Polarization and Strong Infrared Activity in Compressed Solid Hydrogen

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Under a pressure of $\simeq 150$ GPa solid molecular hydrogen undergoes a phase transition accompanied by a dramatic rise in infrared absorption in the vibron frequency range. We use the Berry's phase approach to calculate the electric polarization in several candidate structures finding large, anisotropic dynamic charges and strongly IR-active vibron modes. The polarization is shown to be greatly affected by the overlap between molecules in the crystal, so that the commonly used Clausius-Mossotti description in terms of polarizable, nonoverlapping molecular charge densities is inadequate already at low pressures and even more so for the compressed solid. [S0031-9007(98)07623-6]

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The stretching mode of an isolated hydrogen molecule does not absorb infrared (IR) radiation, since the electric dipole moment vanishes by symmetry and remains zero upon stretching. In the solid the symmetry is lower, and for some structures first-order vibrational IR activity is allowed [1]. Indeed, some IR absorption occurs in the *broken-symmetry phase* (BSP or phase II) [2]. More surprising is the dramatic increase by around 2 orders of magnitude which occurs in the IR absorption when crossing the boundary between the BSP phase and phase III (H-A) at around 150 GPa [3–6].

A considerable effort has been made to try to explain this remarkable behavior. Hemley and co-workers [7] proposed that in phase III the increase in molecular overlap leads to the formation of charge-transfer states between neighboring molecules, which couple to vibrons. Baranowsky [8] invoked a strong ionization of the molecules. Mazin *et al.* [9] neglected the molecular overlap and treated the molecules as point objects polarized by the electric quadrupole (EQ) field of the other molecules (here referred to as EQ model) [10]. Edwards and Ashcroft [11] suggested that a dielectric instability associated with a charge-density wave causes an enhancement of the molecular dipole moments in phase III. Some theories [8] focus on purely static charge, others [7] focus on purely dynamic charge (i.e., displacement induced [12]), and the others [9,11] take the two contributions to be comparable. There is also no agreement on the relative importance of intramolecular [8,9,11] and intermolecular [7] charge transfer [6]. To settle these issues, a careful treatment of the bulk electric polarization, which is the central quantity at play in the physics of IR absorption, is needed.

For that purpose we have used the "modern theory of polarization" [13], which shows how to compute the polarization of a periodic insulating system as a Berry's phase derived from the electronic wave functions. The information about the polarization is therefore in the *phases* of the wave functions, not in the periodic density alone, whose dipole moment is in general ill-defined, depending on the choice of unit cell [14]. The density-based picture is valid only in the Clausius-Mossotti limit of localized, po-larizable units with nonoverlapping charge densities [15] and breaks down whenever significant charge delocalization prevents an unambiguous assignment of the electron density to particular atoms, molecules, or ions. Such overlap effects play an important role in the absorption of light by phonons in ionic systems [15], which typically have a much larger overlap than molecular crystals [12]. But at 150 GPa solid hydrogen has been compressed by almost a factor of 10 [16], hence the motivation for applying the modern theory of polarization to this problem.

Using the Berry's phase approach we have calculated the Born effective charge tensors Z^* [12,17]. In order to compare with experiments done on polycrystalline samples, we used the expression for the oscillator strength $f(j)$ of the contribution of a TO phonon mode j to the dielectric function averaged over all directions [17],

$$f(j) = \frac{4\pi}{\Omega\,\omega(j)^2}\left(\frac{1}{3}\sum_{\alpha=1}^{3}\xi_\alpha(j)^2\right),$$

where $\xi_\alpha(j) \equiv (1/\sqrt{m_p})\sum_k\sum_\beta Z^*_{\alpha\beta}(k)e_\beta(k;j)$, k indexes the atoms in the unit cell of volume Ω, $e_\beta(k;j)$ are the normalized eigenvectors associated with the mode, $\omega(j)$ is its angular frequency, and m_p is the proton mass.

