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SPECTRAL DYNAMICS OF INDIVIDUAL MOLECULES IN SOLIDS

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Abstract Optical spectroscopy experiments on individual chromophores in crystals and glasses are described, and theoretical approaches to understanding the experimental results involving spectral dynamics are discussed.

Optical spectroscopy of dilute chromophores has proven to provide a very useful probe of the structural and dynamical properties of both crystalline and amorphous solids. This is because the transition frequency for a vibronic transition of a chromophore is generally very sensitive to the positions of the nearby atoms, ions, or molecules of the solid.

A typical absorption experiment involves a very large number of individual chromophore molecules, and the absorption line shape in a low-temperature solid is usually inhomogeneously broadened. This means that the line shape simply reflects the distribution of possible transition frequencies for the many chromophores, which is due to a distribution of local environments. Thus in this case it is clear that one can learn something about the structure of the solid from an analysis of the inhomogeneous line shape.[1, 2, 3]

For inhomogeneously broadened line shapes it necessarily follows that no information about time-dependent fluctuations of the chromophore's transition frequency (which I will call spectral dynamics) can be obtained from the line shape itself. This does not mean that such dynamic fluctuations do not occur; it simply means that either their amplitude is much smaller than the inhomogeneous line width or that their time scale is much longer than the inverse of the inhomogeneous line width. In either case these dynamic fluctuations are of great interest because they result from time-dependent changes in the local environments of chromophores, and hence can provide information about solid-state dynamics.

The experimental techniques of fluorescence line narrowing and hole burning were invented, in part, to access this dynamic information. They each involve selective excitation by a narrow-band laser of a nearly resonant subset of chromophores. The resulting fluorescence line shape or hole shape reflects the spectral dynamics of the members of this subset, unobscured by the other chromophores. In a similar vein, in the time-domain photon echo experiment, after the application of a short pulse the inhomogeneous dephasing of all of the chromophores is then rephased by a second pulse, and so the echo decay again reflects only transition frequency fluctuations.

Consider first the case of (substitutional) chromophores in crystals. The above techniques have all been used to measure the chromophore's spectral dynamics,

which in this case are due to phonons. This situation is particularly simple because each chromophore molecule is influenced by the same kinds of phonons. Thus one says that these experiments measure the "homogeneous" line shape, implying that the inherent line shape of each chromophore due to its fluctuating transition frequency is the same. Furthermore, since the time scale for the fluctuations is much faster than the echo decay time (or the inverse of the hole or line width), the homogeneous line shape is always a motionally-narrowed Lorentzian.[4]

The situation of chromophores in glasses, which are much more disordered than crystals, is more complicated for two reasons. First of all, the mechanism for the chromophore's fluctuations is thought to involve two-level systems (TLSs)[5, 6] rather than phonons. These TLSs presumably are distributed randomly throughout the glass, and it follows that different chromophore molecules will have statistically different spectral dynamics. Therefore it does not necessarily make sense to talk about a "homogeneous" line shape for a chromophore in a glass, since the dynamics probed by each chromophore is inherently different. Secondly, there appears to be a very wide distribution of time scales for TLS dynamics in glasses, extending from ps to beyond ks. The most important consequence of this is that experiments that involve different experimental time scales, like photon echoes and hole burning, will give different results.[7]

Suppose that one could measure the absorption line shape of a single chromophore molecule. According to the above discussion, in a crystal each chromophore molecule is expected to have an identical (except for its center frequency) and reproducible Lorentzian "homogeneous" absorption line shape, reflecting the very fast phonon-induced fluctuations. In glasses, each molecule has a different environment of TLSs, and so each molecule should have a different line shape. By measuring the line shapes of many individual molecules one could access the distribution of spectral dynamical behaviors. Such a study can, in principle, provide more information than hole burning or echo experiments, which *average* over the spectral dynamics of many chromophores.

