PHYSICAL REVIEW LETTERS **129,** 035501 (2022)

Compression of D_2 to 460 GPa and Isotopic Effects in the Path to Metal Hydrogen

Paul Loubeyre,[1,2,*] Florent Occelli,[1,2] and Paul Dumas[1,3]
[1]*CEA, DAM, DIF, F-91297 Arpajon, France*
[2]*Université Paris Saclay, Laboratoire Matiere Condit Extremes, CEA, F-91680 Bruyeres Le Chatel, France*
[3]*Synchrotron SOLEIL, L'Orme des Merisiers, F-91191 Gif Sur Yvette, France*

(Received 11 February 2022; accepted 23 May 2022; published 12 July 2022)

How are nuclear quantum fluctuations affecting the properties of dense hydrogen approaching metallization? We report here Raman spectroscopy and synchrotron infrared absorption measurements on deuterium up to 460 GPa at 80 K. By comparing to a previous similar study on hydrogen, isotopic effects on the electronic and vibrational properties in phase III are disclosed. Also, evidence of a probable transition to metal deuterium is observed, shifted by about 35 GPa compared to that in hydrogen. Advanced calculations, quantifying a reduction of the band gap caused by nuclear quantum fluctuations, are compared to the present data.

DOI: 10.1103/PhysRevLett.129.035501

Introduction.—Below 350 GPa, five phases have been disclosed in the phase diagram of hydrogen (deuterium) by Raman and infrared spectroscopy measurements [1–5]. The mass center of each molecule essentially remains on an hcp lattice, as revealed by x-ray diffraction [6–9]. Structural changes have thus been described by orientational ordering of the molecules. Above 300 K, phases I, IV, and V were identified with transition pressures almost independent of the isotopes (H_2, D_2, and HD) [4,5]. Remarkably, for temperatures below 100 K, the stable phases are different with the I-II-III sequence [1–3]. Nuclear quantum fluctuations play a crucial role in understanding the stability of these phases. In phase I, at low temperature, molecules behave as free rotors and the transition to phase II under pressure is seen as a particular solution of the model of coupled quantum rotors. A strong isotopic pressure shift in the I-II transition line exists. Furthermore, *ab initio* simulations explicitly taking into account the nuclear quantum fluctuations (NQF) of the protons (deuterons) have shown that phase II has a different structure for hydrogen than for deuterium, with the existence of a quantum fluxional solid for H_2 (for which an underlying classical structure cannot be clearly identified) [10]. The transition to phase III is associated more to a classical ordering of the molecules [3].

Recently, the exploration of the phase diagram of hydrogen has been extended above 350 GPa, at 80 K, by using synchrotron infrared spectroscopy [11]. The transformation pathway of solid hydrogen toward its metal phase was disclosed by the analysis of infrared absorption (IR) spectra, in terms of structural and electronic properties of solid hydrogen. In phase III, the $C2/c-24$ structure, identified by its IR vibron-phonon fingerprint, was observed to remain stable up to 425 GPa. A progressive zeroing of the transmitted intensity at high wave numbers under pressure was directly related to the evolving electronic direct band gap, decreasing down to about 0.6 eV. Above 425 GPa, a discontinuous evolution to a complete IR absorption down to at least 800 cm^{-1} (0.1 eV) was interpreted as the probable transition to a molecular metal. Infrared absorption measurements are here reported on deuterium, using the identical experimental configuration as for hydrogen, so as to quantify the NQF contribution to the electronic properties of hydrogen approaching its metal state.

Experimental approach.—The experimental procedure is identical to the one used previously in our infrared study of hydrogen at 80 K up to 425 GPa [11]. It is based on two experimental developments. First, sample pressures were generated using the toroidal diamond anvil cell (DAC) [12] to enable overcoming the 400 GPa limit of the conventional DACs [13]. Second, infrared absorption measurements were performed at 80 K using a high-brightness broadband infrared source (SMIS beamline of the SOLEIL synchrotron facility) coupled to a custom-made horizontal microscope equipped with two long-working distance Schwarzschild objectives to cope with the use of a cryostat. Raman spectroscopy and visual sample observation were simultaneously performed. Three runs were devoted to this project, with sample configurations identical to that of the hydrogen study [11]. Yet, only the last run could reach pressures in excess to 400 GPa, somehow reflecting the about 1/4 success rate for the toroidal DAC experiments. Figure 1 illustrates some salient features of the data collected on deuterium in the 400 GPa pressure range. Two photographs show the changes of the sample appearance under white light illumination. A reddish color of the diamond tip is gradually developing above 350 GPa until becoming very dark-red about 460 GPa. That is due to the diamond band gap decreasing in the visible range under the stress at the anvil tip [14]. Such changes of the diamond

