New Ortho-Para Conversion Mechanism in Dense Solid Hydrogen

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Analysis of recent measurements of striking changes in the rate of ortho-para conversion of solid H$_2$ up to 58 GPa shows that the conversion mechanism must differ from that at ambient pressure. A new conversion mechanism is identified in which the emerging excitations are coupled to the converting molecules via electric quadrupole-quadrupole rather than nuclear spin-spin interactions. The latter only initiates conversion while the coupling enhancement associated with the new mechanism is ensured by high compression and a gap closing, with the conversion energy diminishing strongly with increasing pressure.

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The constraints of quantum mechanics link the possible rotational states of the hydrogen molecule to the total of its nuclear spins, leading to two species, ortho with parallel nuclear spins and para with opposite spins. Such a seemingly insignificant difference imparts major differences in the solid-state properties of the material and may be considered one of the most striking macroscopic manifestations of the microscopic laws of quantum mechanics. Characterization of the ortho-para state, and conversion between species, has become an especially important issue for understanding recently observed transformations in solid hydrogen at very high pressure. Ortho-para conversion in solid hydrogen at ambient pressure is mainly due to the magnetic dipole-dipole interaction between the nuclei of two neighboring ortho-molecules [1], with the energy released carried away by phonons [1–3]. With increasing pressure the conversion rate initially follows the density of phonon states and then decreases [4–7], in line with theoretical prediction [3]. Recent conversion rate measurements at higher pressures show, however, that this decrease, after reaching a minimum at a pressure of 2.5 GPa, changes over to a steep and ever accelerating growth to the maximum pressure of the measurements (58 GPa) [8–10]. These remarkable observations have not been explained.

We consider first $J = 2$ rotons and phonons as energy sinks. The $J = 2$ roton is too high for the conversion energy to bridge the gap at pressures below 60 GPa (Fig. 2). One cannot expect the same strong softening predicted for $J = 2$ excitations in pure parahydrogen [11,12] because in ortho-rich mixtures the number of nearest para-neighbors is insufficient for the $J = 2$ wave function to become delocalized. The phonon density of states brings [3] to the

\[ -c^{-2} \frac{dc}{dt} = d(c^{-1})/dt = K, \]  

where $c$ is the ortho-fraction; this equation takes into account the simple fact that two ortho-neighbors are needed for one of them to convert. Figure 1 shows measured inverse ortho-fractions versus time for several pressures. If the conversion rate $K$ were a pressure-dependent constant, the data would fall on straight lines. One can see that deviations from linearity are substantial, especially at higher pressures, implying that $K$ is a strong function of $c$, which can be due to deviations from randomness [10]. But even assuming no diffusion, the very large total slowdown effect implies mechanisms that differ from those considered previously [2,3].

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![FIG. 1. The inverse ortho-concentration vs time for a few representative pressures. The actual conversion is slower even without diffusion (adapted from [10]).](image-url)
conversion mechanism because the respective conversion energy (i.e., the average energy difference between the lowest $J = 1$ state of a molecule and the corresponding $J = 0$ state of the same molecule) decreases with increasing electric quadrupole-quadrupole (EQQ) interaction. At ambient pressure, librions have insufficient energy (about 20 K) to accommodate the relatively large conversion energy. However, this is not true at high pressures (Fig. 2).

The conversion promoting Hamiltonian $H_{ss}$ is the magnetic dipole interaction energy between the nuclear spins of ortho-neighbors. The only path considered so far was that in which the Hamiltonian $H_{ss}$ starts conversion and produces excitations. Another path, inactive at ambient pressure because of the energy conservation law, is that in which $H_{ss}$ serves only to initiate conversion in the chosen molecule at site 0 and not to create excitations. In line with the above reasonings and based on detailed analysis [15] we chose the respective phononless term from the Hamiltonian $H_{ss}$ in the form

$$
\hat{H} = -12\sqrt{14} \mu_0^2 d/2R^4 (\{ {\bf K} \otimes {\bf I}' \}_2 \cdot \{ {\bf C}_1(\omega) \otimes {\bf C}_3(n) \}_2).
$$

Here $\bf K = S_+ - S_-$ and $\bf I' = S'_+ + S'_-$ (primed and nonprimed quantities relate to different molecules), $S_{\pm}$ are the nuclear spins of the atoms in those molecules, $\mu_0$ is the proton magnetic moment, $w$ describes the orientation of the converting molecule, $R$ and $\bf n$ are, respectively, the internuclear distance and its unit radius vector, and we use Rcah’s harmonics and the commonly accepted notation for direct and scalar products of irreducible tensors.

