Infrared activity of vibrational modes in compressed molecular hydrogen: a first-principles study using the geometric phase approach

Infrared activity of vibrational modes in compressed molecular hydrogen: a first-principles study using the geometric phase approach

Kazutaka Nagao and Hitose Nagara

Division of Material Physics, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan

Abstract. The infrared (IR) activities of vibrational modes in molecular solid hydrogen at megabar pressures have been studied by performing a first-principles calculation of the polarizations using the geometric phase approach. We have studied the $Cmc2_1$ and the $Pca2_1$ structures as candidate structures for phase III (H–A or D–A). In the $Cmc2_1$ case, the high-frequency vibron gives higher IR intensity than the low-frequency vibron, which agrees with the experimental results although the effective charge of the high-frequency vibron is much larger than the experimental value. In the $Pca2_1$ case, the high-frequency vibrons give lower IR intensities than the low-frequency vibron, which contradicts the experimental findings. Also, in the $Pca2_1$ case, two IR phonons are possible although one IR phonon is observed in phase III.

Highly compressed solid hydrogen has been explored mainly by means of spectroscopic techniques, Raman scattering and infrared (IR) absorption, up to about 220 GPa [1, 2]. Although the structures for phase II (BSP) and phase III (H–A or D–A) are still vague, the phase boundaries have become clear from observations of discontinuities of vibron frequencies. There have also been observed some fascinating behaviours of Raman- and IR-active vibrational modes, especially around 150 GPa, the II–III phase boundary. One of the most interesting phenomena is the abrupt increase of the absorption of an IR-active vibron at 150 GPa [1, 3], though its origin is still controversial [4–6]. Another is a mid-lying IR-active phonon in the frequency region from 1600 cm^{-1} to 1700 cm^{-1} in phase III, which cannot be observed in phase II [3]. These phenomena can be helpful in screening out the candidate structures.

Cui *et al* studied the number of group theoretically allowed IR- and Raman-active vibrational modes [2]. The group theoretical analysis, however, tells us only whether IR or Raman activity of the mode is a possibility. If a vibrational mode is really IR active, the mode must be accompanied by polarization; in other words, the mode must have an effective charge of sufficient size. In this paper, we study the IR activities of the vibrational modes for some candidate structures by performing first-principles calculations of the polarization and the effective charge. For the candidate structures, we investigate the intensities of some normal modes which are determined in the harmonic approximation, and also compare our vibron effective charges with that obtained from experiment [4]. The structure of phase III is briefly discussed.

11581

Unlike in a finite system, in a system composed of delocalized electrons with a periodic boundary, the calculation of the polarization encounters some difficulties. Thus we make use of the geometric phase (Berry phase) approach [6–8]. If the system has a band gap, the method enables us to calculate the polarization generated by the ionic displacement by the use of the electronic wave function. For the structures in which the ions are displaced according to the motions of IR-active modes, we perform the band calculation using a plane-wave basis. We use the generalized gradient approximation (GGA) to the exchange–correlation energy of the electrons, which keeps band gaps open at higher pressures than the local density approximation (LDA) for molecular hydrogen.

As candidate structures, we choose the $Cmc2_1$ and the $Pca2_1$ structures, in which molecular centres form the hcp lattice and the molecular axes are canted from the c-axis of the hcp lattice. We pick out these structures because the group theoretical analysis tells us that these structures have IR and Raman vibrons and IR phonons, which are experimentally observed in phase III [3]. Also the recent first-principles studies have shown that the behaviours of the frequencies of vibrons and IR phonons in the $Cmc2_1$ and the $Pca2_1$ structures are in good agreement with those observed in experiments at around 150 GPa [9, 10]. In our calculation, the bond length in each structure is optimized: in the $Cmc2_1$ structure, the orientation of the molecules is optimized, and in the $Pca2_1$ structure, the polar and azimuthal angles are set at $\{\theta, \phi\} = \{55.0°, 43.5°\}$.

