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► **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<sub>2</sub> 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-03227604>**

Submitted on 4 Oct 2021

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# High Pressure **Insertion** of Dense H<sub>2</sub> into a Model Zeolite

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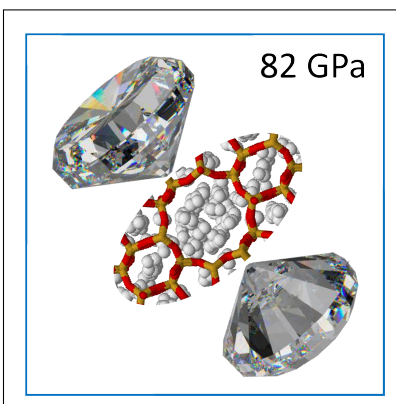
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High pressure, hydrogen, zeolites, Raman spectroscopy, X-ray diffraction, Monte Carlo modelling

### 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  $\text{H}_2$  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  $\text{H}_2$  forms an exotic topologically constrained glassy-like form, otherwise unattainable in pure hydrogen. Raman spectroscopy on confined  $\text{H}_2$  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<sup>1-4</sup> 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<sup>5-20</sup>. 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<sub>2</sub> is a “master” and benchmark system in high pressure sciences.<sup>21</sup> Dense, sub-nano confined states of H<sub>2</sub> 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<sub>2</sub> 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.<sup>22-25</sup> 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<sub>4</sub> filled ice has been found to be stable up to the record pressure of 150 GPa.<sup>26</sup> **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.**<sup>27</sup>

We focused our work on a model, pure SiO<sub>2</sub> 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  $\text{SiO}_4$  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  $\text{H}_2$ ).<sup>28,29</sup> 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  $\text{H}_2$  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.  $\text{H}_2$ -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  $\text{H}_2$ . The number of inserted molecules vs. pressure is non-monotonic with a maximum close to two per  $\text{SiO}_2$  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<sup>30</sup> together with the relevant references.<sup>31–44</sup>

Powder XRD patterns of  $\text{H}_2$ -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  $2\theta$  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  $\text{H}_2$  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).<sup>39–41</sup> Importantly, at the highest pressures, in spite of the increase in line-width, the peaks retained much of their initial integrated intensity (typically