© 2022 American Physical Society

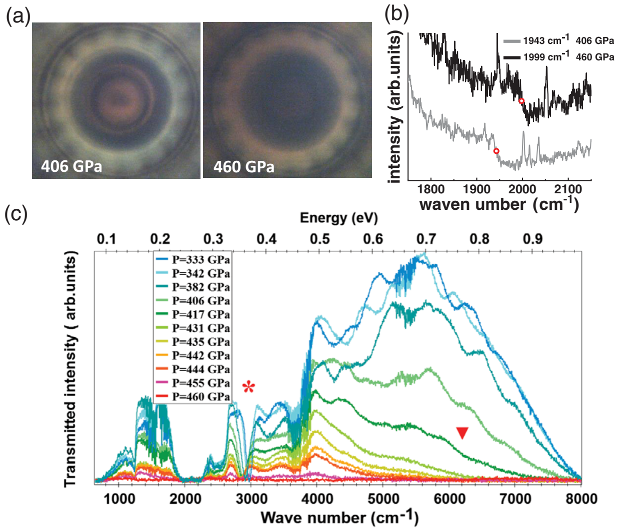

FIG. 1. Selected experimental data (a). Photographs of the deuterium sample under white light illumination above 400 GPa at 80 K. (b) T_{2g} phonon Raman spectra of the diamond anvil tip, with a step shape pointing the wave number used to calculate pressure (as red dot) associated with the diamond tip–D_2 interface. (c) Infrared transmission spectra. Intrinsic absorption features due to deuterium are indicated by the red star pointing to the vibron peak and the red triangle pointing to the zeroing at high wave numbers due to the band gap decrease.

anvil optical properties above 400 GPa have been reproducibly observed [11,12] (transparency is reversibly recovered upon pressure release). Infrared transmission spectra were measured over the 800–8000 cm^{-1} wave number range. The pressure induced changes in the infrared spectra are essentially due to the intrinsic properties of deuterium. Two interesting features are clearly seen: (1) the strong absorption peak around 3000 cm^{-1} which is associated with the D_2 vibron becoming infrared active when entering phase III. This vibron feature broadens and shifts to lower wave numbers with increasing pressure; (2) above 400 GPa, the shape of the infrared spectrum starts to display a zeroing at high wave numbers, evolving toward lower wave numbers with pressure. Finally, a clearly discernible high-frequency step in the T2g phonon Raman spectra of the stressed diamond tip is measured up to the maximum pressure. By using the Akahama 2006-scale [15], the pressure of the deuterium sample is related to the frequency value at half the step, as done for the hydrogen study [11]. The maximum pressure measured is 460 GPa. It is worth noting that if, instead, we would have used the Akahama 2010-scale [8] (as done in a recent report of semimetallic molecular hydrogen [16]), the maximum pressure would then amount to 540 GPa. The error bars in pressure, 10 GPa, is associated with the random uncertainty originating from the stress field at the anvil tip, without accounting for the systematic uncertainty originating from the pressure scale calibration. The evolution of the sample pressure versus the force on the piston (see Supplemental Material, Fig. S1 [17]) features the expected S shape behavior, similarly to a standard DAC compression [12,13].

Discussion.—The absorbance spectra is obtained by calculating $A = -\log_{10}[I(\nu)/I_0(\nu)]$, $I(\nu)$ being the intensity of the raw spectrum at frequency ν and $I_0(\nu)$ that of the reference taken at 134 GPa. The infrared absorption spectra show two peaks [see inset, Fig. 2(a)], which matches the calculated infrared fingerprint of the $C2/c-24$ structure consisting of an intense IR active vibron mode and a less intense phonon mode [18]. This structure is predicted to be the most stable one for phase III, by different *ab initio* calculations, density functional theory (DFT) [18] and quantum Monte Carlo (QMC) [19]. It has 24 atoms in the unit cell, arranged in layers of molecules forming a

