

# Chemically Assisted Precompression of Hydrogen Molecules in Alkaline-Earth Tetrahydrides

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experimental results indicate that the larger the host cation, the longer the  $H_2^{\delta-}$  bond. Analysis of the electron localization function (ELF) demonstrates that the lengthening of the H–H bond is caused by the charge transfer from the metal to  $H_2^{\delta-}$  and by the steric effect of the metal host on the H–H bond. This effect is most

prominent for BaH<sub>4</sub>, where the precompression of  $H_2^{\delta-}$  units at 50 GPa results in bond lengths comparable to that of pure H<sub>2</sub> above 275 GPa.

 $^{\intercal}$ he application of high pressure provides a mechanical route to break covalent bonds and obtain otherwise unachievable chemical states. Hydrogen is the archetypal example: the 1935 prediction of a molecular-atomic transition at extreme compression has inspired decades of experimental research.<sup>1-6</sup> Current data suggests that hydrogen still retains its molecular bond up to pressures of at least 360 GPa,<sup>7-9</sup> pushing the limits of conventional diamond anvil cell experiments. Chemical dopants can assist in the dissociation of quasi-molecular H<sub>2</sub> units by two mechanisms: electronic effects (charge transfer) and confining the molecule to small interstitial locations, the so-called chemical precompression.<sup>10-12</sup> This principle has been extensively used in the production of high temperature superconducting hydrides.<sup>13,14</sup> However, an understanding of the mechanisms involved in H<sub>2</sub> precompression and how the H<sub>2</sub> bonding distances are adjusted by chemical doping have yet to be achieved. In the majority of diamond anvil cell studies reporting the synthesis of metal hydrides, usually only the structure of the host metal can be experimentally determined. This is due to the comparatively weaker X-ray scattering of hydrogen and to the fact that the synthesis conditions of many interesting hydride candidates cannot be routinely reached in neutron diffraction studies. As such, often important information, such as the hydrogen content and the interatomic hydrogen distances, is reliant on theoretical calculations.<sup>15–17</sup> If the hydride contains H<sub>2</sub> units, then Raman spectroscopy can be an efficient method to investigate the high pressure response of the H-H distances of the molecules. Out of the many known

binary metal-hydrogen compounds (group I to XVII), only sodium trihydride and calcium tetrahydride are known to host quasi-molecular hydrogen.<sup>18–20</sup> In these cases, the Raman frequency of the H–H stretching mode (vibron) exhibits a downshift compared to pure molecular hydrogen, and this is related to a lengthening of the bond.

The alkaline-earth metals, except for radium, react readily with hydrogen, forming binary hydrides, MH<sub>2</sub> (M = alkalineearth metal).<sup>21</sup> CaH<sub>2</sub>, SrH<sub>2</sub>, and BaH<sub>2</sub> undergo the same structural phase sequence on compression, from the cotunnite structure (*Pnma*, phase I),<sup>22–25</sup> to the hexagonal Ni<sub>2</sub>In structure (*P6*<sub>3</sub>/*mmc*, phase II). A further transition to an AlB<sub>2</sub>-type structure (P6/*mmm*, phase III), has been experimentally observed in BaH<sub>2</sub>.<sup>21,23,24,26</sup> The structural transitions of the dihydrides are shifted to lower pressures for the heavier alkaline earth metals; e.g., phase III of CaH<sub>2</sub> is predicted at 180 GPa, while phase III of BaH<sub>2</sub> is observed between 40 and 50 GPa.<sup>21–26</sup>

Through a combination of both high temperature and high pressure, interesting compositions were observed in the alkaline-earth-metal-hydrogen system. Superconducting CaH<sub>6</sub> was produced at pressures greater than 160 GPa.<sup>27,28</sup>

