

Vibron effective charges in dense hydrogen

R. J. HEMLEY, I. I. MAZIN(*), A. F. GONCHAROV and HO-KWANG MAO

Geophysical Laboratory and Center for High-Pressure Research

Carnegie Institution of Washington - 5251 Broad Branch Rd. N.W., Washington, DC 20005-1305 USA

(received 22 February 1996; accepted in final form 22 January 1997)

PACS. 64.70Kb – Solid-solid transitions.

PACS. 62.50+p – High-pressure and shock-wave effects in solids and liquids.

PACS. 78.30–j – Infrared and Raman spectra.

Abstract. – We report quantitative intensity measurements of the infrared vibron in the high-pressure molecular phase of solid hydrogen above 150 GPa. The results are analyzed in terms of effective static and dynamic charge. The effective charge reaches $0.04e$ at 230 GPa, which rules out full ionization of the hydrogen molecules to these pressures. The results are consistent with charge transfer associated with orientational ordering in this phase.

Recent high-pressure experiments have generated a wealth of new information on the behavior of hydrogen at very high densities, and one of the most remarkable observations is the large enhancement of the infrared vibron (intramolecular stretching mode) at 150 GPa [1]. This result, now established for H_2 [2], D_2 [3], [4] and HD [3] in the high-pressure molecular phase (phase III), has attracted considerable attention theoretically but has not yet been explained quantitatively [5]-[14]. The role of formal changes in symmetry [4], [5], orientational and structural transformations [1], [3], [4], [6]-[9], intermolecular charge transfer [6], [9]-[11], intramolecular ionization [12], [13], and the development of a charge density wave [14] have been discussed in regard to the intensity increase. Among the more novel proposals are mechanisms that associate the intensity enhancement with radical charge transfer processes and the formation of an ionic state in phase III [12] (see also ref. [15]). Whether or not such electronic symmetry breaking exists is crucial for understanding the pressure-induced changes in hydrogen: it has been proposed that such states form between the lower-pressure insulating and higher-pressure metallic phases, and in general delay the onset of metallization [12], [14], [16]. We report measurements of the infrared vibron together with an analysis of the intensity to test models of phase III of hydrogen. Using newly available information on the dielectric properties of the material, we have determined the pressure dependence of the magnitude of vibron effective charge. The results are consistent with charge transfer associated with orientational ordering of the molecules in phase III.

(*) Present Address: Naval Research Laboratory, Code 6690, Washington, DC 20375-5320 USA.

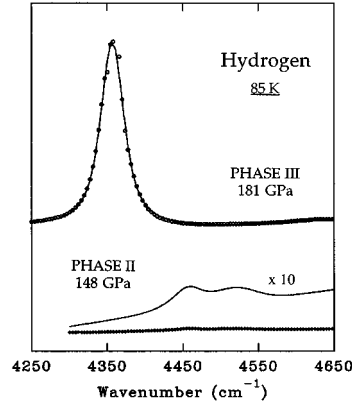


Fig. 1. – Representative infrared vibron spectra in phases II and III of hydrogen at 85 K.

Infrared spectra of hydrogen vibron at megabar pressures (phases II and III) are shown in fig. 1. Although the activity of the infrared vibron is high in phase III [2], [6], the scale of the absorption is not readily clear. In order to quantify this effect, one can introduce an effective charge q_i^* such that the integrated infrared absorption is proportional to $(q_i^*)^2$. The so-called Szigetti effective charge associated with a vibrational mode i is defined as [17]

$$q_i^* = \frac{\nu_i}{e} \sqrt{\pi M_i f_i / N} \frac{3}{\epsilon(\infty) + 2}, \quad (1)$$

where e is the electron charge, M_i is the reduced mass of the vibrational mode, f_i and ν_i are the oscillator strength and frequency of the mode, $\epsilon(\infty)$ is the pressure-dependent high-frequency dielectric parameter, and N is the number density of oscillators. The last factor takes into account the local field (Lorentz-Lorenz) correction, which is needed for comparison with effective charges obtained from microscopic calculations. This factor is strictly valid for an isotropic (cubic) material but differs from the hcp value by only a few percent, and this difference is reduced after averaging over all polarizations. The structures considered here are either hcp (phase I) or structures derived from hcp (phases II and III).

