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Density dependence of the intramolecular distance in solid H_2: A. Spectroscopic determination

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We present an analysis of the measurements of the roton bands in p-H_2 at $T=6$ K. The quadrupole-quadrupole interaction gives the dominant anisotropic contribution up to at least 40 GPa and leads to a splitting of the $J=0\rightarrow2$ rotational transition into three equally spaced branches. In the framework of the Van Kranendonk theory, the effect of the anisotropic interaction can be accounted for and the remaining variation of the roton frequency is then related to the change of the bond length of the H_2 molecule, R_{intra}. The present determination of R_{intra} is semiquantitatively valid but points to an interesting variation, with a minimum around 30 GPa. By analogy with measurements done on I_2 and Br_2, and with *ab initio* calculations, this demonstrates the importance of charge-transfer interaction in dense H_2, even at pressures which are far from the regime of molecular dissociation.

It was predicted long ago that a diatomic molecular solid will progressively lose its molecular character under pressure, ultimately becoming an atomic metal.[1] This phenomenon, called molecular dissociation, has been extensively studied in solid I_2,[2] and observed in IBr,[3] HI,[4] and Br_2.[5] In these cases, it has been found that the molecular dissociation is due to a charge transfer from the intramolecular bond to the intermolecular region which takes place when the intermolecular distance becomes roughly equal to the intramolecular bond length.

Such a transition still remains to be seen in dense solid H_2; the molecular dissociation of H_2 is probably now within experimental reach. Encouragingly, recently two groups have reported a phase transition around 150 GPa in solid H_2 (Refs. 6 and 7) which was attributed to the molecular metallization by band overlap.[7] Optical measurements of reflectivity have been used as evidence of metallization at 149 GPa,[8] However other measurements to 230 GPa do not support this contention.[9] Thus, at the present time there does not exist direct evidence for the experimental realization of metallic molecular hydrogen.

The knowledge of the structural properties of molecular H_2 at very high density is crucial for detailing the transition to its high pressure metallic form. The crystal structure and the equation of state have been measured up to 31 GPa by x-ray[10] and neutron[11] diffraction of single crystals of H_2 and of D_2. The hcp structure was then shown to remain stable up to 150 GPa, from 77 to 300 K, by the continuity of the Raman active transverse optical phonon model.[12] But no information could be obtained on the evolution of the intramolecular bond length, R_{intra}. Direct determinations by x ray, used for I_2,[2] IBr,[3] and Br_2,[5] are impossible and neutron diffraction would require data with an accuracy far beyond what can be obtained in a diamond anvil cell (DAC). Fortunately, due to its small moment of inertia, the H_2 molecule can still be considered as a free rotor even in its solid phase. Therefore this paper aims to give a spectroscopic determination of the intramolecular bond length in solid H_2 up to 40 GPa. Below, we shall analyze the rotational $S_0(0)$ ($J=0\rightarrow2$) Raman line of solid parahydrogen (p-H_2), which has been measured at 5 K up to 54 GPa by Silvera and Wijngaarden.[13]

At low pressure in solid p-H_2, only the $J=0$ rotational level is thermally populated and the $J=0\rightarrow2$ rotational transition is observable. Due to the anisotropic interaction between H_2 molecules, this excitation is delocalized and the coherent rotational motions of the molecules in solid hydrogen give rise to rotational energy bands. In solid hcp, 10 roton modes exist for any value of wave vector K. The even states at $K=0$ are Raman active and their fivefold degeneracy is partially lifted in the solid. As a result, the $J=0\rightarrow2$ transitions, called the $S_0(0)^+$ transitions, can be observed by Raman scattering as three spectral lines. The low energy level, corresponds to $m=\pm1$, the middle one to $m=\pm2$, and the higher one to $m=0$. This was first interpreted by Van Kranendonk[14] with a first-order perturbation theory by taking into account the electric quadrupole-quadrupole interaction, EQQ, which is the only significant anisotropic interaction at low density, between all pairs of molecules distributed on an hcp lattice.

