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ANDERSON TRANSITION IN VIBRONIC EXCITON BANDS OF ISOTOPICALLY MIXED NAPHTHALENE CRYSTALS

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The exciton spectroscopic evidence is presented for the Anderson transition in the vibronic exciton bands of isotopically mixed naphthalene crystals. The sharp reflection spectra of the vibron state are utilized as a microscopic probe to detect the change of the background exciton band from localized to extended character. The experimental critical concentration is in fairly good agreement with the prediction by Economou and Cohen.

I. Introduction

A number of theoretical studies have been devoted to deal with the fundamental aspects of the Anderson transition, such as the critical disorder for the transition, theoretical criterion for the Anderson localization, and so on. However, there has been little experimental information as yet which allows us to make quantitative examination of existing theories. The purpose of this paper is to present the first exciton spectroscopic evidence for the Anderson transition in the vibronic exciton bands of isotopically mixed naphthalene crystals.

II. Experimental

Samples of mixed crystals of normal naphthalene ($C_{10}H_8$, abbreviated hereafter as N-h_8) and deuterated naphthalene ($C_{10}D_8$, N-d_8) were prepared by sublimation of the respective components subjected to zone refinement procedure. The samples were thin flaky single crystals, having shiny *ab* planes as natural surfaces. The reflection spectra were measured at 2K by immersing the sample in pumped liquid helium.

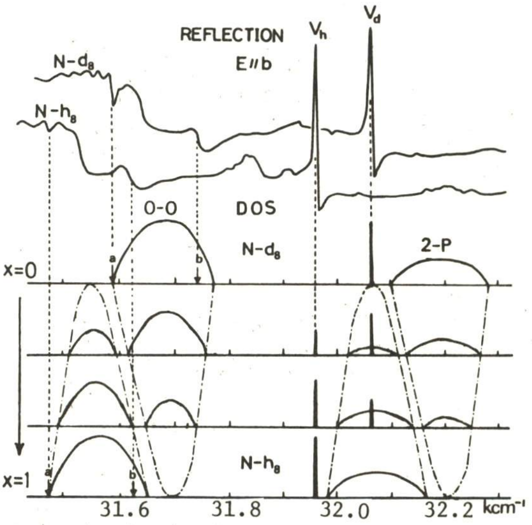
III. Experimental Results on Vibronic Excitons in $(\text{N-}h_8)_x(\text{N-}d_8)_{1-x}$

The first vibronic exciton in naphthalene crystals consists of the one-particle (vibron) and two-particle (2-P) states, both associated with the $^1B_{3u}$ molecular excitation and the non-totally symmetric intramolecular vibration B_{1g} [1]. The 0-0 and the first 0-1 vibronic exciton spectra of pure N-h_8 and N-d_8 crystals are shown in Fig.1 (upper). The two spectra show similar features except an isotopic energy shift of about 115 cm^{-1} (14.3 meV). As the oscillator strength of this exciton is considerably small ($f \lesssim 10^{-3}$), the 0-0 excitons do not show up as prominent reflection anomalies. Weak structures, denoted a and b, correspond to the Davydov components of the respective excitons. Quite sharp reflection peaks, V_h and V_d, are due to the vibron state, an exciton-intramolecular phonon complex formed by the quadratic exciton-phonon interaction [2,3]. Because of small dispersion of the intramolecular phonon, these vibron states are almost localized either on an N-h_8 or an N-d_8 molecule. In pure naphthalene crystals, these vibron spectra are quite sharp, the half width being less than 6 cm^{-1}. On the other hand, in the 2-P state, the exciton and the intramolecular phonon are in an independent motion. As the k=0 components are distributed over the whole band, there is no observable reflection anomaly in this energy region.

