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Observation of Excitons in a Molecular Liquid: Specular Reflection Spectrum of α - Methylnaphthalene

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cies.

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Note added in proof.—It has been called to our attention that M. Porkolab has predicted and calculated the threshold power for the decay of an electron plasma wave into another plasma wave and an ion-acoustic wave.

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Observation of Excitons in a Molecular Liquid: Specular Reflection Spectrum of α -Methylnaphthalene

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The normal-incidence specular-reflection spectrum of liquid α -methylnaphthalene was obtained for the wavelength region from 215 to 400 nm. Comparison of the Kramers-Kronig transform of the reflection spectrum with the absorption spectrum of α -methylnaphthalene in cyclohexane shows the bands of the neat-liquid spectrum shift to lower energy and display significant broadening. These effects support the existence of excitons in molecular liquids.

The existence of excitons in crystalline solids is a consequence of the translational symmetry of the crystal.¹ It has been observed by Rice and co-workers² that liquids also have translational symmetry when compared to the thousands of angstroms wavelength of light characteristic of electronic transitions. Thus, it is reasonable to conjecture that exciton states can exist in liquids.

The initial theory of these workers^{2a} discussed Wannier excitons in a dense liquid in which an excess electron could be described as a plane wave. It was found that scattering processes could be expected to lead to broadening of the exciton states. Later the theory for excitons in liquids was developed^{2b} along the lines of the Fano model of polarization waves in a simple lattice. The structure of the liquid appears explicitly in this construct. An approximate form of this theory,^{2c} which is more applicable to Frenkel excitons, uses a Drude-type model to describe the electronic states; nevertheless, the theory has not been applied to any molecular liquid. However, it is pos-

sible to understand qualitatively what may be expected if excitons do exist in molecular liquids. Two main features should be apparent. The primary one is a broadening of bands because the lifetimes of the electronic excitations will be approximately one tenth the lifetime for typical thermal excitations. The set of exciton levels in the liquid would be expected to appear as an unresolved or poorly resolved spectrum. Secondly, a shift in frequency from that of the solution or vapor spectrum may be expected. While excitons in atomic liquids have been detected,³ molecular liquids have not been investigated.

In an effort to observe excitons in molecular liquids, α -methylnaphthalene was studied in the wavelength region from 215 to 400 nm. Normal-incidence specular-reflection spectra were obtained on samples of the neat liquid using a reflectometer described previously.⁴ The light beam was directly incident on the surface of the liquid which was contained in a small glass boat. This eliminates problems of refractive index

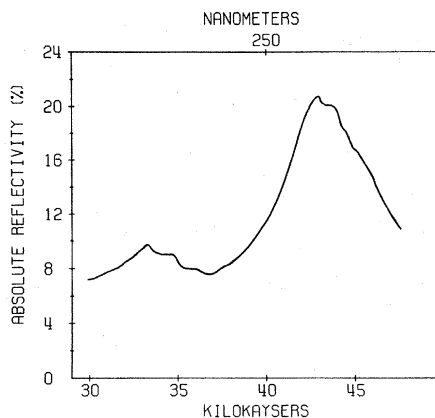


FIG. 1. Specular reflection spectrum of liquid α -methylnaphthalene (1 kayser = 1 cm^{-1}).

change that would arise had the spectrum been obtained through a window in optical contact with the liquid. Intensity readings were taken every 10 \AA with the slits of a Spex 1400 Monochromator set for an average bandpass of 7 \AA . The α -methylnaphthalene was obtained from Eastman Organics and was purified by double distillation over a spinning band column.

The solution spectrum of α -methylnaphthalene in spectroscopic grade cyclohexane was obtained with a Beckman DU-2 spectrophotometer at $10\text{-}\text{\AA}$ intervals. The average bandpass was less than 2 \AA in the region of special interest.

The absorption spectrum of α -methylnaphthalene was obtained by a Kramers-Kronig transform of the reflection data shown in Fig. 1.⁴ Figure 2 shows the solution and neat-liquid spectra. The solution spectrum appears as dashed lines of arbitrary relative intensity. The integrated intensities of the solution and neat-liquid spectra have been obtained. The transition dipole strengths of the neat liquid are 2.25 and 0.30 \AA^2 for the high- and low-energy bands, respectively. The dipole strengths for the solution spectrum are 2.30 and 0.29 \AA^2 . Thus the neat-liquid intensities are not significantly different from those of the solution.