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**Figure 1.** (a) Representative X-ray diffraction patterns of the alkaline-earth tetrahydrides. Tick marks indicate Bragg peaks from the labeled phases. CaH<sub>4</sub>, SrH<sub>4</sub>, and BaH<sub>4</sub> are refined to tetragonal *I*4/*mmm* at 52, 44, and 45 GPa, respectively. Upon decompression, *I*4/*mmm* BaH<sub>4</sub> (and Ba<sub>8</sub>H<sub>46</sub>)<sup>30</sup> undergoes a phase transition to  $Fm\overline{3}m$  BaH<sub>4</sub>. (b) Volume per alkaline-earth atom as a function of pressure. Filled symbols correspond to this work, CaH<sub>4</sub> (brown circles), SrH<sub>4</sub> (green diamonds), *I*4/*mmm* BaH<sub>4</sub> (dark blue squares), and  $Fm\overline{3}m$  BaH<sub>4</sub> (light blue squares). Brown crosses and brown asterisks correspond to CaH<sub>4</sub> from Wu et al.<sup>19</sup> and Mishra et al.,<sup>20</sup> respectively. The open green square is the predicted value of SrH<sub>4</sub> by Hooper et al.<sup>32</sup> The other open symbols correspond to our DFT calculated volumes. (c) *c/a* ratio as a function of pressure for the *I*4/*mmm* structural types.

Strontium polyhydrides have been reported above 70 GPa with a range of stoichiometries:  $SrH_{22}$ ,  $SrH_9$ ,  $Sr_8H_{46}$ ,  $SrH_6$ ,  $Sr_3H_{13}$ , and  $Sr_2H_3$ .<sup>29</sup> Barium polyhydrides have also emerged, with  $Ba_8H_{46}$  at 50 GPa<sup>30</sup> and  $BaH_{10}$ ,  $BaH_6$ ,  $BaH_{21-23}$ , and  $BaH_{12}$  all above 90 GPa.<sup>31</sup>

Here, we synthesize  $CaH_4$ ,  $SrH_4$ , and  $BaH_4$  in a series of diamond anvil cell experiments and study the influence that the metal host has on the  $H_2$  bond. While a combination of both temperature and pressure are required to transform the  $H_2$ 

embedded dihydrides into CaH<sub>4</sub> (50 GPa, 1600 K) and SrH<sub>4</sub> (40 GPa, 1600 K), BaH<sub>4</sub> is formed on room temperature compression alone above 40 GPa. Synchrotron X-ray diffraction measurements of all three compounds revealed isostructural phases adopting I4/mmm symmetry. However, I4/mmm BaH<sub>4</sub> appears as a metastable intermediate phase: both temperature and time lead to a transformation to the theoretically stable Ba<sub>8</sub>H<sub>46</sub>, while  $Fm\overline{3}m$  BaH<sub>4</sub> forms upon decompression. All of the tetrahydrides share common Raman



**Figure 2.** (a) Top: ELF isosurfaces (ELF = 0.44, 0.38, 0.30) for the pure *I4/mmm* M sublattices (M = Ca, Sr, Ba) of MH<sub>4</sub> at 50 GPa (in yellow). Ca, Sr, and Ba atoms are represented as purple, green, and blue spheres, respectively. The ELF values at the octahedral and tetrahedral maxima in Ba (0.477, 0.318) are similar to and lower than those of Ca (0.794, 0.472) and Sr (0.705, 0.406). Bottom: Conventional unit cell of *I4/mmm* MH<sub>4</sub>. (b) Top: ELF isosurfaces (ELF = 0.36) (in yellow) of the *Fm*3*m* Ba sublattice at 10 GPa. The ELF values at the octahedral and tetrahedral maxima are 0.653 and 0.384, respectively. Bottom: crystal structure of R3m BaH<sub>4</sub> at 10 GPa. To analyze the experimental *Fm*3*m*, BaH the R3m space group is used. R3m BaH<sub>4</sub> appears as the most stable in calculations at low pressures, and would correspond to *Fm*3*m* but with orientationally ordered H<sub>2</sub> molecules.

signatures indicating the presence of  $H_2^{\delta-}$  units within the metallic lattice. There is a more pronounced downshift of the  $H_2^{\delta-}$  vibrational Raman frequency with increasing size of the alkaline earth cation, and this can be related to an increase in the H–H intramolecular distance. Electron localization function (ELF) calculations suggest that at a given pressure, the radius of the ELF basin around the  $H_2^{\delta-}$  molecule becomes smaller with increasing atomic number of the alkaline earth cation, causing the lengthening of the  $H_2^{\delta-}$  intramolecular bond. As a result, the intramolecular hydrogen bond lengths of the alkaline-earth tetrahydrides at relatively low pressure (20– 50 GPa), are comparable to those of ultradense elemental hydrogen at 220–275 GPa.

