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.

Given the conversion-initiating interaction, when choosing a conversion mechanism capable of yielding the high rates measured experimentally one must find an excitation which satisfies the following conditions: a strong coupling to the conversion process, energetic feasibility (conservation law), and a sufficient density of states in the proper energy region. There are several promising channels, each deserving detailed consideration. Some of these channels, though essentially insignificant or even inoperative at zero pressure, contain factors that at high compressions outweigh the unfavorable factors. We suggest a new conversion enhancement mechanism, based on the idea of an intermediate state.

The rate of ortho-para (o-p) conversion obeys the equation

$$-c^{-2}dc/dt = d(c^{-1})/dt = K, \tag{1}$$

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].

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

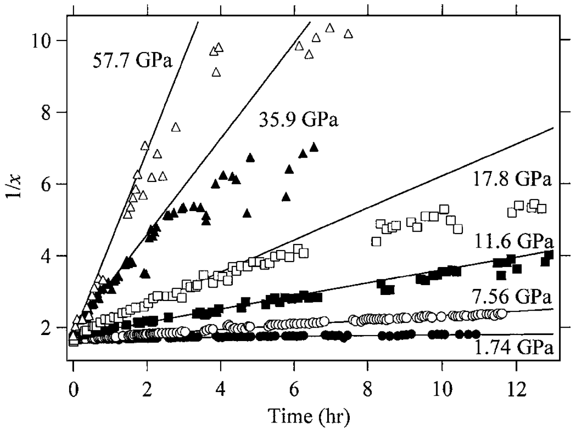

FIG. 1. The inverse ortho-concentration vs time for a few representative pressures. The actual conversion is slower even without diffusion (adapted from [10]).

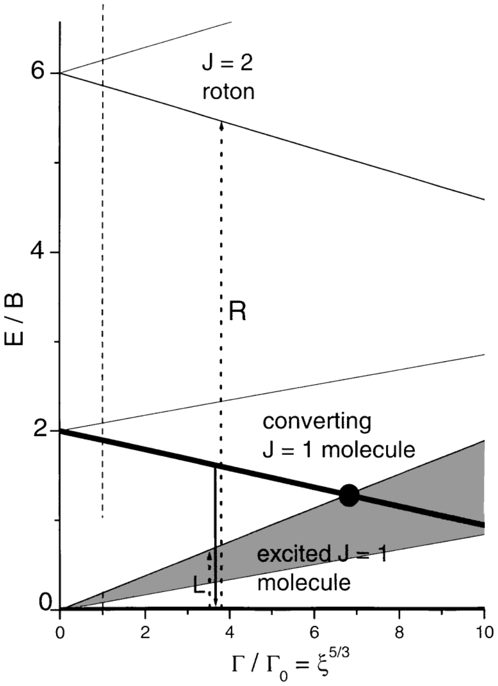

FIG. 2. Energy scheme of conversion transitions involving $J = 1$ and $J = 2$ excitations with varying EQQ interaction. B is the rotational constant. The conversion energy released is from the ground state (thick line) of the converting molecule into the empty states (filled area) of the energy receiving molecule. At $\Gamma \simeq 3.7$ the libronlike excitations (L) are too weak and the $J = 2$ roton (R) is too strong to accommodate the conversion energy. At a critical Γ (large circle) the energy span of the excited molecule is wide enough to take up the conversion energy.

conversion probability the factor $1/\Theta$, where Θ is the Debye temperature. Since the square of the respective coupling constant is the ratio of the kinetic energy of quantum confinement $\Delta_0 = \hbar^2/2MR^2$ (R being the spacing, and M, the molecular mass) to the typical phonon energy Θ, every emerging phonon brings another factor Δ_0/Θ. Since Θ is a much stronger function of the molar density ratio $\xi = \rho(P)/\rho(0)$ than $R^2 \propto \xi^{2/3}$, the phonon related channels are seriously handicapped. Thus, both phonons and $J = 2$ rotons are ineffective. We also disregard the double-conversion mechanism because the respective conversion energy is twice as large as in the single-conversion act, which precludes fulfillment of the energy conservation law up to 100 GPa.