The evolution of the three branches, $\nu(S_0^+(0))_m$, of the roton band has been measured up to 54 GPa at 5 K by Silvera and Wijngaarden.[13] These measurements on p-H_2 have recently been extended to 167 GPa in which an orientational order transition has been observed at 110 GPa.[15] For the purpose of this paper we will only consider the data below 40 GPa, that is in the region where it seems that the features of the Van Kranendonk theory are applicable. Here, the molecules are still freely rotating in an hcp crystal and the perturbation by anisotropic interactions splits the $S_0(0)$ rotational level into three branches, roughly equally spaced. Also the value of the splitting at 40 GPa (40 cm^{-1}) is still much smaller than the average roton energy level (356 cm^{-1}) which means that there is no appreciable mixing of other J rotational states, as supported experimentally by the fact that the orientational order transition takes place at a much higher pressure, $P=110$ GPa.

With increasing pressure, in addition to the EQQ interaction, other components of the anisotropic interaction are expected to become important, mainly that due to repulsive charge overlap.[16] The most general expression for the anisotropic intermolecular forces between two hydrogen molecules can be written[17]

$$V_A(R)=\sum_{i=l_1,l_2} \epsilon_1(R)\sum_m a_m Y_{l_1}^m(\omega_1)Y_{l_2}^m(\omega_2) \ . \tag{1}$$

Because of the homonuclear character of the molecules, only even values of l_1 and l_2 occur. The *ab initio* potential of Schaefer and Meyer,[18] which was fitted to pair measurements by Schaefer and Kohler,[19] was recently shown to be a very good representation of the anisotropic H_2 interaction.[20] If it is expanded in spherical harmonics as in Eq. (1), only the terms with $l_1+l_2<4$ are significant; this expansion can be rewritten in terms of the eigenfunctions of the total internal rotational angular momentum and the coefficient $V_{i,j,k}$ have been tabulated on a grid of intermolecular distances.[19] Van Kranendonk and collaborators[21] have developed a theoretical model to calculate the effect of such an anisotropic interaction on the $J=0\rightarrow 2$ rotational transition. It is sufficient here to recall the main results of this derivation and the reader is referred to extensive reviews for more details.[21,22] Many anisotropic effects can modify the rotational $S_0(0)$ transition, among which the major contributions are (a) the interaction between a molecule and the crystal field; (b) the interaction between pairs of molecules; (c) the three-body interactions between molecules; and (d) the roton anharmonicities.

In a perturbation treatment, these various contributions can be added and one arrives at the following expression for the roton frequencies:

$$\begin{aligned}\nu(S_0^+(0))_m &= \nu + a_m\epsilon_{224}+c_m\epsilon_{202}+\epsilon_{220}\\ &\quad +d_m\epsilon_{222}+\Delta E_m^T+\Delta E_m^A \ .\end{aligned} \tag{2}$$

The ϵ_{ijk} is the contribution due to the V_{ijk} term of the anisotropic potential. For an ideal rigid hcp lattice, ϵ_{202} and ϵ_{222} should be equal to zero; nonvanishing contributions to these terms can be caused by lattice deformations, either steming from lattice vibrations or from deviations from the ideal c/a ratio. Consequently, these two terms are expected to be quite small in dense H_2 and will be neglected in the following. At low pressure, the three-body term ΔE_m^T is due to the energy of quadrupole induced dipoles, resulting in a small effect with less than 10% splitting between the various m levels. The roton anharmonicities term,[23] ΔE_m^A, is the leading contribution of second-order perturbation theory. This term should be proportional to ϵ_{224}^2/B, where B is the rotational constant, and it does not lift the degeneracy of the m levels at $K=0$. Still, the evolution of ΔE_m^A with density is problematical. At $P=0$ GPa, $\Delta E_m^A=0.166$ cm^{-1} and since the EQQ interaction is the dominant term of V_{224}, its evolution should scale as $(V_0/V)^{10/3}$ which would give at 40 GPa a value of 33 cm^{-1} which is nearly equal to the measured total shift of the roton level. This problem was already pointed out by Wijngaarden[22] because this term, being inversely proportional to the rotational constant B, should also give a strong isotopic difference between H_2 and D_2 which is not observed experimentally. Probably with density this term is compensated by higher order terms of the perturbation expansion. The contribution of ΔE_m^A and ΔE_m^T are then difficult to estimate with density. We circumvent this problem by only using low-density data where these terms do not have a significant impact on the results.

