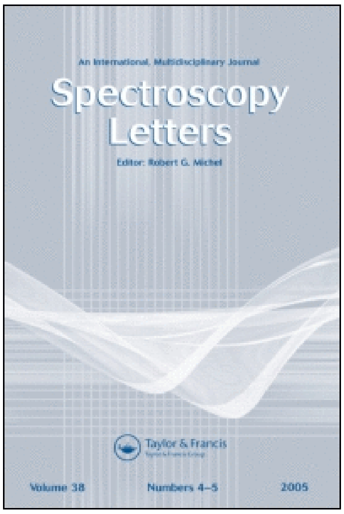

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Stark Hole-Burning Spectroscopy of Cresylviolet Perchlorate in Amorphous Hosts

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Stark Hole-Burning Spectroscopy of Cresylviolet Perchlorate in Amorphous Hosts

Keywords

Cresylviolet perchlorate, Glass, Polymers, Hole-burning, Effective dipole moment change, Stark Effect

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Stark hole-burning spectroscopy is used to investigate the effective dipole moment change of cresylviolet perchlorate (CVP) in various glass and polymer hosts such as ethanol:methanol (EM), polyvinyl alcohol (PVA), poly (2-hydroxyethyl) methacrylate (PHEMA), polyvinylbutyral (PVB), and formamide. The strong correlation between effective dipole moment change of the guest molecule and the holeburning efficiencies of the host matrices illustrates the sensitivity of the dipole moment change as a direct measure of guest-host interactions. Hole-burning is found to be more efficient as the dipole induced reaction field increases. This relationship is discussed in terms of the unusual

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***Permanent Address: Dept. of Electrical Engineering, Yeditepe University, Istanbul 81410, Turkey hole-burning mechanism suggested for this molecule. The effective dipole moment change of cresylviolet perchlorate ranges from 0.14 to 0.59 Debye.

INTRODUCTION

Hole-burning spectroscopy is a valuable tool for high resolution spectroscopic investigation of large molecules for which inhomogeneous molecular interactions with the solvent normally cause broad spectral features [1,2]. The advent of lasers has made possible the ability to obtain narrow spectral lines by burning holes (or more accurately, dips) in the broad absorption or excitation spectra. The holes are usually limited in width to the homogeneous linewidth of the observed species or the laser width.

Several different mechanisms have been identified to explain different observed types of hole-burning spectroscopy. In chemical hole-burning, a photochemical reaction is involved, with the production of a chemical photoproduct responsible for depleting the population of an inhomogenously broadened ensemble at a particular energy. On the contrary, physical hole-burning is presumed to be caused by changes in the physical interaction of the molecular species with its surroundings, resulting in the depletion of molecules with a particular energy with respect to its surroundings. It might be expected that for reasonably efficient photochemical reactions the chemical mechanism would be easier to observe than the photophysical mechanism and this is borne out by numerous experiments. Cresylviolet perchlorate (CVP) shown in figure 1 holds a peculiar position in this regard because it displays some of the features of both types of mechanisms.

The optical properties of many crystalline and polymeric organic solids are frequently dominated by guest molecules. Guest molecules can either be impurities or doping materials. Photochemical hole-burning spectroscopy is a special kind of saturation spectroscopy. With narrow band excitation very narrow and stable photochemical holes can be burned into the absorption bands of guest molecules. From the linewidth and the lineshape of these holes, one can obtain

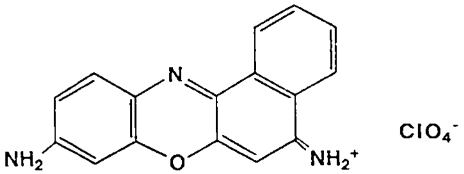

Figure 1. The ionic dye molecule cresylviolet perchlorate.

information about both the host and guest systems [1-7]. In an external field the energy levels of a molecule shift relative to their zero-field values because of multipolar interactions of the molecular charge distribution and polarization effects.

The Stark effect [7] is the shift in spectral lines caused by the application of an external electric field to the molecule. In the case of a homogenous field, a dipole moment gives rise to an energy shift which is linear in field strength, while the shift due to molecular polarizability is quadratic to lowest order. The optical absorption band of a dye molecule therefore shifts in the field, if the dipole moments or the polarizabilities are different in the two electronic states between which the transition occurs. The hole burning technique has been applied to Stark measurments in solids at liquid helium temperature. Since the width of a spectral hole is determined by the homogenous line width, even small shifts caused by field strengths of a few kV/cm, can easily be measured. In amorphous hosts the guest molecules are oriented at random, so that a hole broadens in the electric field without being shifted.

