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Ortho-para conversion of hydrogen at high pressures

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Ortho-para conversion rates in solid H_2 measured as a function of pressure up to 58 GPa are examined theoretically. Analyses of the data provide information on the relative role of diffusion versus intrinsic dependences of the conversion rate on ortho concentration. A theory of the conversion has been developed using a closed-form representation of the conversion promoting nuclear magnetic interaction H_{ss} expanded in spherical harmonics. The mechanisms considered include double conversion, excitations in the $J=1$ and $J=2$ manifolds as conversion energy sinks, and a possibility of intermediate states from which the conversion energy is dissipated via the strong electrical quadrupole-quadrupole (EQQ) interaction. Conversion rates were evaluated for a total of 12 new channels; the two other channels considered previously for moderate pressures have been reconsidered to account for factors that influence phonon-assisted energy dissipation, the most important being the compression-related decrease of the conversion energy (gap closing). Contributions from the standard one-phonon channels with single and double conversion yield fairly good agreement with low-pressure data. The proposed new channel identified as responsible for the observed conversion acceleration is the one in which the conversion Hamiltonian H_{ss} only initiates conversion driving the system to a temporarily nonequilibrium state from which the conversion energy is dissipated via EQQ coupling into excitations within the $J=1$ manifold. Our mechanism predicts a strong and abrupt conversion slowdown at still higher compressions. The abrupt decrease in rate observed at a given pressure at longer times (decreasing ortho fractions) can be explained as due to the inability of slow diffusion to restore the random distribution of ortho species and due to the intrinsic inefficiency of the new channel at low c.

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I. INTRODUCTION

The application of very high pressure has proved to be a singular means by which a broad range of physical phenomena can be explored, from molecular dissociation and metallization to quantum solid-state effects. Ortho-para conversion in solid hydrogen, an ultimately quantum process, is one of the striking examples. Varying pressure opens up and makes possible a spectrum of new conversion mechanisms, ‘‘switching in’’ an ensemble of low-frequency rotational and translational excitations. It is commonly accepted that ortho-para (o-p) conversion in solid hydrogen is well understood for pressures up to a few gigapascals. The main conversion promoting mechanism is the magnetic dipole-dipole interaction between the nuclei of two neighboring ortho molecules[1] whereas the energy released in the conversion process is carried away by phonons. At zero pressure the prevailing energy-removal mechanism is emission of two phonons.[1,2] There must be also a substantial contribution from one-phonon processes owing to the quantum-crystal nature of solid hydrogen.[3] As the pressure is raised to a few gigapascals, the one-phonon process becomes dominant.[3]

The first experiments on o-p conversion date back to the 1930s. The conversion in the solid is a slow process requiring months for a sample to come to equilibrium with respect to the o-p-fraction ratio. Conversion at elevated pressures has attracted interest, in particular, in an attempt to utilize it as a probe of the phonon density of states in the highly anharmonic quantum crystal of hydrogen. The conclusion reached so far was that, as the pressure is increased to a moderate value of several gigapascals, the dominant conversion-energy-removing mechanism becomes the one-phonon emission that accompanies the conversion of one ortho molecule;[3] the relevant density of states, as deduced from conversion rates under pressure,[4–6] mimics roughly what follows from calculations[7] and experiment.[8,9] Hence, the conversion rate is expected to diminish rather rapidly as the pressure is raised. However, as recent conversion rate measurements at high pressures show,[10–13] this decreasing behavior of the rate versus pressure, after reaching a minimum at around 5 GPa, changes over to a steep and ever accelerating growth. There were only general plausible guesses as to what might be the cause for that extraordinary conversion enhancement but no specific model has been suggested.

There are three main factors that influence the magnitude of the ortho-para conversion rate in solid H_2. The first is the mechanism that drives an ortho molecule to convert to the para state; this factor involves various magnetic field sources that make an ortho molecule convert. The second is the channel responsible for carrying away the energy released in the conversion process. The third is the spatial distribution of ortho molecules in the sample. Each channel includes the type of energy-removing excitation, the type of conversion act, and the pathway. The energy sinks to be considered are phonons, $J=2$ excitations, and reorientations within the $J=1$ manifold (which we call librons to distinguish from rotons). We consider two conversion types, the standard (single-conversion) act in which one ortho molecule goes to para state and a double conversion act in which both molecules convert simultaneously. The pathway implies the way the conversion process occurs: in the standard process considered previously for low pressures[1–3] the magnetic nuclear dipole interaction H_{ss} initiates conversion and, simultaneously, ensures energy removal (via phonons). It is, however, possible to separate these two processes; namely, H_{ss} will be needed to promote conversion itself and to drive the system to an intermediate state from which excitations are created via a more ‘‘promising’’ interaction [for instance, electrical quadrupole-quadrupole (EQQ)]. Thus, the standard channel considered previously is a single-conversion process promoted by the nuclear magnetic dipole interaction with one or two phonons emitted. At low pressures the idea of intermediate state is not good because an intermediate state brings to the probability a small coefficient. Yet at higher pressures, this unfavorable circumstance is outweighed by the high power of the compression ratio $\xi=\rho/\rho_0$ (ρ_0 is the molar density at zero pressure) and by other factors.

Experiments on ortho-para conversion in dense hydrogen have been carried out over the pressure range where the solid H_2 adopts the hcp structure and is essentially orientationally disordered. This makes the theoretical task especially difficult, since even at zero pressure there is no theory of the rotational energy spectrum of this highly random system. Moreover, some of the issues pertaining to the general notion of the form of individual parts of the rotational spectrum have not been addressed. Fortunately, there is sufficient experimental evidence for reasonable estimates of the relevant energies to be inferred. In some cases, in order to obtain at least semiquantitative results, we performed calculations for the 100% fcc orientational ordered array of quadrupoles, subsequently introducing reasonable corrections to account for lower ortho fractions and hcp structure. The most promising channel turned to be the one in which H_{ss} only drives an ortho molecule to convert, creating an intermediate state which is momentarily out of equilibrium and which relaxes back to equilibrium-emitting libronlike excitations via the EQQ interaction.

The aim of this paper is to consider all the factors and mechanisms that control ortho-para conversion in an attempt to single out those that can be decisive for very high pressures. The structure of this paper is as follows. In Sec. II we recast the standard nuclear magnetic dipole-dipole interaction Hamiltonian into a closed general form, which is convenient for subsequent calculations. The basic experimental results on conversion from 0.4 to 60 GPa (Refs. 10 and 12) are analyzed in Sec. III in order to examine relevant mechanisms. In Sec. IV we examine in general terms the three basic energy sinks, namely, phonons, $J=2$ excitations (rotons), and ‘‘librons’’ (excitations within the $J=1$ manifold). Calculations for all the channels are in Sec. V; part of the relevant algebra is moved to the Appendix. Section VI contains general discussion and conclusions.

II. HAMILTONIAN

In this section we focus on the conversion promoting Hamiltonian, recasting it to a form suitable for high pressures. The cause that drives an ortho molecule of H_2 to convert is the magnetic field gradient felt by the nuclear magnetic moment of this molecule. In pure hydrogen there are two magnetic field sources. One is the total nonzero nuclear moment of the conversion-promoting ortho neighbor while the other is the magnetic field produced by the rotating motion of the same ortho neighbor. The nuclear spin-spin interaction H_{ss} and the spin-rotation interaction H_{sr} vary with intermolecular distance in the same way ($\propto R^{-3}$) and H_{sr} scales[1] to H_{ss} as $(2-3)\times 10^{-2}$ irrespective of density (pressure). The corresponding correction can be introduced by multiplying the final result by 1.05. So for the sake of simplicity we leave only the prevailing spin-spin term.

The magnetic dipole interaction between the nuclear spins of molecules i and i' is characterized by the energy

$$H_{ss}=-4\sqrt{6}\mu_0^2\sum_{\sigma,\sigma'=\pm 1}\sum_{\nu\tau}C(112;\nu,\tau-\nu)$$

$$\times S^{\nu}_{i\sigma}S^{\tau-\nu}_{i'\sigma'}C^{*}_{2\tau}(\Omega_{i\sigma,i'\sigma'})R^{-3}_{ij}. \qquad (1)$$

Here μ_0 is the nuclear magnetic moment of the proton; $\mathbf{R}_{i\sigma,i'\sigma'}=\mathbf{R}_0+(d/2)(\mathbf{w}'\sigma'-d\mathbf{w}\sigma)$; σ and σ' denote protons, respectively, in molecules i and i'; $S^{\nu}_{i\sigma}$ is the ν spherical projection of the nuclear spin operator of proton σ in molecule i; d is the interatomic distance in the hydrogen molecule; $\mathbf{w}$ and $\mathbf{w}'$ are the unit vectors along the respective molecular axes; $\Omega_{i\sigma,i'\sigma'}$ is the unit vector along the axis connecting the two protons chosen; $C_{2\tau}(\Omega)$ are Racah's spherical harmonics; $C(112;\nu,\tau-\nu)$ are the Clebsch-Gordan coefficients.

Let us express the nuclear spin variables through their linear combinations

$$\mathbf{I}_i=\mathbf{S}_{i+}+\mathbf{S}_{i-}, \qquad (2)$$

which is the total nuclear moment of molecule i, and

$$\mathbf{K}_i=\mathbf{S}_{i+}-\mathbf{S}_{i-}, \qquad (3)$$

which is the operator linking states of different parity of the same molecule.

In these variables the Hamiltonian (1) takes the form

$$H_{ss}=H_{II}+H_{IK}+H_{KI}+H_{KK}. \qquad (4)$$

The same superscripts ii' are omitted. All the terms are similar in form (see below). Analysis of all four can be found in Van Kranendonk's book.[14] We consider first the term $H^{ii'}_{KI}$, which initiates ortho-to-para transitions in molecule i, leaving molecule i' in the ortho state. This term, for brevity denoted as V, is

$$V\equiv H^{ii'}_{KI}=-4\sqrt{6}\mu_0^2\sum_{\tau}Z_{2\tau}$$

$$\times\frac{F_{++}+F_{+-}-F_{-+}-F_{--}}{4}. \qquad (5)$$

Here

$$F_{\sigma\sigma'}=\frac{C_{2\tau}(\Omega_{i\sigma,i'\sigma'})}{|\mathbf{R}_{i\sigma,i'\sigma'}|^3} \tag{6}$$

and we introduced the irreducible rank-2 tensor

$$Z_{2\tau}=\sum_{\mu} C(112;\mu,\tau-\mu)K_i^{\mu}I_{i'}^{\tau-\mu}. \tag{7}$$

In Eq. (5) the sum of the four F's is symmetric under a head-tail permutation of molecule i' and antisymmetric under the same permutation of molecule i. Hence the expansion of this sum in spherical harmonics of the orientation variables of both molecules will contain terms odd in $\mathbf{w}_i$ and even in $\mathbf{w}_{i'}$. The rest will cancel out. Therefore the expression $[F_{++}+F_{+-}-F_{-+}-F_{--}]/4$ can be simply substituted by F_{++} but one should bear in mind terms of what symmetry are to be retained in the expansion.

