

Far vacuum ultraviolet absorption of solid hydrogen

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From the point of view of the electronic structure of their constituents, solid hydrogen and deuterium are the simplest molecular solids and the understanding of exciton states and interband transitions in these systems is of interest. The energy levels of solid deuterium in the range 11–14 eV was studied by optical spectroscopy¹ and by electron energy loss.² We present the results of a spectroscopic study of solid hydrogen and deuterium in the region 900–650 Å (14–20 eV).

Our light source was a windowless helium discharge lamp operated at 40 torr spanning the spectral region 900–600 Å. The lamp was attached through a differential slit assembly to a normal incidence 1 m vacuum monochromator (McPherson 225) equipped with a gold coated grating (1200 lines per mm) blazed at 800 Å. Photoelectric detection was employed. Thin (~200 Å for the pure solids and ~2000 Å for the mixed solid) films of solid hydrogen, deuterium and of neon–deuterium mixtures (2% D₂) were prepared by depositing the gases (Matheson research grade) on a LiF window, coated with lithium³ or with sodium salicylate convertor. The window was attached to a helium flow cryostat and cooled to 6 ± 1 °K.

The absorption spectra of pure solid hydrogen and deuterium (Fig. 1) in the range 14–20 eV are practically identical. The prominent features of these spectra are two broad bands peaking at about 930 Å (13.4 eV) and at 710 Å (17.4 eV). The absorption of deuterium impurity in solid Ne (Fig. 1) in the range 14–17 eV (the upper energy limit being determined by the absorption of the matrix) exhibit just one band peaking at 890 Å (13.9 eV) and no analogue of the 710 Å (17.4 eV) high energy band in the pure solid is exhibited by the impurity spectrum.

The broad bands exhibited by the pure solids at 930 Å (13.4 eV) and at 890 Å (13.9 eV) in D₂/Ne are assigned to the $n=1$ Wannier exciton and impurity states, including large central cell correction, or alternatively, they can be described in terms of a Frenkel state originating from the $X^1\Sigma_g^-C^1\Pi_u$ molecular Werner bands subjected to large nonorthogonality corrections. The large

bandwidth originates from a long vibrational progression which should be also exhibited by a Wannier state.⁴ The onset of the band–band transition in the pure solids is given by⁵ $E_G = I_g + P_+ + V_0 + E_V$ where $I_g = 15.43$ eV⁶ is the gas phase ionization potential, P_+ is the polarization energy, V_0 is the energy of the bottom of the conduction band, while E_V is the half-width of the valence band. From the study of Xe/H₂ and Xe/D₂ spectra $P_+ + V_0 \approx -1 - 2$ eV,⁷ so that setting $E_V \approx 0$, $E_G \approx -13.5 - 14.5$ eV in the pure solids. The guess of $E_G = 14.5$ eV seems to be reasonable in view of the weak absorption band observed in solid H₂ and D₂ around 860 Å (14.4 eV) which may be due to high members of the