When incorporated into alcoholic glasses and polymers, cresylviolet perchlorate shows broad and structureless absorption bands in the UV and visible region even at liquid helium temperature. The reason is probably their sizeable guest-host interaction strength caused by the fact that inhomogeneously broadened $S_0 \rightarrow S_1$, 0-0 transitions and vibronic bands are strongly overlapped. In spite of the broad inhomogeneous absorption bands and the appreciable electron-phonon coupling, very narrow homogeneous line widths, Γ in the MHz regime have been observed for amorphous ionic dye systems at liquid helium temperature.The broad-band detected fluorescence excitation spectra of the S_0 -> S_1, 0-0 band of cresylviolet perchlorate in formamide at 4.2 K has been investigated extensively [19-24].

Measurements of the half-widths of the hole in the frequency and electric field dimensions yield a measure of the extent of dipolar guest-host interactions. 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 often termed "two level" systems [25-39].

EXPERIMENTAL

Excitation spectra were obtained using a Molectron DLII scanning, pulsed dye laser (bandwidth 0.3 cm^{-1}) pumped with a Molectron UVI4 nitrogen laser. Total emission was monitored with a Hamamatsu R818 photomultiplier tube. An average power of 20-30 mW/cm^2 was obtained from the dye laser by using a mixture of Rhodamine 610 and Rhodamine 640 laser dyes. Excitation spectra were scanned with the same dye laser used for burning, but utilizing 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 core diameter of 200 μm (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 6 mm. All measurements were made with the sample immersed in liquid He at 4.2 K.

Cresylviolet perchlorate was obtained from Exciton,Inc. and used without purification.The following hosts were utilized in our experiments:

ethanol:methanol(3:1)(EM), polyvinyl alcohol (PVA), 2-hydroxyethyl methacrylate(PHEMA), polyvinylbutyral(PVB) and formamide. For the polymers, the solution blend method was used for fabrication and the solvent was allowed to evaporate in a glass petri dish to form a thin film. The concentration of CVP in EM was 10^{-5}- 10^{-6} M, and in polymers, was 10^{-4} mole/kg. figures 2 and 3 show the excitation and emission spectra of CVP in PVB, at room temperature.

RESULTS AND DISCUSSION

We have studied the hole-burning mechanism which takes place in the ionic dye molecule cresylviolet perchloride incorporated in polar glasses, alcoholic glasses and polymers at liquid helium temperature. Persistent spectral holes of CVP in different hosts are burned at 4.2 K by narrow-linewidth laser light. The top curve of figure 4 shows a hole burned in the CVP spectrum. The changes in the center of the spectral hole as a function of applied external electric field strength have been investigated for CVP in different hosts, to determine the permanent electric dipole moment difference $\Delta\mu$ of the guest molecule.

In crystals, the spectral holes are normally simply split or shifted by the application of an electric field. Hole-burning Stark spectroscopy in crystals yields information about the nature and symmetry of guest centers. In amorphous solids, the application of an electric field causes the spectral hole to broaden and reduce in depth, because there is a statistical distribution of the electric-field-induced shifts of the electronic levels of the impurity centers. The level shifts of the individual guest molecules are different because they have different orientations and a different local surrounding in the amorphous matrix. Measurements of the half-widths of the hole in the frequency and electrical field dimensions yield a measure of the total effective electric dipole moment difference between the excited and ground states of the impurity center which contains contributions from the guest molecule and the surrounding matrix [10]. The effects of an externally applied electric field on the spectral hole profile of