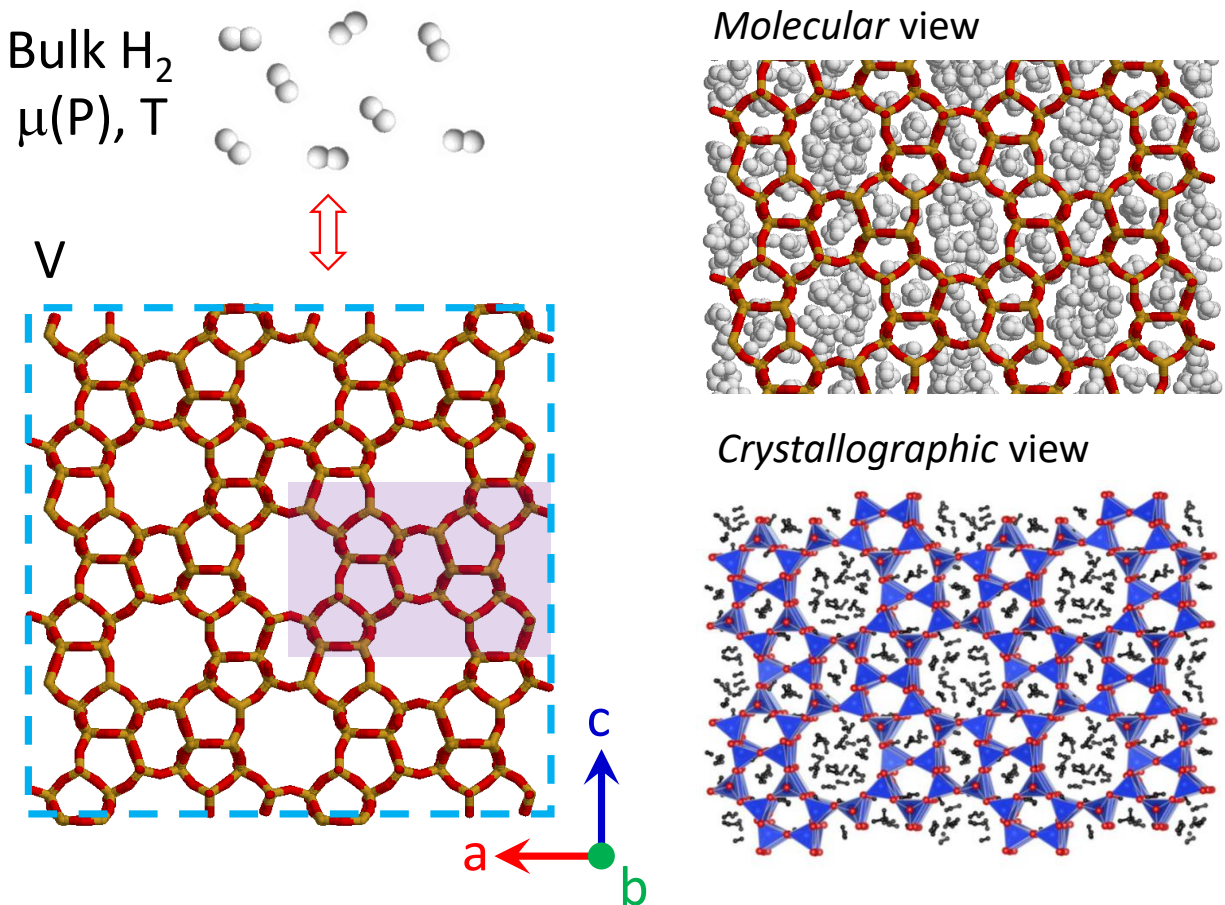


Figure 1: Structure of  $\text{H}_2$ -filled orthorhombic silicalite-1. Left: principles of MC modeling in the Grand Canonical ensemble. Like in real experiments, a zeolite material is set in contact with an infinite reservoir of bulk  $\text{H}_2$ . The purple shaded area denotes the unit cell volume while the blue dashed line indicates the periodic boundary conditions. Right: molecular (top) and crystallographic (bottom) view of  $\text{H}_2$  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  $\text{H}_2$  (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 dumbbells represent the inserted  $\text{H}_2$  molecules. A  $2 \times 2 \times 2$  unit cell is considered here for the sake of clarity.

