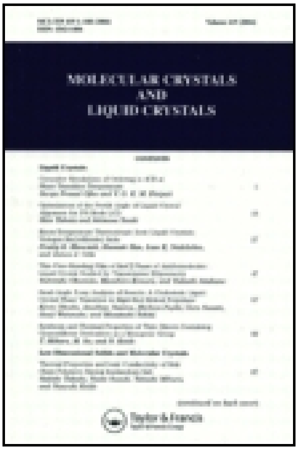

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Fluorescence Resolved Hole Burning of Squaraines in Polymer Matrices

Joachim Wolf [a] & Anne B. Myers [a]
[a] Center for Photoinduced Charge Transfer and Department of Chemistry, University of Rochester, Rochester, NY, 14627-0216

To cite this article: Joachim Wolf & Anne B. Myers (1996): Fluorescence Resolved Hole Burning of Squaraines in Polymer Matrices, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 291:1, 135-142

To link to this article: http://dx.doi.org/10.1080/10587259608042740

Mol. Cryst. Liq. Cryst., 1996, Vol. 291, pp. 135–142
Reprints available directly from the publisher
Photocopying permitted by license only

FLUORESCENCE RESOLVED HOLE BURNING OF SQUARAINES IN POLYMER MATRICES

JOACHIM WOLF and ANNE B. MYERS
Center for Photoinduced Charge Transfer and Department of Chemistry, University of Rochester, Rochester, NY 14627-0216

Abstract Hybrid hole-burning/fluorescence line-narrowing techniques are used to obtain vibrationally well-resolved emission spectra of squaraine chromophores in polymer matrices at 1.4 K. Standard fluorescence line-narrowing spectra of these strongly inhomogeneously broadened systems are complicated by overlapping emission from zero-phonon line (ZPL) and phonon-sideband excited molecules. The ZPL-excited contribution can be reduced either by preferential nonphotochemical hole-burning with narrow-band cw excitation or by partial saturation of the absorption with picosecond pulsed excitation. Subtracting the emission spectra of the ZPL-depleted samples from the initial spectra leaves predominantly ZPL-excited spectra exhibiting enhanced vibrational resolution. These techniques have been used to analyze the vibrational spectra of centrosymmetric squaraines, examine their phonon sideband structures in different polymers, and explore the temperature dependence of the width. We also probe the origin of the low-temperature electronic linewidth by combining cw hole burning linewidths, photon echo decays, and fluorescence lifetime measurements.

INTRODUCTION

Electronic absorption and emission spectra of chromophores in liquid or amorphous solid solutions typically exhibit little or no resolved vibronic structure due to coupling of the electronic transition to the nuclear degrees of freedom of the environment.[1] In liquids one often describes the interaction as a continuous dynamic modulation of the solute's transition frequency by fluctuations in the surrounding solvent. In the solid state the arrangement of solutes in the matrix is approximately fixed, and it becomes useful to distinguish between "homogeneous" broadening of a single chromophore's electronic spectrum due to coupling with matrix or intermolecular phonons and "inhomogeneous" broadening due to the different electronic transition frequencies of chromophores in different local environments. At sufficiently low temperatures the spectra of single chromophores may become quite sharp even though the ensemble-averaged spectra are still severely inhomogeneously broadened, and irradiation with a narrow-band laser in the region of the electronic origin can selectively excite only a small fraction of the chromophores in the ensemble, resulting in relatively sharp emission. This "fluorescence line narrowing" (FLN) technique has been widely used to obtain vibrationally structured emission spectra of matrix-isolated molecules.[2] However, it has significant limitations when the electron-phonon coupling is large (small Debye-Waller factor) and the inhomogeneous broadening is larger than the average phonon frequency, as is often the case in amorphous matrices. Under these conditions the absorption may be dominated by phonon sidebands rather than zero-phonon lines at all excitation frequencies where there is detectable absorbance, giving rise to emission spectra which, while partially "site-selected", are still rather congested.