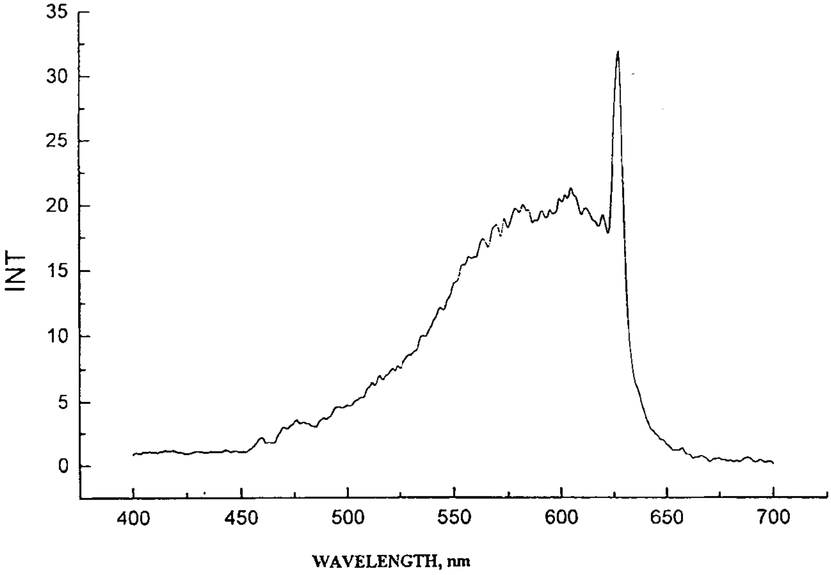

Figure 2. The excitation spectrum of CVP in PVB at room temperature.

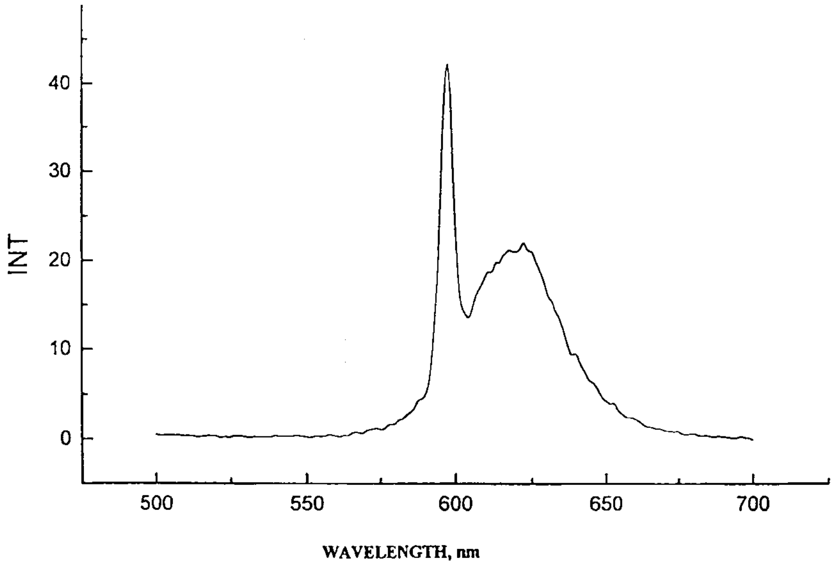

Figure 3. The emission spectrum of CVP in PVB at room temperature.

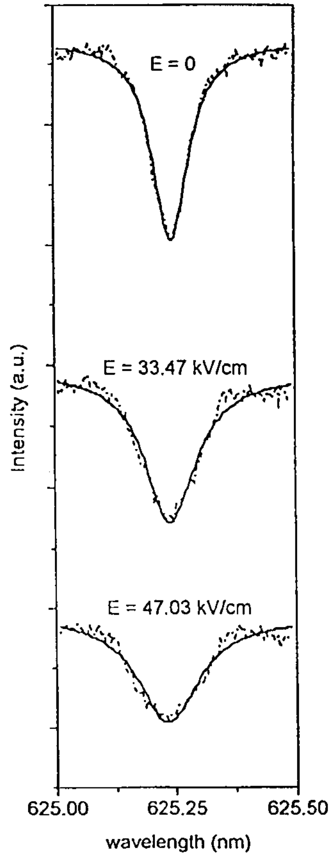

Figure 4. Effect of an external electric field on the spectral hole profile of cresylviolet perchlorate in polyvinylbutyral (PVB).

CVP in PVB, at 625 nm, shown in figure 4. Fields up to 60 kV/cm could be applied without electrical breakdown. From the broadened spectra, full widths at half-maxima (Γ in cm^{-1}) could be measured, and after subtracting out the zero-field width, the broadening versus applied field is plotted. A typical plot is shown in figure 5, where in each graph, data are collected from several samples in

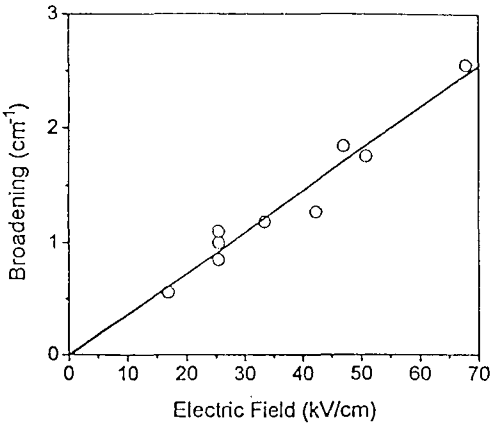

Figure 5. Plot of the spectral hole broadening (cm^{-1}) as a function of applied electric field (kV/cm) for cresylviolet perchlorate in polyvinylbutyral (PVB).

separate experiments, and figure 6, shows the plot of the dipole moment change of CVP as a function of dielectric constant in several hosts.