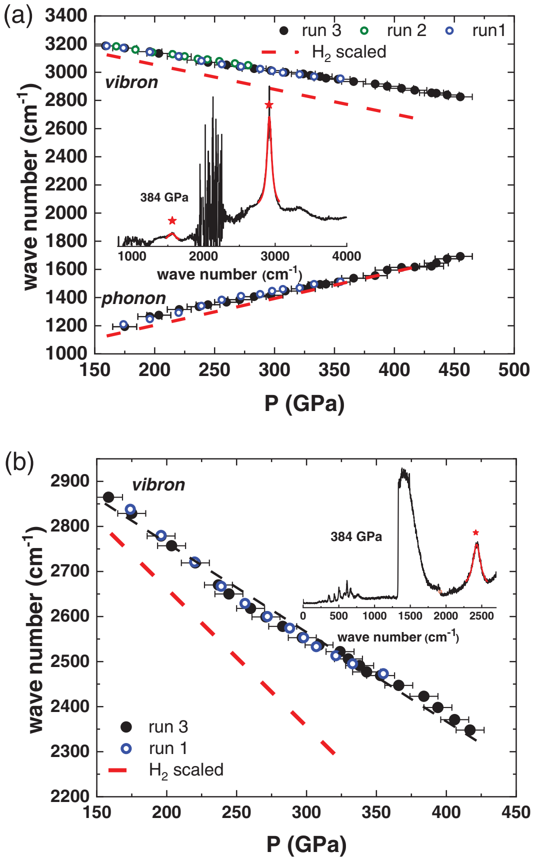

FIG. 2. Wave number versus pressure of the vibron and of the phonon active modes in phase III at 80 K. (a) Infrared measurements, as illustrated by the spectra at 384 GPa (inset). The linear fit of the vibron wave number versus pressure is given by ν_{vibron} [cm^{-1}] = 3374.4 − 1.20P [GPa] and that of the phonon wave number by ν_{phonon} [cm^{-1}] = 945.2–1.62P [GPa]. The scaled hydrogen phonon and vibron curves, as red-dashed lines, are obtained by a scaling of previous hydrogen data [11]. (b) Raman measurements, as illustrated by the spectra at 384 GPa (inset). The linear fit of the vibron wave number versus pressure is given by: ν_{vibron} [cm^{-1}] = 3145.2–1.94P [GPa]. Different symbols indicate different runs.

slight monoclinic distortion of the hexagonal lattice. In Fig. 2(a), the continuous linear pressure evolution of these two modes frequencies suggests that solid deuterium remains in phase III up to 460 GPa. Under the assumption of harmonic oscillators and identical structure and volume, the frequencies in H_2 and in D_2 at a given pressure should differ by a factor of $\sqrt{2}$ as a result of the difference in mass $(\sqrt{m_{D_2}}/\sqrt{m_{H_2}})$. Isotope pressure difference at a given volume, about 1% in the 100 GPa range [6], can be neglected since being much smaller than pressure random uncertainty. As seen in Fig. 2(a), this scaling comparison works well for the phonon while a significant increasing deviation is observed for the vibron. The measurement of the Raman active D_2 vibron frequency is shown in Fig. 2(b). Its continuous linear pressure evolution confirms the stability of phase III. Also, a significant deviation with the H_2-scaled Raman active vibron data is observed. The decrease of the vibron frequency with pressure is indicative of a weakening of the molecular bond. The lower values for the H_2-scaled vibron frequency compared to the D_2 one implies a further weakening of the molecular bond due to NQF. Indeed, it has been calculated that NQF should significantly redshift and broaden the infrared and Raman vibron peaks [20], as observed here for the infrared and Raman vibrons and IR width (Supplemental Material, Fig. S2 [17]). It is interesting to note that the difference between the H_2-scaled and D_2 vibron frequencies is as large as the dispersion of the vibron frequencies calculated using various approximations for the exchange-correlation (XC) functional [21] and so the test of these XC approximations should only be meaningful when NQF are taken into account.