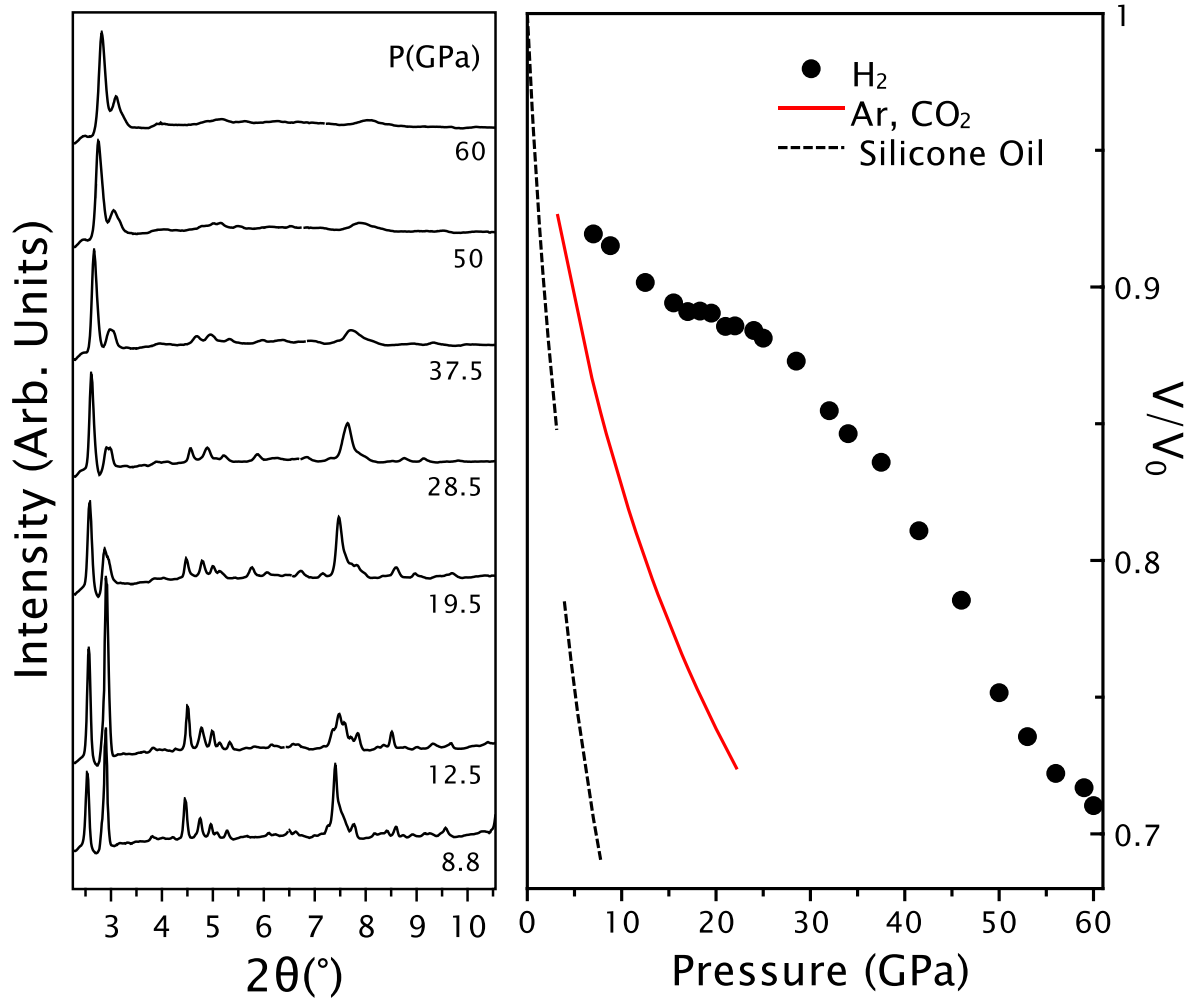


Figure 2: Left panel: Selected powder XRD ( $\lambda = 0.4828 \text{ \AA}$ ) patterns of H<sub>2</sub>-filled silicalite-1, measured upon increasing pressure. A broad Compton scattering background due to air and diamonds has been subtracted. Right panel: experimental pressure behavior for the relative to ambient pressure unit cell volume of H<sub>2</sub>-filled silicalite-1 (filled circles). Error bars are within the size of the circles. Red line: compression curve for Ar and CO<sub>2</sub> filled silicalite-1.<sup>8</sup> Black line: equation of state for silicalite-1, measured in a non-penetrating pressure transmitting medium: silicone oil, where amorphization has been found to occur below 10 GPa.

30-100 %) at low pressure. That suggests that silicalite-1 remains 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<sub>2</sub>-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<sub>2</sub>.<sup>8</sup> The most striking result is the much higher relative volumes of up to 24 % at 25 GPa measured for H<sub>2</sub>-filled silicalite-1 than for Ar or CO<sub>2</sub> filled silicalite-1, clearly indicating that H<sub>2</sub> is much more penetrating than the other two larger systems. Also, the compression curve of H<sub>2</sub>-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<sub>2</sub>, 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> -filled silicalite-1 in the 15-25 GPa pressure interval is now found to be due to H<sub>2</sub>



rapidly entering silicalite-1 to a greater and greater extent upon increasing pressure in this range; here, the filling of H<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>-filled silicalite-1 is thus a hydrogen rich material, with H<sub>2</sub> being physisorbed by the zeolite, and an overall pressure dependent chemical composition: SiO<sub>2</sub>(H<sub>2</sub>)<sub>x</sub>, 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.**<sup>45,46</sup>

At least two remarkable differences emerge between H<sub>2</sub>-filled silicalite-1 and the filling of this zeolite with larger simple systems such as Ar and CO<sub>2</sub>.<sup>47</sup> Firstly, the maximum number of confined H<sub>2</sub> molecules exceeds that for bigger molecules by a factor of 3-4. Secondly, H<sub>2</sub> 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<sub>2</sub> 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.**<sup>45,46,48,49</sup> 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<sub>2</sub>, 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<sub>2</sub>-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<sub>2</sub> vibron for H<sub>2</sub> /silicalite-1 samples, measured upon increasing pres-