In order to obtain from Eq. (5) or (6) the terms responsible for conversion, this energy is expanded in powers of $d/2R$. In fact, this parameter, which is sufficiently small (approximately 0.1) at ambient pressure, appears in H_{KI} in Eq. (5) together with functions of the vectors $\mathbf{w}$ or $\mathbf{w}'$. These functions govern the matrix elements of the transitions involving the final and initial rotational states of the participating molecules. The quantity F in Eq. (6) is a function of two molecular unit vectors $\mathbf{w}$ and $\mathbf{w}'$ and the intermolecular unit vector $\mathbf{n}$. The dipole-dipole interaction (in our case, magnetic) has a specific form which permits this interaction to be represented as a closed and rather simple formula. We demonstrate this procedure[15,16] for $\mathbf{R}=R\mathbf{n}=\mathbf{r}_2-\mathbf{r}_1=r_2\mathbf{n}_2-r_1\mathbf{n}_1$ (assuming, without losing generality, $r_2>r_1$), recasting the known expression[15] as convenient for our purposes:

$$\frac{C_{LM}(\mathbf{n})}{R^{L+1}}=\sum_{l=0}^{\infty} B(L,l)(-)^{L+l}\frac{r_1^l}{r_2^{L+l+1}} \times\{\mathbf{C}_l(\mathbf{n}_1)\otimes\mathbf{C}_{L+l}(\mathbf{n}_2)\}_{LM}, \tag{8}$$

with

$$B(L,l)=\left[\frac{(2L+2l+1)!}{(2L+1)!(2l)!}\right]^{1/2}. \tag{9}$$

Hereinafter we employ the standard definitions[15,17] of the irreducible tensor product of two irreducible tensors $\mathcal{M}$ and $\mathcal{N}$,

$$\{\mathcal{M}_{J_1}\otimes\mathcal{N}_{J_2}\}_{Jm}=\sum_{n} C(J_1J_2J;n,m-n)\mathcal{M}_{J_1,n}\mathcal{N}_{J_2,m-n}, \tag{10}$$

and of the scalar product of two irreducible tensors, say, $\mathcal{R}_L$ and $\mathcal{Q}_L$, of the same rank L,

$$(\mathcal{R}_L\cdot\mathcal{Q}_L)=\sum_{m} \mathcal{R}_{Lm}\mathcal{Q}_{Lm}^{*}. \tag{11}$$

Now we apply Eq. (8) to our case, expanding consecutively in the small-value vectors $d\mathbf{w}/2R$, $d\mathbf{w}'/2R$, and $\mathbf{s}/R$, where $\mathbf{s}$ is the relative displacement of the two interacting neighbors. After simple algebra we finally have

$$\frac{C_{2\tau}(\mathbf{R}_{++})}{R^3} =\sum_{l,m,p=0}^{\infty} S(l,m;p)\frac{(d/2)^{l+m}|\mathbf{s}|^p}{R^{3+l+m+p}}\{\mathbf{C}_l(\mathbf{w})\otimes\{\mathbf{C}_m(\mathbf{w}') \otimes\{\mathbf{C}_p(\mathbf{s})\otimes\mathbf{C}_{2+l+m+p}(\mathbf{n})\}_{2+l+m}\}_{2+l}\}_{2\tau}, \tag{12}$$

where

$$S(l,m;p)=\sqrt{\frac{(5+2l+2m+2p)!}{5!(2l)!(2m)!(2p)!}}. \tag{13}$$

We stress that this expression is exact and complete. Equation (12) allows us to pick easily an arbitrary term of the necessary symmetry. We shall also use a shorter definition

$$\hat{h}(lm;p)\equiv\sum_{\tau} Z_{2\tau}\{\mathbf{C}_l(\mathbf{w})\otimes\{\mathbf{C}_m(\mathbf{w}') \otimes\{\mathbf{C}_p(\mathbf{s})\otimes\mathbf{C}_{2+l+m+p}(\mathbf{n})\}_{2+l+m}\}_{2+l}\}_{2\tau}, \tag{14}$$

with $Z_{2\tau}$ from Eq. (7). The irreducible tensor of rank zero in Eq. (14) is essentially (to within a scalar function) the corresponding partial Hamiltonian.

This result stems from the specific form of the dipolar interaction. We note that the coefficients in Eq. (12) are regular functions of $d/2R$, in contrast to anisotropic interactions of arbitrary form, which generate spherical harmonic expansions with the coefficients explicitly diverging as R tends to d (if both interacting particles are linear molecules) (Ref. 18) or to $d/2$ (if one of the particles is a spherical entity) (Ref. 19).

There is a term in the nuclear spin-spin interaction Hamiltonian (1) or (5), namely, H_{KK}, which can be important at higher pressures. In form it coincides with the term just considered, H_{KI}, but contains odd harmonics of both angular momenta. An analog of the sum in Eq. (5) for this term reads $F_{++}-F_{+-}-F_{-+}+F_{--}$. The Hamiltonian H_{KK} is responsible for processes in which two interacting ortho molecules convert simultaneously. The ratio of the coefficients at $\hat{h}(1,1;0)$ to $\hat{h}(1,0;0)$ is $6(d/2R_0)\xi^{1/3}$. Even with account of the typical proportion of matrix elements this ratio does not seem to be prohibitively small. Previously, this term has been rightfully neglected because in this process the two simultaneous conversion acts release twice as large energy ($2E_{con}\simeq 340$ K), which at low pressures can be in no way dissipated into one or even two phonons.

III. OVERVIEW OF RECENT EXPERIMENTAL RESULTS

We now summarize the results and analyses of recent measurements of ortho-para conversion in solid H_2 at high pressure. NMR measurements, which in principle provide a direct measure of the conversion, have been reported to 12.8

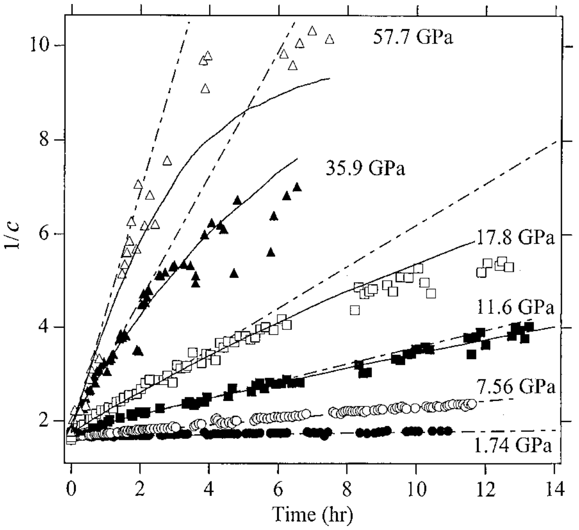

FIG. 1. The inverse ortho fraction vs time for several pressures. The dash-dotted lines are linear fits to short-time data. The solid lines are Monte Carlo best fits (see text).

GPa.[11] Raman measurements have been carried out over a much broader range of pressures from 0.9 to 57.7 GPa, with more extensive data coverage at intermediate pressures and at short times.[10,12] Although Raman spectroscopy provides a less direct measure of the conversion than does NMR, the two data sets are in excellent agreement within their mutual error bars over a broad range of pressures and densities (as discussed further below). In Fig. 1 we show inverse ortho fractions calculated from integrated Raman intensities as a function of time. At short times, all the curves are rather close to straight lines but at longer times the deviations from the linear law are substantial, especially at the higher pressures. These deviations contain valuable information about the kinetics of the ortho system, which can be a result of the simultaneous action of conversion and migration, both of which can be pressure dependent. We compare different methods of analysis in order to draw qualitative conclusions regarding conversion mechanisms and channels.

As we are dealing with solid hydrogen at low temperatures, the conversion is mostly that of ortho-to-para. A typical experimental situation in this case corresponds to a large ortho fraction decaying in time. Since ortho-to-para conversion is caused by the interaction with neighboring ortho molecules, the rate of variation of the ortho fraction c is proportional to the average number of nearest ortho neighbors, M:

$$\frac{dc}{dt}=-\frac{K}{12}Mc \tag{15}$$

or

$$\frac{d}{dt}\left(\frac{1}{c}\right)=K\frac{M}{12c}. \tag{16}$$

By removing c^2 from the right-hand side of Eq. (15) one takes fully into account the simple fact that two ortho neighbors are needed for at least one of them to convert to para. If the ortho distribution is random, then $M=12c$ (12 nearest neighbors in a hcp lattice). If now K is independent of c, Eq. (15) is a second-order rate equation permitting analytical solution:

$$1/c=1/c(0)+Kt. \tag{17}$$

At low pressures and over almost the entire range of temperatures T and ortho concentrations c (except for $T<1.5$ K and $c\leqslant 4\%$), K does not indeed deviate significantly from a constant value during many hours.[4,20] At higher pressures and longer times, deviations from linearity can arise from a nonrandom distribution of ortho molecules as well as from an ortho fraction dependence of the overall K.

The former factor depends to a large extent on the ability of diffusion to restore the distribution to random. Regardless of its mechanism but depending on the interplay of the energy parameters, diffusion can lead to opposite results. If the temperature is high (as compared to the characteristic anisotropic interaction energy between ortho molecules), the equilibrium distribution is random and fast diffusion is capable of efficiently maintaining randomness. In the low-temperature case, when diffusion is faster than conversion, the number of ortho-ortho nearest-neighbor pairs will be substantially larger than in the random distribution, as observed in clusterization at low ortho fractions and low temperatures.

A method for examining the role of diffusion in the restoration of random distributions was described in Ref. 12. Assuming the conversion rate K to be independent of c, the K values were determined by restricting the analysis to the initial decay at very short times (see Fig. 1). The entire data set was also fitted to Eq. (15) or (16) directly, using two methods, a mean-field rate equation based on the work of Schmidt[20,21] and Monte Carlo simulation based on the method developed by Perrell and Haase.[22] As described in Ref. 12, for $c>0.3$, the different approaches are in good agreement, while for $c<0.3$ the random distribution result underestimates the experimental concentrations, the mean-field model overestimates the concentration (as expected for a mean-field model[23]), and the Monte Carlo simulation fits the data quite well. Good agreement with the concentration versus time data is found at all pressures using the Monte Carlo approach (e.g., Fig. 1); however, deviations between the calculations and the experimental data appear to increase at longer times and lower running ortho fractions.[12]

In view of the deviations from the model at lower c, it is also possible that K varies with c. To examine this question, we first note that in general the right hand side of Eq. (16) can be treated as a phenomenological conversion rate parameter K, which depends explicitly on ortho fraction c. This general assumption embraces the effect of diffusion-dependent re-distribution as well. As a test, we analyzed the data from the Raman experiments. First, the experimental points were fitted to a simple polynomial of the second order. The derivative dc^{-1}/dt is then the value of the conversion function at time t, viz., $K(c(t))$. This fitting polynomial can be also used to deduce K_0, the limit value of K at $c=1$, which can be chosen as a universal measure of the conversion rate at a given P. The extrapolation-related corrections

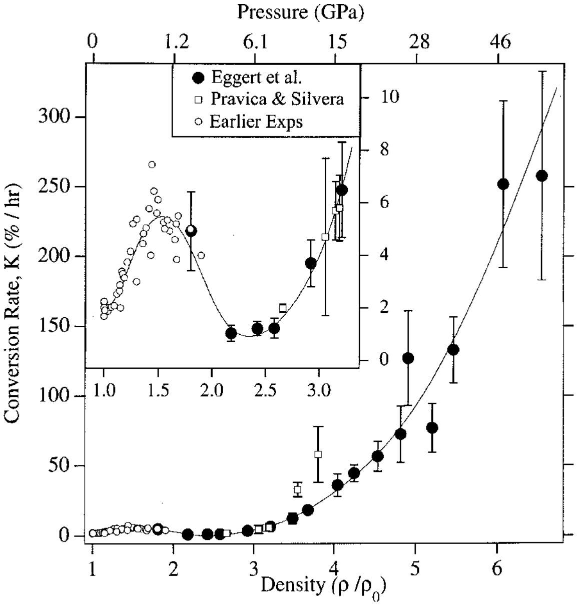

FIG. 2. Measured conversion rates vs density. The points are from Refs. 10 and 12 (solid circles) and Ref. 11 (open squares). The open circles are earlier data from Refs. 4–6. The curves are guides to the eye.

as compared to the values employed in Monte Carlo simulations in all cases but two are insignificant (less than 3%). In this analysis, $K(c)$ is not a constant but a strong function of c, changing substantially (e.g., more than fivefold at 17.1 GPa) as the ortho concentration decreases for all 14 runs at pressures above 3 GPa. Even the three runs at the lowest pressures studied yield results basically consistent with the treatment below; however, those data do not allow drawing unambiguous inferences owing either to an insufficiently long duration of experiment or to experimental uncertainties.

