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Solid HD: anisotropic potentials and structure

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Solid deuterohydrogen is in many respects a typical representative of the family of hydrogen isotope crystals. The main distinguishing and intriguing feature is the eccentricity of the HD molecule. This feature is expected to entail certain peculiarities in the behavior of solid deuterohydrogen, as compared to H_2 and D_2.

The motivation to look into the expected distinctions of the interaction between HD molecules was stimulated by our recent powder x-ray results on the structure of solid deuterohydrogen [1]. In contrast to the earlier measurements [2,3], where the purity of the samples was not reported, our samples were possibly purest. One of our most striking findings was the relatively large (more than 1%) deviation of the c/a ratio, extrapolated to $T = 0$, from the ideal value of $\sqrt{8/3} = 1.633$. It is worth mentioning here that the rather strong electrical quadrupole-quadrupole (EQQ) interaction between $J = 1$ species in the solid homonuclear hydrogens is unable to shift this ratio in the $J = 1$-rich mixtures by more than one tenth of that amount. We have formulated [1] a hypothesis that this deviation of the c/a ratio might be due to the specificity of the anisotropic part of the interaction between HD molecules. The aim of this report is to consider in detail this interaction in solid HD and to understand the implications that stem from the specificity thereof.

Now I shall recall the basic facts about the hydrogen molecule. The forces that bind two hydrogen isotope atoms into a molecule are strong enough to suppress the zero-point intramolecular vibrations and, as a consequence, the internuclear spacing within the molecule as well as the outer molecular dimensions or, in other words, the electron density contour are virtually the same irrespective of what isotopes constitute the molecule. Moreover, the hydrogen molecule is almost spherical, its eccentricity not exceeding 5% [4]. Thus, the static interaction of two isolated hydrogen molecules of any isotopic composition is essentially the same if referred to their geometric centers. But now we must take into consideration the fact that a molecule in the solid vibrates and gyrates around its center of mass rather than geometric center. In the homonuclear molecules such as H_2 or D_2 these two centers coincide, whereas in the HD molecule they do not. This means that the HD molecule vibrates as a whole in the solid not as an almost spherical body (as is the case with H_2) but, which is more important, it rotates in an off-center tumbling manner, rubbing against its partners with the protruding lighter-isotope end (Fig. 1).

The off-center shift of the center of mass along the internuclear axis of the HD molecule, Δ, amounts to one sixth of the internuclear distance. This shift produces an eccentricity more than three times as large as the natural one of 5%.

This report mainly concerns the anisotropic part of the interaction between HD molecules. If, for the time being, we ignore the intrinsic weak eccentricity of the HD molecule, considered with respect to its geometric center, then the main contribution to the anisotropic potential will come from the isotropic part of the po-

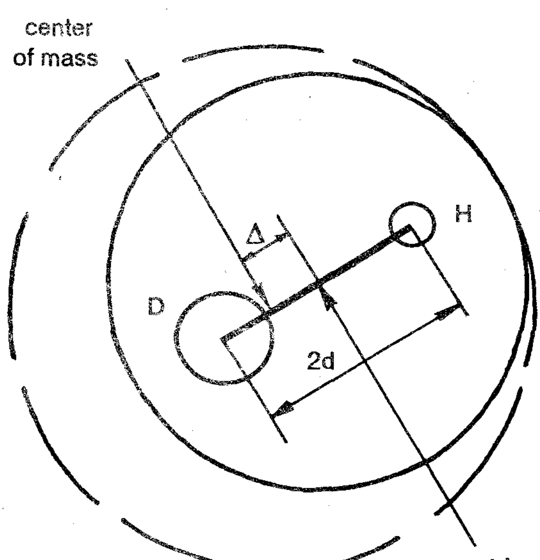

Fig. 1. A schematic representation of the HD molecule. The molecule rotates around the center of mass, which is shifted off the geometric center by Δ. Thus, even a spherical particle will be seen by its neighbors as an anisotropic entity. For HD, $\Delta = 2d/6$, where $2d = 0.7412$ Å is the internuclear spacing.

tential with the proviso that the essentially spherical molecule is rotated not around its geometric center.

Thus, the anisotropic interaction between homonuclear species (H_2, D_2, T_2) comes from:

(i) noncoincidence of the internal distributions of positive and negative charges (EQQ);

(ii) the valence and dispersion contributions due to the very small eccentricity of the outer electron distribution contour.

Unlike in the homonuclear species, the anisotropic interaction between heteronuclear species has an additional term due to the tumbling motion of the molecules around their centers of mass, which are shifted from their geometric centers. Thus, even strictly isotropic forces generate an anisotropic contribution [5]. This contribution, which is important for HD, can be constructed in the following way (Fig. 2).

