PHYSICAL REVIEW B VOLUME 53, NUMBER 22 1 JUNE 1996-II

Calculation of the turnover in the vibrational frequencies of solid hydrogen at high pressures

Marcel I. M. Scheerboom* and Jan A. Schouten
Van der Waals–Zeeman Laboratory, University of Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands

(Received 12 February 1996)

In a theoretical study of solid hydrogen we explain the turnover in both the Raman and infrared frequencies, as well as the large increase of the resonance coupling at high pressures. Moreover, we indicate the reason for the increase of the frequencies in dilute solutions. This has particularly been achieved by calculating the spherically averaged bond-length derivatives of the two-body intermolecular potential energy, while separating this into a static contribution of the molecular charge clouds and a contribution of the fluctuations therein (dispersion). [S0163-1829(96)51222-1]

The vibrational properties of solid hydrogen at ultrahigh pressures continue to draw enormous attention[1–8] because of the suggested implications for the metallization. Until recently the Raman branch of the vibron had been experimentally determined up to 150 GPa,[1] but the infrared (IR) branch only up to 60 GPa.[2] The Raman frequency shows a turnover at 36 GPa. This unexpected phenomenon was attributed to a weakening of the bond between the hydrogen atoms, pointing to the onset of metallization.[1] Later it was recognized that the effect was due to resonance coupling (RC) between the neighboring molecules.[3,4] Several authors have tried to calculate the Raman frequency, but the results at high pressures were rather disappointing,[5–7] moreover, the RC was not addressed in this work. Recently, also the IR spectrum has been measured up to 180 GPa.[4] Also in this case a turnover was found but at much higher pressures. Again it is suggested that there is a relation with the onset of metallization.[4,8]

For our understanding of what is happening, it is of crucial importance to know what is already possible in the molecular approach.[3] This means a quantitative description of the vibrational frequencies only based on a potential, which is a function of the orientations ((Ω_i)), the distances between the centers of mass ((R_{ij})) and the bond lengths ((r_i)). We have performed such a calculation taking data about this potential from literature, without any adjustment to the experimental frequencies and without the assumption of charge transfer or bond weakening. It is shown in Fig. 1 that a turnover is found for the Raman as well as the IR branch. The agreement with the experimental Raman frequencies is very good. The deviation from the experimental IR branch is somewhat larger. The reason for this discrepancy will be explained later. The calculations show that the dispersion is the major cause of the turnover as well as of the resonance coupling.

A study is presented on the vibrational frequencies of solid H_2 at room temperature from the melting line up to 200 GPa. We have calculated the spherically averaged derivatives of the intermolecular potential energy with respect to the bond lengths ((r_i)). It has been suggested that at high pressures the resonance coupling is negligible[6] or could not be extracted[2,3] from the existing *ab initio* data. However, it will be shown that the RC contribution is large and can be fully taken into account in calculating the Raman shift from these data.[9,10] An important aspect of our approach is also the decomposition of the potential in a self-consistent field (SCF) and a London dispersion contribution, using an attenuation function which depends on the bond length. A procedure will be provided for evaluating explicitly the dispersive RC contribution, which must be subtracted in the case of IR.

The first theoretical approach is presented, in which the r_i dependence of the intermolecular potential is evaluated. Before treating the theory in detail we first summarize the well known expressions[3,11,12] resulting in the Raman and IR frequencies, assuming that the derivatives of the intermolecular potential energy with respect to the bond lengths are known.

The Hamiltonian of an isolated molecular *i* is

$$V_0(x_i)=\tfrac{1}{2}\, f\, x_i^2+g x_i^3+h x_i^4, \tag{1}$$

where $x_i=r_i-r_e$ and r_e is the equilibrium bond length; the force constants, *f*, *6g*, and 24*h* are the second, the third, and the fourth derivatives in r_e. By solving the Schrödinger equation one obtains the vibrational transition energy between the 0 and 1 state:[12]

$$E_{\text{vib}}=\hbar\omega_e-2\hbar\omega_e x_e+\cdots, \quad \omega_e=\sqrt{f\mu^{-1}},$$
$$\omega_e x_e=\frac{3}{2}\,\frac{\hbar}{\mu f}\left[\frac{5}{2}\,\frac{g^2}{f}-h\right]. \tag{2}$$