Figure 2 shows the values for K as a function of pressure and density, including the Raman,[10,12] NMR,[11] and the earlier lower-pressure data.[4–6] For the Raman results we show the K values extrapolated to $c=1$. The conversion rate exhibits a strongly nonmonotonic variation with compression: it first slightly increases to a maximum, then decreases to reach a minimum, and then accelerate dramatically. Explanation of this unusual behavior, documented by both Raman and NMR data, is the main objective of the present theoretical study. The rates deduced from Raman and NMR measurements agree well up to $\xi \simeq 3.3$ but tend to diverge at higher compressions. This divergence has led to questions regarding the applicability of the Raman scattering technique for determining the ortho-para composition at high pressures where the mixing of rotational states (and hybridization with the phonon excitation) might preclude an accurate determination of the ortho and para concentrations. As discussed elsewhere,[12] however, these effects have negligible influence on measured Raman intensities. Moreover, there is disagreement for the conversion rates only for the two highest pressures obtained in the NMR study, and these have large uncertainties.[11] Although the differences are just outside the stated uncertainties of the two studies, both studies show the strong increase in rate at similar pressures that is the primary focus of the present theoretical study. We also note that the recent data of Grazzi and Ulivi[13] on conversion in $\mathrm{Ar(H_2)_2}$, taking into account the difference in the number of nearest H_2 neighbors, are consistent with these results for pure hydrogen.

IV. THEORY

A combination of three major factors, viz., the energy sink excitation, the type of conversion act, and the pathway, controls the conversion rate at high pressures. All these three factors are closely linked to the type of partial Hamiltonian in Eq. (14) to be used in calculations. There are three types of excitations capable of carrying away the energy released during conversion or participate in this process. These are phonons, $J=2$ excitations, and collectivized rotational excitations in the $J=1$ manifold. For simplicity, we will sometimes call the $J=1$ excitations librons and the $J=2$ excitations rotons.

Ortho-para conversion of a chosen molecule involves transitions between rotational states of the whole system. Any rotational state $|\{L\}\rangle$ is a state with, strictly speaking, all the N_0 momenta coupled (where $N_0=cN_{tot}$, c is the ortho fraction, N_{tot} is the total number of hydrogen molecules; $\{L\}$ denotes the set of quantum numbers that characterize the state under consideration). This state can be chosen as a product of linear combinations of one-particle rotational wave functions or eigenstates of the EQQ interaction Hamiltonian

$$\mathcal{H}_Q=\frac{1}{2}\sum_{i,j} c_i c_j H_Q^{(ij)}. \tag{18}$$

Here $c_i=0$ if site i is occupied by a para molecule and $c_i=1$ if the site is in the ortho state; the EQQ interaction in the pair (i,j) of ortho molecules can be written in the form [notation as in Eqs. (10) and (11)]

$$H_Q^{(ij)}=\frac{25}{6}\sqrt{70}\Gamma_0\xi^{5/3}(\{\mathbf{C}_2(\mathbf{w}_i)\otimes\mathbf{C}_2(\mathbf{w}_j)\}_4\cdot\mathbf{C}_4(\mathbf{n}_{ij})), \tag{19}$$

where $\xi=\rho/\rho_0$ is the compression ratio, the unit vectors are defined in Eq. (12), and the EQQ interaction constant Γ_0 is

$$\Gamma_0=\frac{6}{25}\frac{q_{11}^2}{R_0^5}. \tag{20}$$

Here R_0 is the nearest-neighbor distance at zero pressure and $q_{11}=\langle 1|\hat{Q}|1\rangle$ is the adiabatic matrix element of the electrical quadrupole moment operator $\hat{Q}$ between purely rotational states with $J=1$. The role of the EQQ interaction is twofold. First, it shapes the rotational energy spectrum and, second, as will be shown later, it can constitute the vortex that produces energy removing excitations, including phonons, because the EQQ interaction couples translational and rotational degrees of freedom.

Temperature can also enter into the interplay between various energy parameters. If the ortho fraction c is high enough and the temperature is low enough (or the pressure is sufficiently high, or both), the o-p mixtures undergo a structural phase transition into the orientationally ordered $Pa3$ phase.[24] All experimental evidence indicates that within the range of pressures and temperatures of the Raman measurements, hydrogen is in the disordered state (e.g., Refs. 10–12 and 25). This increases the difficulty of the calculations.

In the orientationally ordered phase (at high enough ortho fractions c and low enough temperatures T) the spectrum is that of bandlike orientational excitations—librons—whose damping is due to the thermal and para impurity factors. In the orientationally disordered phases (at low c and/or high T) the orientational spectrum is by far more complex. There is no theory for the rotational spectrum of such highly random system as an o-p mixture with c about 50%. Moreover, it can be said that this problem has not been so far even properly addressed. It is true that this problem was partly dealt with but from a different point of view in connection with the problem of quadrupolar glass.[26] Every $J=1$ rotor sees a momentary molecular field, which at extremely low temperatures fluctuates from site to site (the so-called quadrupolar glass) or, at higher temperatures, in both time and space (the completely disordered phase). As the temperature (or, more precisely, the ratio of the temperature to the typical interaction energy) decreases, every quadrupole finds an orientation with minimum energy and stays there. The issue that was under study for a long time is the distribution of quadrupolarizations, which is the local order parameter characterizing this glassy state (see Refs. 27–30). It is reasonable to assume that, irrespective of the structure, the rotational spectra must have a definite span scaled by the EQQ energy parameter $\Gamma=\Gamma_0\xi^{5/3}$. Fortunately, numerous experimental findings are available which not only corroborate this assumption but also allow evaluation of such characteristics of the rotational spectrum as the width (span) and the position with respect to other spectra. We will consider this issue in more detail below. In our calculations, in order to get numeric, however crude, estimates, we will sometimes have to make recourse to the case of ordered state, introducing afterwards corrections to allow for less orientational order and a lower ortho concentration.

We have the following options for the partial Hamiltonians $\hat{h}(LM;N)$ defined in Eq. (14).

$\hat{h}(10;N)$. This term drives one of the interacting molecules to change its parity and leaves the other exactly in the same rotational state. This is the standard conversion Hamiltonian used in all previous rate calculations involving one or two phonons. It can also bring the system to a number of intermediate states, which will dissipate the energy through another interaction(s) and not necessarily into phonons.

$\hat{h}(12;N)$. This term initiates the conversion of the same molecule but by acting on the orientational variables of the other it allows the other molecule to be excited within the states of the same parity; i.e., this term can directly produce a libron (an excitation within the $J=1$ manifold). It can be also elaborated to create additional librons.[31]

$\hat{h}(11;N)$. This term drives *both* ortho molecules to convert simultaneously.

The pathway with intermediate state consists in the following.[32] The Hamiltonian H_{ss} serves only to initiate conversion in the chosen molecule at site 0 and *not* to create excitations. In this way, an intermediate state is produced with molecule 0 in the para state and its surrounding still in the same state as before the conversion act. Because all the EQQ interactions involving the converting molecule have momentarily disappeared, 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, Eqs. (18) and (19), a much stronger one than H_{ss}. In line with the general idea of Berlinsky and Harris,[33] the EQQ Hamiltonian of the intermediate state with molecule 0 in the para state can be written as

$$\mathcal{H}_Q^{(inter)}=\mathcal{H}_Q^{(0)}-\sum_j c_j H_{QQ}^{(0j)}\equiv H_0+V_Q . \tag{21}$$

Here both $\mathcal{H}_Q$ Hamiltonians are described by Eqs. (18)–(20). The Hamiltonian $\mathcal{H}_Q^{(0)}$ with molecule 0 still in the $J=1$ state serves as the unperturbed one. The second term, which means lack of the EQQ interaction between molecule 0 and all other ortho molecules after conversion, may serve as the perturbation:

$$V_Q=-\sum_j c_j(25/6)\Gamma\sqrt{70}\xi^{5/3} \times(\{\mathbf{C}_2(\mathbf{w}_0)\otimes\mathbf{C}_2(\mathbf{w}_j)\}_4\cdot\mathbf{C}_4(\mathbf{n}_{0j})). \tag{22}$$

The idea of intermediate states, which is fruitful at high pressures, does not work at ambient pressure because of the restrictions imposed by the energy conservation law or because the probability is too low.

Prior to going into the analysis for every channel, we formulate the problem of the conversion probabilities in general terms. The probability of the various conversion acts caused directly by the nuclear magnetic dipole interaction is given by

$$W=\frac{2\pi}{\hbar}\sum_{i,f} P_i|\langle f|V|i\rangle|^2\delta(E_i-E_f), \tag{23}$$

where any of the Hamiltonian terms enumerated above can serve as V. Here P_i is the probability of the system to be in the specific initial state $|i\rangle$; E_i and E_f are the energies of the initial and final states. If N phonons are involved, by combining Eqs. (5), (12), and (23), the conversion probability $W(L,M;N)$ due to the relevant term $\hat{h}(L,M;N)$ can be represented as

$$W(L,M;N) =\frac{\gamma_{ss}^2}{\hbar}\left(\frac{d}{2R_0}\right)^{2(L+M)}A(L,M;N)\xi^{2+(2/3)(M+L+N)} \times\sum_{if} P_i\frac{|\mathbf{s}|^{2N}}{R_0^{2N}}|\langle i|\hat{h}(L,M;N)|f\rangle|^2\delta(E_i-E_f). \tag{24}$$

Here $\gamma_{ss}=\mu_0^2/R_0^3$ and

$$A(L,M;N)=192\pi[S(L,M;N)]^2, \tag{25}$$

where $S(L,M;N)$ is as in Eq. (13). Since below 70 GPa the admixture of higher-J states is rather small, we neglect the corresponding compression-related corrections to the matrix elements of any $\hat{h}$.

For an intermediate state, the matrix element in Eq. (23) will be

$$\langle f|V|i\rangle=\sum_{(is)}\frac{\langle f|V_Q|(is)\rangle\langle(is)|H_{ss}|i\rangle}{E_{(is)}}, \tag{26}$$

where summation runs over possible intermediate states with the energies $E_{(is)}$. Here we need to know details of the energy spectrum of the intermediate state.

Since we will be dealing with a number of different channels with long descriptive names, we need some abbreviating nomenclature. The pathway will be denoted as S for the standard one, when H_{ss} serves both to initiate conversion and to create excitations, and I for pathways with intermediate states. The first two numerals of the partial Hamiltonian label will fully describe the type of conversion act. The type and number of sink excitations are placed at the end. For example, $S10\text{-}2p$ denotes the channel considered by Berlinsky and Hardy[2] with the standard pathway via Hamiltonian $\hat{h}(10;2)$ with two phonons born. Channel $S12\text{-}1l$ will mean the standard pathway via the Hamiltonian $\hat{h}(12;0)$ with one libron created.

The quantity we focus on in this paper is the probability W of a given ortho molecule to undergo conversion. The relation between W and the conversion parameter K appearing in the macroscopic equation (15) can be easily obtained if the distribution of ortho molecules remains random during conversion. The decrease of the number of ortho molecules N is proportional to the number of nearest-neighbor ortho pairs N_2: $dN/dt=-2WN_2$. Here the coefficient 2 reflects the fact that either of the two molecules in the pair can convert. In the random approximation, $N_2=6cN$ and we obtain $K=12W$. Exactly the same differential equation holds for double conversion with the modification that the same coefficient 2 implies that both ortho molecules convert simultaneously. Thus, the relation between W and K for double conversion is the same as for single conversion.

A. Phonons

Phonons as the conversion energy sink possess many inviting properties, among which is the wide range of possible energies. In other words, the energy conservation law permits phonons to participate in the conversion process at any pressure. On the other hand, the ever broadening range of allowable phonon energies leads to depletion and low probabilities.