The sharp zero-phonon lines tend to be particularly sensitive to saturation and/or hole burning effects that further reduce their contribution to the total spectrum. As previously demonstrated by Bogner and Schwartz[3] and by Fünfschilling *et al.*[4] and extended by Jankowiak and Small,[5] this sensitivity can be turned into an advantage by utilizing "hole-burning subtracted FLN" spectroscopy.[6] Using an efficient single spectrograph and a CCD detector, we first obtain a fluorescence spectrum under conditions where hole burning is negligible (low intensity and short irradiation time). We then continue irradiating at the same frequency while monitoring the spectrum until the ZPL features in emission are significantly attenuated. Subtraction of the final spectrum from the initial one yields an essentially pure ZPL-excited spectrum showing enhanced vibrational resolution and also displaying the true phonon sideband structure. This technique has proved to be quite useful, but it is applicable to a limited number of systems since it requires that hole-burning occur with a reasonably but not excessively high efficiency. Recently we have also employed a complementary technique of "saturation subtracted FLN" which is useful for systems that have reasonably long excited-state lifetimes but hole-burn inefficiently. Here laser pulses, much shorter than the excited-state lifetime but spectrally narrow enough to accomplish significantly selective excitation, are used to partially deplete the ZPL-resonant molecules by bottlenecking them in the excited electronic state. Subtraction of a properly scaled high-intensity emission spectrum from an undepleted low-intensity spectrum again leaves behind a nearly pure ZPL-excited emission that agrees well with that obtained by hole-burning subtraction for systems that are accessible by both techniques.

EXPERIMENTAL

The experimental details for the hole-burning subtracted FLN spectra are described elsewhere.[6] Samples of about 5×10^6 mol kg^{-1} of bis[2-methyl,4-(dibutylamino)phenyl] squaraine (**I**)[7] in polyethylene (Aldrich, low density) were prepared by mixing the fine polymer powder with the squaraine dissolved in CH_2Cl_2, evaporating the solvent, melting, pressing a thin (ca. 100 μ) film, and quenching in liquid nitrogen. This particular squaraine was chosen because of its relatively high solubility in hydrophobic polymer matrices, presumably due to steric effects of the *ortho*-methyl groups. The films were mounted in either a closed-cycle helium cryostat for variable-temperature experiments from room temperature to 7 K, or in a helium immersion cryostat pumped below the lambda point to achieve a temperature of about 1.4 K. Absorption spectra were measured on a commercial uv-vis spectrophotometer and fluorescence lifetimes were measured with a standard time-correlated single photon counting setup.

The hole-burning subtracted spectra were excited using either about 0.5 mW of power from a cw dye laser (DCM dye, 40 GHz linewidth) or about 25 μW from an external cavity tunable diode laser (<10 MHz linewidth) with a 2 mm diameter spot size at the sample. Spectra were recorded with a 0.5 m single spectrograph and a thinned, back-illuminated, liquid nitrogen cooled CCD. An initial (unburned) spectrum was accumulated for 5 s followed by 100 s of continuous irradiation before accumulation of a final (hole-burned) spectrum for another 5 s. The saturation subtracted spectra were excited using a Nd:YLF-pumped amplified sync-pumped dye laser[8] (DCM in both oscillator and amplifiers) producing about 10 ps pulses at a 500 Hz repetition rate. The partially saturated and unsaturated emission spectra were obtained with pulse energies of about 300 and 10-20 nJ, respectively. This picosecond source was also used for photon echo experiments in the usual 2-pulse configuration. Pump and probe were variably delayed with a motorized delay stage, and the spectrally unfiltered signal was detected with a photomultiplier and boxcar in the background-free direction $2\mathbf{k}_2-\mathbf{k}_1$.

