

Intermolecular coupling and fluxional behavior of hydrogen in phase IV

Alexander F. Goncharov^{1,2,*}, Irina Chuvashova², Cheng Ji^{3,*}, Ho-kwang Mao^{3,*}

¹Key Laboratory of Materials Physics and Center for Energy Matter in Extreme Environments, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei, Anhui 230031, China

²Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road, Washington, District of Columbia 20015, USA

³Center for High Pressure Science and Technology Advanced Research, Shanghai 201203, China

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*corresponding author e-mail: agoncharov@carnegiescience.edu; cheng.ji@hpstar.ac.cn; maohk@hpstar.ac.cn

Significance Statement:

Transformations of solid hydrogen at very high pressures are of fundamental interest as this behavior provides a benchmark for other materials. Molecular hydrogen is expected to transform to a monatomic solid at very high pressures, however intermediate states and their existence remain largely unexplored. Quantum atomic motion is expected to play an increased role for these highly compressed states. Here we revisit hydrogen phase IV, which was reported to exhibit mixed molecular-atomic configurations, to probe the intermolecular interaction in this intermediate regime. By employing concomitantly synchrotron infrared and conventional Raman spectroscopy on the same sample, we do find that the intermolecular interactions are greatly heterogeneous providing unique experimental insights into vibrational dynamics and lattice fluxionality of hydrogen in phase IV.

We performed Raman and infrared (IR) spectroscopy measurements of hydrogen at 295 K up to 280 GPa at an IR synchrotron facility of SSRF. To reach the highest pressure, hydrogen was loaded into toroidal diamond anvils with 30 μm central culet. The intermolecular coupling has been determined by concomitant measurements of the IR and Raman vibron modes. In phase IV, we find that the intermolecular coupling is much stronger in the graphene like layer (G-layer) of elongated molecules compared to the Br₂ like layer (B-layer) of shortened molecules and it increases with pressure much faster in G-layer compared to B-layer. These heterogeneous lattice dynamical properties are unique features of highly fluxional hydrogen phase IV.

Dense hydrogen demonstrates a number of fascinating phenomena (1), and theory predicts even more spectacular behaviors at higher pressures, which remained to be explored (2, 3). Of particular interest is a behavior related to an increase of the kinetic energy and thus quantum atomic motion, which may lead to a change in the character of the chemical bonds (4) or even to a decline in the melting temperature, which can ultimately result in a liquid ground state (5, 6). Hydrogen with the lightest atoms manifests the most suitable system to explore such

1 effects. However, reaching the appropriate states requires very high pressures, which remains
2 technically challenging.

3 Static high-pressure techniques have been recently progressing aggressively stimulated
4 by scientific goals of better understanding materials under extremes (*e.g.* in planetary interiors),
5 competition with dynamic compression techniques, and new advances in first principles
6 calculations. High-pressure molecular hydrogen H_2 is expected to transform to a metallic
7 monatomic state at high pressures (7, 8) [its synthesis is under debate (9)], but the route remained
8 unclear. Until 2012, only three molecular phases of H_2 have been widely recognized: plastic
9 (fully orientationally disordered) hcp phase I and orientationally ordered phases II and III at low
10 temperature and high pressure. While phase II, possessing quantum ordering features (10, 11), is
11 unusual for molecular crystals, phase III was thought to be similar to common orientationally
12 ordered phases in other classical molecular crystals such as diatomics (12). Assuming that this
13 behavior continues to higher pressures, one could expect that higher-pressure H_2 polymorphs
14 would be classically ordered molecular crystals as the DFT theory predicts (12). However,
15 experiments revealed an unusual “mixed molecular and atomic” phase, named phase IV, to
16 crystallize at 225 GPa on compression of phase I via phase III at 295 K (4, 6). The originally
17 identified structural model, *Pbcn* (12), was found to be slightly less stable than *Cmca-4* in DFT
18 calculations (12-14). Recent diffusion quantum Monte Carlo calculations showed that *Pc-48* is
19 more stable at close to room temperatures (15) for phase IV. The model has two types of
20 molecules, elongated molecules in graphene-like layers (G-layers) and shortened molecules in
21 quasi-hexagonal layers (B-layers), to account for the two vibrons with distinct pressure responses
22 (see SI Appendix, Fig. S1 for the illustration of G-layer and B-layer).

23 However, all this classical structural picture has been questioned in molecular dynamics
24 simulations (16-19), showing that the structure of this new phase is highly dynamic, where the
25 atoms in the elongated molecules of G-layers show a diffusive motion, which can be viewed as
26 the rotation of a three-molecule ring and an even longer atomic migration. Thus, the chemical
27 bonds change their space location migrating with time yet preserving the local lattice symmetry
28 at each time; we call this behavior fluxional in analogy with that of some molecular substances at
29 ambient conditions (20). On the other hand, the shortened molecules in B-layers are
30 orientationally disordered but the atoms do not migrate between the molecular sites. Very recent
31 x-ray diffraction (XRD) experiment indicates that phase IV has a hexagonal close-packed (hcp)
32 structure with higher symmetry than all theoretically predicted structures. Fluxional behavior
33 may produce a time average effect to increase the apparent symmetry.

