High-Pressure Insertion of Dense H 2 into a Model Zeolite

Wan Xu, Xiao-Di Liu, Miriam Peña-Alvarez, Hua-Chao Jiang, Philip Dalladay-Simpson, Benoit Coasne, Julien Haines, Eugene Gregoryanz, Mario Santoro

▶ To cite this version:

Wan Xu, Xiao-Di Liu, Miriam Peña-Alvarez, Hua-Chao Jiang, Philip Dalladay-Simpson, et al.. High-Pressure Insertion of Dense H 2 into a Model Zeolite. Journal of Physical Chemistry C, 2021, 125 (13), pp.7511-7517. 10.1021/acs.jpcc.1c02177 . hal-03227604

HAL Id: hal-03227604
https://hal.umontpellier.fr/hal-03227604v1

Submitted on 4 Oct 2021

High Pressure Insertion of Dense H_2 into a Model Zeolite

Wan Xu,[†,‡] Xiao-Di Liu,[*,†] Miriam Peña-Alvarez,[¶] Hua-Chao Jiang,[†] Philip Dalladay-Simpson,[§] Benoit Coasne,[∥] Julien Haines,[⊥] Eugene Gregoryanz,[§,¶,†] and Mario Santoro[*,#,†]

†*Key Laboratory of Materials Physics, Institute of Solid State Physics, HFIPS, Chinese Academy of Sciences, Hefei 230031, China*

‡*University of Science and Technology of China, Hefei, China*

¶*Centre for Science at Extreme Conditions & The School of Physics and Astronomy, The University of Edinburgh, Peter Guthrie Tait Road, Edinburgh, U.K.*

§*Center for High Pressure Science & Technology Advanced Research, 1690 Cailun Road, Shanghai, 201203, China*

∥*Université Grenoble Alpes, CNRS, LIPhy, Grenoble, France*

⊥*ICGM, CNRS, Université de Montpellier, ENSCM, Montpellier, France*

#*Istituto Nazionale di Ottica (CNR-INO) and European Laboratory for non Linear Spectroscopy (LENS), via N. Carrara 1, 50019 Sesto Fiorentino, Italy*

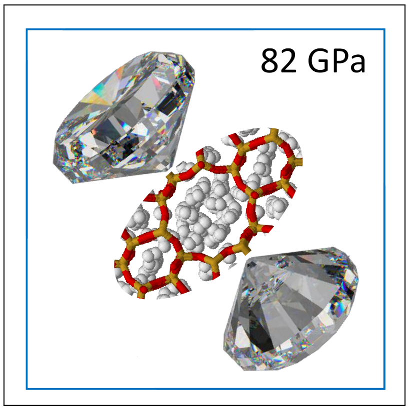
E-mail: xiaodi@issp.ac.cn; santoro@lens.unifi.it

High pressure, hydrogen, zeolites, Raman spectroscopy, X-ray diffraction, Monte Carlo modelling

Abstract

Our combined high-pressure synchrotron x-ray diffraction and Monte Carlo modelling studies show super-filling of the zeolite, and computational results suggest an occupancy by a maximum of nearly two inserted H_2 molecules per framework unit, which is about twice more than observed in gas hydrates. Super-filling prevents amorphization of the host material up to at least 60 GPa, which is a record pressure for zeolites and also for any group IV element being in full 4-fold coordination, except for carbon. We find that the inserted H_2 forms an exotic topologically constrained glassy-like form, otherwise unattainable in pure hydrogen. Raman spectroscopy on confined H_2 shows that the micro-porosity of the zeolite is retained over the entire investigated pressure range (up to 80 GPa) and that inter-molecular interactions share common aspects with bulk hydrogen while they are also affected by the zeolite framework.

Graphical TOC Entry



Zeolites are archetypal micro-porous crystalline systems both natural and synthetic[1–4] with a broad range of industrial applications. Adsorption studies on zeolites at extreme conditions led some of us and other groups to develop a rich and dynamic research area. Particularly, the high pressure insertion of simple dense molecular systems as the guest species in zeolite hosts leads to the formation of exotic guest phases and to unique properties for the host framework[5–20]. Once the latter is supported by inserted guests to form a "molecular spring", it resists the applied pressures. But what would happen if the zeolites are filled by the most penetrating fundamental systems and also the most abundant element in the universe: hydrogen? Indeed, dense H_2 is a "master" and benchmark system in high pressure sciences.[21] Dense, sub-nano confined states of H_2 could be investigated and compared to those of bulk hydrogen at extreme conditions, since these states would add to the general view of such a fundamental element. The highly penetrating character of H_2 could be also compared to other larger molecular and atomic systems to allow us to investigate the ultimate capability of filled zeolites to resist the pressure-induced pore collapse and the consequent pressure induced amorphization (PIA). The utmost removal of PIA can then provide information on the local structure of the framework cation, silicon in our case, at record extreme conditions. Indeed, it is of great interest to search to which extent the 4-fold coordination of silicon can be preserved. In bulk silica, the thermodynamic 4-fold-to-6-fold transformation occurs below 10 GPa, while metastable 4-fold coordinated phases can survive at most up to 20-40 GPa.[22–25] In gas hydrates, similar host-guest systems, the four-connected framework is built up by H-bonded water molecules, instead of being covalently bonded like in zeolites, and it is filled by simple gaseous molecules. Recently, a CH_4 filled ice has been found to be stable up to the record pressure of 150 GPa.[26] On the other hand, cold compression of methane clathrates at GPa has been found to lead to PIA with the amorphous form still being a host-guest gas hydrate.[27]

We focused our work on a model, pure SiO_2 zeolite, silicalite-1 in order to avoid catalytic effects and to investigate how the pore size and shape affect the topology of the confined molecular form under pressure. Silicalite-1 is characterized by a framework of 4-, 5-, 6-, and 10-membered rings of corner-sharing SiO_4 tetrahedra forming interconnected, mutually orthogonal straight and sinusoidal channels, with ambient pressure diameters of close to 5.5 Å (see Figure 1, at 7 GPa, together with inserted H_2).[28,29] Silicalite-1 is produced in crystals of several tens of microns, which makes it very suitable for optical spectroscopy studies.