The effective charge $q_{\alpha,j}$ is a kind of measure of the IR activity of the mode. Here we define $q_{\alpha,j}$ as

$$P_\alpha = \sum_j q_{\alpha,j} u_j$$

where P_α is the α-component of the polarization per molecule and u_j denotes the normal coordinate of the jth mode. For the vibrons and the mid-lying phonons, the motions are practically pure stretching and pure translation of molecules, respectively [10]. Thus we take, as u_j, the change of the bond length in the molecule for the vibronic motion, or the displacement of the molecular centre for the phonon motion. The absorption coefficient is defined by $a(\omega) = -l^{-1} \ln(I/I_0)$, where I_0 and I are the intensities of the incident and transmitted light, respectively, and l is the sample thickness. The absorption coefficient is proportional to

$$J_j = \frac{m_p}{\mu} \left(\left[\sum_\alpha q_{\alpha,j}^2 \right] \middle/ e^2 \right) n_m a_0^3$$

where m_p is the proton mass, μ the reduced mass ($m_p/2$ for the vibron and $2m_p$ for the phonon), e the proton charge, n_m the number density of the molecules and a_0 the Bohr radius.

Figure 1 shows the quantities J_j for some modes in the $Cmc2_1$ and the $Pca2_1$ structures. Let us first assume that $Cmc2_1$ is the structure of phase III. Then the B_2 vibron and the B_2 phonon should be assigned as the IR vibron and the IR phonon experimentally observed in phase III, respectively, because the calculated intensities of those modes are relatively high. In the B_2 vibron mode, the two molecules in the unit cell stretch and shrink out of the phase and the calculated frequency of the out-of-phase vibron is higher than that of the in-phase vibron [9, 10]. In the experiments, the higher-frequency vibron is the IR vibron, which agrees with our assignment of the B_2 vibron. Thus, $Cmc2_1$ as the structure of phase III does not contradict the experimental results. Next, if we assume that $Pca2_1$ is the structure of phase III, the A_1 vibron and the B_1 phonon should be assigned as the IR vibron and the IR phonon, respectively, because those modes are the vibron and the phonon with the
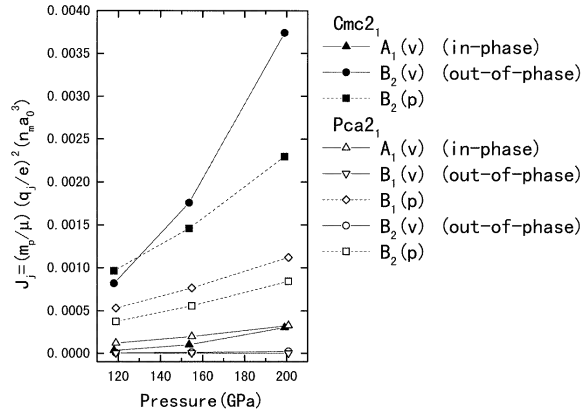
Figure 1. The pressure dependences of the absorption coefficients in the $Cmc2_1$ and the $Pca2_1$ structures. The quantity defined by $J_j = (m_p/\mu)(q_j/e)^2(n_m a_0^3)$ is proportional to the absorption coefficient. Here q_j is defined by $(\sum_\alpha q_{\alpha,j}^2)^{1/2}$. A_1, B_1 and B_2 denote the irreducible representations of the modes. (v) and (p) denote the vibron and phonon modes, respectively.

