

## Importance of anisotropic three-body forces in solid hydrogen

Massimo Moraldi<sup>1,\*</sup> and Lorenzo Ulivi<sup>2,†</sup>

<sup>1</sup>*Dipartimento di Fisica, Università di Firenze, via G. Sansone 1, I-50019 Sesto Fiorentino, Italy*

<sup>2</sup>*ISC-CNR, via della Madonna del piano 10, I-50019 Sesto Fiorentino, Italy*

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We take into account three-body anisotropic forces between molecules to calculate the energy of the  $S_0(0)$  triplet in solid hexagonal close packed hydrogen under pressure. Three-body contributions result in one term depending on the orientation of only one molecule (crystal field term) and two others that couple rotations of different molecules (roton terms). Three-body interactions contribute, to a large extent, to the roton frequencies. Their inclusion in the calculation increases the calculated average frequency of the triplet, even at relatively low density, changing substantially the estimate of the internuclear distance. By contrast, the triplet splitting is substantially unaffected by three-body terms, resulting therefore a good candidate to test anisotropic two-body potential models against experiment.

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The structure and the dynamical properties of solid hydrogen under pressure are exciting subjects of active research.<sup>1-6</sup> In the low-pressure hexagonal close-packed (hcp) phase, the molecules rotate in their lattice sites and  $J$  is a good quantum number. In an ordered crystal (with only para- $H_2$  molecules), the rotational excitation acquires a collective character, due to the anisotropic interaction between molecules. The transition from the ground state (all molecules in the  $J=0$  state) to the state with one  $J=2$  excitation gives rise, in the Raman spectrum, to the  $S_0(0)$  triplet, that has been observed experimentally at low pressure<sup>7</sup> and up to about 110 GPa.<sup>4,8-10</sup> Above this pressure, solid para-hydrogen transforms to an orientationally ordered phase [broken symmetry phase (BSP)], whose crystal structure has been investigated theoretically,<sup>11-13</sup> spectroscopically,<sup>3</sup> and, recently, with more direct methods as x-rays and neutron scattering.<sup>6</sup> Values of the  $S_0(0)$  Raman frequencies and of their pressure evolution contain information on the same anisotropic intermolecular potential components which drive the transition to the BSP.

The quantitative analysis of these data by theories based on known anisotropic pair potentials is extremely problematical and is far from being satisfactory.<sup>4,14</sup> One problem concerns the splitting of the triplet which is always overestimated, as underestimated is the transition pressure to the BSP, if calculated analogously. The other quantity of importance is the average position of the triplet, which depends on the rotational constant and therefore gives information on the intramolecular distance and on its pressure dependence. The information extracted with the analysis of the Raman data depends, however, on our capability to calculate the contribution of the anisotropic potential to the roton energies (average value and splitting) in the solid. The main contribution to the splitting comes from the electric quadrupole-quadrupole interaction, and is generally calculated within first-order perturbation theory.<sup>1</sup> Three other contributions may have importance at high pressure: One comes from different components of the anisotropic pair-wise potential, one from three-body irreducible potential, and finally one from anharmonic effects (second-order perturbation theory).<sup>14</sup> Previous analyses have dealt differently with these contribu-

tions. In Ref. 14, the authors neglect these three contributions in the calculation, and propose an effective many-body contribution to justify the discrepancy of the triplet splitting at high pressure. With regard to the average frequency, they find that the intramolecular distance (that they derive up to about 40 GPa) falls off with pressure, reaches a minimum at about 30 GPa ( $\approx 220$  mol/l), and then increases. Goncharov *et al.*<sup>4</sup> introduce an *ad hoc* interaction component to justify the discrepancy between theory and the experimental triplet splitting. This new component, due to its symmetry, does not contribute to the average frequency.

It is probably worth mentioning here that all of the previous theories do not take into account phonon-roton interactions. Indeed, it has been shown that motional renormalization of the main interaction component, that is, the quadrupole interaction, is less than 5% at 100 mol/l and decreases with increasing density.<sup>15</sup> Also, hybridization effects take place in a limited range of density, and affect only the roton with  $E_{2g}$  symmetry.<sup>1</sup> Such effects have been eliminated by means of an interpolation procedure.