In this work we show the high-pressure insertion of H_2 in silicalite-1 up to 82 GPa. Based on synchrotron X-ray diffraction (XRD) and Monte Carlo (MC) modelling, we show that the insertion leads to an exotic glassy-like form of molecular hydrogen. H_2-filled silicalite-1 is found to be stable up to at least 60 GPa and significantly less compressible than the same zeolite filled by the bigger molecules; this being a consequence of the more penetrating nature of H_2. The number of inserted molecules vs. pressure is non-monotonic with a maximum close to two per SiO_2 unit. Raman spectroscopy shows that the framework porosity is retained up to at least 82 GPa and it provides important clues on inter-molecular interactions.

Our experimental and theoretical methods are described in Supplementary Materials[30] together with the relevant references.[31–44]

Powder XRD patterns of H_2-filled silicalite-1 were measured upon increasing pressure up to 60 GPa (Figure 2), in order to investigate to which extent the framework is stable at high pressures and also to provide inputs for Monte Carlo modelling aimed to determine the amount of stored hydrogen. The large, nanometer scale, unit cell size of silicalite-1 is related to the micro-porosity of the framework and it gives rise to the 101, 011, 200, 020 and 111 diffraction peaks located at very low 2θ angles, down to 2°-3°. The widths of the Bragg peaks increased gradually by a factor of two over the entire pressure range investigated. This can be linked to a gradual increase in deviatoric stress in the solid H_2 pressure medium. We also observed some apparent changes in relative intensity, principally due to the separation of overlapping peaks resulting from changes in the unit cell parameters (Figure SM2 and Table SM1).[39–41] Importantly, at the highest pressures, in spite of the increase in line-width, the peaks retained much of their initial integrated intensity (typically

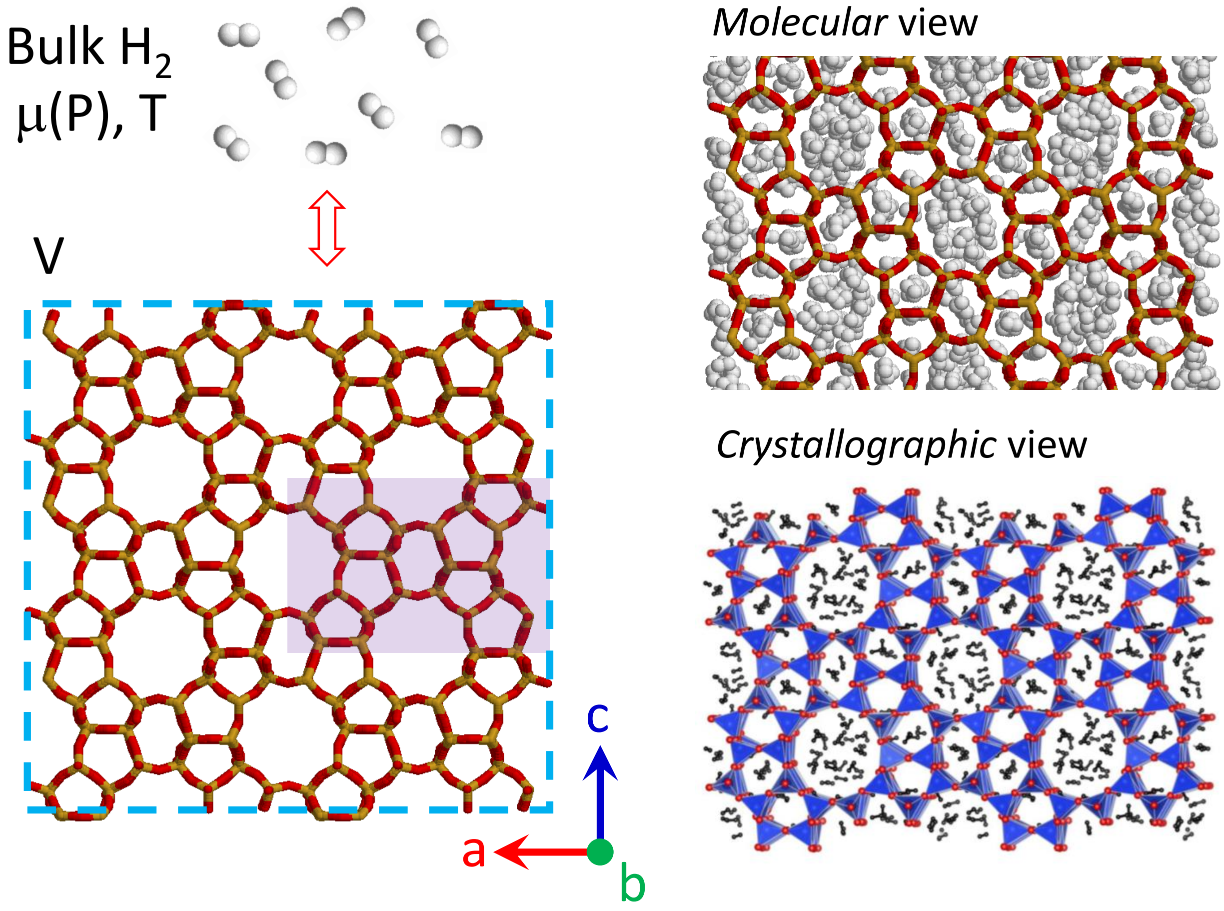


Figure 1: Structure of H_2-filled orthorhombic silicalite-1. Left: principles of MC modeling in the Grand Canonical ensemble. Like in real experiments, a zeolite material is set in contact with an infinite reservoir of bulk H_2. The purple shaded area denotes the unit cell volume while the blue dashed line indicates the periodic boundary conditions. Right: molecular (top) and crystallographic (bottom) view of H_2 inserted in silicalite-1 at room temperature and P = 7 GPa. In the molecular view, the red and orange sticks correspond to the chemical bonds between silicon and oxygen atoms while the white spheres correspond to the hydrogen atoms in H_2 (the sphere radius roughly corresponds to the van der Waals radius of hydrogen). In the crystallographic view, the blue tetrahedra correspond to the silica tetrahedra in silicalite-1 with the red spheres showing the apical oxygens. The black dumbells represent the inserted H_2 molecules. A 2×2×2 unit cell is considered here for the sake of clarity.