We can now rewrite Eq. (2) in the simpler following expression:

$$\nu(S_0^+(0))_m=\nu_0+a_m\epsilon_{224}(\rho)+\epsilon_a(\rho) \tag{3}$$

with $a_{\pm 2}=1$, $a_{\pm 1}=-4$, and $a_0=6$. $\epsilon_a(\rho)$ is the sum of ϵ_{220}, ΔE_m^T, and ΔE_m^A which all have a positive sign and so $\epsilon_a(\rho)$ should be a positive increasing function of the density ρ. We finally note that in the presence of the complete anisotropic interaction of dense H_2, the $J=2$ roton is equally split into three branches, as obtained experimentally to a good approximation, up to 40 GPa.[13]

The mean frequency of the triplet ν_{cm} is given by

$$\nu_{cm}=\tfrac{1}{5}\sum_{m=-2,2}\nu(S_0^+(0))_m=\nu_0+\epsilon_\alpha(\rho) \ . \tag{4}$$

$E_0=hc\nu_0$ is the energy of the $S_0(0)$ rotational level of the H_2 molecule free rotor only perturbed by the isotropic crystal field. The total width, Δ, of the roton branch is easily obtained from Eq. (3) and amounts to

$$\Delta=\nu(S_0^+(0))_0-\nu(S_0^+(0))_1=10\epsilon_{224}(\rho) \ . \tag{5}$$

Δ is thus only related to the V_{224} term of the anisotropic potential. From Schaefer and Kohler,[19] this term is essentially dominated by the EQQ interaction which even at intermolecular separations corresponding to 40 GPa contributes by 96% of the anisotropic interaction. In this case, Δ should be proportional to Q^2/R_1^5, where Q is the quadrupole moment of the H_2 molecule and R_1 the nearest-neighbor distance. For rigid quadrupoles, Q_0, the variation of Δ should consequently scale as $(V_0/V)^{5/3}$ and with the experimental x-ray equation of state[10] one can easily calculate the evolution of Δ with pressure. This calculation is compared in Fig. 1 to experimental data. The agreement is good up to 7 GPa but above this, the calculation largely overestimates the measurements. In fact there is a change in the intramolecular distance, as will be seen below, which should also affect the quadrupole moment Q. With the value of the intramolecular distance obtained below, we have estimated the variation of the quadrupole moment from the calculations of Poll and Wolniewicz.[24] The evolution of Δ now scales as $(V_0/V)^{5/3}(Q/Q_0)^2$ and the agreement with experiment is improved. Still, above 12 GPa, experimental Δ is small-

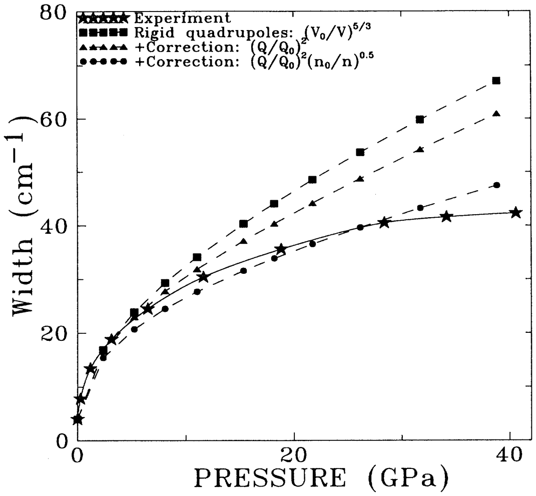

FIG. 1. Pressure dependence of the width, Δ, of the rotational $S_0(0)$ band in solid p-H_2 at 5 K. The stars identify the experimental data; the squares the evolution of Δ if we assume that the anisotropic interaction is due to rigid quadrupoles. The triangles represent the calculation which considers the variation of the quadrupole moment with the bond length of the H_2 molecule. The dots represent the calculations when screening effects are also considered.