In a previous work, we have extended the theory to include all known pair potential components and the second-order terms in the perturbative expansion.<sup>5</sup> To compare with experiments, due to the poor knowledge of the anisotropic pair potential in the solid, in that paper we used a factor to reduce the anisotropic components of the gas-phase potential model.<sup>16,17</sup> The same procedure has been used also by others to calculate the transition pressure and is justified by a density functional theory calculation.<sup>18,19</sup> In this way, we could determine the rotational constant for higher densities than in Ref. 14. The result is that the intramolecular distance shows a minimum, as in Ref. 14 and then rapidly increases with density. The intramolecular distance is not accessible directly from experiments. Actually, a quantum Monte Carlo calculation<sup>20</sup> shows that the intramolecular distance does not change up to a density of about 150 mol/l, which contradicts both the results of Refs. 14 and 5.

In this paper, we demonstrate that three-body effects have large importance for the calculation of the frequencies of the  $S_0(0)$  triplet. To this goal, we do not use in the calculation

any reduction factor for the two-body potential, which is taken equal to the gas-phase one<sup>16,17</sup> throughout this paper. The main three-body contributions are induction effects determined by the molecular quadrupole moment, but corrections due to overlap and dispersion will also be taken into account as described in Ref. 21. Following the work of Piecuch,<sup>22</sup> we have considered three different three-body contributions that we calculate at first order in the perturba-

tion theory. The first contribution  $\varepsilon_{\mu}^{(c)}$  is of “crystal field” type, because it involves the orientation of only one molecule. In terms of purely quadrupolar induction, it would correspond to the interaction of dipoles on molecule  $j$  and  $i$ , both dipoles being induced by the quadrupole moment of molecule 1.

The energies of the triplet at first order in the perturbation theory are

$$\varepsilon_{\mu}^{(c)} = (-1)^{\mu+1} \sum_{L=2}^4 (2L+1) \begin{pmatrix} 2 & L & 2 \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} 2 & L & 2 \\ -\mu & 0 & \mu \end{pmatrix} \sum_{ji} \sum_{\Lambda\Lambda'} \frac{B_{202\Lambda}(R_{1j})B_{202\Lambda'}(R_{1i})}{R_{ij}^3} \sum_{m,n} Y_{2m}(\Omega_{ij})Y_{\Lambda n}^*(\Omega_{1j})Y_{\Lambda'n-m}(\Omega_{1i})(4\pi)^{3/2} \\ \times \frac{75}{\sqrt{6}} (-1)^{n-m} \sum_{m_1} \begin{pmatrix} 2 & 1 & 1 \\ m & m_1+n-m & -m_1-n \end{pmatrix} \begin{pmatrix} L & 2 & 2 \\ 0 & -m_1 & m_1 \end{pmatrix} \begin{pmatrix} 1 & 2 & \Lambda' \\ m_1+n-m & -m_1 & m-n \end{pmatrix} \begin{pmatrix} 1 & 2 & \Lambda \\ -m_1-n & m_1 & n \end{pmatrix}, \quad (1)$$

where  $B_{202\Lambda}(R)$  is related to the dipole induced on a molecule by a second molecule at a distance  $R$  apart.<sup>21</sup> In Eq. (1),  $\begin{pmatrix} JKL \\ mns \end{pmatrix}$  are  $3j$  symbols, and  $Y_{Lm}(\Omega_{ij})$  are spherical harmonics whose argument  $\Omega_{ij}$  is the orientation of the vector joining molecules  $j$  and  $i$  in a fixed frame. The sum over molecules  $\sum_{ji}'$  is limited to  $j \neq 1$  and  $i \neq 1, j$ . If the dipole induction is purely quadrupolar, then  $\Lambda = \Lambda' = 3$  only, and  $B_{2023}(R) = \sqrt{3}Q\alpha/R^4$  with  $\alpha$  the polarizability and  $Q$  the quadrupole moment of hydrogen.<sup>23</sup> In general, the component with  $\Lambda = 1$  also becomes important and, in addition,  $B_{2023}$  is not purely quadrupole-induced.<sup>21</sup> The terms with  $L = 2$  in Eq. (1) are analogous to the one arising from the pair-wise potential component  $V_{202}$  which is known to give a negligible contribution for an hcp lattice with  $c/a = \sqrt{8/3}$ .<sup>1</sup> Indeed, this term is also completely negligible even when taking the  $c/a$  variations<sup>24</sup> with respect to the ideal value into account. The term with  $L = 3$  is zero. The term with  $L = 4$  has the same symmetry properties as the component  $V_{404}$ , postulated in Ref. 4. Even though it is much larger than the  $L = 2$  term, it amounts to a small fraction of the “rotonic” contributions that will be introduced later. Finally, it can be shown that the contribution to the average position of the triplet due to  $\varepsilon_{\mu}^{(c)}$  of Eq. (1) is zero.

