Inhomogeneous Broadening and Excited-Vibrational-State Lifetimes in Low-Temperature Organic Mixed Crystals

A. P. Marchetti

Eastman Kodak Research Laboratories, Rochester, New York 14650

and

W. C. McColgin* and J. H. Eberly*

Department of Physics and Astronomy, University of Rochester, Rochester, New York 14627

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We have determined the extent of residual inhomogeneous broadening in the "sharp" mixed-crystal spectrum of the large organic molecule pentacene; and we report a technique for the direct fluorescence measurement of excited-vibrational-state bandwidths. We have found the lifetime of the 267-cm^{-1} vibronic band in pentacene to be greater than 0.2 nsec.

Large organic molecules in solution have broad optical spectral lines[1] (200–2000 cm^{-1} wide). This is true even at liquid-helium temperatures where rotational and thermal effects are not important. The mixed-crystal technique[2] has long been used to provide much sharper ($\Delta\nu \sim 1-5$ cm^{-1}) molecular spectra for study. The mixed-crystal technique works by locating the subject molecules at identical lattice sites in an appropriate host crystal, thereby eliminating major environmental differences among the subject molecules and thus reducing so-called "inhomogeneous" broadening drastically.[3] Of course once inhomogeneous broadening is eliminated then the width of the sharpened lines can be used to estimate nonenvironmental or "homogeneous" broadening parameters such as the radiative and nonradiative lifetimes of molecular vibronic transitions. A "sharp" mixed-crystal spectrum of pentacene is shown in Fig. 1. The width of the sharp lines shown is about 3 cm^{-1}.

It is unlikely at low temperatures that lifetime broadening, either radiative or nonradiative, can ever account for linewidths of the order of 3 cm^{-1}, and evidence from atomic crystals[3] and Shpol'skii matrices[4] supports speculation[5] that much of the width of these sharp lines is still inhomogeneous. However, in the absence of experimental data the fraction of the width to be assigned to inhomogeneous effects has not been known, and it has not been possible to infer lifetimes from these widths.

In this note we report direct experimental answers to both of these questions. We have determined the extent of residual inhomogeneous broadening in the sharp mixed-crystal spectrum of pentacene; and we have devised a technique that allows the direct measurement of *excited-vi-brational-state nonradiative bandwidths*.

We have worked with the mixed-crystal system of pentacene in a paraterphenyl host crystal [(5 × 10^{-6} mole)/mole]. This mixed-crystal system fluoresces as if each guest pentacene molecule occupies one of four distinct lattice sites, each site giving rise to a system of sharp lines. These systems of lines have origins at the following wavelengths[6]: 5858.4 Å (O_1), 5899.0 Å (O_2), 5920.5 Å (O_3), and 5921.7 Å (O_4), as shown in Fig. 1. If it is accurate to speculate that these sharp lines are still inhomogeneously broadened, then we might speak of the site giving rise to the O_1 lines, for example, as being composed of a distribution of "microsites." The spectral lines of the microsites would be purely homogeneously broadened if they could be isolated.
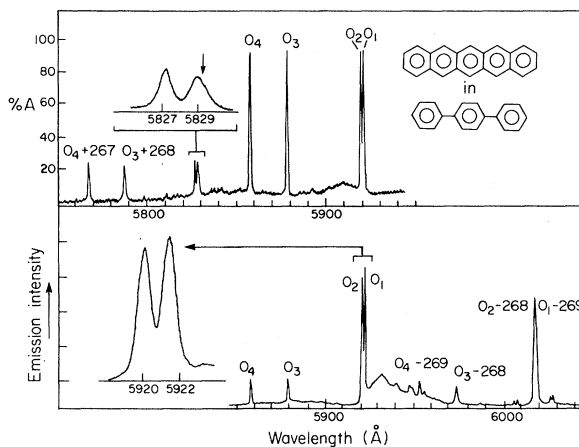

FIG. 1. The normal absorption and emission spectra of pentacene in paraterphenyl at 1.8°K in the region of the four site origins.