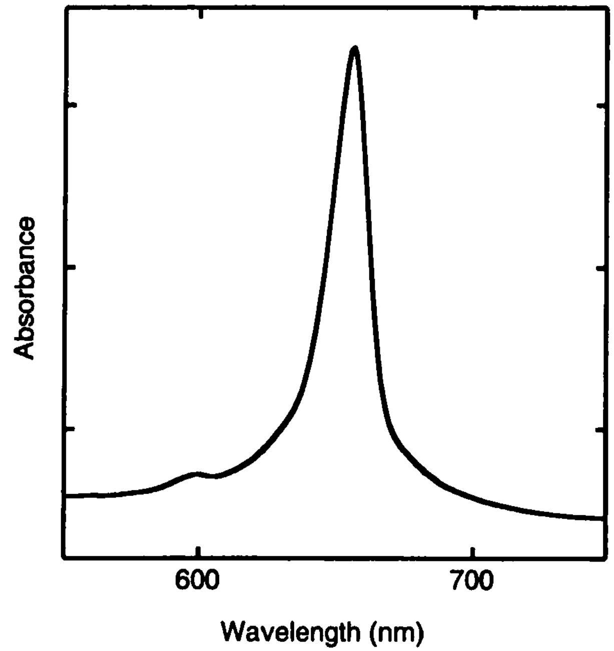

FIGURE 1 Absorption spectrum of **I** in polyethylene at 7 K.

RESULTS AND DISCUSSION

The absorption spectrum of **I** in polyethylene at 7 K (Figure 1) shows very weak vibronic structure. The apparent width of the "origin" (which has some contribution from a moderately active low-frequency vibrational progression as demonstrated by the line-narrowed emission spectra) is about 320 cm^{-1}. Broadband excited fluorescence spectra are similarly unresolved. In contrast, low-intensity laser excitation on the red side of the absorption band produces a highly structured emission consisting of sharp lines due to vibrations of the squaraine alone superimposed on broader features that involve excitation of low-frequency matrix or intermolecular phonons. Higher vibrational levels of the squaraine make a negligible contribution at these excitation frequencies. The broad emission features can result from two mechanisms: excitation of the pure electronic origin followed by emission to a phonon-excited final state, or excitation of the phonon sideband of the electronic origin followed by vibrational relaxation and emission. The contributions of phonon sideband-excited molecules lead to a more congested emission spectrum with weaker ZPL features than if only pure electronic origin transitions were excited.

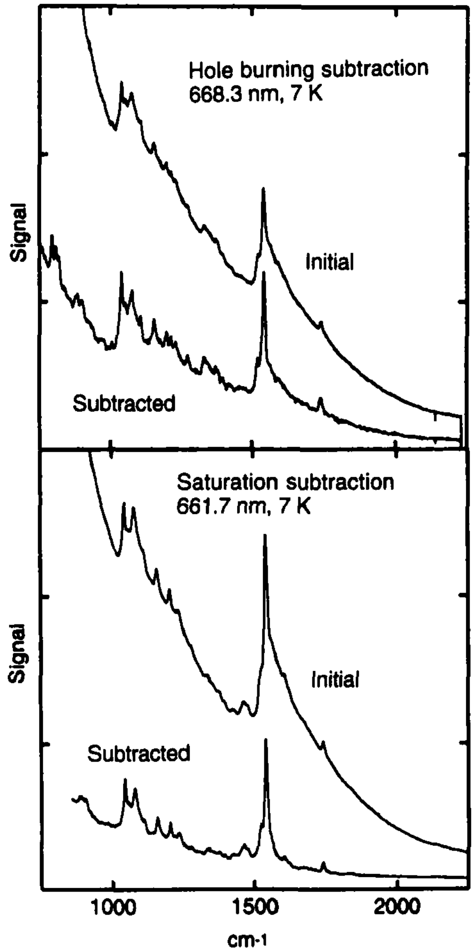

FIGURE 2 Comparison of phonon sideband subtraction methods for **I** at 7 K. Top, hole-burning subtraction at a laser wavelength of 668.3 nm; bottom, saturation subtraction at a laser wavelength of 661.7 nm. In each case the upper curve is the "undepleted" fluorescence spectrum (short irradiation time or low pulse energy) and the lower curve is obtained by subtracting from the upper one an appropriately scaled "ZPL depleted" spectrum (long irradiation time or high pulse energy).

