Density-Dependent Phase Transition and Anisotropic Interactions in Solid Parahydrogen and Orthodeuterium

S. C. Durana and J. P. McTague*
Department of Chemistry,† *University of California, Los Angeles, California 90024*

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Raman scattering studies of the $J=0\rightarrow 2$ rotational transitions in solid parahydrogen and orthodeuterium over the pressure range $0\leq p\leq 3.3$ kbar have revealed a phase transition from hcp to fcc, with the fcc structure being stable at high pressures and hcp stable at low pressures ($\lesssim 0.8$ kbar). In both phases the main anisotropic interaction is molecular electric quadrupole-quadrupole ($\sim R^{-5}$), but we observe significant effects tentatively attributed to correlated zero-point motion.

Solid hydrogen is the simplest molecular solid and can be considered a model system for the study of intermolecular interactions in condensed phases for several reasons. Among them are the following facts: The properties of the isolated molecules are well known; the solid is quite compressible ($-d\ln V/dp\sim 6\times 10^{-4}$ atm^{-1} at $p=0$); and the anisotropic intermolecular interactions can be "turned on" at will by the use of ortho and para modifications and by the introduction of rotational excitations. Because of the small moment of inertia ($B_{\mathrm{H}_2}=60$ cm^{-1}, $B_{\mathrm{D}_2}=30$ cm^{-1}) and the weakness of the anisotropic interactions, the molecular angular momentum J remains a good quantum number even at normal solid densities. At the low temperature of the solid ($T<15$ K) the thermodynamic equilibrium distribution has essentially all the molecules in the $J=0$ state, where they are effectively spherically symmetric, rare-gas-like, Van der Waals molecules.

When grown under ambient pressure, both parahydrogen (p-H_2)[1] and orthodeuterium (o-D_2)[2] form a simple hcp lattice. X-ray evidence[3] shows, however, that when grown on certain substrates an fcc pattern is observed, raising the question of whether the hcp phase is merely metastable, with the fcc modification being kinetically inaccessible under normal growth conditions ($T<0.15\Theta_\mathrm{D}$). It is known, for instance, that the stable low-temperature modifications of o-H_2 and p-D_2 have the molecular centers on an fcc lattice.

We report here rotational Raman scattering studies of the $J=0\rightarrow 2\,[S_0(0)]$ transitions in parahydrogen and orthodeuterium which show that the hcp phase is stable at the densities corresponding to ambient pressure, both for H_2 and for D_2, while the fcc structure is stabilized at slightly higher densities ($\Delta V/V_0\sim 0.15$). Direct measurements of the dependence of the anisotropic intermolecular interactions are also reported as functions of lattice parameters in both the fcc and hcp phases.

Lattice parameters were varied by application of pressures up to 3.3 kbar, generated by transmitting a known uniaxial force through a long hollow stainless-steel compression member to a Bridgman unsupported area piston in contact with the sample, in essentially the same manner as used by Stewart[4,5] for measuring the equation of state. Stewart has shown that, since hydrogen flows under very low shear, essentially hydrostatic pressures can be generated in this manner for pressures greater than a few hundred atmospheres. The three-window high-pressure optical cell was similar to that used by Fitchen.[6] Assignment of unique frequency-pressure relationships, from hysteresis curves of the measured frequency shifts of the Raman bands versus applied force, parallels the equation-of-state determination of Stewart. Knowledge of the crystal structure and the pressure-density relationship then yields the functional dependence of the splittings of the Raman bands on lattice parameter.

Samples of parahydrogen and orthodeuterium were prepared by allowing several cubic centimeters of the pure liquid to remain in contact with a ferrous oxide hydroxide gel catalyst at the normal boiling temperature for approximately 2 h. The samples were then stored in degassed Pyrex bulbs. Only polycrystalline solids could be grown in the high-pressure cell be cause of the low symmetry of the container geometry and the lack of control of suitable temperature gradients during growth. The samples as grown at low pressure were highly cracked and of unsuitable optical quality, but the application of only 100–150 atm pressure caused compaction and the 5145-Å laser light was then readily transmitted.