highest intensities in the $Pca2_1$ structure. However, the A_1 vibron is the in-phase vibron, which has lower frequency than the out-of-phase vibrons (B_1 and B_2 vibrons). Furthermore, two IR phonons (B_1 and B_2 phonons) should be observable because the intensity of the B_2 phonon is comparable with that of the B_1 phonon. Thus, the assumption that $Pca2_1$ is the structure of phase III gives rise to inconsistency with the experimental results.
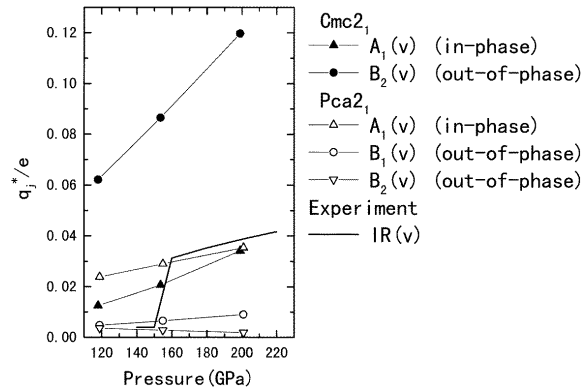
Figure 2. The pressure dependences of the vibron effective charges in the $Cmc2_1$ and the $Pca2_1$ structures. Here q_j^* is defined by $(\sum_\alpha q_{\alpha,j}^2)^{1/2}/\sqrt{3}$, where the effective charge is divided by the factor $\sqrt{3}$ in order to average over the orientation of the crystals for the purposes of comparison with the experimental value. A_1, B_1 and B_2 denote the irreducible representations of the modes. (v) denotes the vibron mode. The experimental data are taken from reference [4].

In order to compare the vibron effective charge estimated from the experiment [4] directly with our result, we pick out the vibron modes and show the vibron effective charges in figure 2. In the $Cmc2_1$ structure, the B_2 vibron, which we have assigned above as the IR vibron, has a magnitude of effective charge considerably larger than that from the experiment. However, we note here that the effect of the large fluctuation of the molecular orientation is not taken into account in our calculation. The orientational fluctuation might

reduce the effective charges even in phase III [5].

In summary, we have studied the IR activities of vibron and mid-lying phonon modes in the $Cmc2_1$ and the $Pca2_1$ structures. In the $Cmc2_1$ structure, the high-frequency (out-of-phase) vibron has higher intensity than the low-frequency (in-phase) vibron. The B_2 phonon is the only possible IR phonon mode of frequency around 1600 cm^{-1}. Our high-frequency-vibron effective charge is too large compared with that from the experiment for phase III. The $Pca2_1$ structure is less plausible because the low-frequency (in-phase) vibron has higher intensity than the high-frequency (out-of-phase) vibrons, which contradicts the experimental findings. Furthermore, in the $Pca2_1$ structure the possibility of two IR phonons contradicts the observation of only one IR phonon for phase III. From our present results, we conclude that $Cmc2_1$ is more favourable than $Pca2_1$ as the structure of phase III. However, we mention that the effective charge tensor is sensitive to the molecular orientation and the bond length. In our calculation, the molecular orientation is not completely optimized in the $Pca2_1$ structure, so we may need to study the structure with different molecular orientations and bond lengths.

References

[1] Mao H K and Hemley R J 1994 *Rev. Mod. Phys.* **66** 671
[2] Cui L, Chen N H and Silvera I F 1995 *Phys. Rev.* B **51** 14 987
[3] Chen N H, Sterer E and Silvera I F 1996 *Phys. Rev. Lett.* **76** 1663
[4] Hemley R J, Mazin I I, Goncharov A F and Mao H K 1997 *Europhys. Lett.* **37** 403
[5] Edwards B and Ashcroft N W 1997 *Nature* **388** 652
[6] Souza I and Martin R M 1997 *Proc. Adriatico Research Conf. on Simple Systems at High Pressures and Temperatures: Theory and Experiment* ICTP Science Abstract No 30, http://www.ictp.trieste.it/ pub_off/sci-abs/smr999 (electronic Proceedings)
[7] King-Smith R D and Vanderbilt D 1993 *Phys. Rev.* B **47** 1651
[8] Resta R 1994 *Rev. Mod. Phys.* **66** 899
[9] Kohanoff J, Scandolo S, Chiarotti G L and Tosatti E 1997 *Phys. Rev. Lett.* **78** 2783
[10] Nagao K and Nagara H 1998 *Phys. Rev. Lett.* **80** 548