Elemental Ca (99.9%, Alfa Aesar), Sr (99.99%, Sigma-Aldrich), and Ba (99%,Sigma-Aldrich) (or BaH<sub>2</sub> (99.5%, ABCR)) were loaded into diamond anvil cells in an argon atmosphere glovebox and subsequently gas loaded with research grade hydrogen (99.9995%) at 0.2 GPa (see Supporting Information for detailed methods). After sample loading, X-ray diffraction measurements indicated that dihydrides (MH<sub>2</sub>) were formed, adopting the Pnma space group. Upon compression, all dihydrides were observed to undergo a phase transformation to  $P6_3/mmc$  space group, with the transition pressures and phase sequences in agreement with the existing literature, Figure S1.<sup>22,23,26</sup> Laser heating  $P6_3/mmc$ CaH<sub>2</sub> in an H<sub>2</sub> atmosphere at 52 GPa to temperatures of 1800 K, yielded the previously reported tetragonal I4/mmm CaH<sub>4</sub>, see Figure 1a (and Figures S1-S4).<sup>19</sup> After laser heating SrH<sub>2</sub> within excess H<sub>2</sub> at a pressure of 44 GPa to temperatures of 1700 K, we observe a complete transformation to I4/mmm SrH<sub>4</sub> upon quench; this phase persisted upon decompression to at least 4 GPa (Figure 1a and Figures S1, S2, S3, and S5).

Both the structure, and the experimentally observed volumes as a function of pressure (Figure 1b), are in good agreement with our own (Tables S1–S4) and previous DFT calculations.<sup>12,32</sup> In a subsequent experimental run, we prepared a sample of Sr embedded in ammonia borane. Ammonia borane can act as a hydrogen source, decomposing at high temperature to produce  $H_2$  and BN.<sup>33</sup> After an initial laser heating at 75 GPa, SrH<sub>2</sub> is formed, and after a subsequent heating, SrH<sub>2</sub> transforms to another compound adopting an  $Fm\overline{3}m$  structure; see Figure S6. We find that the lattice parameters and volumes agree well with those for the recently reported cubic SrH<sub>9</sub>; see Figure S1.<sup>29</sup> Upon decompression, we find that SrH<sub>9</sub> does not decompose to at least 30 GPa.

On room temperature compression of  $BaH_2 + H_2$ , we observe the formation of BaH4 I4/mmm above 40 GPa (Figure 1 and Figures S1-S3 and S5). Although CaH<sub>4</sub> and SrH<sub>4</sub> also adopt an I4/mmm structure, the c/a ratio of 2.17 for  $BaH_4$  is considerably larger than that of either  $SrH_4$  or  $CaH_4$ , where  $c/a \approx 1.6$  (see Figure 1c). In all experiments, the transformation to I4/mmm BaH4 is incomplete, and a considerable fraction of BaH2 was present. Instead of a complete transformation to I4/mmm BaH<sub>4</sub> with time, there is a kinetically sluggish transformation to the documented clathrate type-I  $Pm\overline{3}n$  Ba<sub>8</sub>H<sub>46</sub>. If the I4/mmm BaH<sub>4</sub> sample is laser heated, then there is a complete transformation to Ba<sub>8</sub>H<sub>46</sub>.<sup>30</sup> Upon decompression of either I4/mmm BaH<sub>4</sub> or  $Pm\overline{3}n$ Ba<sub>8</sub>H<sub>46</sub>, a new phase emerges below 27 GPa that can be indexed to an  $Fm\overline{3}m$  structure and is stable to at least 4 GPa (see Figures 1 and S3 and S5). The volume per Ba atom as a function of pressure of the  $Fm\overline{3}m$  structure is similar to that observed for I4/mmm BaH<sub>4</sub>, Figure 1b.