The onset of black deuterium—i.e., deuterium turning totally opaque to transmitted white light [22]—was observed around 340 GPa (see Supplemental Material, Fig. S3 [17]), whereas black hydrogen was observed around 310 GPa. Since identical configuration of both sample and IR bench were used for H_2 and D_2, the transformation to black hydrogen (deuterium) should be related to a similar absorbance spectrum in the visible and so a similar band gap value. It suggests that the band gap is decreasing faster under pressure for H_2 than for D_2. This can be quantified by extracting the band gap from IR absorbance spectra. The absorption edge for a direct band gap should be sharp, hence the low-energy tail observed, as illustrated in Fig. 3(a), suggests the existence of a lower energy indirect electronic band gap. As done previously for the hydrogen study, the direct band gap value is positioned at the junction between the absorbance plateau and the lower energy tail. Yet, doing so the band gap might be underestimated by up to 0.14 eV [11] since the detected absorbance limit is around two due to the low intensity of the signal. The thickness of the D_2 sample being about 1.6 μm thick, the corresponding absorption coefficient is hence about 30 000 cm^{-1}. A recent calculation [23] has shown that this 30 000 cm^{-1} criterion of absorbance gives a reasonable estimate of the direct band gap in the $C2/c-24$ structure, with the true value falling within a $+0.14$ eV uncertainty. It seems reasonable to assume that the absorption spectra of H_2 and of D_2 at a given volume (to a good approximation, pressure) are homothetically shifted in energy due to the NQF, as illustrated in Fig. 3(a). Hence, the direct band gap value should also be shifted by the same amount. The energy at which the absorbance reaches two is more precisely positioned by looking at the transmittance spectra, by pointing the energy for which the IR transmitted intensity goes to zero, as done in Fig. 3(b). By performing the same analysis for the H_2 transmittance spectra (Supplemental Material, Fig. S4 [17]), a very precise shift between the absorbance spectra of H_2 and D_2 can be obtained and thereof, the shift in the direct band gap versus pressure, plotted in Fig. 4(a), can be obtained without having to account for the 0.14 eV uncertainty.

At 460 GPa, a transition to complete IR absorption over the whole infrared spectral range was observed. The sample properties were reversibly measured upon pressure release

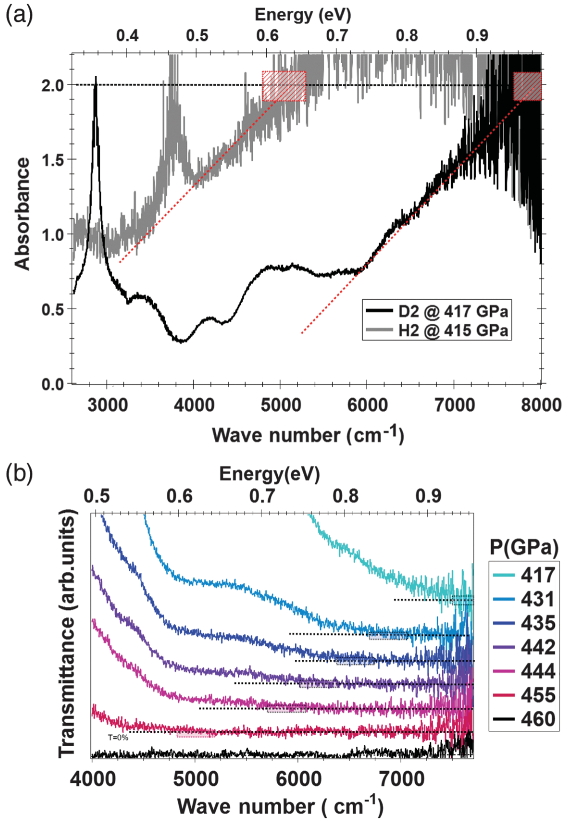

FIG. 3. (a) Comparison of the IR absorbance spectrum measured in H_2 and in D_2 about 415 GPa at 80 K. The red square indicates the position of the direct band gap using the criteria of a 30 000 cm^{-1} absorbance. (b) IR transmittance spectra using a pressure color scale. A different offset in applied for each pressure for better visualization of the onset of the zeroing energy, marked by a rectangle.