To the extent that the residual 3-cm^{-1} widths shown in Fig. 1 are due to inhomogeneous broadening, the microsite lines can be isolated by very-narrow-line laser excitation. If $\Delta\nu$ denotes the *homogeneous* bandwidth of a microsite, then those microsites within $\Delta\nu$ of the exciting laser frequency will be excited and subsequently fluoresce. This technique of optical site selection has been applied to non-mixed-crystal organic-molecular spectroscopy recently.[4,7-9]

In the present experiment, using mixed-crystal pentacene, the sample crystals were immersed in an optical Dewar in liquid helium which was pumped below the λ point to reduce light scattering. Excitation into the first excited vibrational level of the first excited electronic state of the site with origin O_1 (see arrow at 5829 Å in Fig. 1) was provided by a prism-tuned, cw jet-stream dye laser using rhodamine 110. The output of the dye laser was narrowed to about 450 MHz (~ 0.015 cm^{-1}) by using three intracavity etalons. Selection and detection of the 0-0 emission line from the lattice site with origin O_1 was accomplished using a $\frac{1}{2}$-m (Jarrel-Ash) monochromator-photomultiplier system in combination with a scanning Fabry-Perot interferometer.

Figure 2 shows that the optical site-selection technique is able to narrow the already sharp mixed-crystal O_1 line to 0.034 cm^{-1}, that is, by a factor of almost 100. This very large reduction in linewidth not only confirms speculation that even the sharp spectral lines of a single lattice site of mixed-crystal pentacene are almost entirely inhomogeneously broadened, but also shows that the underlying homogeneous line is
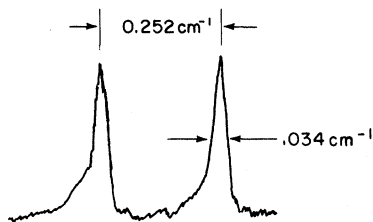
narrower than might reasonably have been expected. From the measured linewidth it is possible to conclude that the lifetime of the first vibrational state must be about 0.2 nsec or longer. Such a relatively long lifetime means that radiative decay can be an active relaxation mechanism. It suggests that in pentacene one might actually observe fluorescence directly from an excited vibrationl state.

In order to justify our conclusion about the vibrational-state lifetime, and to show that our site-selection method offers the general possibility of direct excited-vibrational-state linewidth measurements, it is convenient to refer to the energy-level diagrams in Fig. 3. Each of the sets of levels, labeled 1, 2, ..., 7, represents a different mixed-crystal molecule located at a slightly different microsite. This is the reason the 0*-0 transition frequencies are different. To a first approximation, however, the vibrational spacings 0*-1* are not expected to change from site to site. Levels 0* and 1* are shown with finite widths, indicating roughly their relaxation rates; and 1* is shown with the larger width $\Delta\nu_1$* because it has a rapid nonradiative channel to 0* available to it, while 0* must relax almost completely radiatively.

As shown in Fig. 3, laser irradiation into the 1* band will excite only those microsites whose

FIG. 2. The 0-0 emission from O_1 for pentacene in terphenyl at 1.7°K recorded with a scanning Fabry-Perot interferometer. The arrow in the upper inset of Fig. 1 shows the approximate wavelength of laser excitation into the O_1 267-cm^{-1} vibronic band. The interferometer's repeat interval is shown to be 0.252 cm^{-1}. The optical site-selection linewidth of the O_1 line is 0.034 cm^{-1}. The laser line used for excitation had a width of 0.015 cm^{-1}.
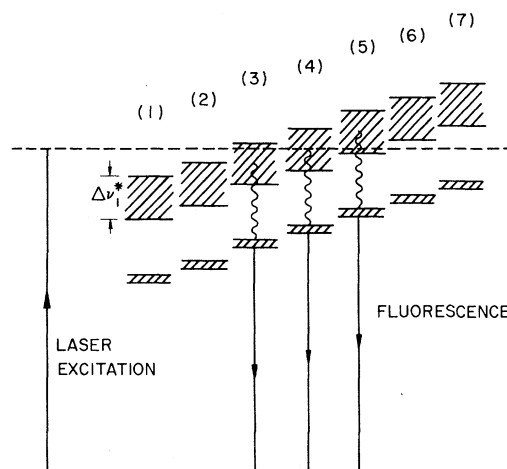

FIG. 3. Excitation and decay scheme used to interpret linewidth data. The 1* level is thought to be broadened by rapid nonradiative decay while the 0 and 0* levels are expected to be very narrow in comparison. The range of 0-0* transition frequencies reflects the presumed existence of a range of "microsites" associated with each type of lattice site in the mixed crystal.