The anisotropic potential due to the off-center shift can be written as a series in the powers of the two vectors, which represent the shifts Δ in each of the molecules, viz., $\omega\Delta$ and $\omega'\Delta$ (they are small as compared to the intermolecular distance at not too high pressures). Re-arranging the expansion into spherical tensors (see Fig. 2) we obtain (I show here only the leading terms, which are not higher than quadratic in Δ)

$$V_{\text{anis}} = V_{cf1} + V_{cf2} + V_{12} + V_x , \qquad (1)$$

where

$$V_{cf1} = U_1(R)[(C_1(\omega)\cdot C_1(\mathbf{n})) - (C_1(\omega')\cdot C_1(\mathbf{n}))] , \qquad (2)$$

$$V_{cf2} = U_2(R)[(C_2(\omega)\cdot C_2(\mathbf{n})) - (C_2(\omega')\cdot C_2(\mathbf{n}))] , \qquad (3)$$

$$V_{12} = U_{12}(C_1(\omega)\cdot C_1(\omega')) , \qquad (4)$$

$$V_x = U_x(R)(\{C_1(\omega)\otimes C_1(\omega')\}_2\cdot C_2(\mathbf{n})) . \qquad (5)$$

Here $\mathbf{n} = \mathbf{R}/R$; ω and ω' are the unit vectors along the shifts in each molecule;

$$C_{Nn}(\mathbf{a}) = (4\pi/(2N+1))^{1/2} Y_{Nn}(\mathbf{a}) ; \qquad (6)$$

Y_{Nn} are the standard spherical functions. Equations (2) to (5) involve scalar and direct products, which are defined, respectively, as

$$(C_N(\mathbf{a})\cdot C_N(\mathbf{b})) \equiv \sum_n (-1)^n C_{Nn}(\mathbf{a}) C^*_{Nn}(\mathbf{b}) ; \qquad (7)$$

$$\{C_1(\omega)\otimes C_1(\omega')\}_{2\nu} \equiv$$
$$\equiv \sum_n C(112; n, \nu-n) C_{1n}(\omega) C_{1\nu-n}(\omega') \qquad (8)$$

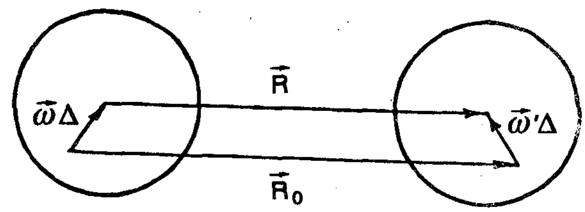

Fig. 2. Interaction of HD molecules. The radius vector **R** sets the frame, in which the interaction of two hydrogen molecules does not depend of the species involved. The vector $\mathbf{R}_0$ separates the centers of mass, around which the molecules rotate and vibrate in the solid.

with $C(112; n, \nu-n)$ as the Clebsch-Gordan coefficients. The interaction contributions of Eqs. (2) to (5) was first derived by Van Kranendonk [5] in a somewhat different form and used to calculate the bandwidth of the $J = 1$ roton in solid HD.

The amplitudes of the interaction terms are

$$U_{cf1} = -\zeta\Phi_1 ; \qquad (9)$$

$$U_{cf2} = (\zeta^2/3)(\Phi_2 - \Phi_1) ; \qquad (10)$$

$$U_{12} = -(\zeta^2/3)(\Phi_2 + 2\Phi_1) ; \qquad (11)$$

$$U_x = -(8/27)^{1/3}\zeta^2(\Phi_2 - \Phi_1) . \qquad (12)$$

Here we introduced the following designations:

$$\Phi_N \equiv R_0^N d^N v_0(R)/dR^N \qquad (13)$$

with $v_0(R)$ as the isotropic potential between hydrogen molecules with respect to their geometric centers;

$$\zeta = \Delta/R_0 = d/3R_0 . \qquad (14)$$

The potentials V_{cf1} and V_{cf2}, when duly summed over the lattice, must have produced the crystals fields of the respective orders. The former cancels out due to the symmetry of the hcp lattice. The other, when summed over an arbitrary hcp lattice, yields a generally nonzero crystal field of the form

$$V_{2c} = \varepsilon_{2c} C_{20}(\omega) \qquad (15)$$

(the reference frame is based on the c axis of the crystal) with

$$\varepsilon_{2c} = \sum_\delta C_{20}(\mathbf{n}_\delta) U_{cf2}(R_\delta) = \sqrt{6}\xi(U_{cf2} + \tfrac{1}{2}R_0 U'_{cf2}) . \qquad (16)$$

Here the summing is over the nearest neighbors δ, and

$$\xi = c/a - \sqrt{8/3} . \qquad (17)$$

As Eq. (16) implies, the crystal field constant ε_{2c} is zero for the ideal c/a ratio.