In fact, single molecule spectroscopy (SMS) experiments have recently become a reality. The first experiments were performed on pentacene (the chromophore) in p-terphenyl crystal.[8, 9, 10] I will focus here on the experiments of Ambrose, Basché, and Moerner,[9, 10] which involved repeated fluorescence excitation spectrum scans of the same chromophore. For each chromophore molecule they found an identical (except for its center frequency) Lorentzian line shape whose line width is determined by fast phonon-induced fluctuations (and by the excited state lifetime), as discussed above. However, for each of a number of different chromophore molecules Moerner and coworkers found that the chromophore's center frequency changed from scan to scan, reflecting spectral dynamics on the time scale of many seconds! The transition frequencies of each of the chromophores seemed to sample a nearly infinite number of possible values. Plotting the transition frequency as a function of time produces what has been called a "spectral diffusion trajectory" (although the frequency fluctuations are not necessarily "diffusive"). These fascinating and totally unexpected results signaled a new mechanism for spectral dynamics in crystals, which must result from very slow molecular dynamics. This behavior has been interpreted as arising from a set of special TLSs in p-terphenyl crystal.[11, 12] Let

me reiterate that because of their slow time scale these dynamics are not manifest in the usual (many-molecule) inhomogeneous absorption spectrum. More recent experiments on the chromophore terrylene (Tr) in hexadecane crystal (a Shpol'skii matrix) showed similar behavior.[13]

Similar spectral dynamics of individual chromophores from repeated fluorescence excitation scans have subsequently been seen in amorphous hosts, for the systems Tr in polyethylene (PE)[14] and tetra-t-butyl-terrylene (TBT) in polyisobutylene (PIB).[15, 16] In at least one instance[16] the chromophore samples far fewer frequencies than in the case of pentacene in p-terphenyl. The spectral diffusion trajectories are assumed to result from the flipping of those TLSs whose dynamics is slower than the scan time.

As mentioned earlier, the study of fluorescence excitation line shapes themselves can also provide a useful probe of the spectral dynamics of individual molecules in glasses. Unlike the case of pentacene in p-terphenyl crystal, where all molecules have the same line shape, individual chromophores in glasses do indeed have a variety of line shapes. This has been seen for perylene in PE, [17] Tr in PE,[18] Tr in polyvinylbutyral, polymethylmethacrylate, and polystyrene,[19] and for TBT in PE and PIB.[15, 16] The spectral broadening presumably is due to the flipping of those TLSs with dynamics faster than the scan time. There is a distribution of line shapes because, as noted earlier, different chromophore molecules are coupled to different sets of TLSs.

A third method for measuring spectral dynamics of individual molecules in glasses involves fluorescence intensity fluctuations during steady-state excitation at a fixed frequency.[20] This method has been applied to the systems of Tr in PE[18, 20] and TBT in PIB.[15, 16] In these experiments the fluorescence intensity fluctuates as the chromophore moves in and out of resonance because of coupling to flipping TLSs. Thus this very clever technique can provide a direct probe of TLS dynamics on all time scales.

It should be clear from the above that SMS presents a terrific opportunity to probe dynamics in both crystalline and amorphous solids at low temperatures. In order to provide a microscopic understanding of spectral dynamics and to analyze experimental results one needs theoretical models. The spectral dynamics in all of the experiments discussed above is assumed to arise from the coupling of the chromophore to one or more TLSs. Theoretical models for just this situation have been developed[21, 22, 23] and the application of these models to the various experiments described above have been discussed in some detail.[12, 23]

I believe that we are now entering a very fruitful period as far as using single molecule spectroscopy to probe molecular dynamics in solids. The spectral diffusion experiments on pentacene in p-terphenyl crystal were ground-breaking in that a new phenomenon was discovered. For this system we have learned a significant amount about molecular dynamics at domain walls and how that is probed by a chromophore. I think this system deserves further study because in this case we are able to identify the nature of the TLSs that appear to be responsible for spectral diffusion, which makes it easier to perform theoretical analysis and consequently to develop a full understanding. In this sense this system has served and will continue to serve as a very useful prototype for more disordered amorphous systems.

Extremely exciting experimental data for glasses are now beginning to emerge. It has been shown that line shape measurements, fluorescence intensity fluctuations, and spectral diffusion trajectories can all be used to probe TLS dynamics on different time scales. Furthermore, as has been emphasized already, these experiments on individual molecules will provide more information than more traditional echo and hole burning experiments that involve an average over the dynamical behavior of many chromophores. At this point what we as a community need is more data. In an ideal world all three of the above experiments would be performed on the same individual molecule at a variety of temperatures, and then would be repeated on many molecules, and all of the above would be repeated for several different systems. Although the basic theoretical apparatus is in place for analyzing these experiments, more refined theoretical results will probably be needed.

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