Partly as a reminder, we consider first the channel S10-1p[3] controlled by the Hamiltonian $\hat{h}(10;1)$ with one phonon serving as the conversion energy sink.[31] The reduced displacements $\mathbf{s}/R_0$ are expressed through the standard phonon variables and their product is subsequently summed over possible phonon states together with the δ function in Eq. (24), producing a weighted density of states of the form

$$f(E)=\frac{1}{R_e^2}\sum_{\kappa}\langle 0|s_\mu|\kappa\rangle\langle\kappa|s_\mu^*|0\rangle\delta(E-\epsilon_\kappa). \tag{27}$$

Here $\kappa=(\mathbf{k},\gamma)$ is the wave vector and the polarization index of the emerging phonon; ϵ_κ is the phonon dispersion law. For varying density the R^{-2} factor scales as $\xi^{2/3}$ [already accounted for in Eq. (24)]; the product $s_\mu s_\mu^*$ supplies ϵ_κ (or the Debye θ) to the denominator; summing over κ yields a function of energy $g_1^{(10)}(E)$. Thus, the extra probability factor due to one phonon will scale as $[\Theta_0/\Theta(\xi)]g_1^{(10)}(E)$ where $\Theta(\xi)$ is the Debye temperature at a given ξ; Θ_0 is the Debye temperature at zero pressure; E is the conversion energy, which for the time being is treated as a constant. The function $g_1^{(10)}(E)$ is nonzero within the range from 0 to a value close to $\Theta(\xi)$. If one assumes that this function retains its mathematical similarity under compression, then it can be represented[3,5] in the form useful for varying volume: $g(E)=G_1(\varepsilon)/\Theta(\xi)$ with

$$\varepsilon=E/\Theta(\xi) \tag{28}$$

and $G_1(\varepsilon)$, the reduced one-phonon density of states, which can be calculated for zero pressure. In other words, this density of states function is set not to vary with pressure while the energy point ε varies between 0 and 1. Finally,

$$W(S10\text{-}1p)\propto\xi^{10/3}[\Theta_0/\Theta(\xi)]^2G_1(\varepsilon). \tag{29}$$

Similarly, for the partial Hamiltonian $\hat{h}(10)$ with two phonons,

$$W(S10\text{-}2p)\propto\xi^{12/3}[\Theta_0/\Theta(\xi)]^3G_2(\varepsilon). \tag{30}$$

It follows that the resulting density-related probability factor for any channel with the partial Hamiltonian $\hat{h}(lm;N)$ with $N\geqslant 1$ phonons involved will be $\xi^n[\Theta_0/\Theta(\xi)]^{N+1}$ with $n=2+2/3(l+m+N)$. For the family of Hamiltonians $\hat{h}(11)$ the density factors for the one-phonon and two-phonon processes are

$$W(S11\text{-}Np)\propto\begin{cases}\xi^4[\Theta_0/\Theta(\xi)]^2, & N=1,\\ \xi^{14/3}[\Theta_0/\Theta(\xi)]^3, & N=2.\end{cases} \tag{31}$$

So one can see that the density dependence of the Debye temperature is a very important factor. At lower pressures, a convenient way to express this dependence is by using the Grüneisen law $\Theta=\Theta\xi^\gamma$, where $\gamma=-\partial\ln\Theta/\partial\ln V$ is the Grüneisen parameter. However, the Grüneisen parameter, which is 2.3–2.4 as derived from heat capacity data[34,35] at ambient pressure, steadily decreases with increasing compression.

The high-pressure Θ values can be deduced from optical phonon frequency measurements.[36] For pressures up to 20 GPa there is the known relationship,[36,37] which when customized to our notation takes the form

$$\ln[\Theta(\xi)/\Theta_0]=\sum_{k=1}^{3} C_k(\ln \xi)^k, \tag{32}$$

with $C_1=2.2188$, $C_2=-0.61192$, and $C_3=0.019666$. In subsequent evaluations we use the Debye θ values deduced[38] from high-pressure optical phonon frequencies measured by Raman scattering[39,40] and represented in the same way as in Eq. (32) with $C_1=2.141$ and $C_2=-0.285$ (the fitting was without C_3). Both C_1 coefficients are zero-pressure extrapolations for the Grüneisen constant.

The shape of the densities of states for one or two phonons is another important factor. We use the representation of Eqs. (29) and (30), in which the shape of the density of states $G_1(\varepsilon)$ and $G_2(\varepsilon)$ is fixed while the argument ε moves to smaller values as the density (and the Debye θ) increases. To get a better insight, the range of variation for both functions $G_1(\varepsilon)$ and $G_2(\varepsilon)$ can be divided roughly into two regions. For example, the one-phonon function (see, for instance, Ref. 3) consists of a low-valued Debye-like part stretching in energy from 0 to $\varepsilon_1 \simeq 40$ K [here $G(\varepsilon) \propto \varepsilon^3/\Theta^2$] and a denser part stretching from ε_1 to $\varepsilon_2 \simeq 120$ K, where to a sensible extent $G(\varepsilon)$ may be roughly considered a constant. To yield a rate of any significance, ε must be within the latter interval. What is happening with decreasing energy is depicted in Fig. 3. The above two edge points are put on the vertical axis and the interval in between is right-incline hatched. A similar favorable interval (90 K $<\varepsilon<240$ K) for two-phonon processes is shown as left-incline hatch. One can see that for single conversion (the lower curve) the moving energy point starts within the two-phonon area, enters the one-phonon interval at $\xi \simeq 1.2$ ($P \simeq 0.06$ GPa), and leaves for good the two-phonon interval at $\xi \simeq 1.4$ ($P \simeq 0.2$ GPa) and the one-phonon one at $\xi \simeq 2.3$ ($P \simeq 3$ GPa). Then it moves deeper into the increasingly unfavorable region, diminishing the probability. This scenario, predicted by previous calculations,[1–3] is corroborated by experimental findings for moderate pressures (see the references in the Introduction). As can be seen from Fig. 3, the double-conversion channels (the upper curve) yield high conversion rates at noticeably higher compressions. All probabilities are affected by the compression-related decrease of the conversion energy, which is discussed in detail in the next subsection. As a result of this decrease, the conversion rate curves will be "compressed."

Phonon densities of states at high pressures should be calculated with account of all the factors discussed above which have been ignored in previous publications. These and some other relevant issues are addressed in another paper.[41]

B. Excitations within the $J=1$ manifold (librons)

Another obviously good candidates for conversion energy sink excitations may come from the rotational subsystem.[42] These excitations, including librons (or reorientations within the $J=1$ manifold) and rotons ($J=2$ excitations), are controlled by the EQQ interactions scaled as R^{-5}. Hence one can expect that the role of this interaction, which is comparatively weak at ambient pressure, will become important with increasing pressure. On the other hand, since the conversion energy is the energy difference between the $J=1$ (surrounded by ortho neighbors in the solid) and $J=0$ states, the pressure-related increase of the EQQ interaction must result in a reduction of the Boltzmann-averaged conversion energy due to the fact that at low enough temperatures all ortho molecules are predominantly in their local ground states. Let us first consider reorientations within the $J=1$ manifold or — for brevity — librons.

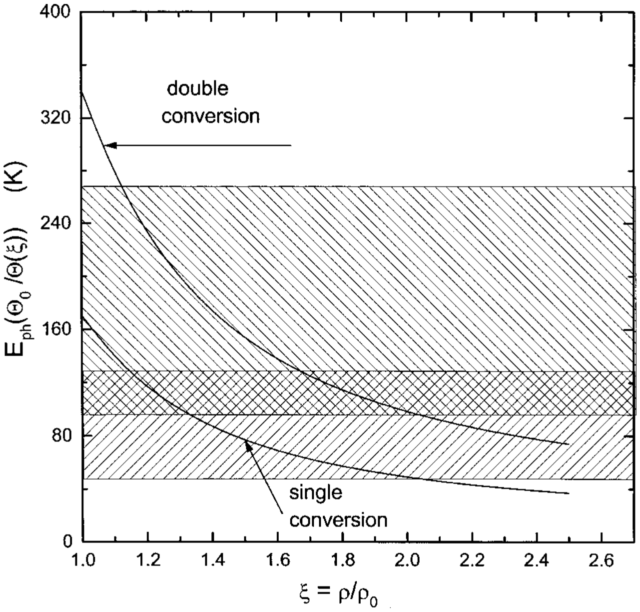

FIG. 3. The ranges where the phonon-related energy removal mechanisms operate. The left-incline and right-incline hatch are for two- and one-phonon processes, respectively; the upper and lower curves represent, respectively, channels $S10$ and $S11$.

The spectrum of librons in the ordered state is well defined and known in sufficient detail (for references and a discussion see Ref. 14). As to the orientationally disordered phase, for the absence of any theory we can only surmise that the spectrum for reorientations within the $J=1$ manifold must have a certain span comparable to the energy band in the ordered state, with a proper allowance for lower ortho fractions. The libronlike excitations within the $J=1$ manifold of a disordered ortho-para mixture must be short ranged and spatially irregular. The respective energy span is determined by the ortho fraction c so that, very roughly in the molecular-field approximation, the span width is proportional to the average number of $J=1$ molecules in the closest surrounding times the characteristic EQQ energy. Thus, the span width Δ_0 is proportional to $\Gamma_0 c \xi^{5/3}$, i.e., depends both on pressure and ortho fraction.

The energy considerations for the channels involving rotational excitations are illustrated in Fig. 4. The energy is counted from the state when the chosen molecule is in the para state. The horizontal axis gives the reduced intensity of the EQQ interaction; the value $\Gamma/\Gamma_0=0$ can be attributed to the free molecule; the value $\Gamma/\Gamma_0=1$ corresponds to ambient pressure. The middle angle symbolizes the spread of rotation energies of the chosen molecule when it is in the ortho state. The lower angle symbolizes the spread for the elementary excitations in the closest surrounding of the chosen molecule

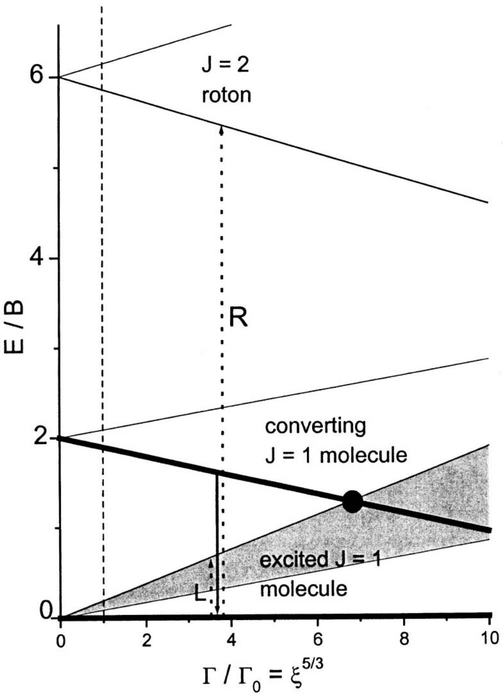

FIG. 4. Energy scheme for single-conversion transitions involving $J=1$ and $J=2$ excitations with varying EQQ interaction. The $J=2$ roton (arrow R) is too energetic to take up the conversion energy. The energy is counted from the state in which the chosen molecule has converted and all other $J=1$ molecules are in their local ground states. Thus, the converting molecule starts from a state with the energy to be released (solid down-pointing arrow) $2B-(2/3)\Delta_0$, where Δ_0 is the compression-dependent energy span. *Another* ortho molecule can now be excited to the libron band (shaded region) to take up a maximum energy of roughly Δ_0 (shown as a dashed up-pointing arrow L) if two-libron states are taken into account. At a critical value of Γ (large circle) the energy span of the excited molecule is wide enough to accommodate the entire conversion energy.

after it has converted. The arrows show conversion transitions; the arrow length is the conversion energy, released if downward and absorbed when upward. As the pressure is increased, the minimum energy to be dissipated decreases considerably. At a certain critical pressure (indicated in Fig. 4 as the large circle) and above, the energy can be dissipated within the $J=1$ manifold.