The $J=0\rightarrow 2$ $[S_0(0)]$ rotational Raman transition is in an experimentally convenient region [$\nu_0\sim 360$

cm^{-1} (H_2) and 180 cm^{-1} (D_2)], and its characteristics have been accurately determined at zero pressure.[7,8] The anisotropic interactions delocalize the excitations, creating bands of rotational excitons. Raman scattering probes only the $K=0$ modes and their frequency differences are determined by the crystal structure and by the detailed nature of the interactions. The most general pairwise interaction for homonuclear diatomic molecules with $J_1+J_2 \leqslant 2$ is

$$V(R_{12}, \omega_1, \omega_2) = V_{00}(R_{12}) + V_{20}(R_{12})[Y_{20}(\omega_1) + Y_{20}(\omega_2)] + \sum_m V_{22m}(R_{12}) Y_{2m}(\omega_1) Y_{2-m}(\omega_2), \quad V_{22m} = V_{22-m}. \tag{1}$$

Here, we have chosen the intermolecular vector as the quantization axis. It is well known that, at zero pressure, the predominant anisotropic interaction is molecular electric quadrupole-quadrupole:

$$V_{220}(\mathrm{EQQ}) = 20\pi\Gamma, \quad \text{where } \Gamma = \tfrac{6}{25} e^2 Q^2 / R^5 12. \tag{2}$$

The Wigner-Eckart theorem gives a relation among the $V_{22m}(\mathrm{EQQ})$:

$$V_{22\pm1}(\mathrm{EQQ}) = \tfrac{2}{3} V_{220}(\mathrm{EQQ}), \text{ and } V_{22\pm2}(\mathrm{EQQ}) = \tfrac{1}{6} V_{220}(\mathrm{EQQ}). \tag{3}$$

Other contributions to the V_{2lm} are not as well characterized, and, in particular, the short-range anisotropic Van der Waals and overlap terms which may become significant at higher densities have been theoretically estimated[9,10] only comparatively crudely. It was one of the goals of the present investigation to attempt to measure their functional form.

Van Kranendonk[11] has shown that, in the hcp structure, the anisotropic interactions split the tenfold degenerate $K=0$, $S_0(0)$ transition into six levels, characterized by m:

$$\psi_m(k=0) = N^{-1/2} \sum_{i=1}^{N/2} [Y_{2m}{}^{(i)}(\Omega_1) Y_{00}{}^{(i)}(\Omega_2) \pm Y_{00}{}^{(i)}(\Omega_1) Y_{2m}{}^{(i)}(\Omega_2)]. \tag{4}$$

Here i indexes the unit cell, containing molecules 1 and 2, and m and Ω are given relative to the hcp c axis. The plus sign is appropriate for the Raman-active levels. In the absence of an external magnetic field, the states ψ_m and ψ_{-m} are degenerate. Thus, only three lines appear in the $S_0(0)$ spectrum, for the most general interaction. In an ideal rigid hcp lattice the V_{20} terms average to zero for first and second nearest neighbors. The EQQ interaction, summed over the entire lattice, splits the Raman-active ψ_m levels into three lines, equally spaced by $\Delta = 3.76\Gamma$. The $\psi_{\pm1}$ state is lowest in energy, followed by $\psi_{\pm2}$. Earlier studies[7,8] have confirmed both the order of the states and the equality, to within 1%, of the energy splittings. However, the magnitude of Δ was observed to be less than that calculated. The presence of a large-amplitude zero-point motion has the effect of renormalizing the interactions. To first order one then replaces the rigid-lattice interaction parameter Γ_0 by a scaled one, $\Gamma_{\text{effective}} = \xi\Gamma_0$. For H_2, previous Raman experiments[7,8] at $p=0$ give $\xi = 0.76$, while for D_2 the value 0.82 is obtained, in reasonable agreement with measurements on other levels by other techniques, and with quantum crystal calculations. One would expect, then, that the EQQ interactions should cause the observed splittings to diverge uniformly, approximately as $R_0{}^{-5}$, as pressure is applied.