A second term is of rotonic type because it involves the orientations of two molecules. In the quadrupolar induction approximation, it can be viewed as the interaction of the dipole induced on molecule  $j$  by quadrupole on molecule 1 with the quadrupole of molecule  $i$ . Explicitly, the equation reads

$$\varepsilon_{\mu}^{(r_1)} = -4\pi \sum_{ji}' \sum_{\Lambda\Lambda'} \frac{B_{202\Lambda}(R_{1j})B_{202\Lambda'}(R_{ij})}{2\alpha} \\ \times \sum_n Y_{\Lambda n}^*(\Omega_{1j})Y_{\Lambda'n}(\Omega_{ij}) \left[ \begin{pmatrix} \Lambda & 2 & 1 \\ n & -\mu & -n+\mu \end{pmatrix} \begin{pmatrix} \Lambda' & 2 & 1 \\ n & -\mu & -n+\mu \end{pmatrix} + \begin{pmatrix} \Lambda & 2 & 1 \\ n & \mu & -n-\mu \end{pmatrix} \begin{pmatrix} \Lambda' & 2 & 1 \\ n & \mu & -n-\mu \end{pmatrix} \right]. \quad (2)$$

The third term, still of “rotonic type,” corresponds to the following mechanism. The quadrupole on molecule 1 induces a dipole on molecule  $j$ , the quadrupole on molecule  $j$  induces a dipole on molecule  $i$ , and finally dipoles on molecules  $j$  and  $i$  interact. We indicate these contributions with the symbol  $\varepsilon_{\mu}^{(r_2)}$ :

$$\varepsilon_{\mu}^{(r_2)} = -4\pi 3\sqrt{10} \sum_{ji}' \sum_{\Lambda\Lambda'} (-1)^{\Lambda+\Lambda'} \frac{B_{202\Lambda}(R_{1j})B_{202\Lambda'}(R_{ji})}{R_{ji}^3} \sum_L \sqrt{(2L+1)(2\Lambda'+1)} \begin{pmatrix} L & \Lambda' & 2 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} L & 1 & 2 \\ 1 & \Lambda' & 2 \end{Bmatrix} \\ \times \sum_M Y_{\Lambda-M}(\Omega_{1j})Y_{LM}(\Omega_{ji})(-1)^M \left[ \begin{pmatrix} 2 & \Lambda & 1 \\ \mu & -M & -\mu-M \end{pmatrix} \begin{pmatrix} L & 1 & 2 \\ -M & -\mu+M & \mu \end{pmatrix} \right. \\ \left. + \begin{pmatrix} 2 & \Lambda & 1 \\ -\mu & -M & \mu+M \end{pmatrix} \begin{pmatrix} L & 1 & 2 \\ -M & \mu+M & -\mu \end{pmatrix} \right]. \quad (3)$$

We have calculated these three-body terms using, for the induced dipole components  $B_{202\Lambda}(R)$ , those reported in Ref. 21. We add the three-body contributions to the two-body

ones (up to second order in the perturbation theory) calculated using for the anisotropic interaction potential, the  $V_{220}$ ,  $V_{222}$  components given by Ref. 16 and the  $V_{224}$ ,  $V_{202}$  given