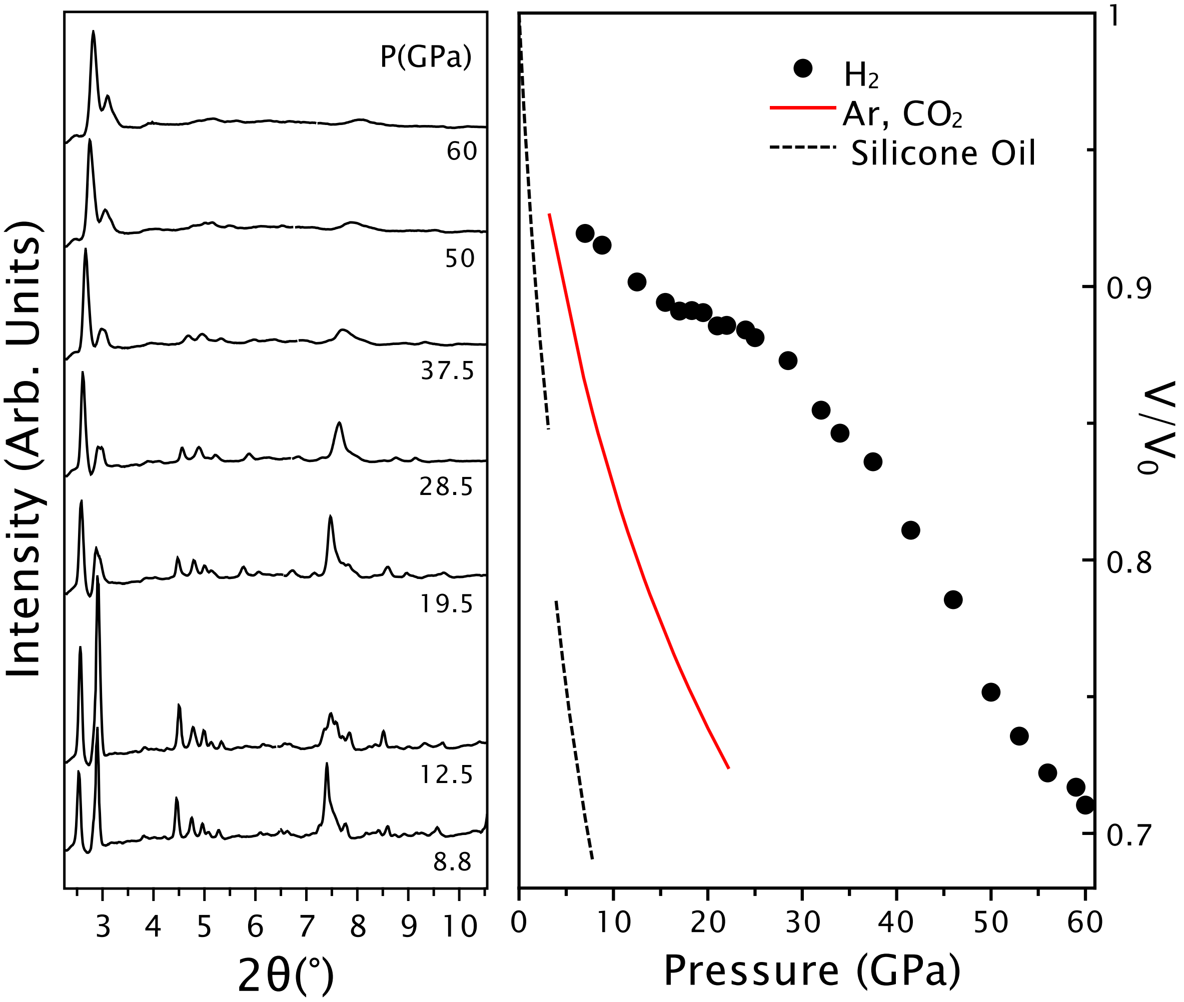


Figure 2: Left panel: Selected powder XRD (λ =0.4828 Å) patterns of H_2-filled silicalite-1, measured upon increasing pressure. A broad Compton scattering background due to air and diamonds has been subtracted. Right panel: experimental pressure behavior for the relative to ambient pressure unit cell volume of H_2-filled silicalite-1 (filled circles). Error bars are within the size of the circles. Red line: compression curve for Ar and CO_2 filled silicalite-1.[8] Black line: equation of state for silicalite-1, measured in a non-penetrating pressure transmitting medium: silicon oil, where amorphization has been found to occur below 10 GPa.

30-100 %) at low pressure. That suggests that silicalite-1 remaines crystalline up to the highest pressure and, consequently, full 4-fold coordination of silicon by oxygen was retained at record pressures among all known group IV compounds, except carbon. Indeed, the thermodynamic transformation pressure from 4-fold to 6-fold coordination in bulk silica is lower by one order of magnitude. LeBail fitting of the XRD patterns (Figure SM3) was used to obtain the pressure behavior of the unit cell volume of H_2-filled silicalite-1 (Figure 2) normalized to its ambient pressure value. We can compare this compression curve with those observed for other penetrating simple gaseous systems such as Ar and CO_2.[8] The most striking result is the much higher relative volumes of up to 24 % at 25 GPa measured for H_2-filled silicalite-1 than for Ar or CO_2 filled silicalite-1, clearly indicating that H_2 is much more penetrating than the other two larger systems. Also, the compression curve of H_2-filled silicalite-1 shows an anomaly. Indeed, a quasi-horizontal inflection point appears at around 19 GPa. Above this point, the curve is convex rather than concave, up to about 50 GPa. This anomaly is suggestive of substantial pressure changes in the filling of silicalite-1 by H_2, a hypothesis that can only be tested on the Grand Canonical ensemble based Monte Carlo (MC) model, whose main outputs are the spatial distribution and the number of inserted molecules per unit cell.