In the lower part of Fig.1, we show the schematic profile of the density of states (DOS) curves of the mixed crystals. The exciton band width in pure crystals is about 185 cm^{-1}(22.9 meV) [4], which is predominantly due to the octapole-octapole interaction between the excited molecules. In the mixed crystals, these excitons show the persistent (two-mode type) behaviour [5]. The DOS's of the vibron states are represented by sharp spikes on the lower energy side of the corresponding 2-P bands. Note that the higher vibron state V_d is located just at the center of the lower branch of the 2-P bands in the mixed crystals. From existing data [1], energy of the lower 2-P state at $x \simeq 0$ is within 12 cm^{-1} from energy of V_d.

The reflection spectra of these vibron transitions in mixed naphthalene crystals are shown in Fig.2. Sharp reflection anomalies, V_h and V_d, in both end crystals persist to exist as doublet structures in mixed crystals. Their spectral shapes are much alike in pure crystals. It should be noted, however, that there is a remarkable difference in the behaviours of the two spectra in mixed crystals: As for the lower component V_h, the spectra are weakened as x decreases, but the spectra for the higher component V_d are significantly broadened for $x>0.2$, and becomes hardly discernible for $x>0.4$. (Weak structure denoted SE is of different origin.)

In order to derive quantitative information from these results, we made spectral shape analysis by assuming a model dielectric function for the respective vibron transitions, in form of



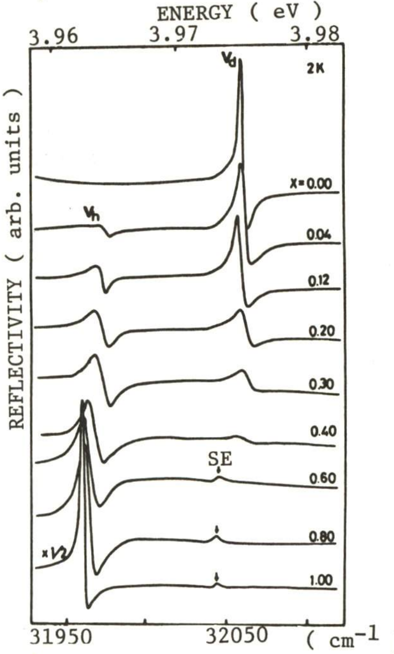


Fig.1 (left): Reflection spectra (upper) and the density of states (lower) of $(N\text{-}h_8)_x(N\text{-}d_8)_{1-x}$

Fig.2 (right): Reflection spectra of vibrons in $(N\text{-}h_8)_x(N\text{-}d_8)_{1-x}$

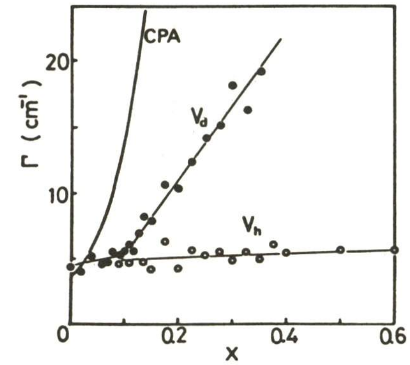


Fig.3 **Damping constants for vibrons in** $(N\text{-}h_8)_x(N\text{-}d_8)_{1-x}$

$$\varepsilon(E) = \varepsilon_\infty + \frac{A_i(x)}{E_{Vi}^2 - E[E + i\Gamma_i(E)]} \;. \qquad (1)$$

Here, ε_∞ is the background dielectric constant, E_{Vi} (i=h or d) is the resonant energy of V_h or V_d, $\Gamma_i(x)$ and $A_i(x)$ are the damping constant and polarizability, respectively, of the corresponding vibron transition. The phenomenological damping constants $\Gamma_i(x)$ obtained from the best fit of the experimental and calculated spectra are plotted in Fig.3 against x. The points for Γ_h are almost equal to $\Gamma = 5$ cm^{-1} independent of x. The points for Γ_d are also of the same magnitude for $x<0.1$, but show an abrupt rise at around $x_c=0.11$, beyond which the experimental points show quite steep increase with x.

