ANTIRESONANCES IN DOPED MOLECULAR SOLIDS—EXPERIMENTAL EVIDENCE FOR CONFIGURATION MIXING OF IMPURITY STATES AND CONDUCTION-BAND STATES

E. S. Pysh,* Stuart A. Rice, and Joshua Jortner

Institute for the Study of Metals and Department of Chemistry, The University of Chicago, Chicago, Illinois

(Received 7 July 1965)

Low-energy electronic transitions observed in the optical spectra of solid insulators show their molecular parentage clearly and are often, though not always, adequately treated in the Frenkel approximation. The optical spectra of solid rare gases and rare-gas alloys, however, represent intermediate excitons which are best described by complementary application of both the Frenkel and Wannier formalisms.[1] One would also expect the higher energy transitions of polyatomic molecules, especially to atomiclike Rydberg states, to result in intermediate excitons, but Rydberg transitions have not previously been studied in any solid phase. The present note describes the absorption spectra arising from acetylene and benzene impurity states in solid krypton in the far ultraviolet region.

The first Rydberg transitions in gaseous acetylene are observed at 8.15, 8.38, and 8.61 eV and have absorption coefficients of 14 680, 1500, and 500 cm^{-1}, respectively.[2] These transitions represent the first three vibrational components of the first $n = 3$ series member. The Rydberg transitions at higher energies are either weaker than this $n = 3$ transition or overlap one another.

Spectra of the doped rare-gas films were taken using a one-meter vacuum ultraviolet scanning monochromator. The gratings used were ruled with 1200 or 600 lines/mm with dispersions of 8.3 and 16.6 Å/mm, respectively. Under the conditions of the experiment the resolution was about 1.0 to 2.0 Å. A capillary discharge light source, operated with hydrogen, provided a line spectrum in the range of this experiment. Gas mixtures were deposited onto a sapphire window coated with sodium salicylate. The sapphire sample holder was attached to a copper rod which extended from the bottom of a liquid-helium cryostat. The temperature of the sample was about 20°K.

Figure 1 shows the absorption spectrum of a krypton matrix doped with 1% acetylene. The sharp rise at 10.2 eV represents the threshold absorption of the krypton matrix. Two dif-
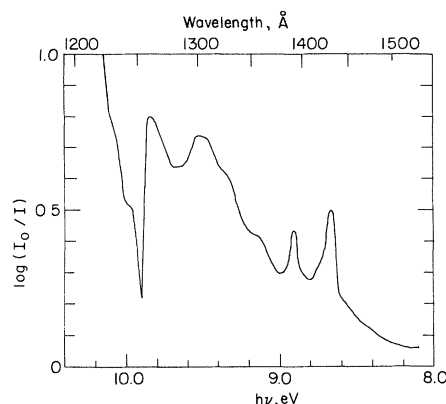

FIG. 1. Absorption spectrum of acetylene-doped (1%) krypton matrix from 1200 to 1520 Å.

fuse absorption bands are observed at 8.67 and 8.90 eV. Below 8.67 eV the absorption drops quickly and levels off below 8.2 eV. By comparison with the gas spectrum, the peaks are identified as the first Rydberg transitions of acetylene. The first two peaks in the solid are separated by 1960 cm^{-1}, compared with 1820 cm^{-1} in the gas, reflecting a vibrational perturbation induced by the matrix. An acetylene-doped (1%) argon film showed absorption peaks at 9.01 and 9.22 eV.

The blue shifts of 0.52 eV in krypton and 0.86 eV in argon of the first Rydberg peak are large but comparable to those shifts observed in rare-gas alloys.[3] The xenon atomic transition $^1S_0$-$^3P_1$ observed at 8.43 eV in the gas phase is blue-shifted 0.58 eV in krypton and 0.79 eV in argon.[1] Recent work in this laboratory shows that the energy shifts in rare-gas alloys reflect a balance between large Coulomb and exchange effects which operate in opposite directions, and that accurate calculations require either a Frenkel scheme modified by the inclusion of large charge delocalization via addition of charge-transfer states, or a pseudopotential formalism together with a model Hamiltonian of a dielectrically screened hydrogenic type.[4]

Gaseous benzene has sharp, strong, and well-separated Rydberg transitions at 8.15 eV, representing the $n = 3$ member of one

series, and at 8.37, 8.68, and 8.85 eV, representing the $n = 3$, 4, and 5 members of a second series.[5] The vibrational components other than the 0-0 bands are much weaker.