The crystal structures of the high-pressure phases have not yet been determined experimentally [5,16]. For clarity we have investigated two of the simplest candidate structures for the compressed solid which have IR-active vibron modes [4] and are also energetically favorable [18,19]. The parameters a (lattice constant), c/a, bond length, and θ of $Cmc2_1$ and $C2/m$ (see Fig. 1) were optimized by minimizing the enthalpy at fixed pressure using a variable cell shape method [20], and they are collected in Table I for several densities [21]. In some cases the centers of the molecules in the two sublattices were allowed to move away from the hcp sites by symmetrical amounts in the yz plane, which does not lower the symmetry while allowing for the manifestation of the instability reported in Ref. [11]. The calculations were done in the local density approximation (LDA) to the density functional theory, with clamped nuclei [22].
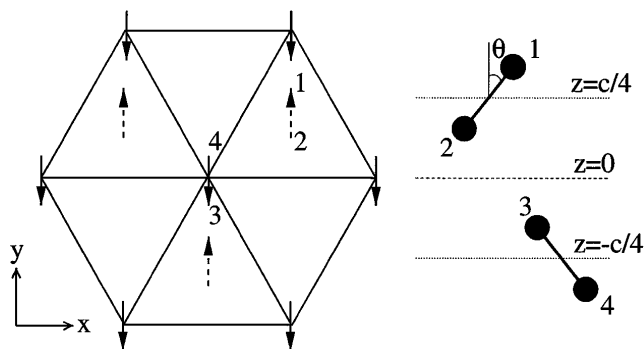
FIG. 1. The $Cmc2_1$ structure viewed along the c axis (left) and in the yz plane (right). The centers of the molecules lie on hcp sites, and the molecules in the two sublattices are tilted away from the c axis by opposite angles θ and $-\theta$. The $C2/m$ structure is identical except that the two molecules are tilted in the same direction by an angle θ.

The existence of a center of inversion between the two molecules in the unit cell of $C2/m$ leads to the relation $Z^*(1) = -Z^*(2) = -Z^*(3) = Z^*(4)$. At 115 GPa we obtained, for atom 2 before (after) the off-site relaxation for the components which do not vanish by symmetry: $Z^*_{xx} = 0.005(0.05)$, $Z^*_{yy} = 0.53(0.96)$, $Z^*_{zz} = 0.07(0.16)$, $Z^*_{yz} = 0.18(0.28)$, and $Z^*_{zy} = 0.08(0.15)$. The pronounced anisotropy of Z^* implies large dynamic charges, since displacements of rigid ions (static charges) give rise to isotropic diagonal Z^* tensors [12]. The smallness of Z^*_{xx} relative to the components in the yz submatrix suggests that most of the charge transfer occurs in the planes of the molecules, since a displacement δx of an atom in the x direction changes the distances to other atoms in that plane to second order only. This analysis establishes that intramolecular and/or in-plane intermolecular charge transfer are the dominant effects, but it does not distinguish between the two. The small off-site relaxation has a large effect on Z^*, revealing a strongly nonlinear dependence of the polarization on the positions of the molecules.

Such large effective charges give rise to very strong IR absorption by the vibron mode in which the two molecules in the primitive cell vibrate out of phase (the in-phase mode is Raman active but IR inactive in this structure [4]). Before the relaxation, the oscillator strength at 115 GPa is about 13 times larger than the experimentally measured value in phase III at 167 GPa, and it increases by a factor of 3.5 upon relaxation (see Table I). Because of closure of the LDA band gap, this structure was not studied at significantly higher pressures.