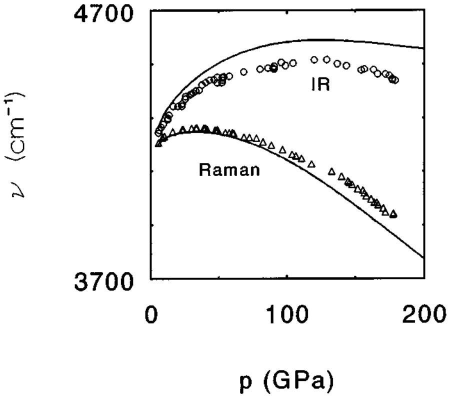

FIG. 1. Theoretical results for the vibrational Raman (lower line) and IR (upper line) frequencies versus the pressure. In the IR results the SCF contribution to the RC is still present. The points are results of Raman [triangles (Ref. 8)] and IR [circles (Ref. 4)] experiments.

ω_e is the harmonic frequency, $\omega_e x_e$ the anharmonicity, and μ the reduced mass.

Consider two molecules i and j. The intermolecular potential energy $\phi(\Omega_i,\Omega_j,R_{ij},r_i,r_j)$, denoted as $\phi(ij)$, can be expanded around r_e:

$$\phi(ij)=\phi(ij)|_{r_i,r_j=r_e}+F_{ij}x_i+F_{ji}x_j+\tfrac{1}{2}G_{ij}x_i^2+\tfrac{1}{2}G_{ji}x_j^2 + C_{ij}x_ix_j+\tfrac{1}{6}H_{ij}x_i^3+\tfrac{1}{6}H_{ji}x_j^3+\tfrac{1}{2}K_{ij}x_i^2x_j+\tfrac{1}{2}K_{ji}x_j^2x_i + \cdots , \tag{3}$$

where F_{ij}, G_{ij}, C_{ij}, H_{ij}, and K_{ij} are the derivatives to the corresponding bond lengths, evaluated at $r_i=r_j=r_e$. These quantities are the central objects of this study. If a lattice is considered, in which the symmetry is such that all the molecules experience identical fields, then the new coordinate $y_i=r_i-(r_e+y_m)$ can be used, where y_m is the change of the equilibrium bond length. In our case this condition is fulfilled since, at room temperature and in the pressure range of interest, hydrogen crystallizes in the hcp structure.[8] In the case of N molecules the one- and two-body terms of Eqs. (1) and (3) can be summed up; the results can be rewritten, such that the linear terms are eliminated:

$$\sum_{i=1}^{i=N} V_0(x_i)+\sum_{i<j} \phi(ij)=\sum_{i=1}^{i=N} [\tfrac{1}{2}f_i'y_i^2+g_i'y_i^3+hy_i^4] + \sum_{i<j} [C_{ij}'y_iy_j+\tfrac{1}{2}K_{ij}y_i^2y_j + \tfrac{1}{2}K_{ji}y_j^2y_i], \tag{4a}$$

$$f_i'=f+\sum_{j\neq i} G_{ij}+\left(6g_i'+\sum_{j\neq i} K_{ij}\right)y_m-12hy_m^2, \tag{4b}$$

$$C_{ij}'=C_{ij}+2K_{ij}y_m, \tag{4c}$$

$$g_i'=g+\tfrac{1}{6}\sum_{j\neq i} H_{ij}+4hy_m, \tag{4d}$$

$$4hy_m^3+3g_i''y_m^2+f_i''y_m+\sum_{j\neq i} F_{ij}=0, \tag{4e}$$

$$f_i''=f+\sum_{j\neq i} [G_{ij}+C_{ij}], \tag{4f}$$

$$g_i''=g+\sum_{j\neq i} [\tfrac{1}{6}H_{ij}+\tfrac{1}{2}K_{ij}]. \tag{4g}$$

It is important to note that in Eqs. (4f) and (4g) one only need to know the *sum* of the mixing and nonmixing coefficients. In the case of Raman spectroscopy the vibrational excitation can be transferred during the process, such that molecule i and its nearest neighbors (NN) vibrate in phase (resonance coupling).[8,11] In Eq. (4a) the y_j of the NN are equal to the y_i and the same form as Eq. (1) arises with solutions as given in Eq. (2). As in Eqs. (4f) and (4g) summations arise of mixing and nonmixing terms. In the case of IR no coupling occurs;[8,11] only the first term in Eq. (4a) has the same form as Eq. (1), giving a similar solution as Eq. (2). The vibrational average of the mixing terms then only give small corrections.