Equations (4) and (5) reflect a coupling of the two molecular angular momenta. The former is an isotropic-Heisenberg coupling, while the latter is algebraically a dipole-dipole coupling, except for the spatial dependence of the interaction constant (I remind here that for the true electrical dipolar interaction the constant is proportional to R^{-3}).

Now about some properties of these two interactions. In line with the standard reasoning regarding the solid hydrogens at low temperatures, we shall consider only the states with $J = 0$ and 1. If we are working in the $J = 1$ manifold, then using the Wigner-Eckert theorem, we can reduce various spherical functions to functions of fixed $J = 1$ operators. What is interesting with the V_{12} and V_x operators, their matrix elements within the $J = 1$ manifold are all *identical zero.* It is this interaction that gives rise to the $J = 1$ roton in solid HD, whose bandwidth has been evaluated [5] to be about 2 K. It is no surprise because this roton is a state that is supported by transitions with the J flipping at a site from 0 to 1 and back. Thus, the above linear couplings will give nonzero interactions only if we have a mixed-J state.

If the problem is reduced to a single-particle one, the rotational wave function Ψ of molecule i can be written in the form

$$\Psi(\omega_i) \sim |0\rangle_i + \sum_\mu a_\mu(i)\, |1\mu\rangle_i\,. \qquad (18)$$

Here $|0\rangle$ and $|1\mu\rangle$ are the eigenfunctions of the momentum J. Note that in the homonuclear hydrogens this would not make sense, because the average of any operator involves strongly forbidden transitions between states of different parity (the so called $o-p$-transitions) and are thereby very small in magnitude. That is, in H_2 or D_2 the both $J = 0$ and $J = 1$ manifolds are almost entirely separated. It is not so in HD.

Let us come back to Eq. (18). The coefficients a_μ are in fact the order parameters. Thus far, there are three independent ones. If we take a homonuclear species, then the confinement strictly to the $J = 1$ manifold imposes the normalization restriction: $\Sigma_\mu a_\mu^2 = 1$. In addition, there is also a symmetry restriction reflecting the fact of head/tail indistinguishability for this homonuclear species. This leaves one linear combination of a_μ as a single independent order parameter.

Before going further with the properties of solid HD, I would like to compare the strengths of various interaction components.

Evaluation of the anisotropic interaction constants for HD as a function of the intermolecular separation was done employing the isotropic model potential suggested by Silvera and Goldman [6], where I took their parameters for the short-range repulsion and the values for the dispersion attraction coefficients as evaluated for H_2 by Mulder et al. [7]. Since the polarizabilities of H_2 and HD differ [8] by less than 0.5%, those values are very good estimates for HD.

In Fig. 3 the anisotropic interaction constants are compared with the strongest intrinsic anisotropic energy of the EQQ interaction. As one can see, all the interactions are weak specifically near the zero-pressure separation of $R_0 \simeq 7$ a.u. = 3.172 Å [1]. The U_{12} value is about –0.2 K per particle at R_0 and goes further down with decreasing spacing. The U_x constant is positive (0.7 K) but changes sign under a very low pressure, or at a slightly closer separation. Now we must take into account the quantum nature of the HD crystal, that is the potentials must be averaged over zero-point vibrations, which are substantial in solid HD. Since the points of intersection of both potential curves with the R axis are close to R_0, this averaging diminishes the interaction constants noticeably, making the evaluated constants and even their sign uncertain. Account of the higher (fourth) terms in Eqs. (11) and (12) «stabilizes» the interaction constants to be: $\overline{U}_{12}$ close to –0.14 K and $\overline{U}_x$ close to –0.32 K. The signs imply that the Heisenberg-like interaction will tend to orient the momenta homogeneously in parallel and the quasi-dipolar one will mainly serve as an anisotropy field that ties the parallel momenta to the crystallographic axes.

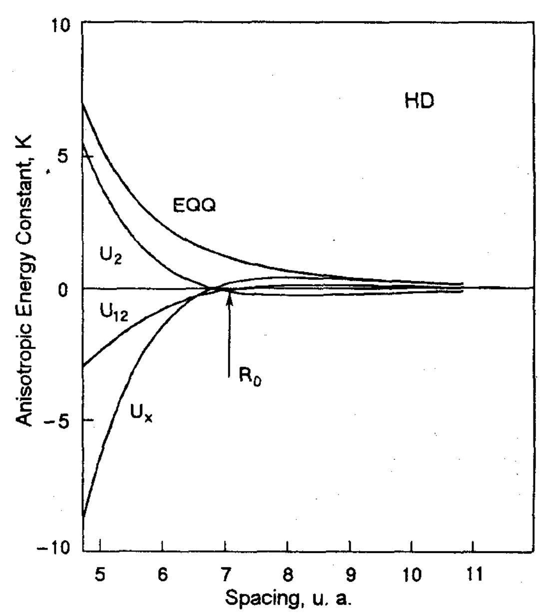

Fig. 3. The constants of the anisotropic interactions between HD molecules. R_0 is the nearest-neighbor separation in solid HD at zero pressure.