The decrease in conversion energy is real, it can be directly seen in inelastic neutron scattering[43,44] or NMR[45] experiments. What is especially important is that this decrease is observed in both fcc and hcp phases. Moreover, with account of the large width of the scattered peak in hcp crystals[44] the shifts in both phases virtually coincide at $c=75\%$. The energy spread for reorientational excitations within the $J=1$ manifold can be rigorously defined for the 100% $J=1$ ordered state. The molecular field splits this level into the ground state $m=0$ singlet and a $m=\pm1$ doublet; the latter is broadened by the off-diagonal part of the EQQ interaction into a band. This band for single-libron excitations at $\mathbf{k}=0$ stretches[46] from 6.2 to 11.3 cm^{-1} (from 8.9 to 16.3 K) with the center of gravity Δ_0 at 8.79 cm^{-1} (12.6 K). The last figure is somewhat below the one that can be estimated (14.4 K) from neutron scattering data.[44] In principle, two-libron excitations[46–48] may also contribute, shifting the upper bound to 21 cm^{-1} (30.2 K). The quantity Δ_0 is the energy distance between the $m=\pm1$ and $m=0$ sublevels of the $J=1$ level for $\xi=1$, $c=1$. Then, $(2/3)\Delta_0$ will be the downward shift of the $m=0$ level caused by the EQQ molecular field. Making use of all the above-quoted figures we find that $E_c=E_0-(2/3)\Delta_0$ or, after rescaling to arbitrary ξ and c and assuming a linear relation, $E_c=E_0-8.4\Gamma_0 c\xi^{5/3}$ with $E_0=2B\simeq170.5$ K.

Here we must add that we do not expect a substantial decrease in effective EQQ energy, similar to the apparent decrease of the operating EQQ interaction that splits the $S_0(0)$ band.[49] We ascribe that "insufficiency" to the effect of a rank-4 crystal field[25] rather than to dielectric screening.[50] If so, any rank-4 field has no direct effect on $J=1$ states, all the matrix elements being zero. Indirect influence through higher-J states is negligible. Thus, as far as the $J=1$ manifold is concerned, the EQQ interaction operates unsuppressed.

C. $J=2$ excitations (rotons)

Let us now consider in more detail the channel where the energy removing agent is a $J=2$ excitation, which we call a roton. There are two arguments that make this channel promising. The first one is the fact that an ortho molecule converting to the para state can go directly to the $J=2$ manifold; i.e., the respective probability is controlled by the Hamiltonian $\hat{h}(10;0)$, which contains the factor d/R_0 to the least power. One can also expect that a noticeable contribution will come from the Hamiltonian $\hat{h}(11;0)$, which drives two ortho molecules to para state simultaneously, one to the $J=0$ and the other to the $J=2$ states. The other argument is the predicted compression-related softening of the $J=2$ roton.[51,52] Unfortunately, this is not directly applicable to ortho-rich mixtures. Here the resonance interaction that broadens the roton state into a band in pure para solid, for which case the theory was developed, is in fact absent because too few para molecules are available in the nearest surrounding.

The energetics of the processes involving direct excitation of one converting molecule into the $J=2$ state is illustrated in the same Fig. 4, where the top angle depicts the roton energy span. At zero pressure and the EQQ interaction for the time being disregarded, the kinetic energy of the roton, $6B$, is prohibitively high and the energy released in a single $(2B)$ or even double $(4B)$ conversion processes is insufficient to bridge that gap. That is, in this case it is not a question of where the energy released is dissipated but where an extra energy to excite the particle into the $J=2$ state is to be found. Thus, to "make" this channel work we must find a cause which lowers the lowest possible levels of the $J=2$, localized or delocalized, so that it connects directly with the $J=1$ submanifold of the converting particle.

Taking the EQQ interaction into account, we recollect (see previous subsection) that at low temperatures the converting ortho molecule sees a typical molecular field created

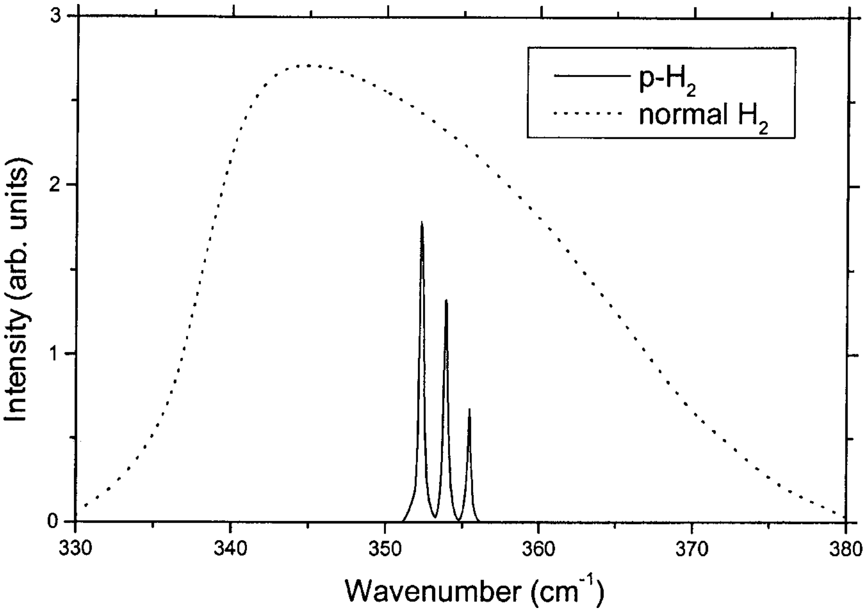

FIG. 5. Comparison of zero-pressure Raman spectra (Ref. 53) of pure p-H_2 and n-H_2. Since the off-diagonal spread is insignificant, the bandwidth reflects the spread of molecular fields of the surrounding $J=1$ molecules that acts on the Raman-excited para molecule.

by its ortho neighbors. The span Δ_0 for a $J=1$ molecule was discussed in the previous subsection. Similar reasonings apply to the process when two neighboring ortho molecules go simultaneously to the para state. Thus, when during conversion the molecule goes from $J=1$ to $J=2$, it finds virtually the same molecular field, which allows us to evaluate the spread by simple rescaling.

Let us now analyze the energy spread of a $J=2$ excitation surrounded predominantly by ortho molecules. The energy of the roton without an EQQ interaction with the surrounding is $6B$. An attempt to look for possibly lowest energies related to the EQQ interaction leaves us with the following options: (i) single conversion, no nearest para neighbors; (ii) single conversion, one or a few para neighbors; (iii) double conversion, no nearest para neighbors; (iv) double conversion, one or a few para neighbors. Here we recall that at low temperatures and high pressures only the lower parts of the respective spans at $2B$ and $4B$ are occupied (see Fig. 4). As an example we give analysis for case (i). The level lowering can be due to the molecular field effect associated only with the diagonal elements of the EQQ interaction of the $J=2$ state with its $J=1$ environment. Speaking in terms of the molecular field, the anisotropic potential created by the $J=1$ molecules surrounding the chosen molecule can be represented in the form $\epsilon_2 C_{20}(\mathbf{w})$. When in the $J=1$ state, the chosen molecule's spectrum is $E(1m)=(2/5)\epsilon_2 A_2(1m)$ with $A_2(10)=1$ and $A_2(1\pm1)=-1/2$. If now the same molecule is in the $J=2$ state, its spectrum is $E(2m)=(2/7)\epsilon_2 A_2(2m)$ with $A_2(20)=1$ and $A_2(2\pm1)=1/2$, and $A_2(2\pm2)=-1$. Since the width of the $J=1$ energy range is known, the ratio $(2/5)A_2(11)$ $(2/7)A_2(22)=7/10$ of the lowest energies sets the slope for the lower boundaries of the $J=2$ range in Fig. 4.

It can be easily verified that either for single or double conversion the lower $J=2$ line meets the energy releasing lines at too large a value of Γ, well over those at which enhanced conversion rates were observed. Account of other options does not give different results, because effect of the off-diagonal elements between para neighbors is of the same order as the diagonal ones between $J=1$ and $J=2$. We must note that the span of roton excitations can be seriously affected by the rank-4 crystal field.[25]

We also give a few pieces of experimental evidence for the energy span of the $J=2$ state in ortho-rich disordered mixtures. One is obtained by comparing the shapes of the $S_0(0)$ band in pure p-H_2 and in normal H_2 at zero pressure. We superimposed these two spectra from Bhatnagar *et al.*[53] in Fig. 5. We point out that, since the off-diagonal spreading effect is inefficient in the case of the normal solid mixture, the domelike feature reflects precisely the spread of $J=2$ state in the inhomogeneous molecular field of the $J=1$ surrounding. A similar effect at high pressures can be seen in Raman spectra for normal o-p composition.[54] The fact that at higher pressures the spread of molecular fields depends on compression can also be seen[10] from conversion-related temporal variations of the $J=3\leftarrow1$ bandwidth at a fixed pressure. Though varying duly with pressure (the spread increases), this effect is strongly moderated by the fourth-harmonic crystal field, which does affect the $J=2$ state. Thus, because at any pressure the minimum energy of the $J=2$ excitations is too high to accommodate the conversion energy, these excitations can hardly serve as energy sink.

V. CALCULATIONS

In this section we evaluate the probabilities of the conversion processes that can occur according to the mechanisms selected in the previous section. We calculate the probabilities separately for several channels or groups of channels. Some of technical details are placed in the Appendix.

The operator part of the conversion promoting Hamiltonians $\hat{h}$ that acts on the angular variables of molecules i and j is proportional to $C_{1\nu}(\mathbf{w}_i)C_{00}(\mathbf{w}_j)$, $C_{1\nu}(\mathbf{w}_i)C_{1\mu}(\mathbf{w}_j)$, or $C_{1\nu}(\mathbf{w}_i)C_{2\mu}(\mathbf{w}_j)$. The rotational transitions initiated by either of these operators take place between states $|\mathrm{i}\{L\}\rangle$ and $\langle \mathrm{f}\{L'\}|$. At low enough temperatures the initial states are those with lowest possible energies. In a general case the proper averaging procedure should be applied. The transitions under consideration are characterized, first, by the energy difference between the two states and, second, by the value of the relevant matrix elements. Both the energy difference and the matrix elements are difficult to calculate accurately for such a highly random system as an ortho-rich o-p mixture.

As the pressure is raised, two things occur. The span widens while the minimum conversion energy E_c decreases. The conversion energy of an ortho molecule is the rotational energy $2B$ (B is the rotational constant of the H_2 molecule) minus the molecular-field ground state energy of that molecule (see Fig. 4). Since the ground-state energy of $J=1$ molecules varies from site to site, conversion energies are distributed over a finite interval, even at zero temperature.

Hereinafter we shall use the following values: the equilibrium intermolecular distance at zero pressure, $R_0=3.788$ Å; the interatomic distance in the molecule, $d=0.7412$ Å; the zero-pressure molar volume $V_0=1/\rho_0=23.16$ cm^3/mol. Hence the values of some quantities: $\gamma_{ss}=2.70\times10^{-9}$ K and $(d/2R_0)^2=0.96\times10^{-2}$. We will use the equation of state from Ref. 55.