Structural searches using  $AIRSS^{34}$  result in a number of candidate structures for  $BaH_4$  with similar energy (all small



**Figure 3.** Raman spectra of the alkaline-earth tetrahydrides upon decompression: (a)  $CaH_4 + H_2$ , (b)  $SrH_4 + H_2$ , and (c)  $BaH_4 + H_2$ . The  $A_{1g}H_2^{\delta-}$  vibrons are marked with solid diamonds. Solid circles mark the  $E_{2g}H_2^{\delta-}$  libron, while the empty circle indicates the  $E_{2g}$  mode corresponding to an  $H_2$  libron coupled to a  $H^-$  lattice mode observed only in  $BaH_4$ . Crosses and asterisks mark the rotational modes and vibron of excess pure hydrogen, respectively.<sup>3</sup>

bandgap insulators, Figures S7-S9). I4/mmm BaH<sub>4</sub> is always competitive but never stable, while  $R\overline{3}m$  is found to be the most stable structure below 25 GPa. The instability of I4/mmm BaH4 in both DFT and experiments suggest that this is an intermediate phase formed as hydrogen migrates through the Ba lattice. The I4/mmm and  $R\overline{3}m$  predicted structures are subgroups of  $Fm\overline{3}m$  in which the symmetrybreaking is generated by the orientation of the H<sub>2</sub> molecules. In the absence of detectable hydrogen scattering, the XRD pattern can be equally well indexed to either  $R\overline{3}m$  or  $Fm\overline{3}m$ . Starting from the  $R\overline{3}m$  structure, we observe in *ab initio* molecular dynamics calculations that H<sub>2</sub> at 300 K went through a number of reorientation transitions on a picosecond time scale. Such reorientations indicate that BaH<sub>4</sub> will have  $Fm\overline{3}m$  symmetry at 300 K, with rotationally disordered H<sub>2</sub><sup> $\delta$ -</sup> molecules.

To investigate the bonding, we study the ELF.<sup>35</sup> Free electrons have an ELF value close to 0.5, while higher ELF values indicate that the electrons are localized, e.g., covalent bonds, lone pairs, and atomic shells.<sup>35</sup> For the empty *I*4/*mmm* Ca/Sr/Ba structures, we identify two ELF maxima types, one centered on the 2*b* sites and elongated along the *c* axis (pseudo-octahedral interstices, Figures 2 and S10) and another type with smaller ELF/volume located on the 4*d* sites, occupying tetrahedral interstices (Figures 2 and S10). The  $Fm\overline{3}m$  Ba ELF topology is equivalent to that of *I*4/*mmm* Ba: octahedral ELF maxima with higher ELF values and tetrahedral

sites of smaller ELF, Figures 2b and S10. The octahedral maxima of the metallic lattices correspond to the sites hosting the  $H_2^{\delta-}$  molecules in the tetrahydrides, and the tetrahedral maxima to the sites hosting the H<sup>-</sup> anions (Table S5). In  $Fm\overline{3}m$ -Ba and in I4/mmm-Ca/Sr the octahedral maxima are almost twice as high as for the tetrahedral ones, showing that these are good sites to localize electrons. However, I4/mmm Ba has a lower ELF at the octahedral site, with a value almost as low as the tetrahedral site, suggesting that the  $H_2^{\delta-}$  units are unfavorable; see Table S5. Indeed experimentally, over time, the I4/mmm BaH<sub>4</sub> structure transforms to Ba<sub>8</sub>H<sub>46</sub>, <sup>30</sup> which has only tetrahedral sites, and to  $Fm\overline{3}m$  BaH<sub>4</sub> in decompression, where the high-ELF octahedral site is more favorable for a molecular hydrogen unit.