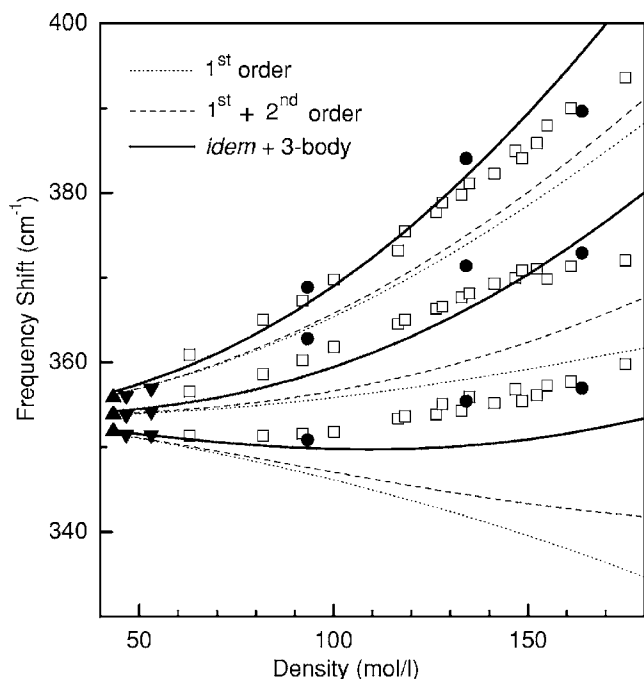


FIG. 1. Frequencies of the  $S_0(0)$  triplet in solid hydrogen. Lines are theoretical results obtained with first-order (dotted lines) and second-order (dashed lines) perturbation theory, using two-body interactions, and adding three-body contribution (solid lines). Symbols are experimental results by various authors ( $\square$  Refs. 8 and 9,  $\bullet$  Ref. 4,  $\blacktriangle$  Ref. 7,  $\blacktriangledown$  Ref. 26).

by Ref. 17, as in our previous work.<sup>5</sup> We have considered a static lattice with  $c/a = \sqrt{8/3}$ , and rotational constants of the isolated molecule.<sup>25</sup> The quantities  $\varepsilon_\mu^{(c)}$  are negligible with respect to the two “roton” terms  $\varepsilon_\mu^{(r_1)}$  and  $\varepsilon_\mu^{(r_2)}$ , that are large and have opposite sign. It is interesting to note that the main effect of the three-body terms is that of uniformly shifting the lines of the triplet, which hardly affects the splitting. The overall contribution of the three-body terms is by no means small, even at relatively low densities as 100 mol/l, being twice as large as the sum of the first-order and second-order two-body terms. It is therefore essential to take this effect into account if one wants to analyze quantitatively experimental data. In this respect, we report in Fig. 1 the results of our computation together with the experimental data<sup>4,7-9</sup> up to a maximum density of 180 mol/l. We notice that the inclusion of the three-body terms leads the calculation to almost coincide with the experimental values, up to a density larger than 100 mol/l, and reproduce satisfactorily these latter up to about 150 mol/l.

For clarity, it is convenient to discuss separately the (weighted) average roton frequency  $\varepsilon_{CM} = 1/5 \sum \varepsilon_\mu$  and the (average) splitting  $\Delta\varepsilon = 1/2(\varepsilon_0 - \varepsilon_1)$ , reported respectively in Figs. 2 and 3. The importance of the successive theoretical corrections is quite different in the two cases. While the successive corrections to  $\Delta\varepsilon$  are relatively small, and seem to indicate a convergence, with respect to both the perturbative and the many-body expansions, the same corrections for  $\varepsilon_{CM}$  are very large. The inclusion of all considered contributions, however, dramatically decreases the large disagreement between the experimental and the computed average frequency,