er. That probably comes from the fact that in dense solid H_2 there exist many-body electronic effects which can lead to a screening of the EQQ interaction. Such effects are difficult to calculate but we can try to estimate them in a mean field way by dividing the EQQ interaction by the dielectric constant of the medium which was estimated from the high pressure measurements of the refractive index n.[25] In this approximation, Δ thus scales as $(V_0/V)^{5/3}(Q/Q_0)^2(n_0/n)^{1/2}$ and we can see in Fig. 1 that the agreement with experimental Δ is reasonably good over the whole density range considered here.

This validates the above analysis which led to the result that the V_{224} term of the anisotropic interaction (essentially the EQQ interaction) is mainly responsible for lifting the degeneracy of the m rotational levels into three branches. This also corroborates two recent works, the NMR measurements of normal H_2 up to 7 GPa (Ref. 26) and the calculation of the dynamics and phase transition in dense H_2 and D_2 up to 100 GPa,[20] which both have shown that the EQQ interaction dominates the anisotropic properties of dense H_2. In the second paper the effect of the reduction of the quadrupole moment, which follows from a shortening of the intramolecular bond, was taken into account for improving the agreement with experiment. In this paper we show that screening effects also have to be considered.

The aim of this analysis is to take out the effect of the anisotropic interaction in order to obtain the $S_0(0)$ rotational transition of the free H_2 rotor. Its energy $E_0=hc\nu_0$ is then directly related to the change of the intramolecular potential due to the isotropic intermolecular interactions. From Eq. (4) the mean value of the triplet is equal to ν_0 plus another term due to anisotropic interactions, $\epsilon_a(\rho)$. This last term is small at low density and its evolution with pressure is unknown. We can only say that it is of positive sign. We will make the hypothesis that this term is negligible over the whole density range considered here. As will be seen below, $E_0=6h/(8\pi^2\mu r_0^2)$, where r_0 is the mean intramolecular distance averaged over vibrational state. Consequently the hypothesis of neglecting $\epsilon_a(\rho)$ comes down to calculating a lower bound for the intramolecular distance.

In the following we then assume that the two protons of an H_2 molecule in the domain solid are interacting through a Morse potential which is a function of three parameters: the location of the minimum r_e, the potential depth $\mathcal{D}$, and the range parameter a. The vibrational and rotational energy levels are then parametrized by the two quantum numbers v and J and are given by the following expression:[27]

$$\begin{aligned}\frac{E_{vJ}}{h}&=\omega(v+\tfrac{1}{2})-\chi_e\omega(v+\tfrac{1}{2})^2\\&\quad+(B_e-\alpha_e(v+\tfrac{1}{2}))J(J+1)\\&\quad-D_eJ^2(J+1)^2\ .\end{aligned}\tag{6}$$

The energy E_0 of the $S_0(0)$ transition, which corresponds to $\Delta v=0$ and $\Delta J=0\rightarrow 2$, is expressed by

$$\frac{E_0}{h}=6(B_e-\alpha_e/2)-36D_e\ ,\tag{7}$$

where

$$B_e=h/(8\pi^2 I_e),\quad I_e=\mu r_e^2,\quad D_e=4B_e^3/\omega^2\ ,$$

$$\omega=a(2\mathcal{D}/\mu)^{1/2}/2\pi,\quad \chi_e=h\omega_e/4\mathcal{D}$$

and

$$\alpha_e=3h^2\omega(1/(ar_e)-1/(ar_e)^2)/(4\mu r_e^2\mathcal{D})\ .$$

The energy E_1 of the $Q_1(0)$ vibrational transition, $\Delta v=0\rightarrow 1$ and $\Delta J=0$, is also simply related to the parameters a and $\mathcal{D}$ of the Morse potential through the relation

$$E_1=\frac{h}{2\pi}\left[\left[\frac{2a^2\mathcal{D}}{\mu}\right]^{1/2}-\frac{ha^2}{2\pi\mu}\right]\ .\tag{8}$$