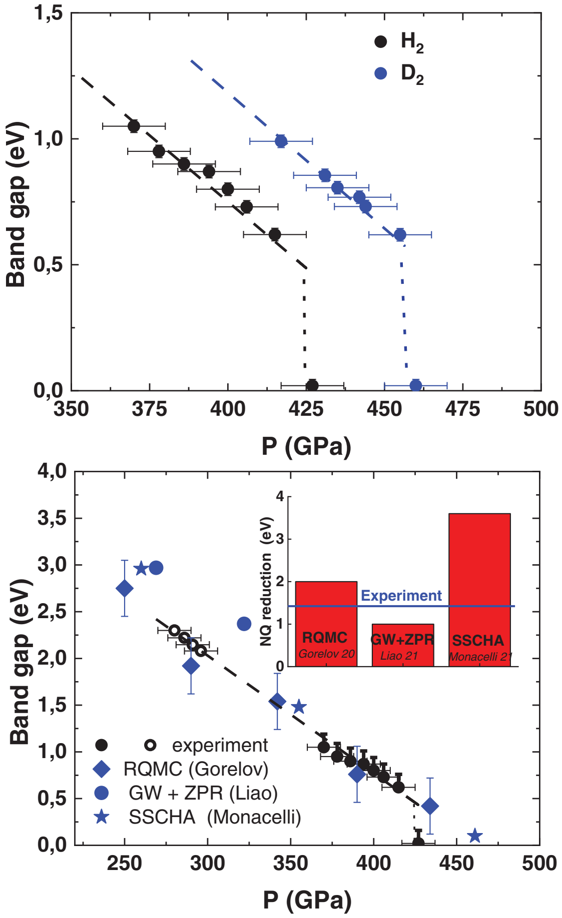

FIG. 4. (a) Relative shift in the pressure evolution at 80 K of the direct band gap in hydrogen [11] and in deuterium. An abrupt evolution to below 0.1 eV is observed for hydrogen and for deuterium, respectively, at 425 and 460 GPa. (b) The band gap value of hydrogen is compared to various calculations taking into account NQF [20,23,24]. In the inset, the reduction of the direct band gap due to NQF is compared to experimental estimate.

(see Fig. S5). Similarly to the hydrogen case, the transition at 460 GPa is thus interpreted as the probable transformation to molecular metal deuterium [11]. Also, it is interesting to note that this transition takes place when the direct band gap reaches about 0.6 eV, both in hydrogen and in deuterium. This seems to indicate that metallization is driven by a band structure effect within the C2/c-24 phase, as proposed by a recent calculation interpreting the discontinuous drop of the direct band gap in hydrogen as an abrupt change of the Fermi surface [25].

The band gap versus pressure at 80 K in solid D_2 is 0.45 eV larger than the one in H_2. For hydrogen as for other materials, the calculated band gap is usually very sensitively dependent on the structural parameters and on the approximation used for the exchange-correlation functional for mean-field-like density functional calculations [26]. Moreover for hydrogen, a significant reduction of the band gap due to NQF has recently been quantified in three studies, which amounts to 2, 1, and 3 eV, respectively, by using a quantum Monte Carlo simulation [23], a renormalized GW band gap by electron-phonon interaction [24] and a DFT calculation including quantum nuclear fluctuations beyond the perturbation theory [20]. The NQF contribution to the band gap should scale as $1/\sqrt{m}$ [20]. The here-measured isotopic shift on the band gap can thus be used to obtain an experimental estimate of the NQF reduction on the H_2 direct band gap which amounts to 1.5 eV. That value is used to benchmark the three advance calculations, as plotted in the inset of Fig. 4(b). Experimental data lies in between the quantum Monte Carlo and the renormalized GW calculations, whereas the stochastic self consistent harmonic approximation one seems to overestimate the NQF contribution. Yet, the three calculations provide H_2 direct band gap values in good agreement with experiment [11].

In summary, pressures in excess of 400 GPa have been reproducibly obtained on the hydrogen systems, here deuterium. Detailed Raman spectroscopy and IR absorption measurements on both H_2 and D_2, enable us to quantify isotopic effects in the structural and in the electronic properties of hydrogen approaching its metal state. Phase III, having most reasonably the $C2/C-24$ structure, is stable up to the metal transition for both isotopes. A significant shift on the direct band gap, by about 0.45 eV, is measured. Thereof, the NQF contribution to the band gap is estimated and its value, 1.5 eV, is used to challenge advanced calculations. Dense hydrogen in the domain of its metallization pressure is indeed a quantum system. The toroidal-DAC is now a well-suited device for advancing the understanding of this fundamental system.