0-1* transition lies within $\Delta\nu$ of the laser frequency. All of those molecules will decay rapidly and nonradiatively to their 0* levels. It is important to observe that these 0* levels will subsequently fluoresce into a band which also[10] has width $\Delta\nu_1{}^* + \Delta\nu_0{}^* \approx \Delta\nu_1{}^*$. Thus, simply by monitoring the 0*-0 fluorescence band, the width of the 1* vibrational level can be detected directly.

We expect, on the basis of our work with other molecules,[8,9] that our conclusions regarding pentacene mixed crystals have fairly general relevance. If this is the case, then the elimination of inhomogeneous broadening by use of optical site-selection spectroscopy will be generally possible, greatly facilitating studies of homogeneous effects such as electron-phonon interactions and vibrational anharmonicities in organic mixed-crystal systems. Even more important will be the immediate improvement possible in measured limits on radiative and nonradiative vibrational lifetimes in large molecules.

Finally we point out an interesting and unexplained distinction between these and earlier results, obtained for tetracene[8] and several other large organic molecules including pentacene.[9] In the previous measurements the subject molecules were in vitreous, not crystalline, hosts but held at liquid-helium temperatures in all cases. The sharpest of these lines, with inhomogeneous broadening removed by the optical site-selection technique, still were about 1 cm^{-1} wide.

In a vitreous host a subject molecule experiences a far greater broadening due simply to environmental irregularities than does a molecule in a crystal, but the limit of fluorescence line narrowing due to excitation by a very narrow-line laser should be the same in the two cases. That is, if the original line is an inhomogeneously broadened envelope of very narrow homogeneously broadened lines, then the homogeneous linewidth provides a lower limit on the extent of possible line narrowing, independent of the degree of inhomogeneous broadening in the original line. The discrepancy between the line-narrowing limit of 0.034 cm^{-1} reported here for mixed crystals, and the limit of about 1 cm^{-1} reported earlier for molecules in vitreous hosts, suggests that even at liquid-helium temperatures the vitreous hosts contribute an unexpected *homogeneous* component of width about 1 cm^{-1} to the subject molecules' total spectral width. It will be very interesting to have optical site-selection results for similar molecules in Shpol'skii matrices, hosts that are intermediate between glasses and crystals.[11]

[1]B. Meyer, *Low Temperature Spectroscopy* (American Elsevier, New York, 1971), pp. 52–56.

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[3]Unfortunately the mixed-crystal technique works relatively rarely for large organic molecules because of the great difficulties in finding suitable crystalline hosts. Ionic atomic mixed crystals are common, of course, and studies of low-temperature, sharp lines with inhomogeneous widths ~1 cm^{-1} are by now well known [for an early example, see A. L. Schawlow, J. Appl. Phys., Suppl. 33, 395 (1962)]. Photon-echo work [see N. A. Kurnit *et al.*, in *Physics of Quantum Electronics*, edited by P. L. Kelley *et al.* (McGraw-Hill, New York, 1966), p. 267] provided the first experimental access to underlying homogeneous widths. More recent work, using direct narrow-line laser excitation is due to A. Szabo, Phys. Rev. Lett. 25, 924 (1970), and 27, 323 (1971).

[4]A preliminary investigation of residual inhomogeneous broadening in molecular Shpol'skii spectra has recently been reported: I. Abram, R. A. Auerbach, R. R. Birge, B. E. Kohler, and J. M. Stevenson, J. Chem. Phys. 61, 3857 (1974).

[5]See, for example, D. B. Fitchen, in *Physics of Color Centers*, edited by W. B. Fowler (Academic, New York, 1968), p. 309; K. K. Rebane, *Impurity Spectra of Solids* (Plenum, New York, 1970), pp. 141–145; J. L. Richards and S. A. Rice, J. Chem. Phys. 54, 2014 (1971); and, more recently, R. M. Hochstrasser and P. N. Prasad, in *Excited States*, edited by E. C. Lim (Academic, New York, 1974), Vol. 1, pp. 114 and 119.