We have observed, however, that at higher pressures the spectra differ not only quantitatively but also qualitatively from this behavior. Figure 1 illustrates two representative spectra for p-H_2. Results are similar for o-D_2. The lower trace was obtained at $p=400$ bar and exhibits the expected triplet structure, while the upper one was observed at $p=890$ bar, and consists of at least four lines, a result inconsistent with the hcp structure. The additional spectral feature at the left appears abruptly with increasing pressure, does not disappear entirely when the pressure is decreased below the observed threshold and increases in relative intensity upon further pressure cycling. The other three bands behave smoothly in both intensity and frequency with pressure. We ascribe the new band to a transition within an fcc phase, which appears between 400 and 890 bar. No volume discontinuity has been noted, a result consistent with the postulated transition. For the fcc structure, group theoretical analysis predicts a T_g and an E_g level, with the T_g level having the lower energy under an EQQ interaction. The EQQ rigid-lattice splitting is $9.57\Gamma_0$. If the new spectral feature is identified as the triply degenerate T_g fcc band and the center of gravity of the fcc levels is the same as that observed for the hcp ones, then the E_g band of the fcc phase would lie almost directly under

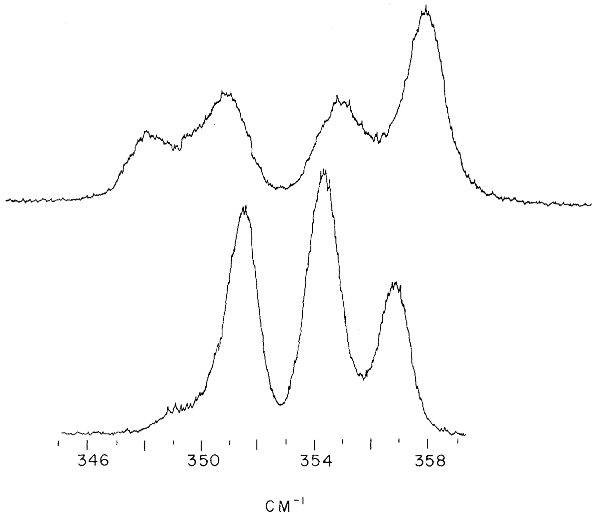

FIG. 1. Raman spectra of the $J=0\rightarrow 2$ transition in parahydrogen at $T\approx 2$ K. The lower trace was recorded at $p=0.40$ kbar on a sample which had been previously cycled to high pressure. Although the sample is predominantly in the hcp phase, a remnant of an fcc phase transition is visible in the region $\nu\approx 349$ cm^{-1}. This feature is clearly seen in the upper trace, recorded at $p=0.89$ kbar, as is the inequality in splittings between the hcp lines and the intensity enchancement of the high-frequency line, assigned to a superposition of the hcp $m=0$ line and the fcc E_g line.

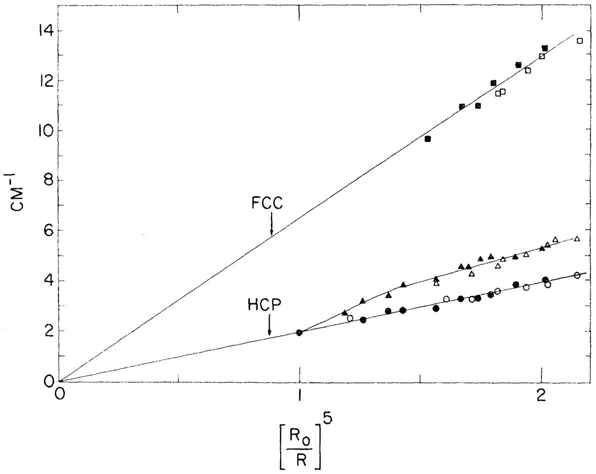

FIG. 2. Frequency splittings observed for both hcp and fcc phases. p-H_2 data are denoted by solid points, while o-D_2 data are represented by open points. Circles, hcp phase $\Delta(\pm 1,\pm 2)$; triangles, $\Delta(\pm 2, 0)$; squares, fcc $\Delta(T_{2g}, E_g)$. All data are referenced to R_0, the lattice parameter of p-H_2 at zero pressure. The lowest density of p-H_2 and o-D_2 points on the lower curve also represent the respective values of $\Delta(\pm 2, 0)$. The lines drawn are visual aids only.

the hcp $m=0$ level, giving $\xi_{\text{fcc}}\approx 0.7\pm 0.1$, the uncertainty arising from the assignment of the lattice parameter. These assignments are consistent with the apparent intensity enhancement with pressure of the high-energy line. In addition, the appearance of a new phase has recently been postulated in order to explain observed hysteresis with pressure of NMR T_1 values,[12] and various thermodynamic anomalies.[13]