We thank O. Marie for focused ion beam machining the toroidal diamond anvils and the gasket holes. We thank F. Borondics and F. Capitani for their assistance at the SMIS beamline of the synchrotron SOLEIL. We are grateful to J. Daillant for facilitating access to the infrared beamline.

---

[*] paul.loubeyre@cea.fr

[1] I. F. Silvera and R. J. Wijngaarden, Phys. Rev. Lett. **47**, 39 (1981).
[2] A. F. Goncharov, R. J. Hemley, H.-k. Mao, and J. Shu, Phys. Rev. Lett. **80**, 101 (1998).
[3] A. F. Goncharov, R. J. Hemley, and H.-k. Mao, J. Chem. Phys. **134**, 174501 (2011).
[4] R. T. Howie, C. L. Guillaume, T. Scheler, A. F. Goncharov, and E. Gregoryanz, Phys. Rev. Lett. **108**, 125501 (2012).
[5] P. Dalladay-Simpson, R. T. Howie, and E. Gregoryanz, Nature (London) **529**, 63 (2016).
[6] P. Loubeyre, R. LeToullec, D. Hausermann, M. Hanfland, R. J. Hemley, H. K. Mao, and L. W. Finger, Nature (London) **383**, 702 (1996).

[7] I. Goncharenko and P. Loubeyre, Nature (London) **435**, 1206 (2005).

[8] Y. Akahama, M. Nishimura, H. Kawamura, N. Hirao, Y. Ohishi, and K. Takemura, Phys. Rev. B **82**, 060101(R) (2010).

[9] C. Ji, B. Li, W. Liu, J. S. Smith, A. Majumdar, W. Luo, R. Ahuja, J. Shu, J. Wang, S. Sinogeikin *et al.*, Nature (London) **573**, 558 (2019).

[10] G. Geneste, M. Torrent, F. Bottin, and P. Loubeyre, Phys. Rev. Lett. **109**, 155303 (2012).

[11] P. Loubeyre, F. Occelli, and P. Dumas, Nature (London) **577**, 631 (2020).

[12] A. Dewaele, P. Loubeyre, F. Occelli, O. Marie, and M. Mezouar, Nat. Commun. **9**, 2913 (2018).

[13] B. Li, C. Ji, W. Yang, J. Wang, K. Yang, R. Xu, W. Liu, Z. Cai, J. Chen, and H.-k. Mao, Proc. Natl. Acad. Sci. U.S.A. **115**, 1713 (2018).

[14] A. L. Ruoff, H. Luo, and Y. K. Vohra, J. Appl. Phys. **69**, 6413 (1991).

[15] Y. Akahama and H. Kawamura, J. Appl. Phys. **100**, 043516 (2006).

[16] M. I. Eremets, A. P. Drozdov, P. P. Kong, and H. Wang, Nat. Phys. **15**, 1246 (2019).

[17] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.129.035501 for details on the materials and methods, supplemental Figs. S1–S6 and Table S1.

[18] C. J. Pickard and R. J. Needs, Nat. Phys. **3**, 473 (2007).

[19] J. McMinis, R. C. Clay, D. Lee, and M. A. Morales, Phys. Rev. Lett. **114**, 105305 (2015).

[20] L. Monacelli, I. Errea, M. Calandra, and F. Mauri, Nat. Phys. **17**, 63 (2021).

[21] H.-C. Yang, K. Liu, Z.-Y. Lu, and H.-Q. Lin, Phys. Rev. B **102**, 174109 (2020).

[22] P. Loubeyre, F. Occelli, and R. LeToullec, Nature (London) **416**, 613 (2002).

[23] V. Gorelov, M. Holzmann, D. M. Ceperley, and C. Pierleoni, Phys. Rev. Lett. **124**, 116401 (2020).

[24] K. Liao, T. Shen, X.-Z. Li, A. Alavi, and A. Grüneis, Phys. Rev. B **103**, 054111 (2021).

[25] M. Dogan, S. Oh, and M. L. Cohen, J. Phys. Condens. Matter **33**, 03LT01 (2021).

[26] M. A. Morales, J. M. McMahon, C. Pierleoni, and D. M. Ceperley, Phys. Rev. B **87**, 184107 (2013).