A. Channel *I*10−1*l*

We start with the channel, which in our opinion is mainly responsible for the rapid increase of the conversion rate at high pressures.[32] This is a channel in which the nuclear magnetic dipole interaction Hamiltonian, Eq. (1), serves only to initiate conversion in the chosen molecule (we put it at the central site 0) and *not* to create excitations. Thus, an intermediate state is produced as explained in the previous section. The difference between this channel and the standard is graphically illustrated in Fig. 6. The coupling is then explicitly contained in the EQQ interaction of the perturbation Hamiltonian, Eq. (22). We use this expression to show how the role of the intermediate state changes with pressure. The relevant coupling parameter is the ratio of the typical EQQ molecular field to the conversion energy. At zero pressure this ratio is roughly 1/10 and, being squared, adds a negligible contribution to the probability of the main channel. However, as the pressure is raised, two factors lead to a fast enhancement of this mechanism. First, the coupling increases as $\xi^{5/3}$ reaching 10 at ξ between 3 and 4, i.e., compensating the small ratio. Second, the conversion energy decreases substantially with increasing density, which adds considerably to the growing efficiency of this channel.

Now, in the general equation for conversion probability the matrix element will take the form (we count the energy from that of the initial state)

$$\langle f|V|i\rangle=\sum_{(is)}\frac{\langle f|V_Q|(is)\rangle\langle(is)|H_{ss}|i\rangle}{E_{(is)}}. \tag{33}$$

Here summation runs over intermediate states with the energies E_{is}. At low enough temperatures we can take that the initial state is the ground state without any excitations. In pure orientationally ordered ortho hydrogen the intermediate state is essentially unique for all the molecules and its energy is the conversion energy E_c, which is pressure dependent. In o-p mixtures the intermediate energies will be distributed over a certain range of finite width, even at zero temperature. Simplifying, we assume that at $T=0$ an o-p mixture can also be characterized by a unique conversion energy, which depends on both pressure and the ortho fraction. The final state will contain the excitations we are looking for, viz., one or two librons.

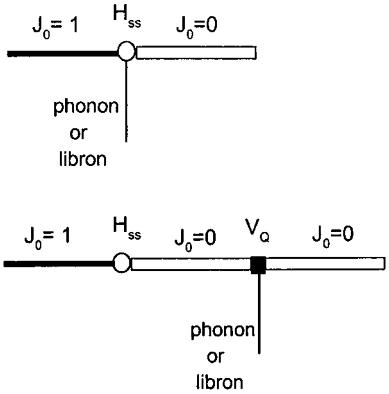

FIG. 6. Vertexes for direct (standard) pathway and a pathway with intermediate state. For standard channels (upper diagram) the nuclear magnetic dipole interaction H_{ss} starts conversion and produces energy sink excitations. In channels with intermediate states, H_{ss} only starts conversion whereas excitations are created through the EQQ interaction.

Depending on what excitation is under consideration, we leave the other subsystem unperturbed. Since we concentrate on librons, we leave all molecular positions fixed. The most promising partial Hamiltonians is $\hat{h}(10)$, since it contains the ratio $d/2R_0$ to the least possible power. The initial state $|i\rangle$ is a product of independent states of the quantities undergoing changes during conversion, viz., $|1m\rangle$ for the nuclear state of the central molecule, $|1m'\rangle$ for the nuclear state of the conversion-promoting molecule, and $|10\rangle$ for the rotational state of the converting molecule respective to its intrinsic reference frame. The intermediate state is the product (following the same sequence) of $|00\rangle$, $|1\mu\rangle$ (μ being the magnetic number of the ortho partner in the final state), and $|00\rangle$.

The conversion probability now is

$$W(10)=\frac{2\pi}{\hbar}\sum_{\mathbf{k}\alpha}P_i\frac{|\langle\mathbf{k}\alpha|V_Q|(is)\rangle|^2}{E_c^2}\times|\langle(is)|H_{ss}|i\rangle|^2\delta(E_c-\epsilon_{\mathbf{k}\alpha}), \tag{34}$$

where $\mathbf{k}$ and α denote the wave and mode numbers of the emerging libron and $\epsilon_{\mathbf{k}\alpha}$ is its dispersion law. The matrix element $\langle(is)|\hat{h}(10)|i\rangle$ can be easily calculated as for the direct phonon-promoted mechanism[2] or as outlined in the Appendix. The result is (we safely sum over the nuclear projection number μ, for the matrix elements of V_Q do not involve nuclear spin variables)

$$\langle (is)|\hat{h}(10)|i\rangle = \frac{10}{567}[1+4\sqrt{2/5}C_{20}(\mathbf{n}_{0i})], \tag{35}$$

where $\mathbf{n}_{0i}$ is the unit vector between molecule 0 and molecule i, which initiated the conversion act. Notice that, once i is fixed, the matrix element of Eq. (35) will affect only one term in the sum over the neighbors in V_Q, Eq. (22). Now the conversion probability takes the form

$$W(10) = A\frac{\gamma_{ss}}{\hbar}\left(\frac{d}{2R_0}\right)^2\frac{\Gamma_0}{E_c^2}\xi^{13/3}\Phi(\varepsilon). \tag{36}$$

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

$$\Phi(\varepsilon)=\sum_{\mathbf{k}\alpha}|\langle\mathbf{k}\alpha|V_Q^{(0)}|(is)\rangle|^2\delta(\varepsilon-\epsilon_{\mathbf{k}\alpha}^{(0)}), \tag{37}$$

where the superscript (0) means that Γ_0 appears in the respective quantities: thereby we normalize all the energies to $\Gamma=\Gamma_0\xi^{5/3}$ and remove the density dependence both from the interaction Hamiltonian and the dispersion law (it is reasonable to assume mathematical similarity for the latter at pressures below 60 GPa). Thus, the entire pressure dependence is shifted to the ε and we calculate as if we have $P=0$. Besides, since theory normally uses Γ as the natural reduction parameter, we will be able to make use of the available numerical estimates. From Eq. (37) it is obvious that the mechanism under discussion will be operative only when the one-libron (and/or two-libron) energy spectrum is broader than the conversion energy. The former broadens fast with pressure while the latter diminishes (see previous section and Fig. 4).

Before presenting the calculations, we once again remark that there is no good theory for the energy spectrum and for elementary excitations in o-p mixtures. Therefore, to construct a semiquantitative theory we begin with the case of the orientationally ordered phase $Pa3$ of pure ortho hydrogen. Then, hoping that the general result do not depend critically on the state of the ortho system (see also our considerations in previous section), we shall introduce corrections to account for the presence of para impurities.

Dealing with librons, it is more convenient to write V_Q in Eq. (22) in the notation of Raich and Etters:[56]

$$V_Q=-6\sqrt{2}\sum_j \gamma(j)[a_j^\dagger+b_j^\dagger+\text{H.c.}] \tag{38}$$

Here H.c. means Hermitian conjugate and $\gamma(j)=\gamma_{0j}^{(01)}$. For definition of $\gamma_{ij}^{(nm)}$ and the quantized operators a and b see Raich and Etters.[56] Remembering that there are four sublattices in $Pa3$ and two excitation modes (clockwise and counterclockwise), we express a and b through their Fourier transforms

$$a_\alpha(\mathbf{k})=\sqrt{4/N}\sum_{j(\alpha)}a_{j(\alpha)}\exp[i\mathbf{k}\cdot\mathbf{j}(\alpha)] \tag{39}$$

and similarly for $b_{j(\alpha)}$. These Fourier transforms can be expressed through the true creation and annihilation operators

$$c_\mu(\mathbf{k})=\sum_\nu V_{\mu\nu}(\mathbf{k})d_\nu(\mathbf{k}), \tag{40}$$

where the subscripts denote modes. The matrix $V(\mathbf{k})$ is the unitary transformation that diagonalizes the equations of motion and yields the true excitations as linear combinations of c, an aggregate variable of a and b. Finally, Eq. (37) takes the form

$$\Phi(\varepsilon)=72\frac{4}{N}\sum_{\mathbf{k}\lambda}\sum_{jj'}\gamma(j)\gamma(j)^*V_{\alpha\lambda}^*(\mathbf{k})V_{\alpha'\lambda}(\mathbf{k}) \times\delta(\varepsilon-\omega_\lambda(\mathbf{k})). \tag{41}$$

This expression can be evaluated only numerically. But to get a rough estimate of the magnitude of Φ we can take the dispersion law for all modes to be the same. Then we get

$$\Phi=18g(\varepsilon)\sum_j|\gamma(j)|^2, \tag{42}$$

where $g(\varepsilon)$ is the complete density of libron states [in our case, the single-mode mode-independent density of states (DOS) multiplied by 8]. In order to be able to use the available numerical calculations by Berlinsky and Harris[33] we use their notation $6\sqrt{2}\gamma^{01}=\zeta^{01}$, which gives $\Phi=3g(\varepsilon)|\gamma^{01}|^2$ with $|\gamma^{01}|^2\simeq 1.36$.

Knowing how E_c depends on ξ (see Sec. IV B) we can calculate the lowest value ξ_0 for this mechanism to be operative. It occurs when the conversion energy (the lower boundary of the middle angle in Fig. 4) meets the uppermost excitation level of the particle that takes up the conversion energy. At a certain value ξ_c, when $E_c(\xi)$ crosses the lowest libron branch, the libron becomes too energetic to accommodate the ever decreasing conversion energy and this mechanism ceases to operate. Using values deduced from measurements, in particular, the libron frequencies obtained by Raman scattering at ambient pressure,[46] we find that the mechanism works (Fig. 4) from $\xi_0\simeq 3.2$ to $\xi_c\simeq 4.9$.

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,[44] 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 ξ values. The effect of para molecules is the evident depletion of the libron spectrum, roughly proportional to $(1-c)$. The rates calculated by this approach are shown in Fig. 7 for pure o-H_2 and for the normal (75% ortho) hcp mixture as short-dashed lines. Both formally diverge at the respective compressions because of E_c in the denominator of Eq. (36) tending to zero. Actually no divergence will occur for the following reasons. We recall that the region of rotational excitations in the $J=1$ manifold (shaded in Fig. 4) is the band of true librons in the orientationally ordered 100% ortho phase. The spectrum of a disordered ortho-para mixture will only qualitatively resemble what is shown in Fig. 4 with the important differ-

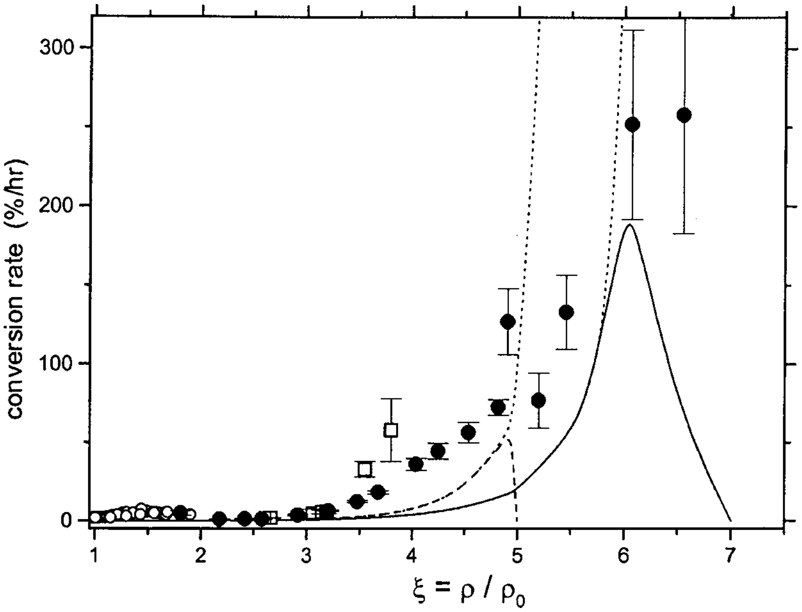

FIG. 7. The conversion rate vs reduced density at high compression. The dashed line is theory for the orientationally ordered pure o-H_2 phase; the solid curve, for (hcp) normal H_2; the dotted lines indicate nominal divergence. The points are from Refs. 10 and 12 (solid circles) and Ref. 11 (open squares). The open circles are earlier data from Refs. 4–6.

ence that the forbidden band (unshaded) will not be empty but contain states owing to areas with fluctuationally reduced ortho concentrations. This means that in reality the evolution of the conversion rate as a function of ξ will be as follows. Above ξ_0 (which depends on ortho fraction) this channel comes into action, growing in efficiency as E_c diminishes with increasing ξ. Then, at a certain value of ξ (between 5.5 and 6 for normal composition) the system finds itself in the depleted region (the forbidden band for librons in the ordered phase) and the efficiency of this channel drops abruptly. Finally, when E_c goes to zero the channel ceases to contribute; generally, conversion must stop at these pressures because the equilibrium ortho concentration becomes large (see Sec. VI for details).