The dielectric function of hydrogen (i.e. refractive index n_H) at very high pressure has been uncertain because of the lack of direct measurements (*e.g.*, ref. [18]). In fact, the dispersion of n_H ($dn_H/d\omega$) has been better determined than the index itself. This problem has been solved by directly measuring both the absorption and reflectivity in the vicinity of the vibron, a measurement which shows that n_H is greater than the refractive index of diamond n_d [19]. Such measurements also provide the optical density and thickness of the sample. We determined f_i for the vibrons i for all phases (I, II and III) by fitting the dielectric function with a Lorentzian function,

$$\epsilon(\omega) = \epsilon(\infty) + f_i \omega_i^2 / (\omega_i^2 - \omega^2 - i\gamma\omega), \quad (2)$$

where ω_i and γ_i are the position and bandwidth of the peak. We find, for example, $q^* = 0.032e$ for the vibron in phase III at 167 GPa and 85 K. In contrast, at the same temperature $q^* = 0.004e$ for the sharp vibron in phase II (at 140 GPa) and $q^* = 0.005e$ for the broad vibron in phase I (at 110 GPa). The latter feature is disorder-induced and strongly temperature

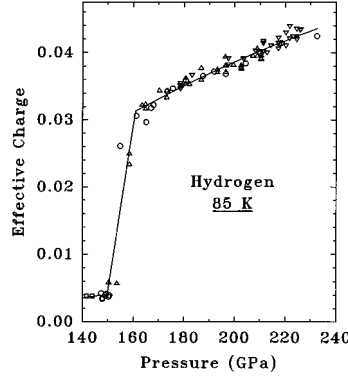


Fig. 2. – Pressure dependence of the effective charge in phases II and III. The circles and squares are from ref. [2], [6]. The triangles are from two separate runs of the present study. The line connecting data between the two phases is a guide to the eye. Points in this intermediate region correspond to mixed-phase samples (incomplete transformation) and were therefore not used in the fit.

and pressure dependent [1], [2], [20], [21]; it is essentially the same as the higher-frequency disorder-induced band observed in phase II (see fig. 1). The pressure dependences of the effective charge associated with the allowed vibrons in phases II and III are shown in fig. 2. We include new measurements with thinner samples to determine accurately the magnitude of the absorption in the high-pressure phase above 200 GPa. The effective charge increases linearly with pressure in phase II, with $dq^*/dP = 5.2 (\pm 0.4) \times 10^{-5} e/\text{GPa}$; for phase III $dq^*/dP = 2.07 (\pm 0.07) \times 10^{-4} e/\text{GPa}$ at the transition and a weak curvature in the pressure dependence of q^* is observed at higher pressures.

We find $q^* = 0.043e$ at 230 GPa, the highest pressure of the measurements [22].

These results can be used to evaluate the hypothesis that hydrogen transforms to an ionic state in phase III (*i.e.* consisting of H^+H^- H^+H^- species). Note that the effective charge defined by eq. (1) includes both the static charge transfer between hydrogen atoms in a molecule (“static charge”) and the dependence of the charge transfer on the molecular bond length (“dynamic charge”). Formally, D , the change of the dipole moment of a hydrogen molecule in the crystal is proportional to the change u of the bond length d ,