Finally, we must remember that the EQQ interaction is also actual for HD and, moreover, it is the most efficient interaction term for $J = 1$ states at low enough pressures. Let us compare the EQQ interaction with the anisotropic interactions inherent only in HD. At $R_0 = 7$a.u. the EQQ constant is 30–40 times stronger than the two interactions under consideration. However, as the pressure is raised, the dipolar interaction, for example, compares with the EQQ one at a pressure of roughly 5 kbar and then exceeds it in absolute magnitude at still higher pressures (shorter distances). Similarly, the Heisenberg-like interaction overtakes the EQQ one in magnitude at a pressure of about 8 kbar. Thus, at pressure above 5–8 kbar the specific anisotropic interactions are likely to become the main factor that will govern the order parameter if such appears.

Summing up, at higher densities, when one might expect a pressure-driven orientational order to appear, there will be three types of interaction ready to compete for the control of the emerging order parameter. More to that, since the Heisenberg-like interaction is nonfrustrative, in contrast to the quasi-dipolar and (especially) EQQ ones, it is expected to be dominating, the other two interaction components serving mostly as the factors that impose crystallography-related restrictions.

Considering the same problem at another angle, the mechanism of a possible pressure-driven transition to an ordered state of forced-nonzero-J states can be completely different from that in D_2 and (hypothetically) H_2, where the order is of collective character, i.e. being due to the total sum of EQQ interactions, which overweighs the energy loss of going to the higher $J = 1$ state. In HD, when both U_{12} and U_x are sufficiently strong (and they are the measure of the $J = 1$ roton band width), the creation of a single $J = 1$ roton can become energetically favorable as compared to the energy of excitation to the $J = 1$ state. This effect is basically the one generally recognized for the origin of zero-point vacancy waves in quantum crystals, when the gain due to the delocalization overweighs the loss of creating a vacancy.

Finally, we shall show that the presence of the specific anisotropic interactions in HD tends to introduce certain changes in the structure parameters of the HD solid. Suppose a spatially dependent distortion appears in the solid. Then the corresponding change of the elastic energy per unit volume in the continuum approximation will have the form (for a hcp structure with the c axis as the z direction)

$$W_{el} = (1/2)c_{11}(u_{xx}^2 + u_{yy}^2) + (1/2)c_{33}u_{zz}^2 + + c_{12}u_{xx}u_{yy} + c_{13}(u_{xx}u_{zz} + u_{yy}u_{zz}) , \quad (19)$$

where

$$u_{ij} = (1/2)(\partial u_i / \partial x_j + \partial u_j / \partial x_i) \quad (20)$$

is the distortion tensor. It is easy to show that

$$u_{zz} = \sqrt{3/8}\,\xi = \sqrt{3/8}\,c/a - 1 . \quad (21)$$

Regretfully, there are no measured or calculated elastic moduli for solid HD, even for zero pressure. So one has to guess, choosing between c_{ij} for H_2, obtained from sound velocities [9], and D_2 at 70 bar (deduced from neutron scattering data [10]).

Equation (20) should be complemented with the rotation-distortion coupling energy terms, one of which is Eq. (16). Similar terms come from U_{12} and U_x. The second-order perturbation theory yields $\xi = -0.0038$ (the sign is definite), which should be compared with the experimental value [1] of −0.015. The agreement is rather good, considering all the uncertainties involved.

Conclusions

1. The specific anisotropic interactions between HD molecules stemming from the fact that the HD molecules rotate not around their geometric centers can account for the structure anomalies found in experiment.

2. At comparatively moderate pressures (below 10 kbar) the specific anisotropic interactions compare with the electrical quadrupole-quadrupole interaction and can be the decisive factor in forming the eventual orientational order parameter to appear in a pressure-driven phase transition.

3. In solid HD, the rotational wave function involved is essentially a mixture of the $J = 0$ and $J = 1$ states at any pressure.

4. The mechanism of the pressure-driven orientational ordering might have a different (as compared to that in the homonuclear hydrogens) nature, the emerging delocalized $J = 1$ roton states being a direct analog of the zero-point vacancy waves suggested for ultimately quantum crystals.

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