We now consider excitations within the $J = 1$ manifold. In a disordered hcp system every molecule is in a molecular field, which varies from site to site and with time. At sufficiently low temperatures, all molecules are in their different ground states; the other two states are excitations, which are local in the molecular field approximation and spread over the neighbors when the off-diagonal terms are taken into account. These delocalized excitations are short ranged but the overall energy spectrum of these excitations has much in common with the libron spectrum of the $Pa3$ array, as far as its span and, to a lesser extent, distribution are concerned. This span, which can be deduced from inelastic neutron scattering [13] or NMR [14] data, is slightly less than the sum of the libron gap and band. The 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, librons 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

$$\hat{h} = -12\sqrt{14}\,\mu_0^2 d/2R^4(\{\mathbf{K} \otimes \mathbf{I}'\}_2 \cdot \{\mathbf{C}_1(\mathbf{w}) \otimes \mathbf{C}_3(\mathbf{n})\}_2). \tag{2}$$

Here $\mathbf{K} = \mathbf{S}_+ - \mathbf{S}_-$ and $\mathbf{I}' = \mathbf{S}'_+ + \mathbf{S}'_-$ (primed and nonprimed quantities relate to different molecules), $\mathbf{S}_\pm$ are the nuclear spins of the atoms in those molecules, μ_0 is the proton magnetic moment, $\mathbf{w}$ describes the orientation of the converting molecule, R and $\mathbf{n}$ are, respectively, the intermoleculer 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

$$\mathcal{H}_{QQ}^{(\mathrm{inter})} = \mathcal{H}_{QQ}^{(0)} - \sum_j c_j h_{QQ}^{(0j)} \equiv H_0 + V_Q. \tag{3}$$

Here c_j is the ortho-occupancy of site j. The Hamiltonian $\mathcal{H}_{QQ}^{(0)}$ 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

$$V_Q = -\sum_j c_j (25/6)\Gamma\sqrt{70}\,\xi^{5/3} \times [\{\mathbf{C}_2(\mathbf{w}_0) \otimes \mathbf{C}_2(\mathbf{w}_j)\}_4 \cdot \mathbf{C}_4(\mathbf{n}_{0j})], \qquad (4)$$

where $\Gamma = (6/25)\,(eQ)^2/R^5$ is the EQQ parameter and $\mathbf{n}_{0j}$ is the unit vector between molecules 0 and j. As shown by recent experiments [17], Γ 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

$$\langle f|V|i\rangle = \sum_{(is)} \frac{\langle f|V_Q|(is)\rangle\langle(is)|H_{ss}|i\rangle}{E_{(is)}}, \qquad (5)$$

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 libron 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

$$W(10) = \frac{2\pi}{\hbar}\sum_{\mathbf{k}\alpha}\frac{|\langle\mathbf{k}\alpha|V_Q|(is)\rangle|^2}{E_c^2} \times \sum_{i,\mu} P_i|\langle(is)|\hat{h}|i\rangle|^2\delta(E_c - \omega_{\mathbf{k}\alpha}), \qquad (6)$$

where $\mathbf{k}, \alpha$ denote, respectively, the wave and mode numbers of the emerging libron and $\omega_{\mathbf{k}\alpha}$ 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 libron energy of roughly 15Γ. But as ξ 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 ξ, the line $[E_{c0} - 15\Gamma_0\xi^{5/3}]$ crosses the ξ axis; i.e., the gap closes and the coupling diverges. In fact, this does not happen because even at smaller ξ this line will leave the region of energies where the libron states are mainly concentrated and this channel will again become ineffective. Thus, this channel operates within a certain range of ξ, 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

$$W(10) = A\frac{\gamma_{ss}}{\hbar}\left(\frac{d}{2R_0}\right)^2\frac{\Gamma_0}{E_c^2}\,\xi^{13/3}\Phi(\varepsilon). \qquad (7)$$