The absorption spectrum of a benzene-doped (1%) krypton matrix is shown in Fig. 2. There is revealed a series of sharp negative peaks corresponding to decreases in absorption. While there is a similarity between the location of the transmission increases and the gas-phase Rydberg levels, there is not a one-to-one correspondence. The striking features of the solid spectrum must represent an interaction between the benzene-molecule states, most likely the Rydberg states, and some matrix configuration, most likely the continuum states of the conduction band. Configuration interaction between discrete atomic states and continuum states has been observed previously to give anomalous line shapes, either strongly asymmetric absorption peaks or transmission windows of the type observed here. Fano is responsible for the development of the theory which describes such anomalous line shapes in terms of a set of parameters related to the relevant dipole and energy matrix elements.[6] Numerous illustrations of the theory are provided by Rydberg series in atomic spectra associated with inner electron or multiple electron excitations which result in autoionization.[7] In particular, argon and krypton show sharp antiresonances of the kind shown in Fig. 2.[8]

Phillips has extended Fano's theory to solids, in which case the conduction band of the solid provides the continuum states.[9] Indeed, Jain has analyzed the spectrum of annealed xenon in this way, and has pointed out that

FIG. 2. Absorption spectrum of benzene-doped (1%) krypton matrix from 1300 to 1600 Å.

stable bound excitons below the direct-absorption threshold are characterized in the optical spectrum by narrow resonances separated by broad antiresonant minima, whereas metastable excitons show broad resonant peaks and sharp narrow antiresonances.[10]

The spectrum displayed in Fig. 2 can be readily explained in terms of transitions to discrete molecular states which overlap the conduction-band states of the matrix. The sharp antiresonance in Fig. 1 at 9.9 eV might similarly represent one of the higher series members of acetylene interacting with krypton conduction-band states, which would imply that the energy gap between the impurity level and the matrix conduction band is between 9.0 and 9.9 eV.

A complete analysis of the line shapes in Fig. 2 is made difficult by the overlapping of neighboring antiresonances. In particular, one cannot evaluate Fano's parameter q^2, which represents the relative transition probabilities to the discrete state, as modified by continuum states and to the band width Γ of unperturbed continuum states. One can only say that since nearly pure transmission windows are observed, with little or no increased absorption, q is much smaller than unity. Since transitions to the discrete states in the gas phase have absorption coefficients as high as 10^3 cm^{-1}, this result implies that the discrete states are greatly modified in the solid. Values of the band width Γ vary from about 0.03 to 0.05 eV, corresponding to a decay rate of ~6×10^{13} sec^{-1} for the metastable state. Since Γ is related to that interaction element, V, of the energy matrix connecting the discrete state, φ, with appropriate continuum states, ψ_i, we have

$$V = \langle \psi_i | H | \varphi \rangle = (\Gamma/\pi)^{1/2} = 0.11 \text{ eV}.$$

The spectrum of solid benzene showed only strong broad continuous absorption in the region from 1600 to 1300 Å. It seems, therefore, that a proper, i.e., free-electron–like, conduction band is required for the appearance of molecular antiresonances. This fact prevents the use of techniques similar to those employed here for the exact location of the photoconducting level in solids whose band structure is more complicated than that of rare gases. One can say in the case of benzene in a rare-gas solid merely that the level is below 8.0 eV, which is certainly a reasonable limit. Photoconductivity experiments on ben-
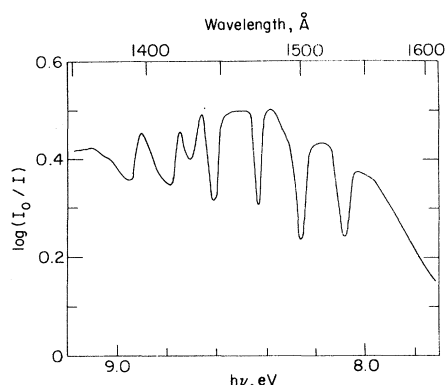
zene-doped matrices would confirm the conclusions of this work, and experiments on solid benzene would locate the band gap where the optical method fails.