IV. Discussion

We now proceed to discuss the possible interpretation of the present results shown in Figs.2,3. The essential point of the results is that the reflection spectra of V_h and V_d exhibit quite different behaviours though they are very similar in pure crystals. We are convinced that such behaviours are attributable to the characteristic energy diagram of the vibronic excitons in mixed naphthalene crystals. According to the DOS curves shown in the lower part of Fig.1, the energy of the V_d state is located just at the center of the lower 2-P band associated with $N\text{-}h_8$ molecules. One may expect, then, that the V_d state is resonantly scattered to the background states, leading to the damping of the V_d state. For the V_h state, such damping effect cannot be expected since there is no overlapping continuum.

Such a resonant scattering effect of a discrete level embedded in a continuum can be dealt with by the coherent potential approximation. The result is shown in Fig.3 by a solid curve (CPA). The predicted Γ_d shows a steep rise with increasing x, but fails to reproduce the discontinuous change as observed. The predicted damping occurs at $x \geq 0$, since the energy of the V_d state is located just at the calculated energy of the $N\text{-}h_8$ impurity level. If this is not the case, the V_d state would not overlap with the 2-P band until either edge of the 2-P band is broadened to the energy of the V_d state, giving rise to a discontinuous x-dependence of Γ_d. However, the actual difference between the two energies is sufficiently small, as mentioned before, and the characteristic x-dependence of Γ_d cannot be attributed to such a superficial effect.

In the CPA calculation, the damping of the discrete V_d state is simply related to the magnitude of the DOS of the overlapping band. However, these background states at small x have the character of impurity states localized on single or cluster guest $N\text{-}h_8$ molecules. We may argue that the vibron state on a particular $N\text{-}d_8$ melecule in mixed crystals is scattered to the 2-P state on these impurity molecules by resonance. However, if the exciton in this 2-P state is localized within a restricted region, it will have a chance to be resonantly transferred back to the original site to form the vibron state again. In this case, there will be no damping of the vibron state. But, with increasing concentration of the guest molecules, a region of the extended states will emerge at the center of the impurity band. If the vibron is scattered to such an extended state, it will have a possibility of escaping far away from the original site, resulting in the effective damping of the vibron state. We presume that this is the situation which actually takes place in mixed naphthalene crystals.

In order to consider a quantitative aspect of the present interpretation, we made a model calculation of the DOS spectra of the vibronic excitons taking account of their localized or extended character. We employed the criterion proposed by Economou and Cohen [6], which is given by a criterion function

$$F(E) = \frac{T}{2\,|E - \Sigma(E)|} \quad . \qquad (2)$$

Here, T is the exciton band width in pure crystals, $\Sigma(E)$ is the CPA self-energy of the exciton. When $F(E)<(>)1$, the region is predicted to be localized (extended). The results of such calculation for the vibronic excitons in mixed naphthalene crystals are shown in Fig.4. According to aforementioned interpretation, the V_d state becomes unstable when the background 2-P states become extended at the center of the band. Present results predict that such transition occurs at the critical concentration somewhere between x_c=0.10-0.15. The experimental result, x_c= 0.11, seems to be in reasonable agreement with this prediction.

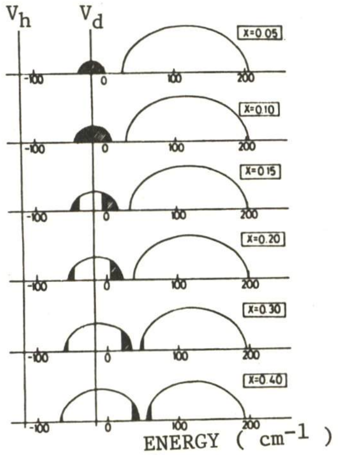


Fig.4 Calculated DOS for the vibronic exciton bands in $(N\text{-}h_8)_x(N\text{-}d_8)_{1-x}$ (The shaded regions are predicted to be localized.)

To summerize, all the experimental results strongly indicate that the V_d state becomes unstable when the background exciton band undergoes the transition from localized to extended character. The sharp vibron spectra in this mixed system are particularly suitable for a microscopic probe to detect the transition. More detailed accounts of the experimental and theoretical results will be described elsewhere.

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