In Figure 1, we report the structure of H_2 filled orthorhombic silicalite-1 at 7.0 GPa, obtained by combining the experimentally determined lattice parameters with Monte Carlo modelling. The zeolite framework is entirely filled by guest H_2 molecules, 127 per unit cell. The state of inserted hydrogen is remarkable. Indeed, this is a disordered, dense glassy-like form within all the investigated pressure range by XRD and MC, i.e. up to 60 GPa. The calculated number of inserted H_2 molecules per unit cell of silicalite-1 by MC as a function of pressure clearly exhibits a maximum (Figure 3, left panel), which corresponds to the anomaly experimentally observed for the pressure behavior of the unit cell volume. The maximum is equal to about 174 and it is located at around 34 GPa. The very low compressibility of H_2 -filled silicalite-1 in the 15-25 GPa pressure interval is now found to be due to H_2

rapidly entering silicalite-1 to a greater and greater extent upon increasing pressure in this range; here, the filling of H_2 hinders the reduction of the host framework volume by strongly reducing the compressibility of the pores. Then, above 30-40 GPa, some amount of previously inserted H_2 is extruded and the volume of silicalite-1 decreases as a result of the combined effect of guest extrusion and normal compression of the filled framework material. H_2-filled silicalite-1 is thus a hydrogen rich material, with H_2 being physisorbed by the zeolite, and an overall pressure dependent chemical composition: $SiO_2(H_2)_x$, with x=1.32-1.82. In fact, this gas content is substantially greater, in terms of number of stored guest molecules, than that experimentally observed so far in any gas hydrate phase at any pressure-temperature condition.[45,46]

At least two remarkable differences emerge between H_2-filled silicalite-1 and the filling of this zeolite with larger simple systems such as Ar and CO_2.[47] Firstly, the maximum number of confined H_2 molecules exceeds that for bigger molecules by a factor of 3-4. Secondly, H_2 is so much more penetrating that even the cages with small openings of 1.4-3.0 Å diameter built up by 5- and 6- membered rings are well filled in this case. We found that the number of H_2 molecules in these cages is equal to 20 per unit cell over all the investigated pressure range, which is 11-16 % of the total amount of inserted molecules. Also, we found that multiple filling of some cages occurs, similarly to several gas hydrates.[45,46,48,49] Interestingly, the non-monotonicity for the pressure behavior of the filling appears to be entirely due to molecules inserted in the channels. All this explains why the volume of the zeolite is so much larger when H_2, rather than bigger guests, is inserted in the framework.

Importantly, the nearest neighbor's intermolecular distance for confined hydrogen is larger than that for bulk hydrogen (Figure 3, right panel) by a few percent, indicating that the H_2-silicalite-1 interaction adds a negative term to the local pressure.

The Raman spectroscopy investigation provides direct information on dynamical properties of the confined dense form of hydrogen. In Figure 4, we report waterfalls of selected Raman spectra of the H_2 vibron for H_2 /silicalite-1 samples, measured upon increasing pres-

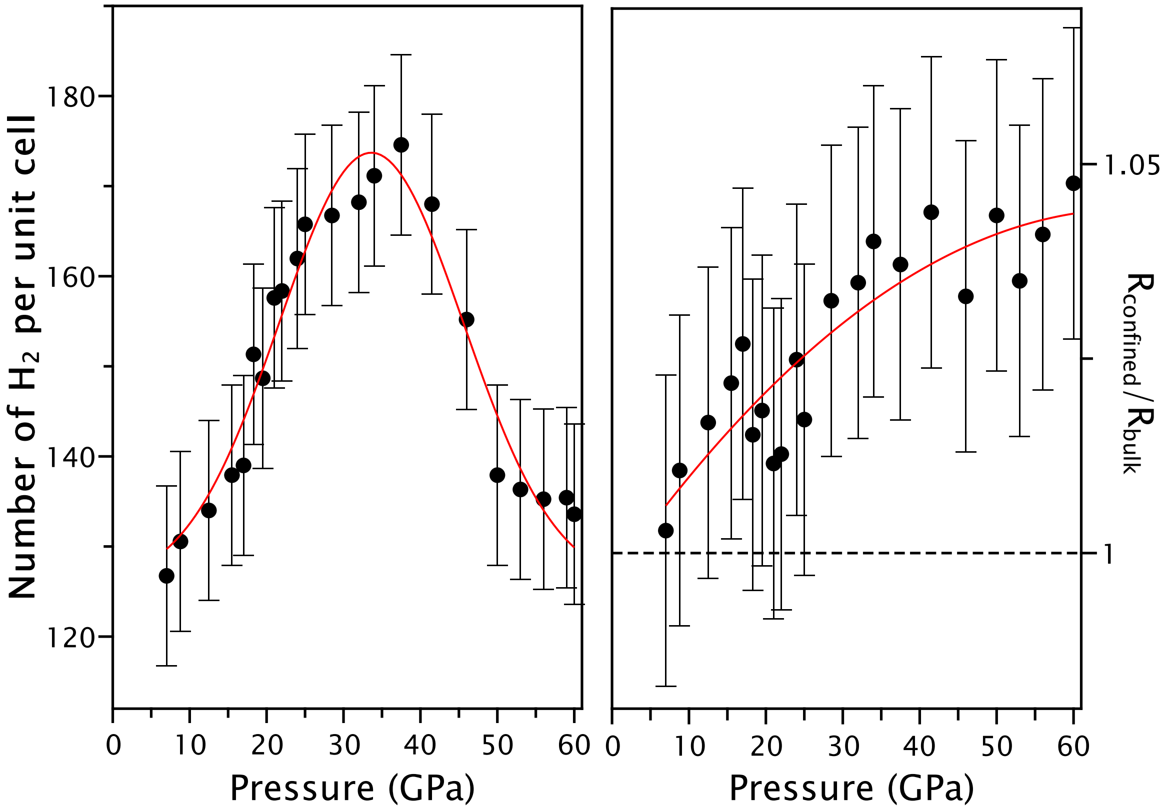


Figure 3: MC calculated pressure behavior of the number of inserted H_2 molecules in silicalite-1 (left) and of the ratio of the nearest neighbor's H_2-H_2 distance for confined hydrogen to that of bulk hydrogen (right). Error bars are due to the simulation and to the evaluation method of the average distances. Red lines through the points are guides for the eye.