The most striking feature in the neat-liquid spectrum is the loss of structure due to broadening. Compared to the great amount of structure observed in the solution spectrum there are only two peaks in the neat-liquid spectrum. These occur at $(35.00$ and $36.10) \times 10^3 \text{ cm}^{-1}$. The latter peak is almost washed out. The peaks are shifted to the red from the solution values by 460 and 800 cm^{-1} , respectively. The two closely spaced low-energy peaks seen in the solution data are gone but can be related to a shoulder in the neat

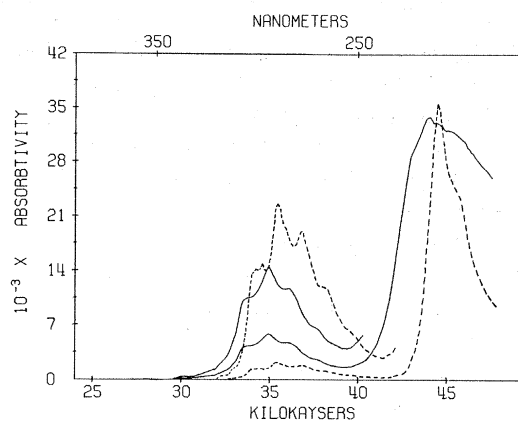


FIG. 2. Solid lines, liquid α -methylnaphthalene absorption spectrum obtained from Kramers-Kronig transform. The low-energy band system is also shown at 3.5 times its true intensity. Dashed lines, the solution spectrum in cyclohexane is shown for comparison but the intensities are only relative. The low-energy solution band is also expanded for purposes of comparison.

liquid occurring at $33.80 \times 10^3 \text{ cm}^{-1}$. This gives a red shift of 630 cm^{-1} . The $38.10 \times 10^3 \text{ cm}^{-1}$ shoulder appearing in solution appears to be red-shifted 550 cm^{-1} in the neat liquid. The $39.53 \times 10^3 \text{ cm}^{-1}$ solution shoulder is not observed.

Also of interest is the extreme broadening of the high-energy band in the neat α -methylnaphthalene. A shoulder appears at $43.30 \times 10^3 \text{ cm}^{-1}$ and a peak at $44.10 \times 10^3 \text{ cm}^{-1}$. There is no red shoulder on this band in the solution spectrum where the peak intensity occurs at $44.44 \times 10^3 \text{ cm}^{-1}$. This would indicate a red shift of 1040 cm^{-1} . The peak in the neat liquid occurs at $45.45 \times 10^3 \text{ cm}^{-1}$. A striking similarity exists between this broadened band and the similar long axis polarized band in crystalline anthracene where the band has been observed⁵ to be metallicly broadened.

The observed frequency shift is somewhat problematic in that the dielectric theory of solvent effects^{6,7} could also be invoked to account for the shift. Nevertheless, dielectric interactions cannot account for the extreme broadening and large energy shifts observed here. Because of the necessity of the calculation of excited-state distribution functions and the need for unavailable parameters such as the friction coefficient, it is not meaningful to provide theoretically² predicted values for the lifetimes and frequency shifts of α -naphthalenes.

Additionally, the results of a recent study⁸ of the two-photon absorption of liquid α -chloronaphthalene suggests a collective electronic state in

the $(32-36) \times 10^3\text{-cm}^{-1}$ region. Thus, the data given above strongly support the existence of excitons in the molecular liquids.

Current efforts are directed toward obtaining the reflection spectra of the anthracene melt and studying the effect of guest molecules on the spectrum of a molecular liquid.

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Simultaneous Ion Heating of He⁺ and Ar⁺ in Linear Turbulent-Heating Experiments

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Turbulent-heating experiments have been carried out in a linear machine with a driving gas of helium mixed with 7% argon in order to see the mass dependence of ion heating. Observation of optical line broadening of the ions showed that both kinds of ions were heated almost simultaneously by almost the same amount during the process. Several mechanisms for ion heating are examined on the basis of the experimental results obtained.

Many experiments on turbulent heating of plasmas have been carried out during the past ten years,¹ resulting in some cases in the heating of ions in the plasma up to a few keV. It has been thought that the mechanism of electron heating is probably an anomalous Ohmic process² of electrons accelerating under the applied electric field. The mechanism of ion heating, however, has not been clear so far. It cannot be explained by the anomalous Ohmic process. This is because, in a coordinate system moving with the ion drift velocity, the excited ion acoustic waves have a phase velocity nearly equal to the sound velocity c_s , which is much larger than the ion thermal velocity; so there exist few particles interacting strongly with the ion acoustic waves if a Maxwellian velocity distribution of ions is assumed.

It should be expected, then, that the ion heating

is due to some process associated with turbulent heating,³ or some other process such as nonlinear Landau damping in which the ion acoustic waves are absorbed by ions. Since the virtual waves are absorbed by the resonant particles, test particles should not be heated as much as the field particles provided the atomic mass of the former is much larger than that of the latter. In this scheme, therefore, the heating rate and the resulting temperature should have an ion-mass dependence when more than two species of ions exist in a plasma and suffer turbulent heating simultaneously.

We have carried out turbulent-heating experiments in a linear magnetic field with a driving gas of helium (93%) mixed with argon (7%), the argon ions playing the role of test particles. The BSG II machine⁴ has been used for the experiment