We will now describe the calculation of F_{ij}, G_{ij}, C_{ij}, H_{ij}, and K_{ij}. The vibrational and molecular motions act on different time scales. As usual,[23] it is assumed that the intermolecular potential can be treated as a time-independent potential with respect to the vibration, and only the average force along the molecular axis will be calculated. First the intermolecular potential energy $[\phi(ij)]$ can be divided in a contribution of the mutual electrostatic interactions and a contribution of the fluctuations therein.[11,13] It should be realized that a SCF calculation only contains the static interaction and not the fluctuations.[14] For large distances the dispersion part can be evaluated[10,11] in the form of three multipoles with coefficients C_k; $k=6,\ 8$, and 10. For smaller values of R_{ij} the dispersive energy is attenuated[11,15] by the overlap of the charge distributions, a process that can be described with an attenuation function (f_{at}), which is 1 for large R_{ij} and becomes zero for $R_{ij}=0$. The spherically averaged form of $\phi(ij)$ becomes

$$\phi(R_{ij})=\phi_{\mathrm{SCF}}(R_{ij})-f_{\mathrm{at}}(R_{ij})\sum_k C_kR_{ij}^{-k}. \tag{5}$$

The Silvera-Goldman (SG) potential[15] for hydrogen (without the many-body term) of this form was based on SCF (Ref. 16) and multipole[10] calculations, which had just become available. We have improved the SCF part by the use of the high level SCF calculations of Ree and Bender[9] for small values of R_{ij}. Recently Hemley and co-workers[17,18] found that a negative short range correction had to be added to this potential. We have rewritten their potential[18] in the original form of Eq. (5). It turned out that we could use the original SG exponential form with slightly adjusted parameters to present the new data and the SCF part of SG at $R_{ij}>0.26$ nm. The attenuation function f_{at} was obtained by substituting this SCF function and the original multipole function[10] in the right-hand side of Eq. (5) and the empirical potential[18] in the left-hand side. Thus the potential used by us reproduces the experimental *p-V* curve. We make use of the fact that a direct relation exists between f_{at} and ϕ_{SCF}, because the attenuation process is due to the overlap of the charge distributions. This relation can be deduced by plotting $f_{\mathrm{at}}(R_{ij})$ versus $\phi_{\mathrm{SCF}}(R_{ij})$ for various values of R_{ij} (see Fig. 2). The points in Fig. 2, corresponding to equidistant values for R_{ij} can be represented by the functional form (line in Fig. 2):

$$f_{\mathrm{at}}(\phi_{\mathrm{SCF}})=[1+0.46055(1-\exp(-13.222\phi_{\mathrm{SCF}}\phi_0^{-1})) + \phi_{\mathrm{SCF}}\phi_0^{-1}+0.01842(\phi_{\mathrm{SCF}}\phi_0^{-1})^2]^{-1}, \tag{6}$$

where $\phi_0=6.649\times 10^{-20}$ J. The linear part of the plot, which is most important for this work, is due to the fact that in this region the overlap energy completely dominates ϕ_{SCF}.

The r_i derivatives of the distinct parts of Eq. (5) can be determined with the help of the *ab initio* data.[9,10] The ϕ_{SCF} has been calculated for four standard orientations (T, P, ,X, and L), seven values of R_{ij} (including infinity), and five values of r.[9] For each orientation (and fixed *Rij*) the

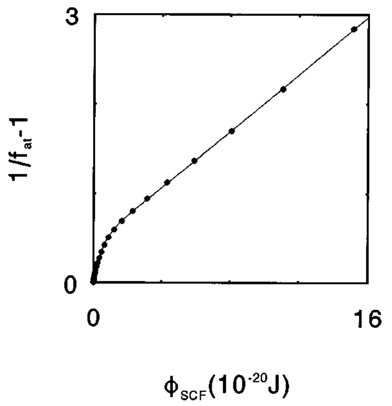

FIG. 2. The reciprocal attenuation function minus one versus the intermolecular SCF energy. The points correspond to equidistant R values; the line is Eq. (6).