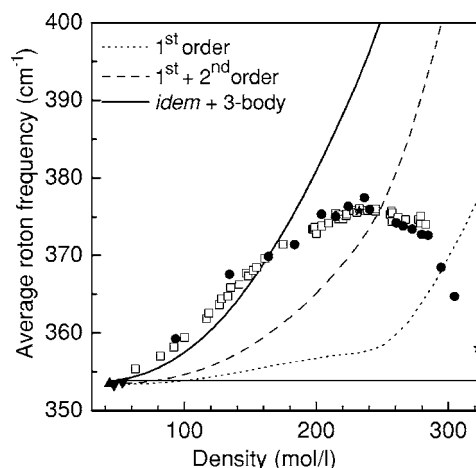


FIG. 2. Average frequency of the  $S_0(0)$  triplet in solid hydrogen. The symbol  $\star$  refer to experimental results of Ref. 10 the other symbols and lines as in Fig. 1.

leading to a reasonable agreement up to about 150 mol/l. We want to stress that this agreement is obtained using in the computation the molecular constants of the free molecule, in particular the rotational constant  $B_0$ . In our previous work,<sup>5</sup> three-body contributions were not taken into account, and a significant variation of the internuclear distance was needed, to obtain agreement with the experiment. The inclusion of three-body forces in the calculation leads us to conclude, in the limits of the hypothesis made in this work but in contrast to other work,<sup>5,14</sup> that pressure effects on the molecular bond are negligible up to 150 mol/l. Above this pressure, the experimental average frequency presents a large softening, which is not reproduced by any computation, where successive corrections do not seem to lead to a convergence.

Considering the average splitting  $\Delta\varepsilon$  (see Fig. 3), we stress that the three-body correction to the first-order two-

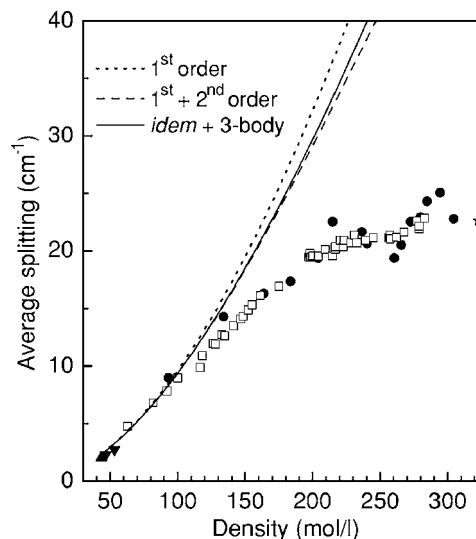


FIG. 3. Splitting  $[1/2(\varepsilon_0 - \varepsilon_1)]$  of the  $S_0(0)$  triplet in solid hydrogen. Lines and symbols as in Fig. 2.

body perturbation theory is very small. Such a result is reasonable. Indeed, while the main two-body anisotropy component has the form of two interaction quadrupoles and scales as  $Q^2/R^5$ , with  $R$  the intermolecular distance, a typical three-body term involves also the induction of a dipole through the polarizability  $\alpha Q^2\alpha/R^8$ . The ratio of the two terms amounts to  $\alpha/R^3$ , which is about 10% when  $R=2$  Å (about 300 mol/l). By the same reasoning, four-body contributions amount to a fraction  $\alpha^2/R^6$  of two-body terms and can thus be neglected over all densities considered in the paper. This makes the theoretical results quite dependable, and allows for a fruitful comparison with experiment. In particular, the small effect of three-body forces in the calculation demonstrates that the splitting depends mainly on the pair-wise components of the interaction. We are thus led to attribute the large discrepancy of experimental and calcu-

lated splitting to a poor knowledge of the anisotropic pair potential at short distances.

To conclude, we have taken into account all possible contributions listed in Ref. 14 and explicitly calculated the effect of three-body forces, demonstrating their importance, mainly for the determination of  $\epsilon_{CM}$ . On the other hand, three-body forces are negligible for the calculation of the triplet splitting. This experimental quantity can thus serve to determine the anisotropic two-body interaction potential. The models for the latter, available in the literature, have been tested and given poor results for reproducing the experimental data. All of these model are too repulsive, which calls for a careful re-examination of pair-wise potential components at the short intermolecular distances that are reached in high pressure experiments.

\*Electronic address: moraldi@fi.infn.it

†Electronic address: lorenzo.ulivi@isc.cnr.it

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