34 Previous optical spectroscopy investigations (4, 21-23) demonstrated that phase IV has
35 Raman and IR spectra, distinct from the phases discovered earlier, characterized by the presence
36 of two vibron modes (in G-layers and B-layers); the lower frequency vibron modes (ν_1) show a
37 softening and broadening behavior under pressure which is consistent with the molecules in the
38 G-layers to be very short lived (16, 17). In contrast, the higher frequency vibron (ν_2) corresponds
39 to shortened molecules in B-layers. However, Raman and IR experiments have been performed
40 separately making it difficult to compare the results, especially concerning the splitting between
41 the IR and Raman modes. The difference between IR and Raman frequency of a vibron mode

provides valuable information on the intermolecular coupling of the mode. Here, we report the results of concomitant IR/Raman experiments on the same sample yielding reliable information about the intermolecular coupling in both G- and B-layers. We find that the intermolecular coupling in the two types of layers are very different, with that in the G-layers being much stronger and increasing more rapidly with compression compared to that in B-layers.

Two (out of a dozen attempts) diamond anvil cell experiments were successful in reaching pressures in excess of 200 GPa which are needed to reach phases III and IV of hydrogen at 295 K. One was performed to 240 GPa using conventional single beveled diamonds with 40 μm tip diameter. The other one used toroidal anvils (24, 25) machined with focused ion beam (FIB) from conventional beveled anvils with 50 μm tip diameter, yielding a 30 μm diameter tips (Fig. 1a). The use of the novel anvil configuration eventually target at achieving higher pressures than using the conventional beveled anvils. These anvils were coated (using sputtering) with alumina of 50-100 nm thickness. Rhenium was used as the gasket. Hydrogen was loaded at room temperature, being pumped up to 150 MPa using a compressor. The sample dimensions were approximately 10 μm at 160 GPa, as shown in Fig. 1b, and 6 μm at the highest pressure of 280 GPa.

The IR spectra of the vibron modes (Fig. 2a) show an increase in intensity at the transition to phase III, where one strong vibron mode is observed (26). Above 224 GPa, this mode abruptly splits giving rise to a doublet (Fig. 2a). The lower-frequency ν_1 , corresponding to the G-layer molecules, softens and broadens with pressure, while the higher-frequency ν_2 , corresponding to B-layer molecules, is almost pressure independent and is gaining the intensity. The distinct pressure responses of the two bands indicate the existence of two types of molecules in phase IV. Concomitant Raman measurements at the same conditions (Fig. 2b) show a similar behavior of the Raman vibron band albeit the frequencies are shifted to lower energies. This energy distinction is because Raman and IR vibron modes have different vibration patterns for the molecules that belong to the same unit cell: in-phase for Raman and out-of-phase for IR active modes. Thus, the Raman-IR splitting value represents the strength of the intermolecular coupling (27, 28). The intermolecular coupling is commonly represented as Van Kranendonk's hopping matrix elements ε_{ij} (29), that correspond to intermolecular coupling strengths. For instance, the difference in the Raman and IR vibron frequency in hcp phase I of hydrogen is 6ε , where $\varepsilon/2$ corresponds to the pair interactions between nearest neighbor molecules. Under pressure, the intermolecular coupling normally increases representing a normal tendency for compression of molecular crystals, where intermolecular distances contract much faster than intramolecular (these can even expand) due to heterogeneity of the interatomic interactions. This behavior has been established for phases I, II and III of hydrogen, but phase IV reveals an anomalous behavior as elaborated below.

Our combined concomitant IR-Raman experiments allow determining the splitting of the vibrational band independently of the pressure measurements. This is critical to accurately characterize the splitting, since such determination has been performed based on separate IR and Raman measurements, in which pressure determination could suffer a large uncertainty [e.g. Ref. (30)]. Here, based on our improved measurements, we find a sharp increase of the intermolecular

coupling strength with pressure in molecules belonging to G-layers (Fig. 3b) especially in phase IV. The intermolecular coupling between molecules in B-layers is obviously weaker. This two-type-molecule scenario develops in phase IV with the G-layer molecules becoming fluxional. At these conditions (≥ 270 GPa), the whole inter-intra-molecular bonding concept is about to break down in G-layer because the difference between intra- and inter-molecular bond strength becomes much less substantial. Moreover, the molecules in G-layers are short living as they decompose and recombine within a picosecond time scale (16, 17); this dramatically increases anharmonic effects. On the other hand, the intermolecular coupling in B-layers is much weaker demonstrating an intriguing bonding distinction between molecules in G- and B-layers, which also results in a charge transfer and band gap opening (17) stabilizing the structure. Concerning the intermolecular bonding anisotropy, it can be explained naïvely as due to a difference in the intramolecular bond lengths in G- and B-layers which leaves a complementary length for the intermolecular bonds in these adjacent layers. Thus, phase IV of hydrogen manifests a Peierls distortion of some kind.