Nearly pure ZPL-excited spectra can be obtained through either of the subtraction methods. Figure 2 compares the original, undepleted fluorescence spectra with the hole-burning subtracted and saturation-subtracted ones at a temperature of 7 K. The two subtraction techniques yield nearly the same spectra, with small differences that may be due to the fact that the spectra were obtained at somewhat different wavelengths. Figure 3 shows more complete emission spectra obtained with both techniques. The vibrational frequencies and relative intensities are much more clearly evident in the subtracted spectra, allowing the first detailed ground-state vibrational analyses of squaraine chromophores to be performed as we have detailed elsewhere.[6] These subtracted spectra also reveal the true shapes and intensities of the phonon sidebands and allow the phonon frequencies and Debye-Waller factors in different matrices to be compared.[9]

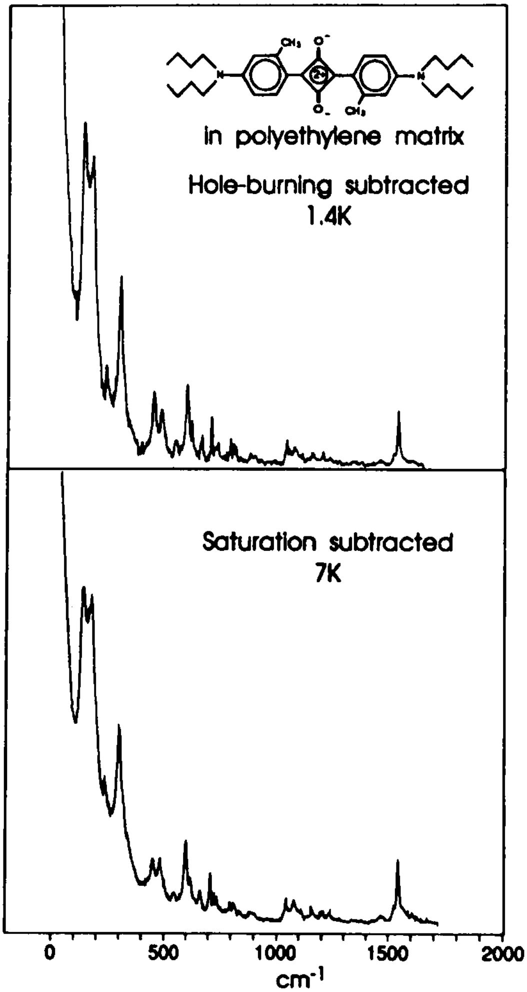

FIGURE 3 Line-narrowed fluorescence spectra of **I** in polyethylene by the hole-burning subtraction technique at 1.4 K (top) and by the saturation subtraction technique at 7 K (bottom).

These subtraction procedures are useful because the ZPL-resonant molecules undergo both saturation and hole burning more efficiently than do the phonon-wing resonant ones. In the picosecond saturation experiments the effect arises from ground-state depletion of the ZPL-resonant molecules at the high pulse energies. At low pulse energies each member of the ensemble makes a contribution to the fluorescence intensity that is roughly proportional to its linear absorption cross section at the laser frequency. The ZPL-resonant molecules, while few in number, make a substantial contribution to the emission since their peak absorption cross sections are so large. At high pulse energies, however, the leading edge of the pulse transfers most of the ZPL-resonant molecules into the excited state (the measured fluorescence lifetime of 4.3-4.4 ns at both room temperature and 7 K greatly exceeds the pulse duration), leaving the trailing edge of the pulse to excite mainly phonon wing resonant molecules. The phonon wing resonant molecules therefore make a larger relative contribution to the fluorescence spectrum at high pulse energies. The cw hole-burning subtraction technique presumably works for a similar reason: the ZPL-resonant molecules absorb more photons in the beginning and are therefore more likely to undergo a hole-burning event that removes them from resonance, leaving a larger fraction of phonon wing resonant molecules at later times.

