MONOLAYER SURFACE RAMAN AND FLUORESCENCE SPECTROSCOPY OF THE ANTHRACENE CRYSTAL

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Résumé : L'observation du spectre d'excitation de la fluorescence de l'exciton de surface d'un cristal d'anthracène non recouvert et recouvert d'un film d'azote, nous a permis de mettre en évidence un mode de phonon de surface d'énergie plus basse que le mode correspondant dans le volume. La forme de raie de cette structure et son comportement lorsque la surface est recouverte, sont analysés en termes de diffusion Raman résonnante de surface, de relaxations intra-surface et vers le volume et de couplage entre la surface d'anthracène et le film déposé.

Abstract : We report evidence for of a surface lattice phonon with lower energy than its bulk counterpart, by observation of the excitation spectrum of surface exciton fluorescence for uncoated and N_2-coated anthracene crystal (001) face. The line-shape of this surface structure and its behaviour on surface coating are analysed in terms of surface resonant Raman scattering, intrasurface and surface-to-bulk relaxation processes and coupling between the anthracene surface and the N_2 film.

I - INTRODUCTION.

Organic molecular crystals with bulk electronic excitons of the Frenkel type, may present also monolayer surface and sub-surface collective excitations (Site Shift Surface Excitons) due to the specific environment (lacking or different van der Waals interactions) seen by surface molecules. Their existence on a particular face of the crystal, is simply related to the dominant intraplane character of the excitation energy exchange sum $I(\vec{k})$, for a wave-vector direction normal to this face. At the opposite of Surface Polaritons, that are non-radiative evanescent modes extending one wave length deep into the crystal (macroscopic surface), Surface Excitons are radiative bidimensional Frenkel excitons, localized essentially on the first few monomolecular layers of the crystal {1}.

In the anthracene crystal, organized as a stack of $(\vec{a},\vec{b})$ planes very weakly coupled by coulombic dipolar interactions, such surface and sub-surface exciton resonances have been observed for the first singlet-singlet transition ($\sim$25000 cm^{-1}){2}. As the exciton-photon coupling is quite strong for this transition and correlatively the light penetration into the crystal very shallow, the polariton dispersion behavior leads, at low temperature, to a high and broad bulk reflectivity of the (001) face, on which surface exciton resonances appear as interference figures. (See I, II and III on the upper spectrum on Fig. 1). The surface origin of these structures, that do not appear in the reflectivity spectra of the other crystal faces, has been unambiguously established by observing their reversible low energy shift upon coating of the crystal surface with a transparent layer of frozen gas {2}.

Due to their bi-dimensional character, surface excitons coupled to the radiation field, have a high radiative unstability ($\tau \sim$ picosecond) that overcomes intrasurface and surface-to-bulk non radiative relaxation processes {3}. This accounts for the very weak fluorescence lines I and II (see lower spectrum on Fig. 1) observed on the high energy side (+ 207 cm^{-1} and + 6 cm^{-1}) of the bulk fluorescence origin (E^{oo}_{vb} = 25093 cm^{-1}), at the same energy as surface reflectivity structures, and exhibiting the same behavior upon surface coating {4}. Line I (E^{oo}_{sb} = 25300 cm^{-1}), interpreted as the collective emission from the lowest Davydov component of surface
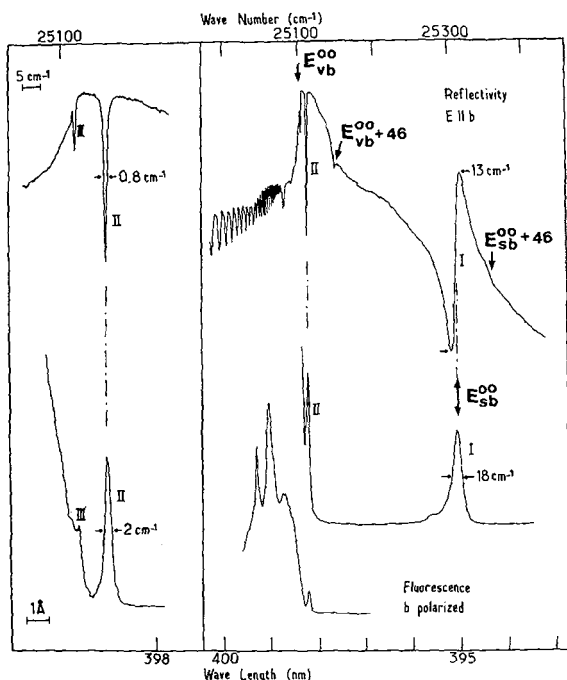
*(L.A. 283 du C.N.R.S.)