So the measurements[28] of the energy of the $Q_1(0)$ vibrational transition in solids of para-H_2 and of ortho-D_2 are expressed by two relations given by Eq. (8) with their respective different reduced masses μ, from which the evolution of the parameters a and $\mathcal{D}$ can be inverted, as was done recently by Ashcroft.[29] Knowing that, the equilibrium intramolecular distance r_e is obtained from the nonlinear equation (7) and the energy level of the rotational $S_0(0)$ transition, E_0, is determined from the experimental values of the triplet, as explained above, that is from Eq. (4) with $\epsilon_a(\rho)=0$.

Since the period of vibration is very small compared to the period of rotation, it is plausible to use a mean B_0 value of the rotational constant for the lowest vibrational states. From Eq. (7), it is given by

$$B_0=B_e-\alpha_e/2=h/(8\pi^2\mu r_0^2) . \qquad (9)$$

In this case, r_0 is the mean value of the intramolecular distance for the lowest vibrational state whereas r_e is the minimum of the intramolecular potential.[27]

In Fig. 2 we show the values of r_e and r_0, calculated in the above-described procedure. As expected, the extrapolation of the two curves to $P=0$ gives values of r_e and r_0 which are 0.4% greater than the measured values for the free molecule,[30] in agreement with the fact that in the low-pressure solid the dispersion forces are known to stretch the H_2 molecule.[17] However, the evolution with pressure of the intramolecular distance is quite surprising. First, as expected for a molecule compressed by a crystal field, it starts to decrease with increasing pressure, but then around 30 GPa its evolution levels off and then starts to increase again. In the last part of this paper we will try to understand the physical reasons of such a behavior by comparing it to the measurements on other diatomic molecular solids, I_2 and Br_2, and also to the *ab initio* calculations in dense solid H_2. Before that, it should be noted that since the calculated values of r_e and r_0 are lower bounds of their real values, if $\epsilon_a(\rho)$ were not negligible contrary to what has been assumed above, the shape of the evolution of R_{intra} would still be the same and its minimum would occur at an even lower pressure. Also, as seen in Fig. 2, the difference between r_0 and r_e increases with pressure and this indicates that the bonding force is becoming more anharmonic under pressure, in agreement with the quantum Monte Carlo simulations.[31]

The mean intramolecular distance r_0 has been measured for molecular solids I_2 and Br_2 up to their molecular dissociation by x-ray diffraction. In x-ray measurements the uncertainty is quite large and amounts to 0.05 Å, and so within these error bars no appreciable change of r_0 could be detected in both systems.[2,5] However, preliminary energy x-ray absorption fine structure (EXAFS) measurements on Br_2,[32] which should be a very sensitive method, indicate that r_0 starts to decrease, hits a plateau, and then r_0 increases again, when approaching the molecular dissociation. Still, the curve obtained in this preliminary measurement is only qualitatively correct since the data acquisition and the treatment of the spectrum need to be improved for more quantitative results. Further experiments are planned for the coming year. These experimental determinations of r_0 in different molecular diatomic solids are compared in Fig. 3 to the present spectroscopic determination of r_0 in solid p-H_2; the relative variation of r_0 in arbitrary units is plotted as function of the reduced density $\rho^*=\rho/\rho_m$, where ρ_m is the density of the molecular dissociation given by the Herzfeld criterion.[33,34] It is seen that the evolution of r_0 in solid Br_2 is similar to the one determined here in solid p-H_2. In general, it is expected, from perturbation calculations, that r_0 should decrease with increasing density, that is when the molecule is compressed by the crystal field.[35] It could happen that with the change of the anharmonicity of the intramolecular potential, although the equilibrium bond length, r_e, is decreasing, its average value over vibration, r_0, increases. But this is not the case here since as it can be seen in Fig. 2, r_e and r_0 are both increasing. In fact, the following explanation developed for the analysis of the measurements on I_2 should also be valid here.[36] On compression of the molecular solid, the electronic charge density is going from the intramolecular bond to the intermolecular region and therefore the bonding of the molecule diminishes. The evolution of r_0 is consequently the result of two competing effects: the compression of the molecule