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[9]W. C. McColgin, Ph. D. dissertation, Department of Physics and Astronomy, University of Rochester, 1975 (unpublished).

[10]The width of the fluorescence band will be the same as the width $\Delta\nu_1{}^*$ only if there is perfect site coherence during the nonradiative 1*-0* decay. If there is not, the observed fluorescence width may be larger than $\Delta\nu_1{}^*$ because of spectral diffusion, due for example to

excitation-exchange scattering among the sites during the nonradiative process. Thus, in the present case, our measurement also puts a limit of about 0.2 nsec on the time for spectral diffusion in low-temperature pentacene.

[11]Unfortunately, the Shpol'skii-matrix measurements reported by Kohler *et al*. (see Ref. 4), were instrument-limited, with resolution on the order of 0.4 cm^{-1}, not narrow enough to pin down the residual homogeneous width of the lines measured.

Detection of Optical Surface Guided Modes in Thin Graphite Films by High-Energy Electron Scattering*

C. H. Chen and J. Silcox†
School of Applied and Engineering Physics, Cornell University, Ithaca, New York 14853
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High-angular-resolution ($\sim 8 \times 10^{-6}$ rad), high-energy (75 keV), electron scattering from graphite thin films demonstrates energy losses due to the excitation of optical surface guided modes. Measurements of the dispersion offer considerable support for the aniso-tropic dielectric constant proposed by Tosatti and Bassani.

In this Letter, we report the observation for the first time of peaks in characteristic electron energy-loss spectra which can be clearly identified with the excitation of guided surface waves in a thin-film specimen. Such waves can most readily be visualized as electromagnetic waves propagating in the thin film in a wave-guide fashion. These excitations are contained within the usual surface-plasmon formalism[1] and become significant at long wavelengths in thin films of materials in energy regimes where the dielectric constant is greater than unity. Thus in the neighborhood of a strong absorption edge, the surface excitations above the edge are of surface-plasmon nature [provided the dielectric constant becomes sufficiently negative, i.e. $\epsilon(\omega) < -1$], whereas below the edge they become guided surface waves. In the infrared, in materials where a strong absorption edge arises as a result of surface-phonon effects, the equivalent excitation to the surface plasmon at that edge is the surface polariton, whereas the guided-mode equivalent has been identified as a wavelike "bulk" mode.[2] In the present case we are concerned with a situation in which the basic physical cause of the absorption edge is a normal interband transition. However as the system in question, graphite, is anisotropic some complexities are introduced into this simple picture.

Specifically, we report high-angular-resolution, energy-loss data as a function of scattering angle θ for a specimen of graphite, 75 nm thick, tilted so that the c axis (normal to the specimen plane) makes an angle of 60° with the incident beam. We demonstrate the existence of three surface modes

in the energy range between 4 and 11 eV at the smallest scattering angles. At large angles a single peak corresponding to a volume excitation is observed. In between, the volume and surface terms in the scattering probability cancel each other—a corresponding gap is seen in the excitation spectrum. The volume peak occurs precisely at the point where disagreement arises between the electron energy-loss measurements of Zeppenfeld[3] and the optical observations of Willis, Feuerbacher, and Fitton[4] using photoemission and secondary-electron emission and Klucker, Skibowski, and Steinmann[5] using reflectivity measurements with synchrotron radiation. The observations reported here resolve that discrepancy and offer evidence in favor of the dielectric constants proposed by Tosatti and Bassani.[6] The interpretation demonstrates the necessity for a complete calculation of the energy-loss probabilities including both anisotropic dielectric constants and retardation.

The apparatus and techniques have been described previously.[7,8] Briefly a Hitachi HU11A electron microscope is used to provide a 75-keV electron beam parallel to 8×10^{-6} rad incident on the specimen while lenses after the specimen are adjusted to provide a long effective camera length (~ 25 m). A Wien electron spectrometer mounted underneath the electron microscope provides the energy analysis with an energy resolution ~ 0.5 eV. The entrance slit to the spectrometer is placed over the central electron beam and allows the passage of electrons scattered at different angles to the incident beam. The spectrometer deflects electrons in a direction perpendicular to