

least one of the possible vibrationally relaxed S_1 states of acyclic 1,3 dienes and lends further support to the doubly twisted (bicyclobutane-like) conformation on the basis of which one predicts that a 1,5 antarafacial shift is possible for either a *cis-s-trans* or a *trans-s-cis* configuration, independently of the faster shift taking place prior to relaxation in *cis-s-cis* conformers. This prediction was tested in irradiating the methyl d_3 *cis*-penta-1,3-diene in which the migration of deuterium could be significantly reduced to the benefit of other processes: we found indeed that Φ (3-methylcyclobutene) increases by a factor of 2.8 rela-

tive to the non-deuteriated molecule.

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T2

Photophysics of Organic Crystal Surfaces

M. R. PHILPOTT

IBM Research Laboratory, Monterey and Cottle Roads, San Jose, Calif. 95193 (U.S.A.)

J.-M. TURLET

Laboratoire d'Optique Moleculaire, Université de Bordeaux I, 33405-Talence (France)

Surface, subsurface and bulk exciton transitions have been observed in aromatic hydrocarbon crystals by means of low temperature (2 K) reflection spectroscopy. Because of their sensitivity to surface conditions, deposited films etc., the surface exciton transitions act as probes of physical and chemical processes occurring near the surface. This has been demonstrated by observing the effects of photo-oxidation and condensed gas films on the b-polarized reflection spectrum of the 4000 Å transition of anthracene. Figure 1 shows the shift in the main surface transition caused by a thin film of gas condensed on the (001) face at temperatures below 20 K. Condensed films of N_2 , O_2 , Ar, Kr and Xe shift the surface of 100 cm^{-1} to lower energies. Methane films gave a shift of 100 cm^{-1} . Figure 2 demonstrates that disruption of the crystal surface by photo-oxidation obliterates the fine structure in the low temperature spectrum due to surface and surface transitions. Spectrum 1 was

recorded before and spectrum 2 after photo-oxidation of the (001) face of an anthracene crystal.

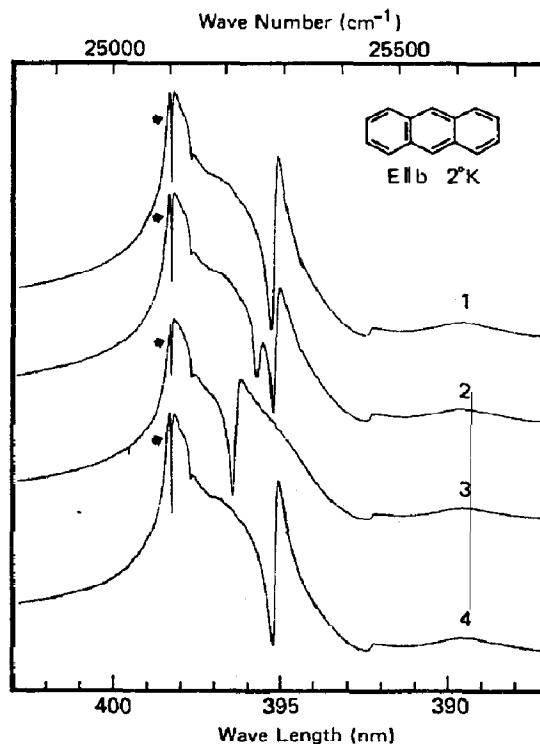


Figure 1. Reflection spectra of crystals with a solid air coating.

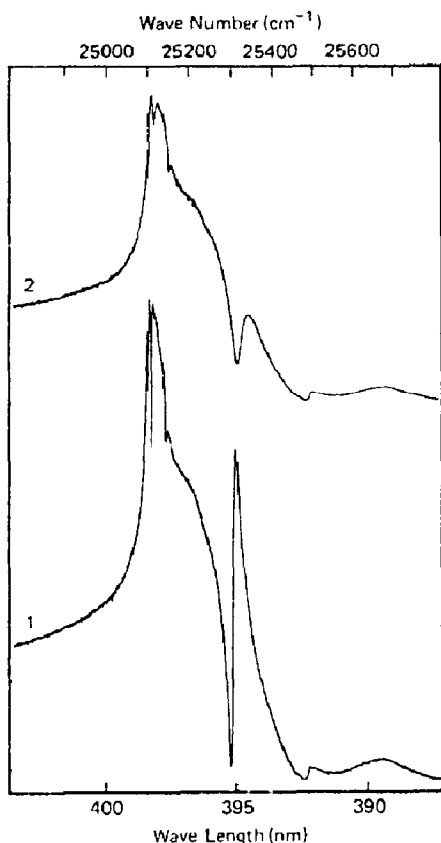


Figure 2. Reflection spectra of anthracene crystal before (1) and after (2) photo-oxidation.

T6

Vibrational Relaxation in Condensed Media

S. H. LIN, H. P. LIN and D. KNITTEL
Department of Chemistry, Arizona State University, Tempe, Az. 85281 (U.S.A.)

A master equation approach has been developed to describe the vibrational relaxation and a model for calculating the rate constant of vibrational relaxation in condensed media based on the assumption that the short-range repulsive portion of the intermolecular force is responsible for inducing the vibrational relaxation has been presented [1, 2].

In this investigation, we are concerned with the temperature effect on vibrational relaxation and the vibrational energy transfer from the vibrationally excited donor to the acceptor. For the temper-

ature effect, we present numerical results to show the temperature dependence of the rate constant of vibrational relaxation and to discuss the validity of the rate constants obtained from the use of the weak coupling approximation and the strong coupling approximation. It is shown that although the temperature effect is extremely large over the temperature range $T = 0$ to $T = \theta_E$, the Einstein temperature of the medium, for the temperature range $T = 0$ to $T = 0.3 \theta_E$, the rate constant varies slowly with temperature.

For the vibrational energy transfer, we derive the master equation to describe the time dependent behavior of the excited donor, and the expression for the rate constant of vibrational energy transfer. The master equation is solved to study the temporal behavior of the excited donor as a function of the acceptor concentration. Numerical results are presented to demonstrate the theoretical results.

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T8

C_2^- Molecular Ion: Long Range Electron Tunnelling and $B^2 \Sigma_u^+ \leftrightarrow a^4 \Sigma_u^-$ Intersystem Crossing in Rare Gas Lattices

V. E. BONDYBEY

Bell Laboratories, Murray Hill, N.J. 07974 (U.S.A.)

The $B^2 \Sigma_u^+$ fluorescence of C_2^- displays an extreme Personov effect — narrowing in emission of an inhomogeneously broadened absorption spectra excited by monochromatic light. The temperature dependent single site emission spectra are consistent with Rebane impurity spectra theory and quadratic electron-phonon coupling. C_2^- appears to be a substitutional guest in Ar, Kr, and Xe, and to displace two or more atoms in Ne. The principal vibrational relaxation pathway within the B state involves sequential steps through two vibrational levels of the previously predicted (yet unobserved)