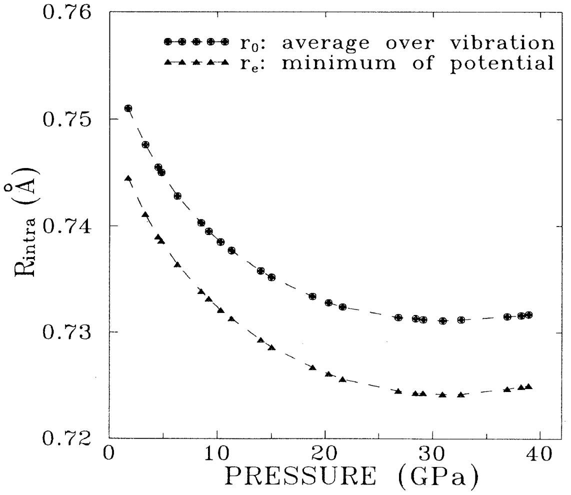

FIG. 2. Spectroscopic determination of the intramolecular distance of H_2 in p-H_2 solid at 5 K. The dots identify the minimum of the intramolecular potential and the triangles the mean value of the lowest vibrational state.

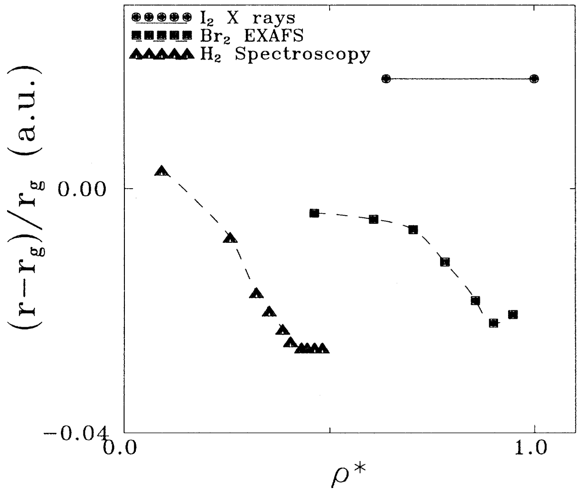

FIG. 3. Qualitative variations of the intramolecular distance r of various molecules in their dense solids. The relative variation to the gas value r_g is plotted in arbitrary units versus ρ^x, the density divided by the density of the molecular dissociation. The dots identify the x-ray measurements of I_2 (Ref. 2); the squares are the EXAFS measurements of Br_2 (Ref. 32); the triangles are the present spectroscopic determination.

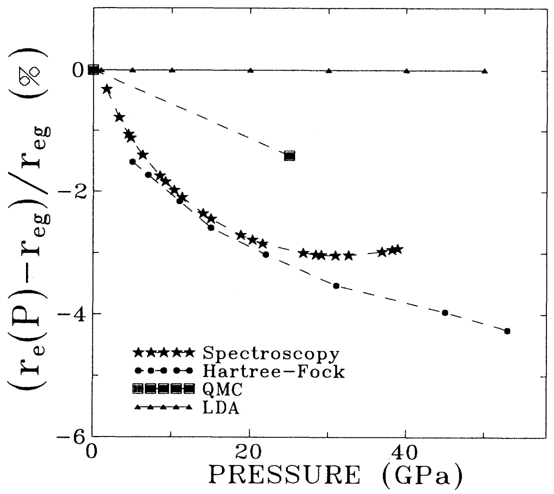

FIG. 4. Relative variation of the minimum of the intramolecular potential of H_2, r_e, to its gas value, r_{eg}. The stars identify the present spectroscopic determination; the dots are the Hartree-Fock type calculation (Ref. 38); the squares are the quantum Monte Carlo calculations (Ref. 31); the triangles are the LDA calculations (Ref. 39).