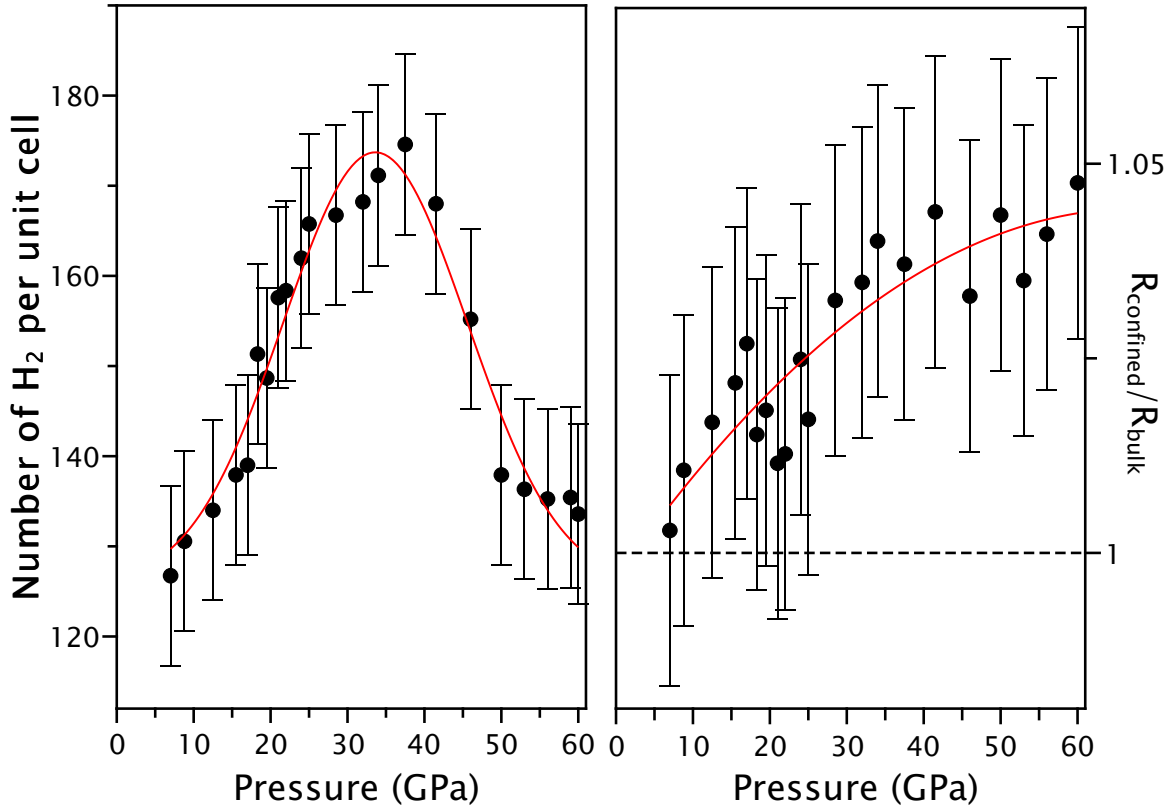


Figure 3: MC calculated pressure behavior of the number of inserted H<sub>2</sub> molecules in silicalite-1 (left) and of the ratio of the nearest neighbor's H<sub>2</sub>-H<sub>2</sub> distance for confined hydrogen to that of bulk hydrogen (right). Error bars are due to the simulation and to the evaluation method of the average distances. Red lines through the points are guides for the eye.