The Hamiltonian $H_{ss}$ produces an intermediate state with molecule 0 in the $J = 0$ state and its surrounding still in the same state as before the conversion act. This is not an equilibrium state; the coupling between the translational and rotational degrees of freedom tends to relax both the molecular positions and quadrupole directions to a new equilibrium, causing new excitations to be created. The coupling is explicitly contained in the EQQ Hamiltonian. In line with the general idea of Berlinsky and Harris [16], the EQQ Hamiltonian of the intermediate state with molecule 0 in the $J = 0$ state can be restructured as

$$
H_{QQ}^{(\text{inter})} = H_{QQ}^{(0)} - \sum_j c_j h_{QQ}^{(0)} = H_0 + V_Q. \quad (3)
$$

Here $c_j$ is the ortho-occupancy of site $j$. The Hamiltonian $H_{QQ}^{(0)}$ with molecule 0 still in the $J = 1$ state serves as the unperturbed one. The second term denotes lack of the EQQ interaction between molecule 0 and all other ortho-molecules after conversion. The perturbation $V_Q$ can be represented as
\[ V_Q = - \sum c_j(25/6)\Gamma \sqrt{70} \xi^{5/3} \times \left[ (C_2(w_0) \otimes C_2(w_j))_4 \cdot C_4(n_0) \right], \quad (4) \]

where \( \Gamma = (6/25) (eQ)^2 / R^5 \) is the EQQ parameter and \( n_0 \) is the unit vector between molecules 0 and \( j \). As shown by recent experiments [17], \( \Gamma \) grows with compression as \( R^{-5} \), unlike the splitting of the \( J = 2 \) Raman line [18] where the crystal fields play a decisive role at high pressures. It can be shown that the asymptotic form of the EQQ interaction at pressures below 70 GPa is applicable better than to within 10% [19].

Now, the matrix element in the general expression for conversion probability takes the form

\[ \langle f|V|i \rangle = \sum \langle f|V_Q|(is) \rangle \langle (is)|H_{ss}|l \rangle / E_{(is)}, \quad (5) \]

where the summation runs over possible intermediate states with the energies \( E_{(is)} \). In pure ordered \( o-H_2 \) the intermediate state is unique for all the molecules and its energy is the pressure-dependent conversion energy \( E_c \), which is equal to the zero-pressure conversion energy minus the librion gap. In disordered (hcp) \( o-p \) mixtures the intermediate energies are distributed over a certain range [13], even at \( T = 0 \) K. Simplifying, we assume that at \( T = 0 \) K an \( o-p \) mixture can also be characterized by a unique energy, which depends both on pressure and ortho-fraction. The conversion probability is now

\[ W(10) = \frac{2\pi}{\hbar} \sum_{k} \frac{[k\alpha|V_Q|(is)]^2}{E_c^2} \times \sum_{i,j} P_j[(is)|\hat{h}|i)]^2 \delta(E_c - \omega_{k\alpha}), \quad (6) \]

where \( k, \alpha \) denote, respectively, the wave and mode numbers of the emerging librion and \( \omega_{k\alpha} \) is its dispersion law.

Equation (6) clearly shows how the role of the intermediate state changes with pressure. At zero pressure this channel is inactive since \( E_c \) is much larger than the typical librion energy of roughly 15\( \Gamma \). But as \( \xi \) increases, the former decreases while the latter grows so that this channel opens up at a certain pressure. Being a square of the ratio of the EQQ interaction to the conversion energy \( E_c \), the relevant coupling constant scales as \( \xi^{5/3} / [E_{c0} - 15\Gamma_0 \xi^{5/3}]^2 \). The efficiency of this channel increases very fast not only due to the large exponent of \( \xi^{13/3} \) but also due to the closing conversion gap. At a critical \( \xi \), the line \([E_{c0} - 15\Gamma_0 \xi^{5/3}] \) crosses the \( \xi \) axis; i.e., the gap closes and the coupling diverges. In fact, this does not happen because even at smaller \( \xi \) this line will leave the region of energies where the librion states are mainly concentrated and this channel will again become ineffective. Thus, this channel operates within a certain range of \( \xi \), above which the rate is expected to drop abruptly to values that are ensured by other, less efficient (e.g., phonon-mediated) channels.

The matrix element \( \langle (is)|\hat{h}|i \rangle \) can be easily calculated as for the direct phonon-promoted mechanism [2,15]. The conversion probability becomes

\[ W(10) = \frac{A \gamma_{ss}}{\hbar} \frac{(d)}{2R_0} \frac{\Gamma_0}{E_c^2} \xi^{13/3} \Phi(e). \quad (7) \]

Here \( A = 640 \pi / 9, \ e = E_c / \Gamma, \ \Gamma = \Gamma_0 \xi^{5/3}, \) and

\[ \Phi(e) = \sum_{k\alpha} |(k\alpha|V_Q(0)|(is))|^2 \delta(e - \omega_{k\alpha}(0)), \quad (8) \]

where the energies are normalized to \( \Gamma = \Gamma_0 \xi^{5/3} \). Thus, the entire pressure dependence is shifted to \( e \).