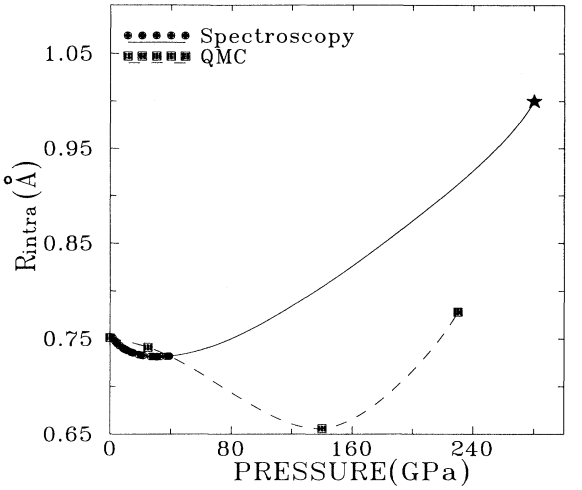

FIG. 5. Variation of the intramolecular distance of the H_2 molecule in the solid under very high pressure. The squares are the quantum Monte Carlo calculations (Ref. 31); the dots identify the present spectroscopic determination and the star is a hypothetical value as explained in the text.

which tends to decrease it and the progressive loss of the intramolecular bonding by charge transfer to the intermolecular region which tends to increase it. As seen in Fig. 3, in solid I_2, charge transfer is dominant over the whole solid density. In solid Br_2 it becomes important for reduced densities greater than 0.8. Surprisingly in solid H_2 it appears to be significant for reduced densities even as low as 0.4, which are quite far from molecular dissociation. It is also interesting to remark that the minimum of the intramolecular bond length corresponds to the maximum of the frequency of the vibronic $Q_1(0)$ mode.[28] The two effects appear to be correlated and related to charge transfer, which seems to invalidate the recently proposed interpretation of the maximum of the $Q_1(0)$ curve in terms of anharmonic effects.[29,37]

In Fig. 4 we compare our spectroscopic determination of the relative variation of r_e to its calculation by the most sophisticated *ab initio* methods. For pressure below 20 GPa, the spectroscopic determination is in very good agreement with the Hartree-Fock type calculation of Raynor.[38] In this density range the molecule is mainly compressed by the crystal field and the molecular basis set of the Hartree-Fock calculation is particularly suited for that. But at higher pressures, charge transfer effects come into play and they are not well described in such a calculation since it presupposes that the electrons are principally localized on closed-shell molecular units. Finally, the large discrepancies between these various theoretical calculations [Hartree-Fock,[38] quantum Monte Carlo,[31] and local density approximation (LDA)[39]] stress the fact that although H_2 has the simplest electronic configuration, its quasiexact description by *ab initio* methods is certainly far from being achieved.

In order to extrapolate our determination of r_0 to higher pressures, we have made the following assumptions: (i) the structure mhcp in which the molecules are ordered along the c axis is stable near the molecular dissociation, as suggested from recent experimental measurements[12] and calculations;[40] (ii) the value at the molecular dissociation is taken to be equal to 2 cm^3/mole, which is the value given by quantum simulations[31] and the Herzfeld criterion[34]; (iii) the molecular dissociation occurs when the intramolecular distance is of the same order as the nearest-neighbor H-H intermolecular distance. Assuming various c/a ratios between 1.63 and 1.58, the intramolecular distance obtained in this way is always of the order of 1.02 Å, which is plotted in Fig. 5 as a star. The trend of the evolution of r_0 over the whole pressure domain of the molecular H_2 solid is then very similar to the one obtained by quantum simulation.[31]

Ree and Bender[16] have calculated by the configuration integral (CI) method the dependence of the H_2-H_2 pair potential on the bond length and obtained that r_e should shrink as the two H_2 molecules come closer. The increase of r_e observed above 30 GPa apparently contradicts this calculation. However, in dense solid H_2 many-body effects have to be considered and probably could resolve this disagreement. Still, it remains to understand why charge transfer between two H_2 molecules is taken place for such low reduced densities in solid H_2.

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