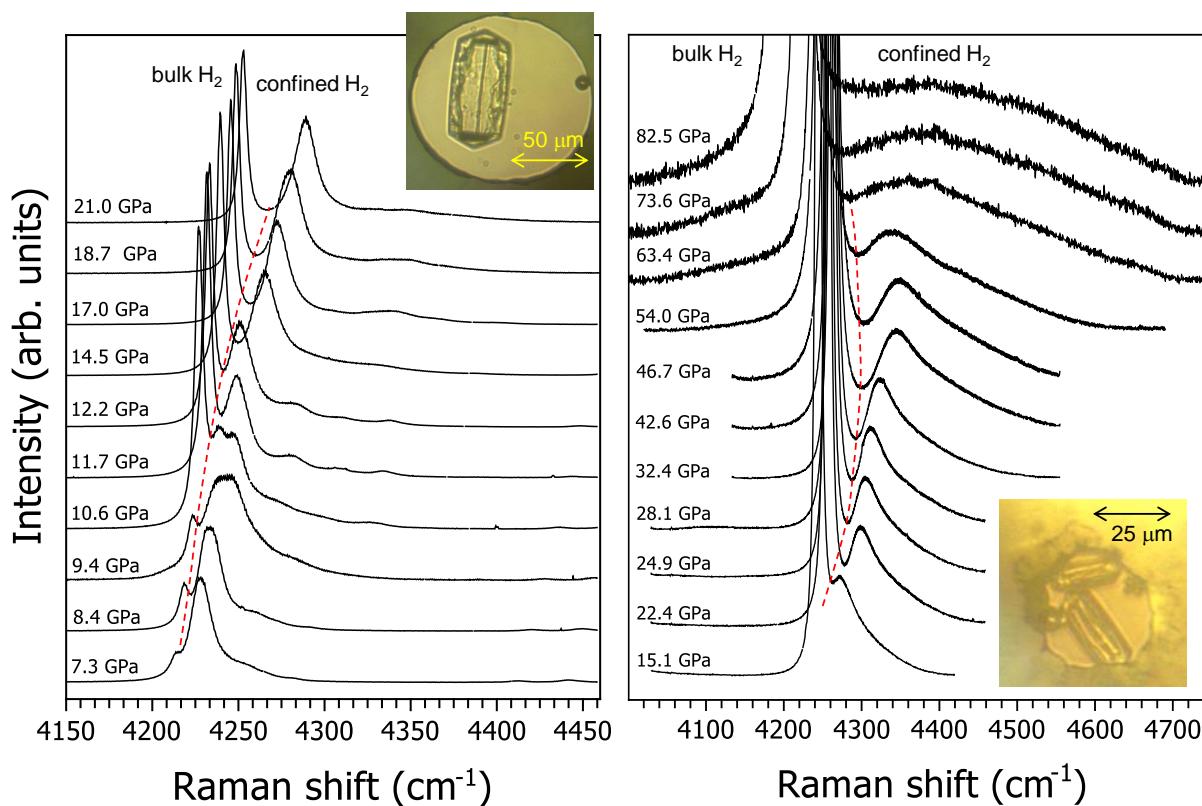


Figure 4: Selected Raman spectra of H<sub>2</sub>-filled silicalite-1 crystals in the frequency range of the H<sub>2</sub> vibron, measured upon increasing pressure. Left (right) panel: spectra measured on top of a silicalite-1 crystal of 80 × 40 × 40 μm<sup>3</sup> (30 × 15 × 15 μm<sup>3</sup>) initial size. Red dashed lines separate the bulk and the confined H<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> peak due to bulk hydrogen layers surrounding the crystals and several blue shifted extra peaks which can be easily attributed to confined dense H<sub>2</sub>. 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> is indeed found to be in a glassy-like state

In Figure 5, we report the pressure shift of the H<sub>2</sub> frequency for the most intense peak in confined H<sub>2</sub> and for bulk H<sub>2</sub> measured in this work up to 82.5 GPa, and also for isolated H<sub>2</sub> impurities in three crystalline matrices: Ne, Ar and D<sub>2</sub>.<sup>50</sup> The pressure behavior for the confined H<sub>2</sub> frequency is remarkable: it is systematically higher than that of the Raman frequency for pure H<sub>2</sub> and, more importantly, in both cases we observe a maximum, which is located at around 50 GPa in confined H<sub>2</sub> and 35 GPa in pure H<sub>2</sub>. 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<sub>2</sub> frequency for confined hydrogen can be easily traced back to the H<sub>2</sub>-H<sub>2</sub> vibrational coupling<sup>50-53</sup> (and references therein. See also SM). The Raman frequency being blue shifted in confined H<sub>2</sub> and the maximum being at higher pressures with respect to bulk H<sub>2</sub> 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<sub>2</sub> neighbors. An extreme case in this respect is that of