B. Phonon-assisted channels

Now we focus on the conversion processes involving phonons. A detailed analysis of the effect of all the important factors on the phonon spectral densities at high pressures can be found in another publication.[41] We first consider the double-conversion channels and then address modifications to the standard ones.[2,3] In line with the reasons formulated in the previous section, the new promising candidates, are the channels $S11\text{-}1p$ and $S11\text{-}2p$. Making use of Eqs. (13), (14), and (25), we represent the respective probabilities in the form

$$W(S11\text{-}Np)=\frac{\gamma_{ss}^2}{\hbar}\xi^{(10+2N)/3}A(N)\left(\frac{d}{R_0}\right)^4 D(11;N), \tag{43}$$

with [cf. Eq. (13)]

$$A(N)=12\pi[S(1,1;N)]^2=\begin{cases}498960\pi, & N=1,\\ 6486480\pi, & N=2,\end{cases} \tag{44}$$

and

$$D(11;N)=\sum_{i,f} P_i|\langle i|\hat{h}(11;N)|\rangle|^2\delta(E_i-E_f)(|\mathbf{s}|/R_0)^{2N}. \tag{45}$$

The dependence on ξ is partly ‘‘removed’’ from the last expression (note the dependence on R_0).

In line with the reasoning of the previous section, any quantity $f(E)$ that has the form of the density of phonon states is to a good approximation a uniform function of its argument. This function scales to the inverse Debye θ and, hence, for an arbitrary Θ it can be recast as $f(E)=\Theta^{-1}G(\varepsilon)$ with ε as in Eq. (28). Finally (details of the relevant algebra can be found in the Appendix and in Ref. 41) we have for the probability of a double-conversion act involving two ortho molecules:

$$\begin{aligned}W(S11\text{-}Np)&\\ &=\frac{\gamma_{ss}^2}{\hbar}\left(\frac{d}{R_0}\right)^4\frac{\pi}{27}\\ &\quad\times\begin{cases}19600\xi^4[\Theta_0/\Theta(\xi)]^2\tilde{f}_2^{(1)}(\varepsilon), & N=1,\\ 43120\xi^{4/3}[\Theta_0/\Theta(\xi)]^3\tilde{f}_2^{(2)}, & N=2.\end{cases}\end{aligned} \tag{46}$$

Here we introduced the complete densities of states, $f_i^{(j)}$, where i is 1 for single conversion and 2 for double conversion; j denotes the number of phonons involved. If we ignore the angular-dependent parts of $f_i^{(j)}$, they coincide with the ‘‘isotropic’’ j-phonon densities of states. We do not need to write similar expressions for the single-conversion channels $S10\text{–}Np$ with one[3] or two[2] phonons. The role of various corrections for the two-phonon density of states for channel $S10\text{-}2p$ can be found in Ref. 41.

All the four standard phonon-assisted channels $S10\text{-}1p$, $S10\text{-}2p$, $S11\text{-}1p$, and $S11\text{-}2p$ are efficient below $\xi\simeq 2.5$. We found that Berlinsky's calculations[3] for the one-phonon channel $S10\text{-}1p$ change noticeably if corrected to account for two important factors, namely, the compression-related decrease of the conversion energy and the $\Theta(\xi)$ relationship obtained from Raman vibron frequencies [see Eq. (32) and the accompanying discussion] as opposed to the simplified Grüneisen-law dependence used previously. The former manifests itself in a "constriction" of the K vs ξ dependence as compared to that calculated with a compression-independent conversion energy. The latter correction results in slightly higher rates, especially at higher densities. In Fig. 8 we show conversion rates for the single-conversion and double-conversion one-phonon channels $S10\text{-}1p$ and $S11\text{-}1p$. Details of these calculations can be found in Ref. 41. It is interesting that the total of these two channels is fairly close to the result of Berlinsky[3] calculated only for channel $S10\text{-}1p$ but without account of the two effects just mentioned. The agreement with experiment looks good, considering the remarks below.

Owing to an extra $\Theta(\xi)$ in the denominator [cf., for instance, Eq. (46)], the two-phonon channels are strongly suppressed even at moderate pressures. Channel $S10\text{-}2p$ contributes noticeably[1,2] at very low pressures, as shown in Fig. 8. Since the energy released in a double-conversion two-phonon act is roughly twice as large as in a single-conversion act, channel $S11\text{-}2p$ comes into play at compressions above $\xi \simeq 1.13$, contributing little against the background of channel $S10\text{-}1p$.

Conversion rates for all the standard phonon-assisted channels were calculated within harmonic approximation. Since solid hydrogen is a quantum crystal, at least at lower pressures, the large intrinsic anharmonicities should produce substantial contributions at phonon energies close and even above the maximum allowable harmonic bounds for one-phonon and two-phonon states, as correctly noted by Berlinsky.[3] The sharp one-phonon peak predicted by harmonic calculations is likely to be broadened (and perhaps disappear, agreeing with experiment) as a result of quantum anharmonicities and temperature.

C. Channel $S12\text{-}1l$ with direct creation of librons

Because of the same energy conservation considerations this channel operates within the same range of ξ as $I10\text{-}1l$. The respective probability can be written in the form (we omit details of calculation)

$$W(I12\text{-}1l) \simeq \frac{9408\pi}{125}\frac{\gamma_{ss}^2}{\hbar\Gamma_0}\xi^{7/3}\left(\frac{d}{2R_0}\right)^3\rho_{\mathrm{lib}}(E). \qquad (47)$$

This channel is of little significance because the probability contains the small parameter $d/2R_0$ to the third power and lacks the closing gap factor.

D. Other channels

We also considered several other channels, which turned to be by far less efficient within specific ranges of compressions as compared to those already evaluated in detail above. Among them are channels with the $J=2$ level as the intermediate state and channels $I10\text{-}1p$ and $I10\text{-}2p$, which are similar to $I10\text{-}1l$ but producing phonons rather than librons to carry away the conversion energy. We do not show them in Fig. 7.

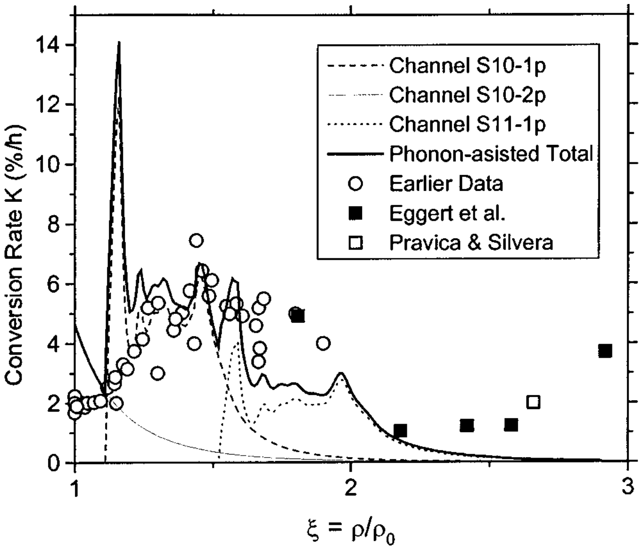

FIG. 8. Conversion rates at moderate pressures as calculated in this theory compared to experiment. The solid envelope is a sum of the contributions of standard single-conversion and double-conversion channels $S10\text{-}1p$ and $S11\text{-}1p$, standard two-phonon single-conversion channel $S10\text{-}2p$, and direct libron-assisted channel $S12\text{-}1l$. The latter (not shown to avoid overcrowding) starts contributing at $\xi \geqslant 2.5$ but remains small. Earlier calculations for channels $S10\text{-}1p$ and $S10\text{-}2p$ have been duly corrected (see text). The points are from Refs. 10 and 12 (solid squares) and Ref. 11 (open squares). As in Fig. 7, the open circles correspond to earlier data (Refs. 4–6).

VI. DISCUSSION AND CONCLUSIONS

Any conversion mechanism depends strongly on compression. The new mechanism, which is capable of explaining qualitatively the steep conversion rate enhancement in H_2 pressurized to 60–70 GPa (see Fig. 7), is strongly sensitive also to the ortho fraction c. This is because both the average conversion energy and the span of $J=1$ excitations that take up this energy are strong functions of c at a given pressure. At relatively high ortho concentration (roughly 60%–75%) the new mechanism predicts an abrupt slowdown for pressures higher than those studied. This happens when excitations within the $J=1$ manifold grow too energetic to accommodate the progressively decreasing average conversion energy. This slowdown, discussed in Sec. V A and depicted in Fig. 7, is a direct consequence of high compression. There is also another possible reason for conversion to stop at still higher pressures because of the decreasing conversion energy, since at high c the deviations in the spatial distribution of ortho species from random are unimportant, which allows the conversion equation to be cast in the form[11] $dc/dt = -Kc(c-c_{\mathrm{eq}})/(1-c_{\mathrm{eq}})$ where $c_{\mathrm{eq}}(T)$ is the equilibrium ortho concentration. This equation can be represented in the form of Eq. (15): $dc/dt = -K_{\mathrm{eff}}(c,T)c^2$ with

$$K_{\mathrm{eff}}(c,T)=K(c)\,\frac{1-c_{\mathrm{eq}}/c}{1-c_{\mathrm{eq}}}, \tag{48}$$

where $K(c)$ is the true conversion rate parameter. The equilibrium ortho concentration c_{eq} can be approximately written as $(3/4)\exp[-E_c(\xi)/T]$. At low temperatures and moderate pressures, c_{eq} is very small and the fraction in the right-hand side of Eq. (48) is virtually unity. With increasing pressure the conversion energy E_c goes down, presumably even to zero, and the effective conversion rate can be a strong function of c and/or T. Moreover, it can even become negative, entailing upconversion from para to ortho.

At low ortho fractions, there are two possible mechanisms that can result in an abrupt conversion slowdown at long experimental times (decreased ortho concentrations), observed most distinctly at the higher pressures. The first is related to the spatial distribution of ortho molecules. The combined action of diffusion, temperature, and EQQ interaction can result in substantial deviations of this distribution from random. If the diffusion of ortho species is sufficiently fast and the temperature is high compared to the EQQ attraction, a random distribution of ortho molecules will be maintained at any time. If diffusion is fast and the EQQ is strong (compared to the temperature), the o-p mixture will phase separate into areas rich in o-H_2 and p-H_2. If diffusion is slow, the distribution will evolve with the fluctuationally high-concentration areas will be depleted first so that the distribution is nonrandom and conversion slows down. Previous analyses of conversion rate data[10,12] were based on the assumption that the conversion rate is independent of ortho fraction and diffusion is the only conversion-controlling factor. Under these restrictions, the best-fit Monte Carlo simulations (without the return term) to the experimental data assuming no diffusion gave good agreement, especially at lower pressures (cf. Fig. 1). The second possible mechanism for behind the long time is directly related to the energetics of our new proposed conversion pathway. When progressing in time, conversion reduces ortho species and brings the system out of the energy overlap (see Fig. 4) necessary for the new mechanism with high conversion rates to be operative. This will happen irrespective of the diffusion rate but will be enhanced by slow diffusion and the associated deficiency of ortho-ortho nearest neighbors. We think that both long-t slowdown mechanisms operate in parallel, the importance and contribution of each depending on the specific experimental situation.