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:

$$|\Delta\mu| = 59.6\ \Gamma/(2EL) \qquad (2)$$

Where E is the applied electric 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 ($L=(\varepsilon+2)/3$).

In the EtOH/MeOH host as well as in the polymeric PHEMA, PVA and PVB, it was possible to burn observable holes in a relatively short period of time (in some cases, seconds). The hole burning is photochemical and photophysical in nature and involves a hydrogen bonding mechanism. In Table 1, we summarize

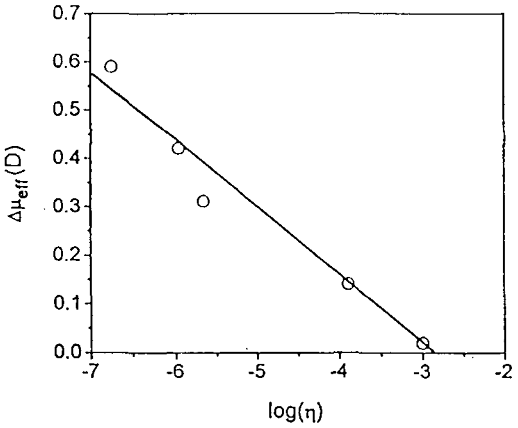

Figure 6. Plot of the effective dipole moment change (| $\Delta\mu_{eff}$ |) in the first excited state of cresylviolet perchlorate as a function of logarithm of hole-burning efficiency (log(η)) in various hosts.

Table 1. Effective dipole moment change (| $\Delta\mu_{eff}$ |), hole-burning efficiency (η) and dielectric constant (ε) for cresylviolet perchlorate in various hosts at 4.2 K.

Host	ε	η	| $\Delta\mu_{eff}$ |
Formamide	109	8.5 x 10^{-2}	<0.02
Ethanol:Methanol	26.6	1.3 x 10^{-4}	0.14 ±0.02
PVA	5.2	2.2 x 10^{-6}	0.31 ±0.04
PHEMA	4.0	1.1 x 10^{-6}	0.42 ±0.04
PVB	3.6	1.8 x 10^{-7}	0.59 ±0.10

the effective dipole moment change data for CVP in different hosts. Additional broadening due to the process of spectral diffusion has been observed in some cases. However, at short burning times, broadening is often negligible [17,22]. As a check, we measured zero-field hole-width at the end of our experiments, and no broadening was observed due to the spectral diffusion. 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 Stark line shape is modulated by a Gaussian distribution of effective dipole moments. Resulting line shape convolutions have been invoked to obtain an average value for the induced dipole moment change $|\Delta\mu_{eff}|$ as a measure of the magnitude of dipolar coupling.

The holes were detected by measuring the excitation spectra.The quantum efficiency η is the yield of stable photoreacted molecules per absorbed photon. We have used the formula of Iino et al. [40] to calculate η. Systems with high values of the efficiency are usually assumed to display chemical hole burning, while lower values are assumed to be photophysical in nature. According to measured η values, hole-burning is photochemical in EM and appears to be photophysical in the hosts, PVA, PVB and PHEMA. Only a small solvent effect is observed from the 0-0 band peak-to-peak position and the distance from excitation and fluorescence spectra. There are good correlations between ε,η and $\Delta\mu$ as it is seen in Table 1. For the experimental convenience all the experiments described in this work were performed at a constant temperature of 4.2 K. In figure 6 we show the correlation between the effective dipole moment change and the logarithm of the hole burning efficiency. Note that it is linear over four decades of the scale. We take this to be striking confirmation of the proposed mechanism of hole burning, which involves dipole-dipole interactions of the guest molecule with the two level system of the host.

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Abbreviations

EM = Ethanol:Methanol
PVA = Polyvinyl alcohol
PVB = Polyvinyl butyral
PHEMA = Poly-(2-hydroxyethyl)-methacrylate
CVP = Cresylviolet perchlorate

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