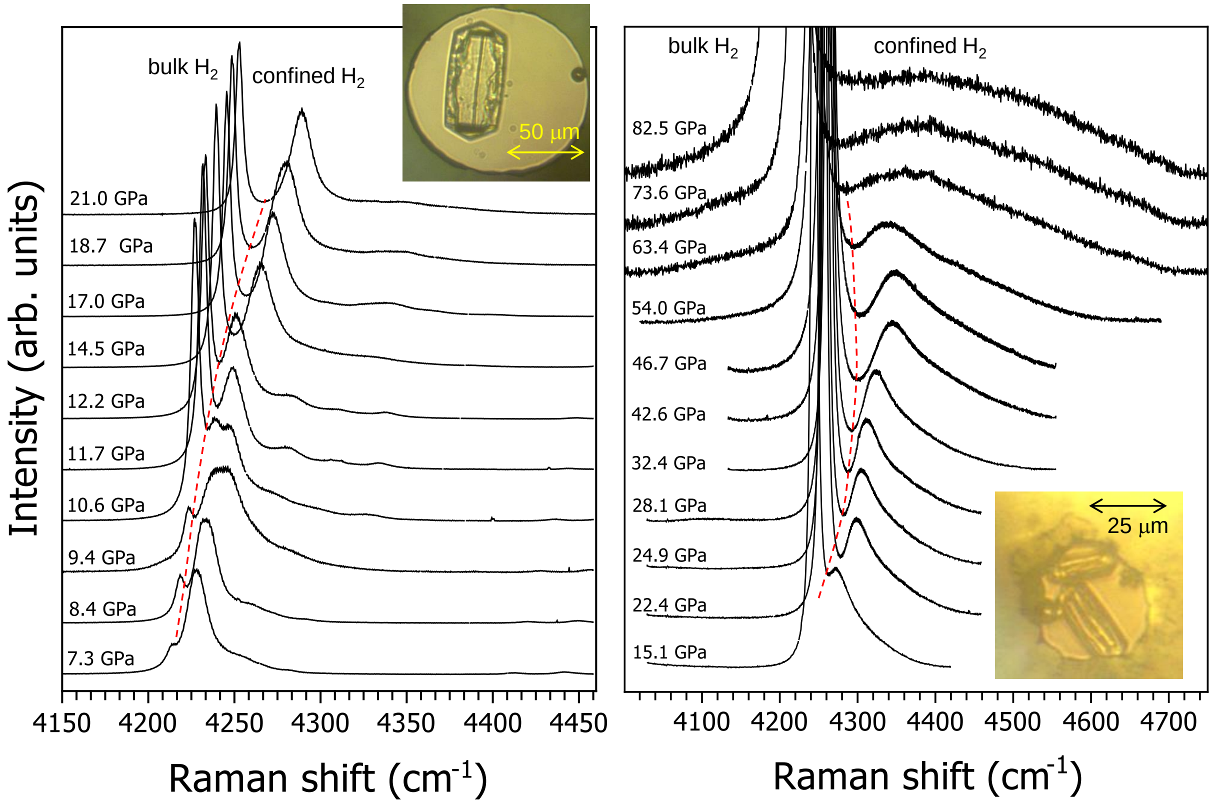


Figure 4: Selected Raman spectra of H_2-filled silicalite-1 crystals in the frequency range of the H_2 vibron, measured upon increasing pressure. Left (right) panel: spectra measured on top of a silicalite-1 crystal of 80×40×40 μm^3 (30×15×15 μm^3) initial size. Red dashed lines separate the bulk and the confined H_2 peaks. Insets: silicalite-1 crystals in the gasket holes, at 0.4 GPa and 4.2 GPa, in the left and right panels, respectively, immersed in H_2 as the pressure transmitting medium. Ruby chips are also present for pressure measurements.

sure on silicalite-1 crystals up to 82.5 GPa. In the spectra, we observe the pure H_2 peak due to bulk hydrogen layers surrounding the crystals and several blue shifted extra peaks which can be easily attributed to confined dense H_2. The blue shift, which increases with pressure, is the net result of the modified intermolecular interactions in confined hydrogen and the interaction between the guest molecules and the internal walls of the porous host. Spectra measured on larger silicalite-1 crystals show up to 4-5 partially resolved peaks for confined hydrogen (Figure 4, left panel), likely to be ascribed to H_2 guest molecules located on distinct host crystallographic sites of silicalite-1 and, as a consequence, experiencing different interactions. These peaks are much broader than the peak of bulk H_2 and they broaden upon increasing pressure till they merge. This finding is compatible with confined hydrogen being highly disordered around the different crystallographic sites corresponding to the distinct peaks, in full agreement with the combined XRD/MC outcome where confined H_2 is indeed found to be in a glassy-like state

In Figure 5, we report the pressure shift of the H_2 frequency for the most intense peak in confined H_2 and for bulk H_2 measured in this work up to 82.5 GPa, and also for isolated H_2 impurities in three crystalline matrices: Ne, Ar and D_2.[50] The pressure behavior for the confined H_2 frequency is remarkable: it is systematically higher than that of the Raman frequency for pure H_2 and, more importantly, in both cases we observe a maximum, which is located at around 50 GPa in confined H_2 and 35 GPa in pure H_2. In addition, in confined hydrogen, a frequency jump occurs around 62 GPa, beyond the pressure range of our XRD investigation, which probably relates to a major structural change in silicalite-1 such as a yet unknown phase transition. The origin of the maximum in the H_2 frequency for confined hydrogen can be easily traced back to the H_2-H_2 vibrational coupling[50–53] (and references therein. See also SM). The Raman frequency being blue shifted in confined H_2 and the maximum being at higher pressures with respect to bulk H_2 suggest that vibrational coupling is weaker in the confined form. This is due the larger inter-molecular distance (see Figure 3) and to the reduced number of H_2 neighbors. An extreme case in this respect is that of