data for infinity (two times the intramolecular energy, which is the same for all orientations) were subtracted from those at finite R_{ij} value. The results can be fitted with a cubic function of r and a standard deviation smaller than the numerical rounding error of ϕ_{SCF}. In Ref. 9 the r_i of the two molecules were not varied independently. Making use of Eq. (3) and setting $r = r_i = r_j$ gives the coefficients of the cubic fit. The r_e was derived from a third order expression of the values for infinity. Next, the coefficients of the cubic fit were spherically averaged with the method used by Ree and Bender.[9] From Eq. (3) it follows that the result for the linear coefficient gives twice the averaged F_{ij}, while the quadratic coefficient gives the sum of the averaged G_{ij} and C_{ij}. The cubic coefficient gives twice the quantity $(1/6H_{ij} + 1/2K_{ij})$. With the help of Eqs. (2) and (4) one can evaluate the SCF contribution to the Raman shift. This includes the RC contribution, which should not be present in the IR determination and will, therefore, give too large values for the IR frequency. The rounding error prevents the evaluation of a reliable fourth derivative of ϕ_{SCF}. The derivatives of f_{at} are achieved by assuming that Eq. (6) holds for all values of r_i.

Meyer[10] presented multipole coefficients for various values of r. With the help of these values and of the first six terms of Eq. (3), one can determine the first derivative F_{ij} and once again the *sum* of G_{ij} and C_{ij}. Fortunately, in this case the mixing coefficient (RC) for the C_k can be evaluated separately by deriving the following relation:

$$\frac{d^2 C_k}{dr_i dr_j} = Q_k \left(\frac{dC_k}{dr_i} \right)^2 C_k^{-1}, \tag{7}$$

where Q_k is only dependent on k. For that purpose we extended the work of Thiéry *et al.*[19] on C_6 to the C_8 and C_{10}. The C_k are functions of the polarizability (α) and the ionization energy *(I)*. From the relation between these two quantities[13,19] also a relation of C_k with its derivatives can be obtained by using the Slater-Kirkwood approximation,[13,19] which holds very good for H_2. The first r_i derivative of C_k from Meyer's data appeared to be consistent within about 1.5% with these relations. Our results are $Q_k = 10/9$, 17/18, and 26/25 for $k = 6$, 8, and 10 respectively. Note that for the dispersion it is possible to separate the RC contribution, but not to evaluate the third and fourth r_i derivative, needed for a possible contribution to the anharmonicity.

To calculate the frequencies we have first performed the summations of Eqs. (4b)–(4g) on an ideal hcp lattice. For the dispersive RC only the NN contributions were taken into account. The room temperature pressures, determined with the equation of state of Ref. 17, were between 5.5 and 200 GPa. The $J = 1$ vibron was considered and so $\omega_0 = 4155$ cm^{-1} was taken as the value of the isolated molecule.[11] The results have been plotted as lines in Fig. 1 along with the experimental Raman[8] and IR (Ref. 4) data.

The Raman calculation shows very good agreement with experiment. The turnover behavior is well described and is due to the fact that the dispersive contributions become dominant. The attenuation contribution to the dispersive effect is positive and in magnitude about 15%, which is a considerable amount. The IR results are somewhat too high, because they still contain the RC of the SCF, which turns out to be much smaller than the RC of the dispersion. Note that the calculated IR curve is also going through a maximum. Taking only the SCF contribution into account, the frequency increases with pressure and the shift with respect to ω_0 is 1900 cm^{-1} at 200 GPa. The anharmonicity hardly changes up to 30 GPa, whereas above this pressure it increases rapidly up to almost twice the value of the lowest pressure. We also have decreased the *c/a* ratio of the hcp lattice with 5%, which is about the expected deviation at 1.8 GPa.[20,24] It only gives a decrease of 3 cm^{-1} at the highest pressure.