The symmetry of the $Cmc2_1$ structure dictates the following form for the effective charge tensors:

$$Z^*(1) = \begin{pmatrix} -a & 0 & 0 \\ 0 & -b & c' \\ 0 & d' & -e \end{pmatrix}, \quad Z^*(2) = \begin{pmatrix} a & 0 & 0 \\ 0 & b & c \\ 0 & d & e \end{pmatrix},$$

$$Z^*(3) = \begin{pmatrix} -a & 0 & 0 \\ 0 & -b & -c' \\ 0 & -d' & -e \end{pmatrix},$$

$$Z^*(4) = \begin{pmatrix} a & 0 & 0 \\ 0 & b & -c \\ 0 & -d & e \end{pmatrix}.$$

The calculated values for several densities are shown in Table II. The anisotropy is again very large, but the overall values are somewhat smaller than for $C2/m$. Both vibrons are IR active in this structure [4]: the out-of-phase vibron has a large oscillator strength (see f_o in Table I) in reasonable agreement with the measured values in phase III, whereas the in-phase vibron (f_i in Table I) is about an order of magnitude weaker. In contrast to experiment [4], the calculated f_i would be large enough to be detected. The intensity of the absorption grows rapidly with pressure, in agreement with the behavior in phase III [4,6,7]. The effect of off-site relaxation of the molecules is again significant, with the oscillator strengths of the vibrons increasing 18-fold for the in-phase mode (polarized along the c axis) and 4-fold for the out-of-phase mode (polarized along y in Fig. 1) at 115 GPa.

In this structure there is a net spontaneous polarization $\mathbf{P}_0$ along the c axis. Similarly to the in-phase vibron, there is a large increase in $\mathbf{P}_0$ due to the small off-site

TABLE I. Optimized parameters (except for $r_s = 2.0$) and in-phase (f_i) and out-of-phase (f_o) vibron oscillator strengths for several pressures. Pressures in GPa are obtained using the equation of state of Ref. [16], angles are in degrees, and the other quantities are in atomic units (a.u.). The experimental results for phase III are from Ref. [6].

Structure	P	r_s	c/a	r_{bond}	θ	f_i	f_o
$C2/m$	115	1.52	1.588	1.456	69.5	0	0.169
$C2/m$ [a]	115	1.52	1.583	1.460	70.6	0	0.589
$Cmc2_1$	13	2.0	1.576	1.445	54.0	10^{-6}	9×10^{-6}
$Cmc2_1$	115	1.52	1.576	1.445	54.0	0.0008	0.011
$Cmc2_1$ [a]	115	1.52	1.574	1.451	56.6	0.014	0.049
$Cmc2_1$	152	1.47	1.571	1.443	55.2	0.0026	0.026
$Cmc2_1$	167	1.45	1.570	1.443	55.6	0.004	0.034
$Cmc2_1$	180	1.43	1.569	1.443	55.9	0.0059	0.044
Phase III	167					≈ 0	0.0134

[a]Centers of the molecules are off site (see text). The off-site displacement in a.u. of the upper molecule in Fig. 1 is $\delta y = -0.1$, $\delta z = -0.01$ ($C2/m$), and $\delta y = -0.07$ ($Cmc2_1$).

TABLE II. Effective charges in atomic units for the optimized (except for $r_s = 2.0$) $Cmc2_1$ at several densities.

r_s	a	b	c	d	e	c'	d'
2.0	0.018	0.0033	0.042	0.040	−0.0005	0.028	0.044
1.52	0.022	0.144	0.208	0.271	0.0088	0.069	0.193
1.52[a]	0.050	0.298	0.243	0.348	0.087	−0.014	0.091
1.47	0.020	0.204	0.260	0.347	0.015	0.069	0.216
1.45	0.018	0.229	0.283	0.380	0.017	0.068	0.223
1.43	0.017	0.254	0.307	0.413	0.020	0.065	0.228

[a]Centers of the molecules are off site (see text).

relaxation, at 115 GPa from -1.43×10^{-4} **z** to -1.30×10^{-3} **z** in atomic units. This can be qualitatively understood using the EQ model: when the molecules are on hcp sites the EQ field at the sites points along the y direction, so that $\mathbf{P}_0$ (in-phase IR activity) is due solely to the anisotropy of the molecular polarizability (derivatives of the EQ moment and polarizability). However, if the molecules are off-site there is a component of the EQ field along the c axis at the molecular centers, which is expected to lead to a larger increase in $\mathbf{P}_0$ and in-phase IR activity than in out-of-phase IR activity.