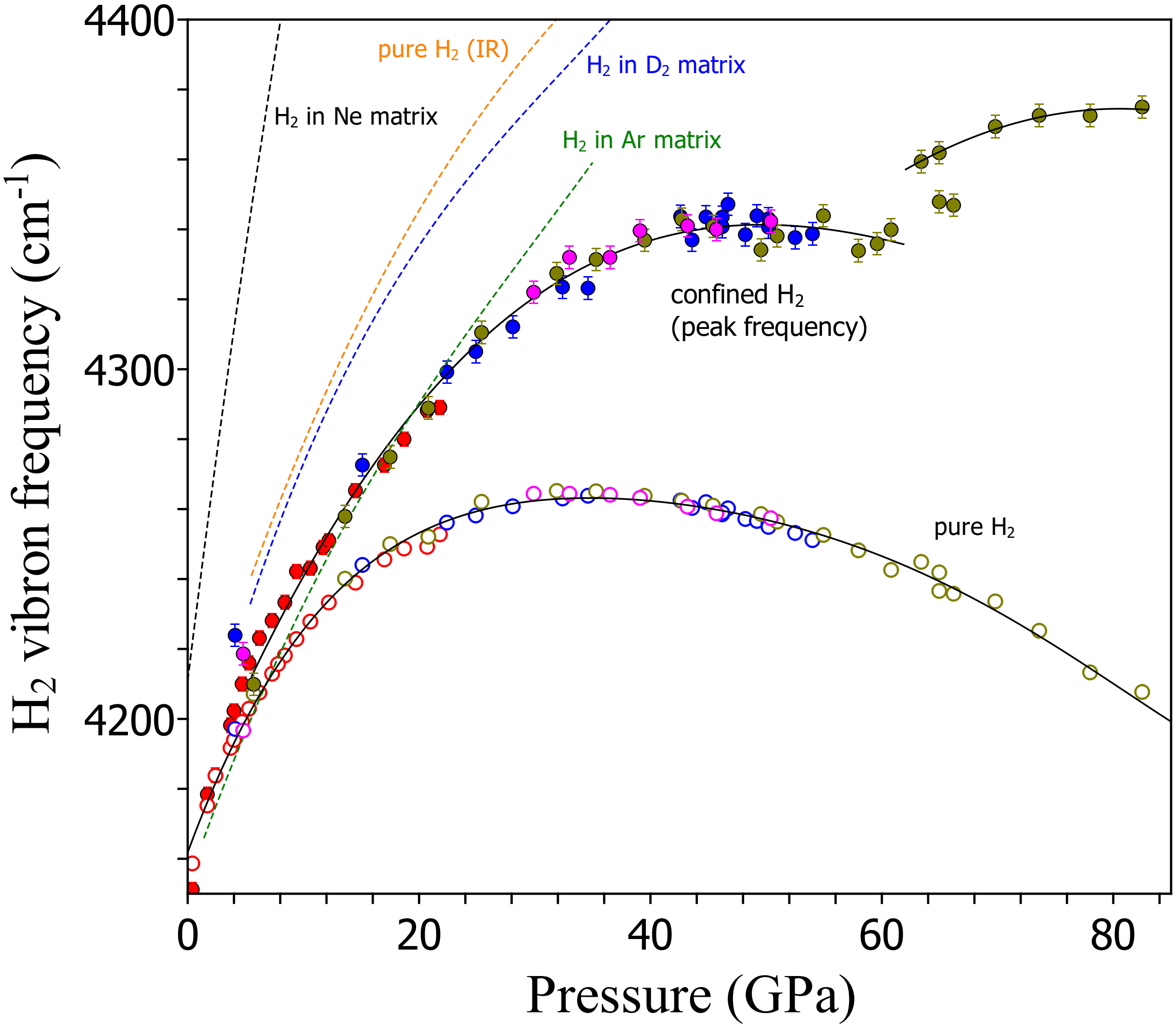


Figure 5: H_2 frequency vs. pressure for different materials and compounds. Full and open dots: this work, values for confined in silicalite-1 and bulk H_2, respectively (see text for details). Black lines: guides for an eye through these two data sets. Error bars are mainly due to the fitting procedure of peaks for confined H_2. Other lines: pressure shift for H_2 as a single molecule impurity in Ne (black), D_2 (blue) and Ar (green) matrix, respectively.[50] Orange line: pressure shift for the IR active H_2 frequency in pure hydrogen.[51–53]

molecules in the cages of silicalite-1, where the number of H_2 neighbors drops to 1 or 0 and the vibrational coupling is nearly or entirely switched off. This case likely corresponds to the highest frequency components in the Raman frequency distribution for confined hydrogen (Figure 4). The Raman spectra of the rotational peaks (Figure SM4)[39–41] show that confined H_2 is a near free rotor, the rotations of which are somewhat more hindered than for pure hydrogen.[54]

Our investigation uncovered an exotic form of dense hydrogen inserted in a zeolite. Which is the Mbar/multi-Mbar fate of H_2-filled zeolites? Which is the fate of silicon coordination in gas filled framework materials and, more generally, of host-guest systems where the host is a covalent or H-bonded network and the guest is a simple atom or molecule, and which is the potential to synthesize novel H rich systems in this way? All these questions among others build up an entirely unexplored field, initiated here and left to future intriguing studies.

Acknowledgement

The research was supported by the Chinese Academy of Sciences President's International Fellowship Initiative Fund (2019VMA0027), the National Natural Science Foundation of China (Grant Nos.11874361, 51672279, 11774354 and 51727806), the CAS Innovation Grant (CXJJ-19-B08), the Science Challenge Project (No.TZ2016001), and the CASHIPS Director's Fund (Grant No. YZJJ201705). We also acknowledge the PRIN project ZAPPING, number 2015HK93L7, granted by the Italian Ministry of Education, Universities and Research, MIUR. MPA acknowledges the support of the European Research Council (ERC) Grant Hecate Ref. No. 695527 and UKRI Future leaders fellowship Mrc-Mr/T043733/1.

Supporting Information Available

The Supporting Information is available free of charge at `https://`

- Experimental and computational methods
- Supplementary GCMC results.
- Supplementary XRD results.
- H_2-H_2 vibrational coupling.
- Supplementary Raman Spectroscopy results

References

(1) Breck, D. W. *Zeolite molecular sieves: structure, chemistry and use*; Krieger, 1984.

(2) Galarneau, A.; Di Renzo, F.; Fajula, F.; Vedrine, J. *Zeolites and mesoporous materials at the dawn of the 21st century: proceedings of the 13th International Zeolite Conference, Montpellier, France, 8-13 July 2001*; Elsevier, 2001.

(3) Auerbach, S.; Carrado, K.; Dutta, P. *Handbook of zeolite science and technology*; Vol. 1170.

(4) Chipera, S. J.; Apps, J. A. Geochemical stability of natural zeolites. *Reviews in Mineralogy and Geochemistry* **2001**, *45*, 117–161.

(5) Hazen, R. Zeolite molecular sieve 4A: anomalous compressibility and volume discontinuities at high pressure. *Science* **1983**, *219*, 1065–1067.

(6) Lee, Y.; Vogt, T.; Hriljac, J. A.; Parise, J. B.; Hanson, J. C.; Kim, S. J. Non-framework cation migration and irreversible pressure-induced hydration in a zeolite. *Nature* **2002**, *420*, 485–489.