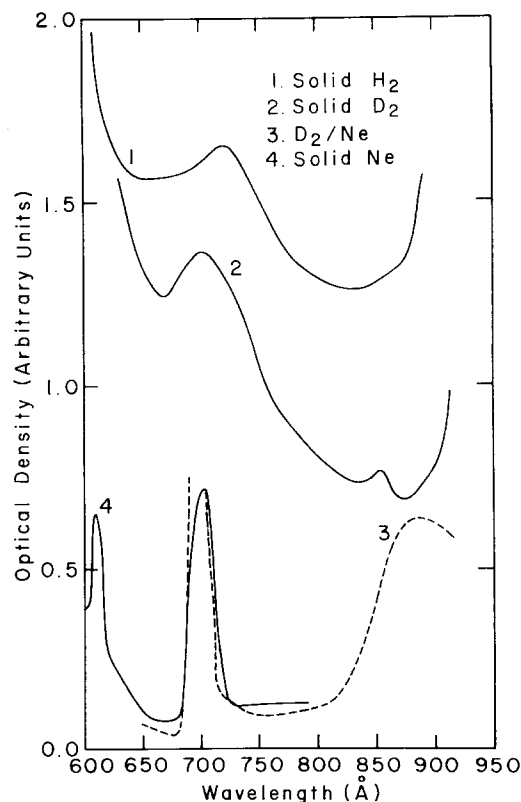


FIG. 1. Absorption spectra of (1) solid H₂, (2) solid D₂, and of (3) 2% D₂ in solid Ne. The absorption spectrum of (4) solid Ne is presented for the sake of comparison with (3). Films deposited and measured at 6 °K.

Wannier series. For the D_2/Ne impurity states we have the matrix ionization potential $E_G = I_g + P_+ + V_0$, as for $Ne(s)$ $V_0 = +0.5$ ⁵ we expect $E_G = I_g = 15.5$ eV. This high onset for the direct transition in the solid Ne is consistent with the blue shift of the $n=1$ state (0.5 eV) of D_2/Ne relative to the pure solids. The absorption spectra of solid H_2 , D_2 , and D_2/Ne in the range 14.5–20 eV have no parentage in the electronic excitations of the isolated molecule.⁶ The high molecular Rydberg states and the ionization continuum are replaced in the dense medium by high Wannier states followed by the interband transitions.^{4,8}

The broad band (width ~ 2.5 eV) peaking at 710 Å (17.4 eV) in the pure solids is assigned to the interband transition. The alternative interpretations are rejected. We do not assign this transition to saddle point excitons⁹ in view of previous objections raised in the interpretation of the spectra of solid rare gases.¹⁰ Also, metastable excitons originating from two electron excitations are expected to be located at higher energies. Our interpretation is consistent with the absence of the corresponding transition in D_2/Ne .

The absorption coefficient $A(\hbar\omega)$ for the direct transition from the valence band $|v, \mathbf{k}\rangle$ to the conduction band $|c, \mathbf{k}'\rangle$ (where $\mathbf{k} = \mathbf{k}'$) is⁹ $A(\hbar\omega) = \sum_{\mathbf{k}} |\mu_{cv}(\mathbf{k})|^2 \delta[E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar\omega]$. Assuming that the transition moment $\mu_{cv}(\mathbf{k})$ is reasonably constant

throughout the Brillouin zone $A(\hbar\omega)$ monitors $\sum_{\mathbf{k}} \delta[E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar\omega]$, i. e., the joint density of states (JDOS). We propose that the broad optical absorption in the range 14.5–18 eV monitors the JDOS of solid H_2 and D_2 and as the valence band is expected to be narrow the major contribution originates from the conduction band. These pure solids are unique as in view of their simple electronic structure no interference from the metastable exciton originating from one electron transition from lower lying conduction bands will be encountered. Thus, the density of states in the conduction band can be directly monitored from optical spectroscopy.

¹G. Baldini, Jap. J. Appl. Phys. Suppl. I 4, 613 (1965).

²L. Schmidt, Phys. Lett. A 36, 87 (1971).

³N. Kristianpoller and D. Dutton, Appl. Opt. 3, 287 (1964).

⁴B. Katz, M. Brith, B. Scharf, and J. Jortner, J. Chem. Phys. 50, 5195 (1969).

⁵B. Raz and J. Jortner, Chem. Phys. Lett. 9, 222 (1971).

⁶(a) H. Beutler and H. O. Jünger, Z. Phys. 100, 80 (1936); (b) G. R. Cook and P. H. Metzger, J. Opt. Soc. Am. 54, 968 (1964).

⁷A. Gedanken, B. Raz, and J. Jortner, Chem. Phys. Lett. 14, 326 (1972).

⁸A. Gedanken, B. Raz, and J. Jortner, J. Chem. Phys. 59, 1630 (1973).

⁹J. C. Phillips, Solid State Phys. 18, 55 (1966).

¹⁰D. Beaglehole, Phys. Rev. Lett. 15, 551 (1965).