Since any theory for the energy spectrum in disordered (and even ordered) \( o-p \) mixtures is lacking, we construct a semi-quantitative theory, considering first the case of the orientationally ordered phase of pure \( o-H_2 \), and then introduce corrections. For ordered \( o-H_2 \), we express \( C_2(w_j) \) in Eq. (4) through creation operators [20] to get finally

\[ \Phi(e) = \frac{72}{N} \frac{4}{\delta_e} \sum_{k\alpha} \sum_{jj'} \gamma(j) \gamma(j') \exp[i \mathbf{k} \cdot (j - j')] \times [V_{a\lambda}(k) + V_{a\lambda}^*(k)] \times [V_{a\lambda}(k) + V_{a\lambda}^*(k)] \delta(e - \omega_{k\alpha}(k)). \quad (9) \]

This expression can be evaluated only numerically. A rough estimate, the accuracy of which is difficult to assess, of the magnitude of \( \Phi \) can be obtained by taking the dispersion law for all modes to be the same and making use of available numerical calculations [16]. By definition, the conversion rate \( K \) is \( 12W(1,0) \), which gives

\[ K(1,0) = 7.21 \xi^{8/3} \frac{\Gamma_0 \xi^{5/3}}{E_c^2} g_0(e). \quad (10) \]

We now calculate how \( E_c \) depends on \( \xi \) and the lower boundary of \( \xi \) for the mechanism to be operative. By definition, \( E_c \) is the difference between the conversion energy in the gas, \( E_{c0} = 2B = 170.5 \) K, and the energy per \( J = 1 \) molecule in the ground state. Using values deduced from measurements [21] (in particular, the librion frequencies obtained by Raman scattering at ambient pressure [22]), we find that the mechanism works from \( \xi_0 \approx 3.2 \) to \( \xi_c \approx 4.9 \) (Fig. 2).

Going from fcc to hcp results in a narrower spread of states within the \( J = 1 \) manifold. As can be inferred from inelastic neutron scattering results [13], for ortho-fractions of \( \sim 75\% \) the bottom level in hcp is shifted upward by about 1.5 K. This gives \( \xi_0 = 3.7 \) and \( \xi_c = 7.2 \); i.e., the mechanism is shifted to larger compressions. Another important feature is that the excited states are expected to occupy a broader interval, which brings about a rarified density of states but makes the channel operative over a wider stretch of \( \xi \) values. The effect of para-molecules is the evident depletion of the librion spectrum, roughly proportional to \( (1 - c) \). At \( \xi \) between 5.5 and 6 the rate starts to diminish and terminates at 7.2. The rates calculated by this approach are shown in Fig. 3 for pure \( o-H_2 \) and for a
FIG. 3. The conversion rate vs reduced density at high compression. The points are from [8,10] (solid circles) and [9] (empty squares). The open circles are earlier data (see [8,10]) and the shaded area shows the theory from [3]. The dashed line is theory for the orientationally ordered pure $^2\text{H}_2$ phase, the solid curve, for (hcp) normal $^2\text{H}_2$; the dotted lines indicate nominal divergence. Inset: Low density region.

normal (75% ortho) hcp mixture. Other new channels (a total of 14) contribute for $\xi$ from about 2.5 to 6 but do not lead to an abrupt increase [15].

In conclusion, analysis of conversion rate data reveals a mechanism that differs from that employed to explain low-pressure data. The steep increase in conversion rates at high pressures can be explained by a conversion channel that involves an intermediate state in which new excitations are created due to the EQQ coupling between rotational momenta. The enhancement may be ascribed to a gap closing that arises when the EQQ interaction becomes sufficient to substantially diminish the conversion energy released because of the lowering of the ground-state level of the ortho-molecule suffering conversion. This concentration-sensitive channel comes into play at compressions $\xi$ between 3 and 4 and ceases to operate at higher values ($\xi = 6$ and 7), depending on the ortho-concentration. Thus, this theory predicts a significant reduction in the conversion rate at $>80$ GPa; extending the measurements to higher pressure will thus provide a critical test of the present theory.

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[19] The use of the EQQ interaction is justified as follows. Over the pressure range examined, the characteristic dimension of the charge distribution of the molecule (derived from $Q = er^2$) is considerably less than the interatomic separation $R$ such that $r/R < 0.25$. As a result, the energy of the hexadecupolar interaction does not exceed 8% of the quadrupolar energy. Moreover, we are concerned with matrix elements between $J = 1$ states and between $J = 0$ and $J = 2$ states, for which the hexadecupolar matrix elements are zero.