(7) Lee, Y.; Hriljac, J. A.; Vogt, T. Pressure-induced argon insertion into an auxetic small pore zeolite. *The Journal of Physical Chemistry C* **2010**, *114*, 6922–6927.

(8) Haines, J.; Cambon, O.; Levelut, C.; Santoro, M.; Gorelli, F.; Garbarino, G. Deactivation of pressure-induced amorphization in silicalite SiO_2 by insertion of guest species. *Journal of the American Chemical Society* **2010**, *132*, 8860–8861.

(9) Lee, Y.; Liu, D.; Seoung, D.; Liu, Z. X.; Kao, C. C.; Vogt, T. Pressure- and Heat-Induced Insertion of CO_2 into an Auxetic Small-Pore Zeolite. *Journal of the American Chemical Society* **2011**, *133*, 1674–1677.

(10) Santoro, M.; Gorelli, F.; Haines, J.; Cambon, O.; Levelut, C.; Garbarino, G. Silicon carbonate phase formed from carbon dioxide and silica under pressure. *Proceedings of the National Academy of Sciences* **2011**, *108*, 7689–7692.

(11) Niwa, K.; Tanaka, T.; Hasegawa, M.; Okada, T.; Yagi, T.; Kikegawa, T. Pressure-induced noble gas insertion into Linde-type A zeolite and its incompressible behaviors at high pressure. *Microporous and Mesoporous Materials* **2013**, *182*, 191–197.

(12) Santoro, M.; Gorelli, F. A.; Bini, R.; Haines, J.; Van Der Lee, A. High-pressure synthesis of a polyethylene/zeolite nano-composite material. *Nature Communications* **2013**, *4*, 1557.

(13) Seoung, D.; Lee, Y.; Cynn, H.; Park, C.; Choi, K.-Y.; Blom, D. A.; Evans, W. J.; Kao, C.-C.; Vogt, T.; Lee, Y. Irreversible xenon insertion into a small-pore zeolite at moderate pressures and temperatures. *Nature Chemistry* **2014**, *6*, 835.

(14) Gatta, G.; Lee, Y. Zeolites at high pressure: A review. *Mineralogical Magazine* **2014**, *78*, 267–291.

(15) Vezzalini, G.; Arletti, R.; Quartieri, S. High-pressure-induced structural changes, amorphization and molecule penetration in MFI microporous materials: a review. *Acta Crystallographica Section B: Structural Science, Crystal Engineering and Materials* **2014**, *70*, 444–451.

(16) Santoro, M.; Dziubek, K.; Scelta, D.; Ceppatelli, M.; Gorelli, F. A.; Bini, R.; Thibaud, J.-M.; Di Renzo, F.; Cambon, O.; Rouquette, J. et al. High Pressure Synthesis of All-Transoid Polycarbonyl [-(C=O)-]$_n$ in a Zeolite. *Chemistry of Materials* **2015**, *27*, 6486–6489.

(17) Scelta, D.; Ceppatelli, M.; Santoro, M.; Bini, R.; Gorelli, F. A.; Perucchi, A.; Mezouar, M.; Van Der Lee, A.; Haines, J. High pressure polymerization in a confined space: conjugated chain/zeolite nanocomposites. *Chemistry of Materials* **2014**, *26*, 2249–2255.

(18) Santoro, M.; Scelta, D.; Dziubek, K.; Ceppatelli, M.; Gorelli, F. A.; Bini, R.; Garbarino, G.; Thibaud, J.-M.; Di Renzo, F.; Cambon, O. et al. Synthesis of 1D polymer/zeolite nanocomposites under high pressure. *Chemistry of Materials* **2016**, *28*, 4065–4071.

(19) Santoro, M.; Gorelli, F. A.; Bini, R.; Haines, J. Intermolecular Interactions in Highly Disordered, Confined Dense N_2. *The Journal of Physical Chemistry Letters* **2017**, *8*, 2406–2411.

(20) Santoro, M.; Veremeienko, V.; Polisi, M.; Fantini, R.; Alabarse, F.; Arletti, R.; Quatieri, S.; Svitlyk, V.; van der Lee, A.; Rouquette, J. et al. Insertion and Confinement of H_2O in Hydrophobic Siliceous Zeolites at High Pressure. *The Journal of Physical Chemistry C* **2019**, *123*, 17432–17439.

(21) Gregoryanz, E.; Ji, C.; Dalladay-Simpson, P.; Li, B.; Howie, R. T.; Mao, H.-K. Everything you always wanted to know about metallic hydrogen but were afraid to ask. *Matter and Radiation at Extremes* **2020**, *5*, 038101.

(22) Hemley, R. J. High-pressure behavior of silica. *Reviews of Mineralogy* **1994**, *29*, 41–81.

(23) Prokopenko, V.; Dubrovinsky, L.; Dmitriev, V.; Weber, H.-P. In situ characterization

of phase transitions in cristobalite under high pressure by Raman spectroscopy and X-ray diffraction. *Journal of Alloys and Compounds* **2001**, *327*, 87–95.

(24) Haines, J.; Léger, J.; Gorelli, F.; Hanfland, M. Crystalline post-quartz phase in silica at high pressure. *Physical Review Letters* **2001**, *87*, 155503.

(25) Bykova, E.; Bykov, M.; Černok, A.; Tidholm, J.; Simak, S. I.; Hellman, O.; Belov, M.; Abrikosov, I. A.; Liermann, H.-P.; Hanfland, M. et al. Metastable silica high pressure polymorphs as structural proxies of deep Earth silicate melts. *Nature Communications* **2018**, *9*, 1–8.

(26) Schaack, S.; Ranieri, U.; Depondt, P.; Gaal, R.; Kuhs, W. F.; Gillet, P.; Finocchi, F.; Bove, L. E. Observation of methane filled hexagonal ice stable up to 150 GPa. *Proceedings of the National Academy of Sciences* **2019**, *116*, 16204–16209.

(27) Tulk, C. A.; Klug, D. D.; Molaison, J. J.; dos Santos, A. M.; Pradhan, N. Structure and stability of an amorphous water–methane mixture produced by cold compression of methane hydrate. *Physical Review B* **2012**, *86*, 054110.

(28) Olson, D.; Kokotailo, G.; Lawton, S.; Meier, W. Crystal structure and structure-related properties of ZSM-5. *The Journal of Physical Chemistry* **1981**, *85*, 2238–2243.