More insight into the physics of polarization can be obtained by looking at the electron density. In Fig. 2a we show the density along the axis of a molecule for several pressures. The asymmetry induced by the crystal field can be seen most clearly in Fig. 2b. If the molecules can be considered to be separate polarizable objects, as in the Clausius-Mossotti model, then the asymmetry of the three-dimensional molecular density will determine the polarization. For example, in the EQ model [9,10] the intramolecular part of the asymmetry $a(\xi)$ scales as $1/r_s^4$ (assuming that the molecular EQ moment and polarizability do not change much with pressure [23]). Indeed, this is the case at low and moderate pressures ($r_s \gtrsim 2.0$), as can be seen in Fig. 2b from the agreement in the intramolecu-
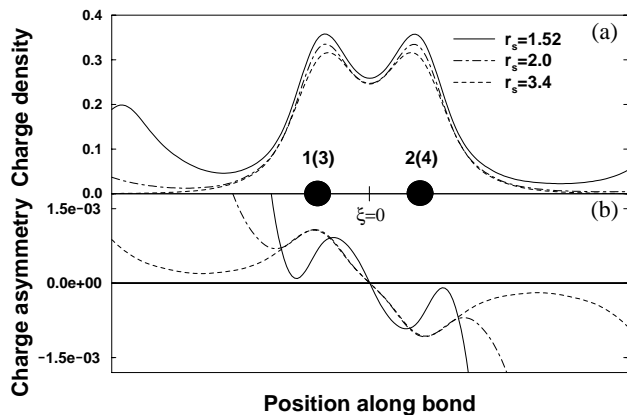

FIG. 2. (a) Electron density $n(\mathbf{r})$ in a.u. for the hcp-centered $Cmc2_1$ along a line joining atoms 1(3) and 2(4) of Fig. 1. (b) Asymmetry along that line, defined as $a(\xi) = [n(\xi) - n(-\xi)]/2n_0$, where n_0 is the maximum electronic density in the hydrogen atom [11]. For $r_s = 3.4$, $a(\xi)$ was multiplied by $(3.4/2.0)^4$ for comparison with $r_s = 2.0$.
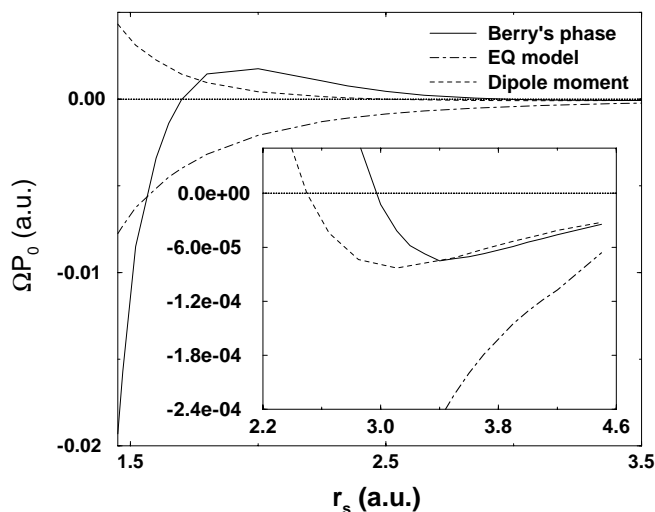
lar region between the curve for $r_s = 2.0$ and the scaled curve for $r_s = 3.4$. However, the scaling clearly does not hold up to the megabar range, since the intramolecular $a(\xi)$ would have to be around 3 times larger for $r_s = 1.52$ than for $r_s = 2.0$, whereas it is found to be slightly smaller and decreasing with pressure in that range. Therefore in the megabar range the EQ fields alone do not account for the local field acting on the molecules, contrary to the model used in Ref. [9].

