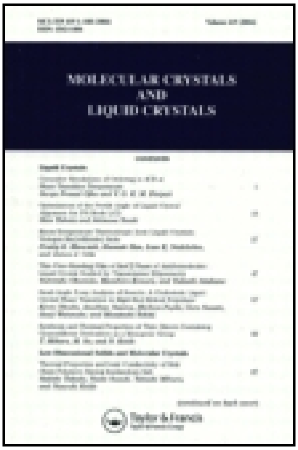

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Spectroscopy of Organic Crystal Surfaces

J. M. Turlet [a] & M. R. Philpott [b]
[a] Laboratoire d'Optique Moleculaire, Université de Bordeaux l, 33405, Talence, France
[b] IBM Research Laboratory, Monterey and Cottle Roads, San Jose, California, 95193, U.S.A.

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Spectroscopy of Organic Crystal Surfaces

J.-M. TURLET†
Laboratoire d'Optique Moleculaire, Université de Bordeaux I, 33405—Talence, France

M. R. PHILPOTT
IBM Research Laboratory, Monterey and Cottle Roads, San Jose, California 95193, U.S.A.

In the vicinity of the 4000 Å singlet transition of anthracene crystals the reflection spectrum off the (001) face consists of a series of bands corresponding to transitions from the ground level to vibronic levels of the excited electronic state. At temperatures below 20°K the b-polarized reflection band of the O—O transition contains anomalous structure consisting of several narrow reflectivity minima within the region of high reflectivity.[2] The energy interval spanned by this "stop band" is nearly 300 cm^{-1}, see spectrum 1 of Figure 1. Until the recent observation of similar minima in the O—O_b reflection band of the first singlet transition in tetracene crystals,[3] these structures had no counterpart in the spectra of transitions of similar intensity in any other organic solid. According to the theory of surface exciton states[4,5] a transition to a surface level lying within the energy range spanned by the reflection band of the bulk crystal transition (the so-called stop band) creates a narrow minimum or antiresonance by an interference mechanism. Outside the stop band a surface transition is observable as a peak in the reflection spectrum.

Obviously any electronic phenomenon associated with molecules in the crystal surface should be very sensitive to perturbations of the surface region. In this note we describe changes observed in reflection spectra recorded at 2°K resulting from the deposit of solidified gas layers on the (001) surface at temperatures between 5 and 20°K. Comparison of spectra from the same crystal shows shifts only for the minima, thereby revealing that portion of

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† IBM Postdoctoral Fellow 1974–75.

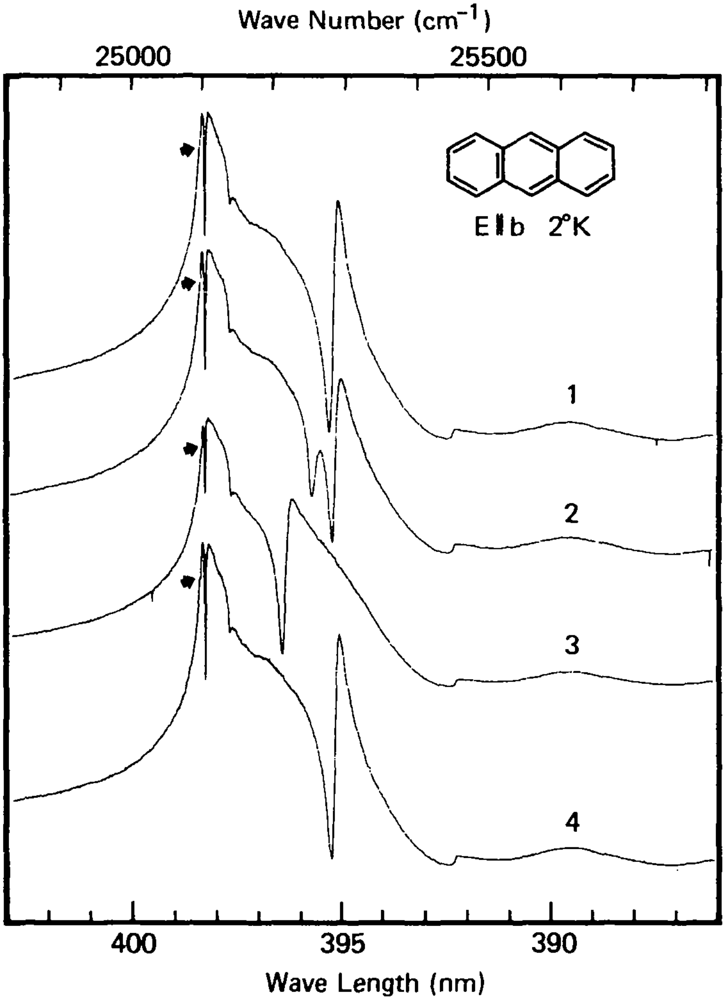

FIGURE 1

the spectrum generated by processes in the bulk crystal and that portion due to surface phenomena. The gases used in the experiments were air, CH_4, C_2H_4, Ar, Kr, Xe, N_2 and O_2. We made the most detailed study for solidified air since this is the most likely contaminant on the surface of a sample in a low temperature reflection or fluorescence experiment.