All of the alkaline-earth tetrahydrides exhibit intense Raman activity, (see Table S6 for DFPT predictions<sup>37</sup>). Experimentally, we see the double-degenerate  $E_{2g}$  mode between 400 and 1100 cm<sup>-1</sup>), which is attributed to modes associated with the angular degrees of freedom of the  $H_2^{\delta-}$ , referred as libration.<sup>38,39</sup> As seen in Figure 4a for all the tetrahydrides, the  $H_2^{\delta-}$  libration hardens substantially with pressure. Moreover, there is also a strong dependency of the frequency on the host alkaline earth metal atomic number, with Ba exhibiting the highest upshift. Previous works have calculated the effect on the Raman modes of a single  $H_2$  molecule when trapped in cages of various sizes.<sup>38</sup> By this means, compression of the cage leads to an upshift in the libron frequency.<sup>38,39</sup> This agrees well



**Figure 4.** (a) Raman shift as a function of pressure of the  $E_{2g} H_2^{\delta-}$  librational modes. The dotted line is a guide to the eye. (b) Raman shift as a function of pressure of the  $A_{1g} H_2^{\delta-}$  vibron. The dashed line corresponds to pure  $H_{2\nu}^3$  the dotted lines provide a guide to the eye. (c) Intramolecular H–H bond length estimates as a function of pressure. Symbols represent the  $H_2^{\delta-}$  bond lengths (*r*) calculated using the empirical relationship  $\nu r^3$ , where  $\nu$  is the Raman vibrational frequency.<sup>36</sup> The dashed line represents the corresponding values of pure  $H_2$ .<sup>3</sup> Hollow symbols and asterisks correspond to H–H distances obtained from DFT calculations.



**Figure 5.** (a) Charges as a function of pressure based on the ELF topology of the metals ( $M^{x+}$ , x+ is the charge), hydrogen atoms located in the tetrahedral sites ( $H^{y-}$ , y- is the charge) and molecular hydrogen located in the octahedral sites ( $H_2^{\delta-}$ ,  $\delta -$  is the charge). b) Radius of the  $H_2^{\delta-}$  ELF basin along the line joining its middle point and the alkaline-earth metals across the *I*4/*mmm ab* plane, and the octahedral diagonal in  $R\overline{3}m$ . Insert: A metallic atom of the *I*4/*mmm ab* plane corner hosting one  $H_2^{\delta-}$  in the center perpendicular to the plane, blue is for Ba, green for Sr and purple for Ca,  $H_2$  molecule is pink. c) Radius of the  $H_2^{\delta-}$  ELF basin across the *I*4/*mmm c* axis. Insert: *I*4/*mmm c* axis with 2 metallic atoms on the corners hosting one  $H_2^{\delta-}$  ELF basin radius.

with the alkaline-earth tetrahydrides hosting H<sub>2</sub> molecules within octahedral cages, and the libron frequency increases going from larger basin of Ca to the smaller basin of Ba, Figure 2 and Table S5. Both I4/mmm and  $Fm\overline{3}m$  BaH<sub>4</sub> exhibit similar libron Raman frequencies and pressure dependency, which is understandable as in both configurations the H<sub>2</sub> molecules are hosted by octahedral cages. The most intense band, above 3000 cm<sup>-1</sup> (Figure 3), corresponds to the  $A_{1g}$  mode resulting from the H–H intramolecular stretching of the  $H_2^{\delta-}$ , vibron (see Figure 3 and Figure S11).<sup>19,32</sup> The  $H_2^{\delta-}$  vibron frequency and bandwidth depends strongly on the hosting cation. The Raman spectra presented in Figure 3 were measured during decompression of the tetrahydrides (see also Figure S12). At

25 GPa, the intramolecular vibron has a frequency of 3800 cm<sup>-1</sup> for CaH<sub>4</sub>, 3750 cm<sup>-1</sup> for SrH<sub>4</sub>, and 3500 cm<sup>-1</sup> for BaH<sub>4</sub>. The H<sub>2</sub><sup> $\delta$ -</sup> vibron broadens with pressure, an effect observed in pure H<sub>2</sub> and attributed to the reduced lifetime of the molecule.<sup>3</sup> Figure 4b shows the Raman shift of the H<sub>2</sub><sup> $\delta$ -</sup> vibron as a function of pressure together with a comparison with pure H<sub>2</sub>.<sup>3</sup> In all the alkaline-earth tetrahydrides, the H<sub>2</sub><sup> $\delta$ -</sup> vibron softens rapidly in compression, more markedly as the alkaline earth atomic number increases.