In Ref. [11] the intramolecular $a(\xi)$ was interpreted as an estimate of the dipole moment of the molecule in the solid. For molecules centered on hcp sites, the asymmetry was found to be small and, assuming that the effective charges scale with the static moment, the vibron oscillator strengths were predicted to be too small compared to experiment [11]. Instead, we have found for the same structures oscillator strengths even larger than experiment (see Table I). Furthermore, the intramolecular $a(\xi)$ is comparable for $r_s = 1.52$ and $r_s = 2.0$ (see Fig. 2b), and yet the oscillator strengths of the vibrons are ~1000 times larger for $r_s = 1.52$. Factors that may explain these large discrepancies are the following: (i) $a(\xi)$ does not represent the full three-dimensional asymmetry; (ii) effects of dynamic charge transfer are not included in $a(\xi)$; and (iii) molecular overlaps, even if small, may be important, as can be seen in Fig. 2, where it is clear that for the higher densities $a(\xi)$ is large in the intermolecular region, where the density is small. This is related to the fact that the outer regions of the molecules are most easily polarizable [24].

At low enough densities the Claussius-Mossotti model must be correct; however, to our knowledge there has never been a thorough investigation of *how low the density must be for this limit to apply*. This is now possible using the modern theory of polarization [13]. Here we present results for the $Cmc2_1$ structure as a function of density. (We emphasize that this is not meant to represent real hydrogen at low pressure, where the molecules are not oriented but instead behave as quantum rotors [25,26], but is sufficient to establish the desired points regarding the sensitivity of the polarization to the molecular overlap.) In Fig. 3 we plot the spontaneous polarization per unit cell as a function of r_s, together with the value given by the EQ model and the dipole moment for a particular choice of cell [27]. According to the interpretation of $a(\xi)$ given in Ref. [11], atoms 1 and 3 in Fig. 1 seem to have an excess

FIG. 3. Spontaneous polarization per unit cell as a function of r_s for the hcp-centered $Cmc2_1$. The structural parameters are the optimized parameters for $r_s = 1.52$ (see Table I). The Berry's phase result is compared with the value given by the EQ model, using the quadrupole moment and polarizability of the H_2 molecule quoted in Ref. [26], and with the "dipole moment" of the charge density in a unit cell [27]. The inset shows the polarization at large r_s on an expanded scale.

of electron charge. In a Clausius-Mossotti framework this would lead to a net polarization along minus z, and that is indeed the result of the EQ model (and also of the dipole moment for $r_s > 2.5$), but between $r_s \simeq 1.7$ ($\simeq 50$ GPa) and $r_s \simeq 3.0$ (around atmospheric pressure) the Berry's phase polarization has the *opposite* sign. Most surprising is the fact that the corrections to the models are so large even at low pressures (large r_s). The fact that the three quantities in Fig. 3 start to converge to each other only for $r_s \gtrsim 3.0$ suggests that the Clausius-Mossotti limit is reached only at very low, or even *negative* pressures.

In summary, we have presented the first *ab initio* calculations of the intensity of IR absorption in solid hydrogen, showing that intense vibron IR activity is found in some structures due to large dynamic charges. The strong dependence of the effective charges on the symmetry and structural parameters offers a plausible explanation for the observed difference in IR absorption in the different phases. The physics of polarization of solid hydrogen appears to be more subtle and less amenable to simple models than was previously assumed. This seems to be caused by the very delocalized nature of the induced dipoles, which extend out to the tails of the molecular charge density [24]. This renders the bulk polarization very sensitive to even small overlaps between the molecules and becomes increasingly more important at higher pressures. These findings may be relevant for other molecular solids, since the Clausius-Mossotti picture is usually assumed in the treatment of IR absorption in such systems [28].

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