$$D(u) = q(d)u + [\partial q(d)/\partial d]ud = (q + q_d)u = q^*u, \quad (3)$$

where $q(d)$ and $q_d = d[\partial q(d)/\partial d]$ are the static and dynamic charges, respectively. The experimentally accessible quantity is their sum, the effective charge $q + q_d$, which in phase III is far greater than that in phases I and II, but still significantly less than the static charge of fully ionized hydrogen molecules in a crystal structure with a symmetry-allowed IR transition (*i.e.* $q^* \approx 1$). We conclude that the measured effective charge suggests that the maximum static charge transfer is of order 4% of an electron charge [23]. Further, it might be tempting to connect vibron softening at the transition with the change in electrostatic energy associated with charge transfer to an ionic state. For example, for an unpolarized molecule with total energy $W(d) = m(2\pi\nu)^2(d - d_0)^2$, the charge transfer q associated with a hypothetical ionic state would add $\Delta W(d) \sim -q^2/d$ and $\partial^2 W/\partial d^2 \approx 2m(2\pi\nu)^2 - 2q^2/d^3$. The observed frequency discontinuity $\Delta\nu$ of $\sim 100 \text{ cm}^{-1}$ would then correspond to $q \approx 0.4e$, which is an order of magnitude larger than the experimental number of $0.04e$.

This analysis shows that the transition to phase III is not associated with a large charge transfer in a formally ionic state but instead must reflect other changes in the material.

Experimental data indicate that the softening and effective charge are related linearly, an effect that can be easily explained if both quantities are linear in an order parameter; in particular, this is supported by measurements of the temperature dependence of the IR intensity and frequency shift [21]. Recent measurements demonstrate that phase III is transparent down to 0.15 eV (to at least 200 GPa) [19], with no sign of the theoretically predicted band-overlap metallization (see also ref. [24]). The present results point to the importance of orientational ordering (*e.g.*, ref. [21], [25]-[29]) rather than ionization in stabilizing the insulating molecular phase at these pressures.

We showed previously that charge transfer can occur between two molecules as a result of an antiphase molecular vibration (intermolecular charge transfer) [6], [10]. In principle, both intermolecular and intramolecular charge transfer can create a macroscopic polarization, but the restrictions of crystal symmetry for intermolecular charge transfer to be active in infrared absorption appear to be more severe. The crystal structure of phase III is not known. Applying the methods developed in ref. [5], [30], we consider structures in which the molecular centers form the same lattice but differ by the manner in which the molecules are oriented. Previously discussed hcp-based structures $P6_3/mmc$ (“hcp-c”), $Pca2_1$ or $P2_1/c$ are examples (*e.g.*, ref. [1], [4], [5], [26]-[28]). The electrostatic field and macroscopic polarization induced by intermolecular charge transfer does not depend on molecular orientation and vanishes in these structures. The effect of intramolecular charge transfer, however, is different and is orientation dependent. Another interesting example is the hypothetical $P6_3/m$ structure, the hexagonal analog of cubic $Pa3$. Although this structure has two crystallographically inequivalent molecules, it does not allow for the intermolecular charge transfer activity as well. Intermolecular charge transfer thus requires more complex structures, such as that suggested in ref. [9]. On the other hand, for intramolecular charge transfer (*i.e.* polarization of individual molecules), the condition is rather general: the two atoms in a molecule should be crystallographically inequivalent. Indeed, calculation of the vibron intensity for a lattice of ordered quadrupoles assuming the $Pca2_1$ structure (which allows for molecular polarization) gives an estimate for the total effective charge in the range of the measurements ($q^* = 0.06e$) [21].

To summarize, we have shown that the strong vibron infrared activity in phase III is not due to full intramolecular ionization (which does not occur in the currently investigated pressure range) and this rules out proposed fully ionic states for dense hydrogen up to 230 GPa. Intramolecular charge transfer associated with symmetry breaking of the molecules can give rise to the observed infrared response; that is with the condition that the two atoms in a molecule are crystallographically inequivalent. In complex structures both intermolecular and intramolecular effects may be allowed, and the relative roles of these two processes in dense hydrogen remain to be determined. Charge transfer processes and associated orientational ordering may delay the onset of band overlap.

We thank M. HANFLAND, V. V. STRUZHIN, M. LI, and J. F. SHU for assistance and many useful discussions. This work was supported by the NSF and NASA.