Fig. 1 - Reflectivity and fluorescence spectra of the (001) face of a sublimation grown anthracene monocrystal at 1.7 K.

exciton on the first monomolecular layer, is of particular interest for surface study, since it is 200 cm^{-1} far apart from any bulk emission.

We took advantage of this last point to investigate the vibration modes of surface molecules for uncoated (helium-anthracene interface) and coated (frozen nitrogen-anthracene interface) crystal (001) face, using a technique combining excitation spectra of the surface emission (line I) with gas condensation experiment. It allowed us to unveil very weak surface structures from the bulk vibronic background, while practically no surface information may be extracted from the reflectivity spectrum of the vibronic region, where numerous broad and intense bulk modes overlap. The general theory of the exciton-vibration coupling, leading in the anthracene crystal to mixed vibron and two-particle states, as well as the experimental results concerning the dominant 1400 cm^{-1} and 390 cm^{-1} intramolecular anthracene modes, have been discussed elsewhere {5,6}. We present here, for the first time to our knowledge, the experimental evidence of a surface lattice phonon mode on an organic molecular crystal, and analyse the line shape of the surface structures in terms of specific relaxation dynamics of the surface excitation.

II - EXPERIMENTAL RESULTS.

All surface experiments have been done with sublimation-grown monocrystals((001) plates, a few microns thick), starting from extensively zone refined anthracene. More experimental details, as well as the description of the technique used to condense gas on the surface, may be found in {1,2,5} and in the references therein. Bulk Raman experiment was performed at 5K on a melt grown sample (2 mm thick), using the 4579.39 Å Ar$^+$ line of a 171 Spectra Physics laser, normally incident on the (001) face and a U 1000 Jobin Yvon double monochromator to detect the 90° scattered beam.

At low temperature (1.7K), the $\vec{b}$ polarized reflectivity spectrum (upper spectrum on Fig. 1) exhibits at the energy E_{vb}^{oo} + 46 = 25138 cm^{-1}, the neat dip already ascribed {2} to the bulk phonon sideband involving the 49 cm^{-1} Ag lattice phonon mode observed in Raman spectroscopy {7}. On the same spectrum, with careful attention, one may observe at about E_{sb}^{oo} + 46 ≃ 25342 cm^{-1}, a slope discontinuity that might be the surface counterpart of the bulk phonon sideband mentionned above. However no de-
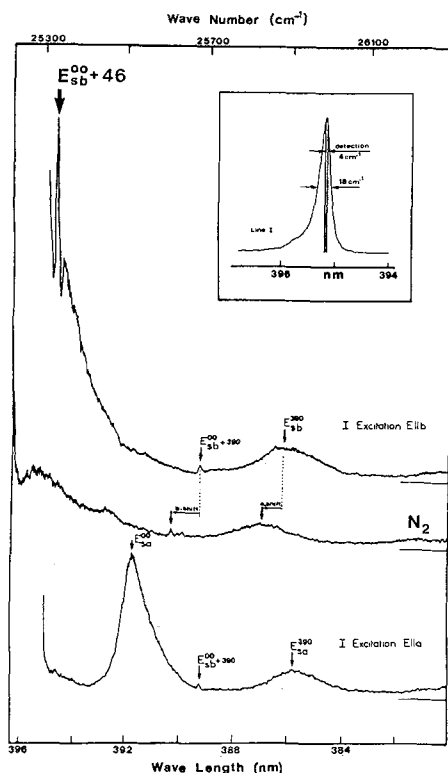
Wave Number (cm⁻¹)

Fig. 2 - Excitation spectra of the surface emission (line I) of the (001) face of a sublimation-grown anthracene monocrystal at 4.2 K : for E//b and uncoated crystal surface (upper spectrum); for E//b and N_2 coated crystal surface (middle spectrum); for E//a and uncoated crystal surface.
    The schematic profile of the b polarized structure, with the three regions A, B, and C, is represented above.

finite information can be extracted from a so diffuse structure.