Here $A = 640\pi/9$, $\varepsilon = E_c/\Gamma$, $\Gamma = \Gamma_0\xi^{5/3}$, and

$$\Phi(\varepsilon) = \sum_{\mathbf{k}\alpha}|\langle\mathbf{k}\alpha|V_Q^{(0)}|(is)\rangle|^2\delta(\varepsilon - \omega_{\mathbf{k}\alpha}^{(0)}), \qquad (8)$$

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

Since any theory for the energy spectrum in disordered (and even ordered) o-p mixtures is lacking, we construct a semiquantitative 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 $\mathbf{C}_2(\mathbf{w}_j)$ in Eq. (4) through creation operators [20] to get finally

$$\Phi(\varepsilon) = 72\,\frac{4}{N}\sum_{\mathbf{k}\lambda}\sum_{jj'}\gamma(j)\gamma(j)^*\exp[i\mathbf{k}\cdot(\mathbf{j} - \mathbf{j}')] \times [V_{\alpha\lambda}^*(\mathbf{k}) + V_{\tilde{\alpha}\lambda}^*(\mathbf{k})] \times [V_{\alpha'\lambda}(\mathbf{k}) + V_{\tilde{\alpha}'\lambda}(\mathbf{k})]\delta[\varepsilon - \omega_\lambda(\mathbf{k})]. \qquad (9)$$

This expression can be evaluated only numerically. A rough estimate, the accuracy of which is difficult to assess, of the magnitude of Φ 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

$$K(1,0) \simeq 7.21\xi^{8/3}\,\frac{\Gamma_0\xi^{5/3}}{E_c^2}\,g_0(\varepsilon). \qquad (10)$$

We now calculate how E_c depends on ξ and the lower boundary of ξ 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 libron frequencies obtained by Raman scattering at ambient pressure [22]), we find that the mechanism works from $\xi_0 \simeq 3.2$ to $\xi_c \simeq 4.9$ (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 ~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 ξ values. The effect of para-molecules is the evident depletion of the libron spectrum, roughly proportional to $(1 - c)$. At ξ 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

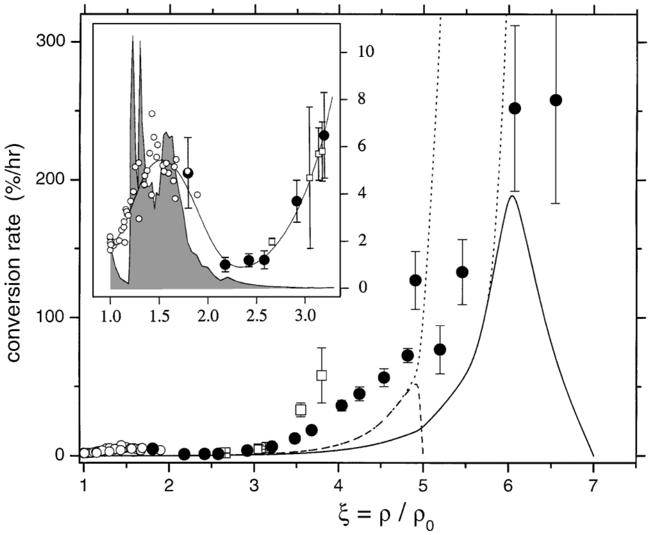

FIG. 3. The conversion rate vs reduced density at high compression. The points are from [8,10] (solid circles) and [9] (empty squares). The open circles are earlier data (see [8,10]) and the shaded area shows the theory from [3]. The dashed line is theory for the orientationally ordered pure o-H_2 phase, the solid curve, for (hcp) normal 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 ξ 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 ξ 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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