The extrapolation of the Raman shift to zero pressure gives a value of 16 cm^{-1} below ω_0, which is 5 cm^{-1} lower than the experimental value.[21] This is possibly due to lack of data for the r_i derivatives of ϕ_{SCF} above $R_{ij} = 0.26$ nm. In the present work we divided the SCF values for F_{ij} by those of ϕ_{SCF} and fitted this ratio linearly to make the extrapolations for $R_{ij} > 0.26$ nm, needed to calculate the contributions of the next nearest neighbors and further. Inspection learns, that if we use an extrapolation such that agreement with experiment at $p = 0$ is achieved, perfect agreement will be obtained with the experimental Raman shift over the whole pressure range.

If it is assumed, that the r derivatives of the intermolecular energy for H_2 and D_2 are identical, one can calculate the Raman shift of D_2 by substituting twice the reduced mass of H_2 in Eq. (2). It turns out, that up to 80 GPa the Raman shift of D_2 (Ref. 8) is well described; above 80 GPa the deviation becomes larger than that of H_2, at the highest pressure being 30 cm^{-1} larger. A possible explanation is that above 80 GPa the r_i derivatives of D_2 are slightly different from that of H_2. Another possibility is that at the highest pressures the r_i derivatives are not fully correct,which has a different influence on H_2 than on D_2.

We note that the remarkably large increase of the frequencies of H_2, diluted in He or Ne,[3] can now easily be explained. The dispersion effect is roughly proportional to the dispersive energy itself, which decreases enormously in an environment of He and Ne, causing the upwards effect. This also explains why the influence of low pressure is negative in pure systems, while it is positive in diluted systems, and why N_2 diluted in He shows the same effect.[22]

[*] Deceased.

[1] H. K. Mao, P. M. Bell, and R. J. Hemley, Phys. Rev. Lett. **55**, 99 (1985).

[2] I. F. Silvera, S. J. Jeon, and H. E. Lorenzana, Phys. Rev. B **46**, 5791 (1992).

[3] P. Loubeyre, R. LeToullec, and J. P. Pinceaux, Phys. Rev. B **45**, 12 844 (1992).

[4] M. Hanfland, R. J. Hemley, H. K. Mao, and G. P. Williams, Phys. Rev. Lett. **69**, 1129 (1992).

[5] S. Chakravarty *et al.*, Phys. Rev. B **24**, 1624 (1981).

[6] R. J. Wijngaarden, A. Lagendijk, and I. F. Silvera, Phys. Rev. B **26**, 4957 (1982).

[7] S. Raynor, J. Chem. Phys. **87**, 2795 (1987).

[8] H. K. Mao and R. J. Hemley, Rev. Mod. Phys. **66**, 671 (1994).

[9] F. H. Ree and C. F. Bender, J. Chem. Phys. **71**, 5362 (1979).

[10] W. Meyer, Chem. Phys. **17**, 27 (1976).

[11] J. van Kranendonk, *Solid Hydrogen* (Plenum, New York, 1983).

[12] G. Herzberg, *Spectra of Diatomic Molecules* (van Nostrand, New York, 1950).

[13] J. O. Hirschfelder, C. E. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1964).

[14] H. Margenau and N. R. Kestner, *Theory of Intermolecular Forces* (Pergamon, Oxford, 1971).

[15] I. F. Silvera and V.V. Goldman, J. Chem. Phys. **69**, 4209 (1978).

[16] A. K. McMahan, H. Beck, and J. A. Krumhansl, Phys. Rev. A **9**, 1852 (1974).

[17] R. J. Hemley *et al.*, Phys. Rev. B **42**, 6458 (1990).

[18] T. S. Duffy, W. L. Vos, C. S. Zha, R. J. Hemley, and H. K. Mao, Science **263**, 1590 (1994).

[19] M. M. Thiéry and V. Chandrasekharan, J. Chem. Phys. **67**, 3659 (1977).

[20] H. K. Mao *et al.*, Science **239**, 1131 (1988).

[21] E. J. Allin and S. M. Till, Can. J. Phys. **57**, 442 (1979).

[22] M. I. M. Scheerboom and J. A. Schouten, Phys. Rev. E **51**, R2747 (1995).

[23] J. Belak, R. LeSar, and R. D. Etters, J. Chem. Phys. **92**, 5430 (1990).

[24] J. Hu, H. K. Mao, J. Shu, and R. J. Hemley, in *High-Pressure Science and Technology*, edited by S. C. Schmidt, J. W. Shaner, G. A. Samara, and M. Ross (AIP, New York, 1994), p. 441.