The $\vec{b}$ polarized excitation spectrum (upper spectrum on Fig. 2) of the surface emission (line I), presents, at the opposite of the reflectivity spectrum, a very intense and sharp peak (A) at the energy $E_{sb}^{oo} + 46 = 25344.3 \pm 0,5$ cm⁻¹, followed on the high energy side, by a dip (B) and a broad band (C). We can note already (see the inset on Fig. 2) that its bandwidth (7.2 cm⁻¹), corresponding roughly to the excitation plus detection bandwidths, is much thinner than the excited band (18 cm⁻¹). Upon surface coating with frozen nitrogen, the peak (A) is drastically affected and changes to a broad band, shifted to lower energies (middle spectrum on Fig. 2) roughly like the $\vec{b}$ polarized emission E_{sb}^{oo}.

III - DISCUSSION.

Obviously, the location, the shape and the behavior upon surface coating of the structure $E^{oo} + 46$ described above, permit to assign it to the "46 cm⁻¹" (more exactly 45.1 ± 1.0 cm⁻¹) Ag lattice phonon sideband associated with the surface exciton E_{sb}^{oo}. From a general view point, covering the pure electronic and vibronic region, this last result once again confirms the overall translational equivalence ($\delta \sim 200$cm⁻¹) of surface states with bulk states. However several particularities exist in the shape, the energy value and the surface coating behavior of the surface phonon structure and must be now analysed in order to find the specificity of surface molecules.

The shape of the structure $E_{sb}^{oo} + 46$ in the excitation spectrum of the surface emission (line I), differs greatly from the stepwise shape expected for a two particle absorption edge (see bulk reflectivity for instance). According to the model we proposed recently {6}, this result reflects a strong energy dependence of the relaxation inside the surface excitonic band : the peak (A) originates from the direct re-

laxation of the exciting photon (E_{sb}^{oo} + 46) into a surface 46 cm^{-1} phonon and a Raman scattered photon in resonance with the surface radiant state E^{oo} ; this is basically a Surface Resonant Raman Scattering process. The broad band (C_{sb}^{b} arises from creation of a $E_{sb}^{k\neq o}$ surface exciton and a 46 cm^{-1} surface phonon, followed by intrasurface relaxation to the surface radiant (k=o) state E_{sb}^{oo}, while the dip (B) reveal a quenching of this intrasurface process by any other non-radiative channel as for instance surface to bulk relaxation.

According to this assignment of the peak A as a Raman line, the surface phonon frequency that we quoted (45.1 ± 1.0 cm^{-1}) must be compared with its bulk counterpart equally deduced from Ramam spectroscopy. In order to improve the accuracy of the last reported value {7} , we recorded the bulk Ramam spectrum of anthracene at 5K and found 49.35 ± 0,1 cm^{-1} for the symmetric mode Ag and 56.97 ± 0,1 cm^{-1} for the antisymmetric mode Bg corresponding to the vibration mainly around the normal molecular axis. This significant lowering of the vibrational energy of the molecules on the crystal surface, due to a lack of van der Waals interactions, is the evidence of a possible reconstruction of the surface monolayer, as it was already suggested by dispersion analysis of the surface exciton.{5,6}

Finally, upon N_2 coating of the crystal surface, we observed a drastic perturbation (broadening and shift to lower energies) of the sharp surface phonon structure that may reflect either an inhomogeneous broadening due to the different local environment created by the frozen N_2 layer, or an homogeneous broadening of the anthracene surface phonon through it coupling to the acousto-optical phonons of α $-N_2$ in the 50 cm^{-1} region.

IV - CONCLUSION.

In this study, observation of surface emission excitation spectrum jointly with surface coating experiment, has proved a very sensitive technique to unveil very weak surface structures from an intense bulk background. No doubt that this nondestructive method of surface study may bring informations of great value on the organization of the crystal molecules on the first few monomolecular layers, as well as on the structure and the coupling of films deposited on the surface.

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