REFERENCES

- [1] MAO H. K. and HEMLEY R. J., *Rev. Mod. Phys.*, **66** (1994) 671.
- [2] HANFLAND M., HEMLEY R. J. and MAO H. K., *Phys. Rev. Lett.*, **70** (1993) 3760.
- [3] HEMLEY R. J. and MAO H. K., in *Elementary Processes in Dense Plasmas*, edited by S. ICHIMARU and S. OGATA (Addison-Welsey, Reading, Mass.) 1995, p. 269.
- [4] CUI L., CHEN N. H. and SILVERA I. F., *Phys. Rev. B*, **51** (1995) 14987.
- [5] ZALLEN R., MARTIN R. M. and NATOLI V., *Phys. Rev. B*, **49** (1994) 7032.
- [6] HEMLEY R. J., SOOS Z. G., HANFLAND M. and MAO H. K., *Nature*, **369** (1994) 384.
- [7] SURH M. P., *Bull. Am. Phys. Soc.*, **39** (1994) 335.
- [8] EDWARDS B. and ASHCROFT N. W., *Bull. Am. Phys. Soc.*, **39** (1994) 336; EDWARDS B., ASHCROFT N. W. and LENOSKY T., *Europhys. Lett.*, **34** (1995) 519; EDWARDS B. and ASHCROFT N. W., private communication.
- [9] TSE J. and KLUG D. D., *Nature*, **378** (1995) 595.
- [10] SOOS Z. G., EGGERT J. H., HEMLEY R. J., HANFLAND M. and MAO H. K., *Chem. Phys.*, **200** (1995) 23.
- [11] SOOS Z. G. and MUKHOPADHYAY D., *Chem. Phys. Lett.*, **245** (1995) 194.
- [12] BARANOWSKI B., *Polish J. Chem.*, **69** (1995) 981.
- [13] ASHCROFT N. W., in *Elementary Processes in Dense Plasmas*, edited by S. ICHIMARU and S. OGATA (Addison-Welsey, Reading, Mass.) 1995, p. 251.
- [14] ASHCROFT N. W., *Physics World*, **8** (1995) 43.
- [15] BARANOWSKI B., *Polish J. Chem.*, **66** (1992) 1637.
- [16] SIRINGO F., PUCCI R. and ANGILELLA G. G. N., private communication.
- [17] SZIGETTI B., *Proc. R. Soc. London, Ser. A*, **204** (1950) 51.
- [18] HANFLAND M., HEMLEY R. J. and MAO H. K., *Phys. Rev. B*, **43** (1991) 8767.
- [19] HEMLEY R. J., MAO H. K., GONCHAROV A. F., HANFLAND M. and STRUZHNIKIN V. V., *Phys. Rev. Lett.*, **76** (1996) 1667.
- [20] HANFLAND M., HEMLEY R. J., MAO H. K. and WILLIAMS G. P., *Phys. Rev. Lett.*, **69** (1992) 1129.
- [21] MAZIN I. I., HEMLEY R. J., GONCHAROV A. F., HANFLAND M. and MAO H. K., to be published in *Phys. Rev. Lett.*
- [22] This is based on a linear extrapolation of the phase-III vibron frequency with pressure. The vibron frequency has been calibrated against ruby R_1 fluorescence to 180 GPa (ref. [2]) and can be fit linearly with pressure over the measured range.
- [23] This is true unless q and q_d have opposite signs and there is an accidental cancellation in the effective charge.
- [24] CHEN N., STERER E. and SILVERA I. F., *Phys. Rev. Lett.*, **76** (1996) 1663.
- [25] ASHCROFT N. W., *Molecular Systems under Pressure*, edited by R. PUCCI and G. PICCITO (Elsevier, New York, N.Y.) 1991, p. 201.
- [26] KAXIRAS E., BROUGHTON J. and HEMLEY R. J., *Phys. Rev. Lett.*, **67** (1991) 1138.
- [27] KAXIRAS E. and BROUGHTON J., *Europhys. Lett.*, **17** (1992) 151.
- [28] MAZIN I. I. and COHEN R. E., *Phys. Rev. B*, **52** (1995) R8597.
- [29] GONCHAROV A. F., MAZIN I. I., EGGERT J. H., HEMLEY R. J. and MAO H. K., *Phys. Rev. Lett.*, **75** (1995) 2514.
- [30] ZALLEN R. M., *Phys. Rev.*, **173** (1968) 824.