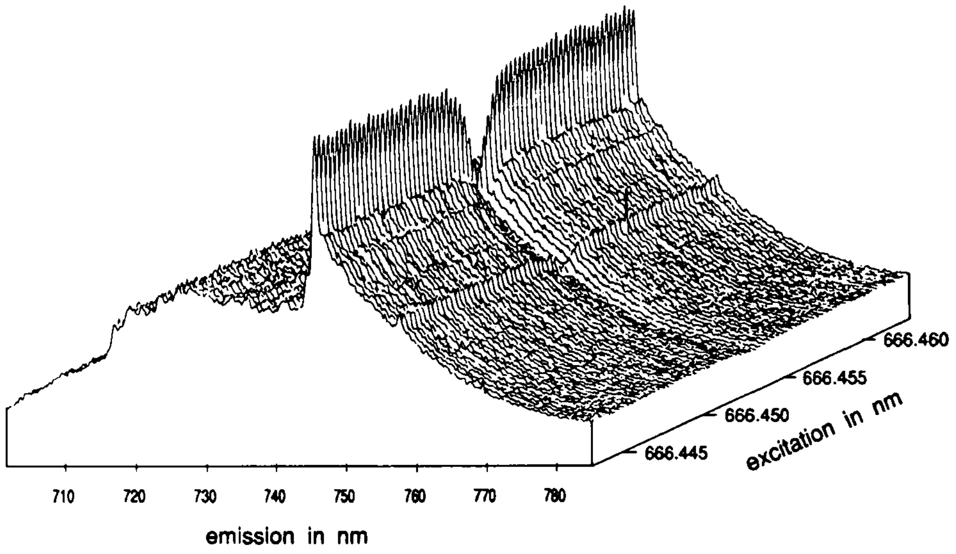

FIGURE 4 Resolved fluorescence excitation spectrum of I in polyethylene at 1.4 K following hole burning at 666.453 nm. The hole was burned with 40 μW on a 2 mm spot in 60 s, and was read with about 4 μW and 1 s per spectrum.

Even if the vibronic structure of the fluorescence is not of interest in itself, spectrally resolving the emission can aid in detecting the holes burned in the absorption spectrum and in analyzing the source of their breadth. Figure 4 shows a three-dimensional plot (intensity versus excitation and detection wavelength) of the fluorescence from a cw hole-burned sample. The hole in the excitation spectrum is much more pronounced when detected at the zero-phonon peak of an emission feature than when integrated over the entire emission spectrum. Thus by resolving the fluorescence it becomes feasible to detect holes at burning fluences where the hole depth in direct transmission or total fluorescence detection is very small, simplifying the extrapolation to zero burning fluence needed to extract the true homogeneous linewidth.

It is well known that in glassy matrices hole burning and photon echo techniques often do not yield the same apparent homogeneous linewidth due to the existence of spectral diffusion processes on a variety of time scales.[10,11] In polyethylene at 1.4 K, the hole width of 0.028 cm^{-1} shown in Figure 4, which is within 10% of the width extrapolated to zero burning fluence, corresponds to a homogeneous linewidth of 0.014 cm^{-1}, about an order of magnitude greater than the lifetime-limited width obtained from the fluorescence lifetime of 4.4 ns. Preliminary photon echo measurements give a decay time of about 700 ps with red-edge excitation, indicating some pure dephasing contribution to the homogeneous width but much less than that implied by the hole-burning experiment. The difference presumably signals spectral diffusion processes that act on time scales intermediate between the subnanosecond waiting time for the photon echo experiment and the >60 s needed to burn and read the holes in the cw hole-burning experiment.