Conversion rate measurements[13] in the Ar$(H_2)_2$ compound at high pressures also show an abrupt acceleration of the conversion at roughly around the same compressions as in pure hydrogen. However, even taking into account that the hydrogen nearest neighbors in Ar$(H_2)_2$ are fewer, the conversion rates are still substantially lower than in H_2. This effect can be explained by a depletion of states in the $J=1$ manifold due to the presence of argon atoms. This is a sure indication that the channels responsible for the removal of conversion energy in Ar$(H_2)_2$ involve rotational, rather than translational, excitations. We did not address other possibilities for conversion mechanisms at very high pressures. Among these we should mention the expected breakdown of the very notion of ortho and para species,[57] which in particular may become efficient in connection with the charge transfer in phase III.[58]

Summing up we formulate the following conclusions.

(i) Recent measurements of the pressure dependence of the ortho-para conversion rate in solid H_2 provide a basis for testing a broad suite of possible conversion mechanisms, including the role of quantum diffusion. Monte Carlo simulations indicate that at a given pressure the variation of the conversion rate with time (or ortho fraction) can be explained by the absence of diffusion, which results in a nonrandom distribution of ortho species that slows conversion. An additional independent contribution to this slowing can arise from the predicted strong intrinsic dependence of the rate on the ortho fraction at high pressure.

(ii) We derive a new closed-form expression for the spherical harmonic expansion of the nuclear magnetic dipole interaction Hamiltonian H_{ss}, which is mainly responsible for the conversion. Any of the partial conversion-promoting Hamiltonians can be conveniently picked from this expansion. Several new factors are taken into consideration, among which are double conversion (when both interacting ortho molecules go to para state) and excitations within the $J=1$ manifold (librons or their analog in disordered ortho-para mixtures) serving as sinks for the conversion energy released.

(iii) The conversion energy, which is counted from the ground-state level of the converting $J=1$ molecule, decreases with compression due to the increasing offset caused by the random EQQ molecular field felt by the converting molecules. We call this phenomenon $J=1$ gap closing. This phenomenon turns to be of great importance at high pressures.

(iv) We suggest a new channel of ortho-para conversion in solid hydrogen that is efficient at high pressure, namely, one in which H_{ss} only starts the conversion act and brings the system to an intermediate state from which the energy-removing excitations are produced via the EQQ interaction. This conversion channel with excitations in the $J=1$ manifold as the energy sink is responsible for the strong conversion enhancement at high compressions $\xi>3$. Gap closing adds substantially to the conversion enhancement at high pressures. Theory predicts an abrupt slowdown of the conversion as the pressure is increased further (above 65–70 GPa for 65%–75% ortho).

(v) We have calculated conversion rates for a new phonon-assisted channel $S11\text{-}1p$ with two interacting ortho molecules going to the para state simultaneously during the same conversion act. We have also reconsidered the channel $S10\text{-}1p$ calculated previously by Berlinsky[3] to take into account the correct dependence of the Debye temperature, which scales the ultimate harmonic energy, on the density ratio ξ as well as the gap closing. A sum of the conversion rates due to these two phonon-assisted channels agrees well with the older results on conversion rates at moderate pressures.

(vi) The abrupt decrease of the observed conversion rate at long experimental times as the ortho concentration decreases to around 20% or lower arises from two factors. One is due to the lack of diffusion, which results in a preferential depletion of regions with high ortho concentrations, leading to nonrandom distributions. The other is a strong sensitivity of the new channel to the span of $J=1$ excitations and hence the ortho fraction c.

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APPENDIX

To illustrate how the phonon-related conversion rate probabilities are calculated we take channel $S11\text{-}1p$, which is the direct double conversion with one phonon emitted, as an example. To calculate $D(11;1)$ as in Eq. (45), we rewrite Eq. (14) in explicit form

$$\begin{aligned}\hat{h}^{(1)}&(1,1;1)\\ &=\sum_{\tau,\varphi,\mu,\nu,\lambda} C(112;\mu,\tau-\mu)K_{\mu}K'_{\tau-\mu}C(132;\varphi,\tau-\varphi)\\ &\quad\times C_{1\varphi}(\mathbf{w})C(143;\nu,\tau-\varphi-\nu)C_{1\nu}(\mathbf{w}')\\ &\quad\times C(154;\lambda,\tau-\varphi-\nu-\lambda)\\ &\quad\times\frac{|\mathbf{s}_{ij}|}{R_0}C_{1\lambda}(\mathbf{s}_{ij})C^{*}_{5,\tau-\varphi-\nu-\lambda}(\mathbf{n}). \qquad \text{(A1)}\end{aligned}$$

The initial state of the two molecules involved is a product of the rotational states $|1M\rangle$ and $|1M'\rangle$ and of the nuclear spin states $|1m\rangle$ and $|1m'\rangle$. The final rotational states are all zeros plus the quantum numbers of the emitted phonon. Making use of the known matrix elements[2] for nuclear-spin and rotational transitions we obtain the corresponding probability matrix element, which is a function of all the variables (M,M',m,m'):

$$\begin{aligned}\mathcal{P}^{(1)}&\equiv\langle i|\hat{h}(1,1;1)|f\rangle\\ &=\frac{1}{3}(-)^{M+M'}C(112;\overline{m},m-m')\\ &\quad\times C(132;\overline{M},M+m-m')\\ &\quad\times C(143;\overline{M',M}+M'+m-m')\sum_{\lambda} C(154;\lambda,M\\ &\quad+M'+m-m'-\lambda)C_{5,M+M'+m-m'-\lambda}\\ &\quad\times(\mathbf{n})\frac{|\mathbf{s}_{ij}|}{R_0}\langle 1\text{ph}|C_{1\lambda}(\mathbf{s}_{ij})|0\rangle. \qquad \text{(A2)}\end{aligned}$$

Here $\langle 1\text{ph}|C_{1\lambda}(\mathbf{s}_{ij})|0\rangle$ means the matrix element between the states with no phonons and one phonon labeled κ, which includes its wave vector $\mathbf{k}$ and polarization γ. It is implied that this matrix element will be multiplied by its Hermitian conjugate and the product will be summed over M, M', m, m', and κ. Since every of the four initial rotation states are independent and have three components and assuming that all of them are equally probable, for the probability of the initial state we have $P_i=1/27$.

We note that the matrix element $\mathcal{P}^{(1)}$ has only one inner summation index (over λ), which enables us to simplify it effectively. Substituting the longest string of indices (but without λ!, which is the inner summation index for the probability) $M+M'+m-m'$ for N and excluding m', we have

$$\begin{aligned}\mathcal{P}^{(1)}=&\frac{1}{3}(-)^{M+M'}C(112;\overline{m},N-M-M')C(132;\overline{M},M+N)\\ &\times C(143;\overline{M',N})\sum_{\lambda} C(154;\lambda,N-\lambda)\\ &\times C_{5,N-\lambda}(\mathbf{n})\frac{|\mathbf{s}_{ij}|}{R_0}\langle\kappa|C_{1\lambda}(\mathbf{s}_{ij})|0\rangle. \qquad \text{(A3)}\end{aligned}$$

Now the variable m appears only in the first Clebsch-Gordan (CG) coefficient. Thus, the summation over m in the relevant expression for the probability will yield (we apply the unitarity rule) $\Sigma_m\,[C(112;\overline{m},N-M-M')]^2=5/3$. In other words, the first CG is equivalent to $\sqrt{5/3}$. The same procedure can be applied in Eq. (A3) consecutively to the next two CG coefficients to obtain

$$\begin{aligned}\mathcal{P}^{(1)}\Rightarrow&\sqrt{\frac{35}{9\sqrt{3}}}\sum_{\lambda}\frac{|\mathbf{s}_{ij}|}{R_0}\langle 0|C_{1\lambda}(\mathbf{s}_{ij})|1\text{ph}(\mathbf{k},\gamma)\rangle\\ &\times C(154;\lambda,N-\lambda)C_{5,N-\lambda}(\mathbf{n}), \qquad \text{(A4)}\end{aligned}$$

where only one variable to be summed after squaring, viz., N, is left.

Inserting the matrix element $\mathcal{P}^{(1)}$ into the sum of Eq. (45) we have

$$\begin{aligned}D(11;1)=&\frac{35}{81\times 243}\left(\frac{s}{R_0}\right)^2\sum_{N\lambda\lambda'\kappa} C(154;\lambda,N-\lambda)\\ &\times C(154;\lambda',N-\lambda')C_{5N-\lambda}(\mathbf{n})C^{*}_{5N-\lambda'}(\mathbf{n})\\ &\times\langle 0|C^{*}_{1\lambda'}(\mathbf{s})|\kappa\rangle\langle\kappa|C_{1\lambda}(\mathbf{s})|0\rangle\,\delta(\epsilon_{\kappa}-\varepsilon), \qquad \text{(A5)}\end{aligned}$$

where ϵ_{κ} is the phonon dispersion law. To simplify this expression we apply first the rule $C_{l_1m_1}(\mathbf{n})C_{l_2m_2}(\mathbf{n})=\Sigma_L C(l_1l_2L;00)C(l_1l_2L;m_1m_2)C_{L,m_1+m_2}(\mathbf{n})$, then the known renaming trick[17]

$$\begin{aligned}C(abe;&\alpha\beta)C(edc;\alpha+\beta,\delta)\\ &=\sum_{f}\sqrt{1+2f}\sqrt{1+2e}\\ &\quad\times W(abcd;ef)C(bdf;\beta,\delta)C(afc;\alpha,\beta+\delta), \qquad \text{(A6)}\end{aligned}$$

where $W(abcd;ef)$ is the Racah coefficient, and, finally, the orthogonality rule $\Sigma_m C(abc_1;m,N-m)C(abc_2;m,N-m) = \delta_{c_1c_2}$ In the end we arrive at

$$D(11;1)=\frac{35}{27\times 81}(\chi_0+\chi_2). \tag{A7}$$

Here

$$\chi_0^{(1)}=\frac{1}{33R_0^2}\sum_{\lambda}\langle s_\lambda s_\lambda^*\rangle_\varepsilon , \tag{A8}$$

where we use the definition

$$\langle A_m B_n\rangle_\varepsilon=\sum_{\kappa}\langle\kappa|A_m|0\rangle\langle 0|B_n|\kappa\rangle\delta(\epsilon_\kappa-\varepsilon). \tag{A9}$$

The function χ_0 is easily expressed through the standard phonon density of states

$$f_0(E)=(1/3)\sum_{\mu}\langle s_\mu s_\mu^*\rangle_E . \tag{A10}$$

The other term in Eq. (A7), $\chi_2^{(1)}$, is a spectral function that can be reduced to the form

$$\chi_2^{(1)}=\frac{1}{33}\sqrt{\frac{2}{3}}\sum_{\lambda\lambda'} C_{2\lambda'-\lambda}(\mathbf{n})C(112;\lambda',\overline{\lambda})\frac{\langle s_\lambda s_{\lambda'}^*\rangle_\varepsilon}{R_0^2}$$
$$\equiv\frac{1}{11}f_2(\varepsilon). \tag{A11}$$

Finally,

$$D(11;1)=\frac{35}{24057}[f_0(\varepsilon)+f_2(\varepsilon)]$$
$$=\frac{35}{72171}\frac{1}{R_0^2}\left\langle\left[(\mathbf{ns})^2+\frac{s^2}{3}\right]\right\rangle_\varepsilon , \tag{A12}$$

where **n** is the unit vector along the intermolecular axis. Both spectral functions $f_0(\varepsilon)$ and $f_2(\varepsilon)$ have been calculated in the harmonic approximation by Berlinsky[3] assuming that the intermolecular interaction is central and can be described by a single force parameter. In contrast to the case of monoconversion[2,3] with the Hamiltonian based on $\hat{h}(10)$, in our case the contribution of the spectral function $f_2(\varepsilon)$ is appreciable. Calculations for other phonon-assisted channels that take into account several factors not considered in Berlinsky's calculations can be found in another paper.[41]

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