Spectrum 1 (top) of Figure 1 is the *b*-polarized reflection spectrum of a cleaved crystal before coating the surface with a transparent layer of solidified air. The minima attributed to surface transitions are located at ca. 3954 Å (I) and ca. 3984 Å (II). The arrows in all spectra show the location of a minimum (III) that has not been observed previously, at ca. 3985 Å on the long wavelength edge of the stop band.

Spectra 2 and 3 in the figure show the effect of solidified air on the reflection spectrum. Similar spectra were obtained when N_2 and O_2 were used separately. The formation of the satellite minimum at 5 Å to the red of minimum I in spectrum 2 was also observed after a first exposure of (001) to other gases. Spectrum 3 was obtained after exposing the crystal to more gas. Further exposures to gas did not bring about any further shift of minimum I, thereby implying that the surface had been saturated. The shift in minimum I between 1 and 3 is approximately 11 Å (60–70 cm^{-1}). The shift of minimum II was very small, less than 0.5 Å. The other gases used in our experiments also shifted minimum I by approximately 11 Å except CH_4 which gave a shift of 15 Å. To remove the solidified air deposit the crystal was allowed to warm slowly to temperatures in excess of 100°K in a steady stream of He gas. Then after cooling the sample back to 2°K the spectrum 4, which is almost identical to spectrum 1, was obtained.

The large shift of minimum I implies an association with an excitation close enough to the surface to be perturbed by the deposit. The barely detectable shift of minimum II suggests it corresponds to an exciton lying deeper where molecular properties are intermediate between the surface and bulk crystal regions. Since only the minima are shifted the rest of the reflection band is a property of the bulk crystal. In particular the chimney-like structure between 3985 and 3975 Å, the region of highest reflectivity containing minimum II, is not affected by transparent surface layers. We conclude therefore that the sharp drop in reflectivity terminating in the small minimum at 3978 Å is due to some relaxation process in the bulk region of the crystal.

Irradiation of crystals immersed in liquid He with radiation from an Hg lamp did not cause any change or loss in fine structure in the region 4000 to 3950 Å. In other experiments, crystals known to have the spectrum 1 in Figure 2 were irradiated in air with an Hg lamp for short periods at 300°K. Irradiation for periods less than one minute partially destroyed minima I and II and also caused the overall loss in reflectivity visible in spectrum 2 of Figure 2. Irradiation for periods longer than one minute completely destroyed all the fine structure. These observations indicate that disruption of the surface by photo-oxidation affects the surface and subsurface transitions most, leaving the spectrum of the bulk crystal transition relatively undisturbed.

Finally we conclude by noting that the observations reported here imply that the sensitivity of surface states to thin overcoatings can be utilized to differentiate surface from bulk phenomena in other crystals, and to probe structural and chemical changes in films in contact with organic solid surfaces.

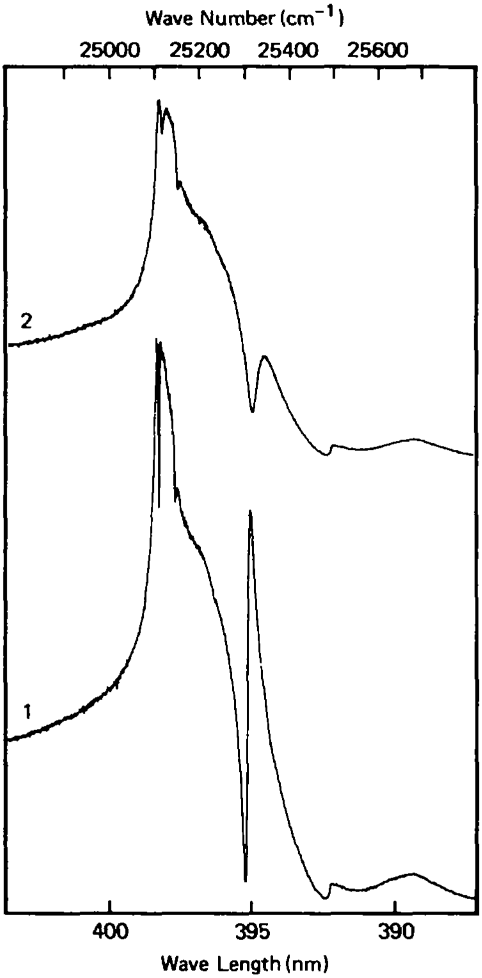

FIGURE 2

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