Recently, technical breakthroughs have been made and XRD data of hydrogen at above two megabar pressures became available, and disclosed the crystal structure of phase IV (31). Based on XRD results, the phase transitions along the 295 K isotherm, from phase I to phases III and IV, appear to be iso-structural. XRD probes the scattering from electrons which are located in between two hydrogen atoms in one molecule, thus captures an averaged over the time positions of the mass centers of H_2 molecules. Noteworthy, vibrational spectroscopy is complementary to XRD since the former is sensitive to the local symmetry of molecules. Even though the XRD results suggest the mass center of H_2 molecules sit on hcp-like lattice in phase IV, Raman and IR data clearly indicate the emerging of two types of distinct H_2 molecules, while XRD is insensitive to such symmetry breaking in the molecular level. By considering both XRD and spectroscopy data, when the hcp brillouin zone gets highly distorted under strong compression (31), hydrogen appears to develop two types of molecules, in phase IV, with one being strongly interacting with neighbors and fluxional in G-layers and the other with weaker intermolecular coupling in B-layers. Since the molecules in G-layers are fluxional, the time averaged symmetry in both of the layers is still hexagonal, thus consistent to the XRD measurements (Fig. S3). With further compression, the intensified intermolecular interactions between the G-layer molecules may eventually lead to equal inter-molecular and intra-molecular distances, viz. the breakdown of the molecular configuration. At 280 GPa, our experiment demonstrates that the bandgap is still open in phase IV (Fig. 4), in agreement with previous observations (4). Vibrational spectroscopy represents a unique way of probing this unusual high-pressure behavior capturing a local atomic configuration to which it is very sensitive.

Methods

We performed the experiments at a newly constructed system at the beamline BL01B of the Shanghai Synchrotron Radiation Facility (32, 33). The system combines synchrotron Fourier-Transform (FT-IR) spectroscopy with a broadband laser visible/IR and conventional laser Raman spectroscopy in one instrument. The all-mirror custom confocal IR microscope was used in a

1 transmission mode and the FT-IR spectra were recorded with a mercury-cadmium-telluride
2 (MCT) detector with the $0.05 \times 0.05 \text{ mm}^2$ crystal dimensions in the spectral range of 700-10000
3 cm^{-1} . The synchrotron beam diameter was about 10 μm measured in the IR spectral range (33).
4 The transmission IR measurements were performed in a single-channel mode using the IR
5 spectrum of the same sample measured at the condition where IR absorption was relatively weak
6 (*e.g.* in phase I) (27) as the reference. The same IR optics was used to measure visible and IR
7 transmission spectra with the Raman spectrometer equipped with array CCD and IR detectors.
8 The Raman microscope objective lens (Mitutoyo 50 X, NA=0.4) is interchangeable with the IR
9 reflective objectives diverting the optical path to the Raman spectrometer. A 660 nm single-line
10 solid-state laser was used to excite the Raman spectra in a back scattering geometry and the
11 signal was analyzed using three narrow bandpass holographic notch filters and a single grating
12 500 mm focal length spectrograph equipped with a CCD detector. Raman and IR experiments
13 were performed at 295 K at the same nominal pressure measured with Raman spectra of the
14 stressed diamond (34) and finely corrected using the spectral position of the main Raman vibron
15 band as presented in Ref. (30).

Figure Captions:

Fig. 1. Loading of hydrogen with the toroidal diamond anvils. (a). scanning electronic microscope image of the diamond tip machined with FIB. (b). optical microscope image of the loaded hydrogen sample in the transmitted and reflected light at approximately 160 GPa.

Fig. 2. Synchrotron IR and Raman spectroscopy in compressed hydrogen up to 280 GPa at 295 K. (a) IR spectra of the vibron modes in phases III and IV. (b) Raman spectra of phase IV as pressure increases; left and right panels show the libron plus phonon modes and the vibron modes, respectively. The vibron modes denoted as ν_1 and ν_2 correspond to the strongly and weakly bounded G and Br₂ layers, respectively. The results are in a qualitative agreement with previous measurements (4, 6, 21-23). (c) Configuration of G-layers and B-layers in the P_c -48 model (15). G-layers contain the elongated molecules (blue intramolecular bonds) associated in quasi-hexagons (yellow intermolecular bond), while the B-layers consist of shortened molecules (green bond). Only two layers are shown projected along the c -axis.

Fig. 3. (a) Raman and IR vibron frequencies as a function of pressure: symbols are from this work; pressure is determined via Raman measurements of the stressed anvils and further corrected to match the position of the main Raman vibron mode ν_1 according the calibration of Ref. (30); an uncertainty of the frequency determination is smaller than the size of the symbols except for the last pressure point, where an asymmetric ν_1 IR peak was observed; the IR results of Ref. (22) agree fairly with Zha et al. (23) and are not shown. (b) intermolecular coupling represented by the difference between the IR and Raman vibron frequencies: symbols are from this work and dashed lines are theoretically calculated (14); the results below 205 GPa are compared to previously measured in phase III (35).

Fig. 4. Optical absorption spectrum of hydrogen at 280 GPa obtained concomitantly with IR and Raman spectroscopy measurements of Fig. 2.

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