If the only interaction in the system were renormalized EQQ, both the splittings of the hcp triplet would diverge approximately as R^{-5} from the zero-pressure value of $\Delta(\pm 1, \pm 2)=\Delta(\pm 2, 0)$ $=2.00$ cm^{-1} for hydrogen and 2.56 cm^{-1} for deuterium. Furthermore, the splitting of the fcc phase doublet would also diverge as R^{-5} from its appearance onward. Figure 2 illustrates the experimental energy differences (in cm^{-1}) as a function of $(R_0/R)^5$ for both phases, for both p-H_2 and o-D_2. R_0 is the lattice parameter of hydrogen at zero pressure, and deuterium is plotted at its measured lattice parameter as though it were hydrogen. The fcc data provide no surprising information. To within the experimental error and the accuracy of the knowledge of the equation of state and lattice parameters at zero pressure, hydrogen and deuterium scale with lattice constant and the predominant anisotropic interaction is the EQQ interaction. As a reference, at the highest pressure reported, the molecules are on the average at a separation corresponding to the bottom of the Lennard-Jones well as opposed to the classical turning point at zero pressure.

The hcp phase, however, exhibits an unusual behavior. The lower curve for this phase is the energy difference between the ± 2 and 0 band and appears to exhibit only an EQQ dependence. The splitting between the ± 2 and ± 1 bands diverges from the ± 2 and 0 band difference upon application of the smallest pressures attainable and uniformly increases. The solid line through the data points is only meant to serve as a visual reference and not as an implied functional form. Such an unsymmetrical divergence of the hcp phase triplet is quite unexpected. It cannot result from a pairwise additive force of nearest neighbors in a rigid lattice. Noolandi[14] has provided a theory of dielectric screening, a pseudo-three-body interaction, which would result in an unsymmetrical divergence, but it predicts that this effect would cause the ± 2 and 0 band difference to be anomalous qualitatively and is an order of magnitude too small quantitatively to explain the present observations. Van Kranendonk and Sears[15] have ascribed such a difference to an alteration of the ratio c/a. This is ruled unlikely since $\Delta(c/a)$ would have to increase greatly as pressure was applied to quantitatively match the data. Hydrogen supports little shear and it is not physically apparent why the crystal would tend to become less than close packed as the material is squeezed.

It has been pointed out by Ebner and Sung[16] that, although terms such as the V_{20} sum to zero over close-packed nearest neighbors in a rigid lattice, this is not in general true when zero-point motion is appreciable. If this is the case here, then the anomalous splitting should reflect both the detailed nature of the correlations in zero-point motion and the significant non-EQQ interactions. Detailed quantum crystal calculations are needed in order to test this hypothesis, and are currently in progress, as are experiments at higher pressures. Furthermore, since a quantitative interpretation of the splittings depends on the equation of state, a redetermination of it is needed, and is being pursued.

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*Alfred P. Sloan Foundation Fellow

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Optical Detection of Paramagnetic Resonance of the Self-Trapped Exciton in KBr

A. Wasiela, G. Ascarelli,* and Y. Merle d'Aubigné
Laboratoire de Spectrométrie Physique,† *38041 Grenoble-Cedex, France*

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Paramagnetic resonance of the self-trapped exciton has been studied in KBr. The general features of the spectra confirm the validity of Kabler's model of a V_K center having trapped an electron. We describe special aspects of the optical technique used to detect the resonance.

Intrinsic luminescence in alkali halides is known to occur through radiative decay of the self-trapped exciton.[1,2] The hole is highly localized on two adjacent, covalently bonded, halide ions, so that the self-trapped exciton may be regarded as an X_2^{--} molecular ion in an excited level or as a V_K center (self-trapped hole) having trapped an electron.[3,4] In most of the alkali halides, two emission bands are observed. On the basis of lifetime measurements[3] and studies of linear polarization and of circular polarization[5] in a magnetic field, the high- and low-energy bands have been assigned to transitions originating from a spin singlet and a spin triplet, respectively. The existence of a long-lived emission band, showing temperature-dependent circular polarization in a magnetic field,[5] suggests the possibility of optical detection of the paramagnetic resonance of the triplet state. Using simple techniques described by Geschwind,[6] we have detected the resonance of the self-trapped exciton in NaCl, RbBr, and KBr. The last mentioned