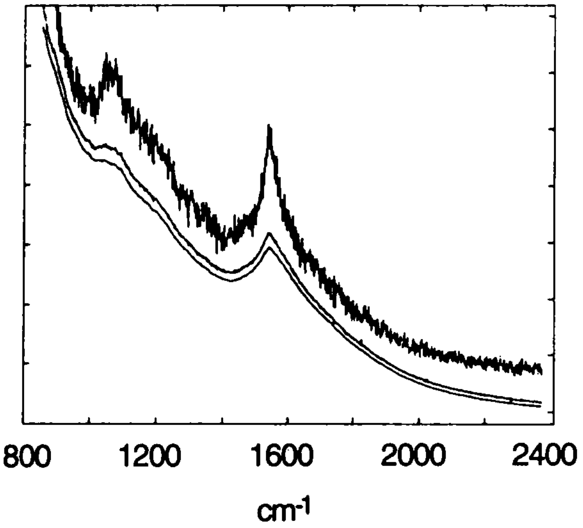

FIGURE 5 Saturation subtracted hole burning of **I** in polyethylene at 50 K. From bottom to top are shown a depleted (high pulse energy) fluorescence spectrum, a scaled low pulse energy spectrum, and their rescaled difference.

The rapid increase in spectral diffusion rate with increasing temperature typically makes hole burning very difficult to observe at temperatures above 20 K or so. The cw hole-burning subtracted fluorescence line narrowing technique loses its utility at elevated temperatures for the same reason, as the "initial" and "hole-burned" fluorescence spectra cease to be distinguishable. However, the saturation subtraction technique continues to work at higher temperatures due to the much shorter time over which spectral diffusion can act. The saturation subtracted fluorescence spectra demonstrate some line narrowing even at 50 K as shown in Figure 5, although the resulting line shapes depend somewhat on the choice of subtraction parameter. While the apparent widths of our line-narrowed fluorescence spectra at the lower temperatures are entirely instrument limited, above about 20 K they exhibit clear broadening with increasing temperature. If the part of the emission that remains after subtraction still represents the contribution from purely ZPL-excited molecules, these spectra may be interpreted as giving the temperature dependence of the electronic homogeneous linewidth on a subnanosecond time scale.

CONCLUSIONS

The subtracted fluorescence techniques described here are likely to find their greatest application in studies of the matrix and temperature dependences of Debye-Waller factors and phonon wing bandshapes. The combination of these and other experimental studies with appropriate theoretical modeling should lead to a better understanding of the coupling of "solvent" and intermolecular modes to electronic transitions of solutes which will be applicable to liquids and high-temperature glassy solids as well as cryogenic systems.

ACKNOWLEDGEMENTS

This work was supported by NSF grants CHE-9407966 (to A.M.) and CHE-9120001 (the Center for Photoinduced Charge Transfer). We thank Dr. Kock-Yee Law of Xerox Corp. for providing the squaraine samples.

REFERENCES

1. J.L. Skinner and W.E. Moerner, J. Phys. Chem., 100, 13251 (1996).
2. M. Orrit, J. Bernard and R.I. Personov, J. Phys. Chem., 97, 10256 (1993).
3. U. Bogner and R. Schwarz, Phys. Rev. B, B24, 2846 (1981).
4. J. Fünfschilling, D. Glatz and I. Zschokke-Gränacher, J. Lumin., 36, 85 (1986).
5. R. Jankowiak and G.J. Small, Chem. Res. Toxicol., 4, 256 (1991).
6. J. Wolf, K.-Y. Law and A.B. Myers, J. Phys. Chem., 100, 11870 (1996).
7. K.-Y. Law, J. Phys. Chem., 91, 5184 (1987).
8. D.L. Phillips, J.-M. Rodier and A.B. Myers, Chem. Phys., 175, 1 (1993).
9. J. Wolf and A.B. Myers, Macromolec. Symp., in press.
10. L.R. Narasimhan, K.A. Littau, D.W. Pack, Y.S. Bai, A. Elschner and M.D. Fayer, Chem. Rev., 90, 439 (1990).
11. S. Völker, Annu. Rev. Phys. Chem., 40, 499 (1989).