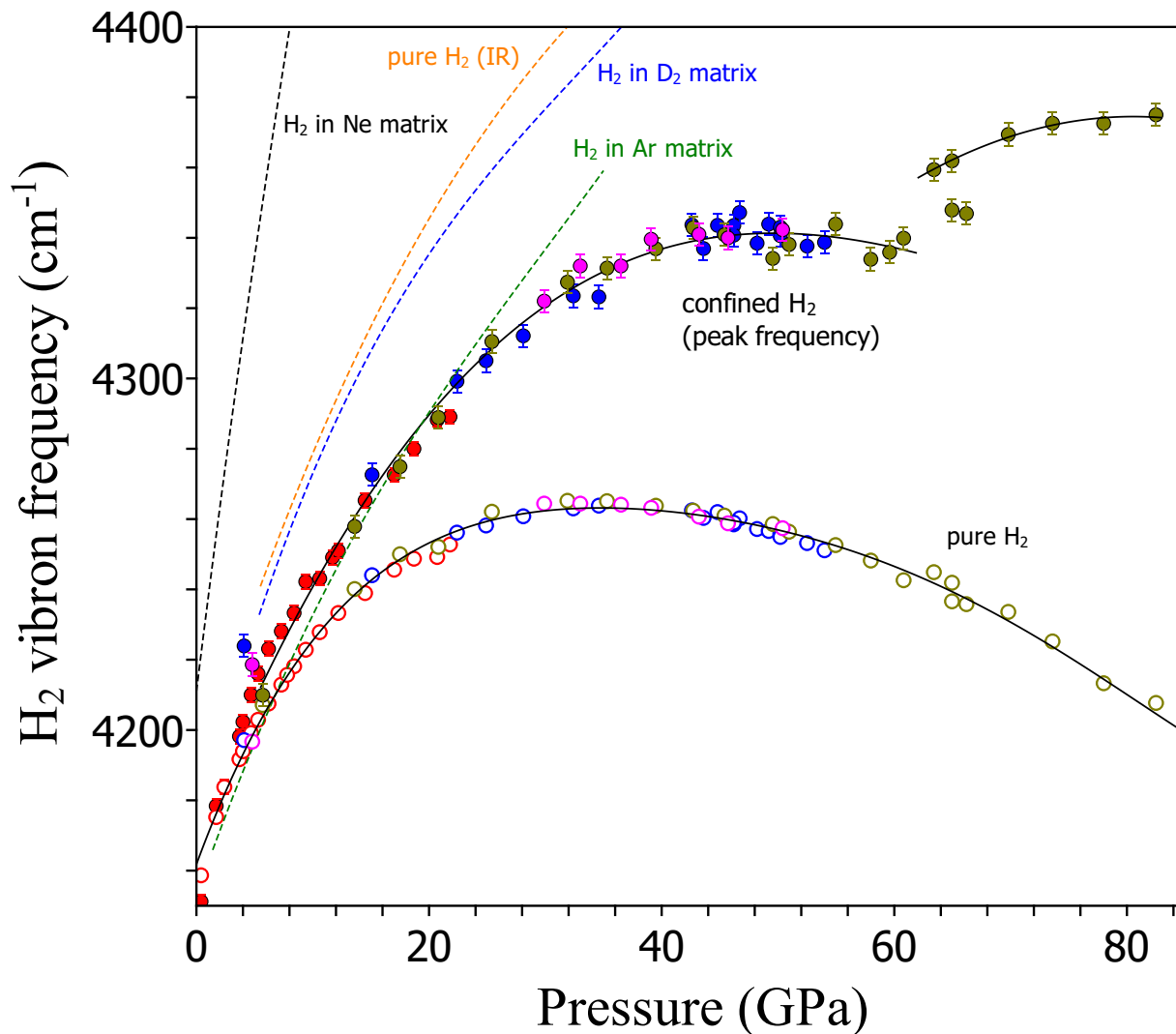


Figure 5:  $\text{H}_2$  frequency vs. pressure for different materials and compounds. Full and open dots: this work, values for confined in silicalite-1 and bulk  $\text{H}_2$ , respectively (see text for details). Black lines: guides for an eye through these two data sets. Error bars are mainly due to the fitting procedure of peaks for confined  $\text{H}_2$ . Other lines: pressure shift for  $\text{H}_2$  as a single molecule impurity in Ne (black),  $\text{D}_2$  (blue) and Ar (green) matrix, respectively.<sup>50</sup> Orange line: pressure shift for the IR active  $\text{H}_2$  frequency in pure hydrogen.<sup>51-53</sup>

molecules in the cages of silicalite-1, where the number of H<sub>2</sub> 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)<sup>39-41</sup> show that confined H<sub>2</sub> is a near free rotor, the rotations of which are somewhat more hindered than for pure hydrogen.<sup>54</sup>

Our investigation uncovered an exotic form of dense hydrogen **inserted** in a zeolite. Which is the Mbar/multi-Mbar fate of H<sub>2</sub>-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<sub>2</sub>-H<sub>2</sub> vibrational coupling.
- Supplementary Raman Spectroscopy results

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