It is important to note that the interpretation of the observations reported here in terms of configuration mixing of impurity states and conduction-band states provides support for a recent extension of Frenkel-Davydov exciton theory to include ion-pair exciton states.[4,11] It appears that even in cases where the tight-binding approximation is a good first-order approximation, the crystal states are not accurately described in terms of having a one-to-one parentage in only free molecule states, but rather that delocalization of the excitation must always be considered.

We wish to thank the Directorate of Chemical Sciences of the Air Force Office of Scientific Research and the U. S. Public Health Service for financial support. We have also benefited from the use of facilities provided by the Advanced Research Projects Agency for materials research at the University of Chicago.

*National Science Foundation Fellow.

[1]G. Baldini, Phys. Rev. 128, 1562 (1962); 137, A508 (1965).

[2]T. Nakayama and K. Watanabe, J. Chem. Phys. 40, 558 (1964); E. S. Pysh, Thesis, University of Chicago, 1965 (unpublished).

[3]Note that there is a bump in Fig. 1 at about 9.1 eV which may correspond to the 8.61-eV transition in acetylene shifted by about 0.52 eV. It should also be noted that the line shapes of the absorptions at 8.67 and 8.90 eV are not completely symmetric. The origin of this asymmetry in line shape is at present unknown. There may be some configuration mixing of impurity states and host states. In contrast, the spectrum of benzene in argon and krypton shows pronounced anti-resonances, which unambiguously indicate configuration mixing of host and impurity states. It is possible that the very large and sharp dip in absorption at about 9.9 eV for acetylene in krypton might similarly represent one of the higher series members of acetylene interacting with krypton conduction-band states. The behavior of benzene and acetylene as impurities in these solids is then seen to be logically connected by the magnitude and the differences in excitation energies of the Rydberg states of the two compounds relative to the energy gap between the ground state and the conduction band of the host matrix.

[4]S. Webber, S. A. Rice, and J. Jortner, J. Chem. Phys. 41, 2911 (1964); 42, 1907 (1965).

[5]W. Price and R. Wood, J. Chem. Phys. 3, 439 (1935); P. G. Wilkinson, Can. J. Phys. 34, 596 (1956).

[6]U. Fano, Phys. Rev. 124, 1866 (1961); U. Fano and J. W. Cooper, Phys. Rev. 137, A1364 (1965).

[7]H. Beutler, Z. Physik 93, 177 (1935); R. Madden and K. Codling, Phys. Rev. Letters 10, 516 (1963).

[8]J. Samson, Phys. Rev. 132, 2122 (1963).

[9]J. C. Phillips, Phys Rev. (to be published).

[10]K. P. Jain, Phys. Rev. 139, A544 (1965).

[11]S. Choi, J. Jortner, S. A. Rice, and R. Silbey, J. Chem. Phys. 41, 3294 (1964); R. Silbey, J. Jortner, and S. A. Rice, J. Chem. Phys. 42, 1515 (1965); R. Silbey, J. Jortner, M. Vala, and S. A. Rice, J. Chem. Phys. 42, 2948 (1965).

ELECTROCALORIC EFFECT AND A NEW TYPE OF IMPURITY MODE*

G. Lombardo and R. O. Pohl

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York
(Received 21 July 1965)

Measurements of the thermal conductivity of mixed alkali-halide crystals[1] indicated the existence of a large number of resonant scattering mechanisms characterized by angular frequencies between 1.9×10^{11} and 1.9×10^{13} rad sec^{-1} (1 and 100 cm^{-1}). They have been attributed to impurity modes.[2] Some of these modes with energies over 10 cm^{-1} have since been investigated in the far infrared.[3] Very little is known about the modes of lower energy.

We have found an electrocaloric effect in KCl doped with LiCl. This cooling upon adiabatic depolarization at low temperatures was first suggested[4] for paraelectric crystals and observed in SrTiO$_3$.[5] Recently the electrocaloric effect has also been observed in KCl doped with KOH.[6] It was explained by an alignment of OH$^-$ dipoles. Our experiments concern an alignment of dipoles due to monatomic impurities and are used to study low-frequency impurity modes.

The crystals were grown under chlorine atmosphere from chlorine-treated starting materials by Mr. D. Bower.[7] The LiCl concentrations were determined by Dr. R. K. Skogerboe.[7] The electric fields were applied by means of gold electrodes evaporated onto the large faces of samples cleaved to approximately $2 \times 3 \times 0.2$ cm^3. The gold-film area was kept smaller than the crystal faces in order to minimize the dan-