(29) Hay, D. G.; Jaeger, H. Orthorhombic-monoclinic phase changes in ZSM-5 zeolite/silicalite. *Journal of the Chemical Society, Chemical Communications* **1984**, 1433–1433.

(30) *See Supplemental Material [url] for description of experimental and theoretical details and analysis of Results which includes Refs. [30-43]*

(31) Mao, H.; Bell, P.; Shaner, J. t.; Steinberg, D. Specific volume measurements of Cu, Mo, Pd, and Ag and calibration of the ruby R 1 fluorescence pressure gauge from 0.06 to 1 Mbar. *Journal of Applied Physics* **1978**, *49*, 3276–3283.

(32) Akahama, Y.; Kawamura, H. Pressure calibration of diamond anvil Raman gauge to 310 GPa. *Journal of Applied Physics* **2006**, *100*, 043516.

(33) Howie, R. T.; Gregoryanz, E.; Goncharov, A. F. Hydrogen (deuterium) vibron frequency as a pressure comparison gauge at multi-Mbar pressures. *Journal of Applied Physics* **2013**, *114*, 073505.

(34) Prescher, C.; Prakapenka, V. B. DIOPTAS: a program for reduction of two-dimensional X-ray diffraction data and data exploration. *High Pressure Research* **2015**, *35*, 223–230.

(35) Carvajal, J. R. Recent developments of the program FULLPROF, in commission on powder diffraction (IUCr). *Newsletter* **2001**, *26*, 12–19.

(36) Fei, Y.; Ricolleau, A.; Frank, M.; Mibe, K.; Shen, G.; Prakapenka, V. Toward an internally consistent pressure scale. *Proceedings of the National Academy of Sciences* **2007**, *104*, 9182–9186.

(37) Desbiens, N.; Boutin, A.; Demachy, I. Water condensation in hydrophobic silicalite-1 zeolite: a molecular simulation study. *The Journal of Physical Chemistry B* **2005**, *109*, 24071–24076.

(38) Coasne, B.; Galarneau, A.; Di Renzo, F.; Pellenq, R. Intrusion and retraction of fluids in nanopores: effect of morphological heterogeneity. *The Journal of Physical Chemistry C* **2009**, *113*, 1953–1962.

(39) Leachman, J. W.; Jacobsen, R. T.; Penoncello, S.; Lemmon, E. W. Fundamental equations of state for parahydrogen, normal hydrogen, and orthohydrogen. *Journal of Physical and Chemical Reference Data* **2009**, *38*, 721–748.

(40) McCarty, R. D.; Hord, J.; Roder, H. M. *Selected properties of hydrogen (engineering design data)*; US Department of Commerce, National Bureau of Standards, 1981; Vol. 168.

(41) Kunz, O.; Klimeck, R.; Wagner, W.; Jaeschke, M. *The GERG-2004 Wide-Range Reference Equation of State for Natural Gases and Other Mixtures GERG TM15 2007*; VDI-Verlag, 2007.

(42) Darkrim, F.; Levesque, D. Monte Carlo simulations of hydrogen adsorption in single-walled carbon nanotubes. *The Journal of Chemical Physics* **1998**, *109*, 4981–4984.

(43) Desbiens, N.; Demachy, I.; Fuchs, A. H.; Kirsch-Rodeschini, H.; Soulard, M.; Patarin, J. Water condensation in hydrophobic nanopores. *Angewandte Chemie International Edition* **2005**, *44*, 5310–5313.

(44) Garberoglio, G.; Skoulidas, A. I.; Johnson, J. K. Adsorption of gases in metal organic materials: comparison of simulations and experiments. *The Journal of Physical Chemistry B* **2005**, *109*, 13094–13103.

(45) Loveday, J.; Nelmes, R. High-pressure gas hydrates. *Physical Chemistry Chemical Physics* **2008**, *10*, 937–950.

(46) Mao, W. L.; Koh, C. A.; Sloan, E. D. Clathrate hydrates under pressure. *Physics Today* **2007**, *60*, 42–47.

(47) Coasne, B.; Haines, J.; Levelut, C.; Cambon, O.; Santoro, M.; Gorelli, F.; Garbarino, G. Enhanced mechanical strength of zeolites by adsorption of guest molecules. *Physical Chemistry Chemical Physics* **2011**, *13*, 20096–20099.

(48) Kuhs, W. F.; Chazallon, B.; Radaelli, P. G.; Pauer, F. Cage Occupancy and Compressibility of Deuterated N_2-Clathrate Hydrate by Neutron Diffraction. *J. Inclusion Phenom. Mol. Recogn. Chem.* **1997**, *29*, 65–77.

(49) Mao, W. L.; Mao, H. K.; Goncharov, A. F.; Struzhkin, V. V.; Guo, Q. Z.; Hu, J. Z.; Shu, J. F.; Hemley, R. J.; Somayazulu, M.; Zhao, Y. S. Hydrogen Clusters in Clathrate Hydrate. *Science* **2002**, *297*, 2247–2249.

(50) Loubeyre, P.; LeToullec, R.; Pinceaux, J. Raman measurements of the vibrational properties of H_2 as a guest molecule in dense helium, neon, argon, and deuterium systems up to 40 GPa. *Physical Review B* **1992**, *45*, 12844–12553.

(51) Moshary, F.; Chen, N. H.; Silvera, I. F. Pressure dependence of the vibron in H_2, HD, and D_2: Implications for inter-and intramolecular forces. *Physical Review B* **1993**, *48*, 12613–12619.

(52) Hanfland, M.; Hemley, R.; Mao, H.; Williams, G. Synchrotron infrared spectroscopy at megabar pressures: Vibrational dynamics of hydrogen to 180 GPa. *Physical Review Letters* **1992**, *69*, 1129–1132.

(53) Hanfland, M.; Hemley, R. J.; Mao, H.-k. Novel infrared vibron absorption in solid hydrogen at megabar pressures. *Physical Review Letters* **1993**, *70*, 3760–3763.

(54) Peña-Alvarez, M.; Afonina, V.; Dalladay-Simpson, P.; Liu, X.-D.; Howie, R. T.; Cooke, P. I.; Magdau, I. B.; Ackland, G. J.; Gregoryanz, E. Quantitative rotational to librational transition in dense H_2 and D_2. *The Journal of Physical Chemistry Letters* **2020**, *11*, 6626–6631.