When pure molecular hydrogen is compressed to above 30 GPa, there is a turnover in the intramolecular vibron frequency and a lengthening of the H-H bond.40-44 For instance, the H–H bond lengthens from 0.718 at 6 GPa in phase I to 0.84 Å when entering phase IV at 225 GPa,<sup>3,45,46</sup> and this is manifested by a 650 cm<sup>-1</sup> drop in the  $H_2$ - $\nu_1$  frequency.<sup>3</sup> Comparing the  $H_2^{\delta-}$  vibron in the alkaline tetrahydrides with the vibron of pure  $H_2$ - $\nu_1$ , we observe that pressures of only 60 GPa for CaH<sub>4</sub>, 40 GPa for SrH<sub>4</sub> and 20 GPa for BaH<sub>4</sub> are sufficient to reach values seen in H<sub>2</sub> at 225 GPa (Phase IV). Using the empirical formula relating the Raman shift of the H-H vibron with the bond lengths (r),  $\nu r^3$  proportional to a constant, and the H-H bond length of pure H<sub>2</sub> at 6 GPa as a reference,<sup>36</sup> we plot the H-H bond lengths as a function of pressure in Figure 4c, together with the bond lengths calculated from our DFT calculations. If the theoretical optimization of the internal coordinates of I4/mmm BaH<sub>4</sub> is constrained to the experimental lattice parameters, the H-H distances are larger (e.g., 2.2% at 50 GPa) but still retain the molecular bond. Even at the lowest pressures reached experimentally in this study, all the tetrahydrides show H-H distances corresponding to those of pure H<sub>2</sub> above 220 GPa. Compared to other metal hydride systems, NaH<sub>3</sub> exhibits a downshift of the  $H_2^{\delta-}$  vibron, at around 4100 cm<sup>-1</sup> in contrast to 4250 cm<sup>-1</sup> in pure  $H_2$  at 50 GPa.<sup>18</sup> This further demonstrates that the effect of H<sub>2</sub> chemical precompression is more pronounced in systems with heavier metallic hosts.

It has been long suggested that electron transfer from an electropositive metal to  $\mathrm{H}_2^{\delta-}$  would contribute to the stretching and weakening of the H–H bond via the population of the  $\sigma^*$ orbitals.<sup>11,12</sup> We have calculated the ELF basin charges and the Bader charges using the Quantum Theory of Atoms in Molecules (QTAIM  $^{47})$  for the different  $\rm MH_4$  theoretically optimized structures, see Figure S13-S15. As shown as a function of pressure in Figure 5a the alkaline earth metal donates electrons to H<sup>-</sup> and H<sub>2</sub><sup> $\delta$ -</sup>. Ca and Sr charges are similar and higher in value than the Ba charge.<sup>48–50</sup> The charge of the hydrogen anion, H<sup>y</sup>, decreases in compression (in absolute numbers-toward neutral charge) regardless of the structure. Within the I4/mmm tetrahydrides, the  $H^{y^-}$  charge is highest (the most negatively charged) in Sr and then decreases for Ca and furthermore for Ba, while  $R\overline{3}m$  BaH<sub>4</sub> is smaller than its tetragonal analogue. Both the positive charge of the metallic cations and the negative charge of the  $H^{y}$  must contribute to the population of the  $\sigma^*$  H<sub>2</sub><sup> $\delta$ -</sup> orbitals, Figure 5a. However, within the I4/mmm structure, the  $H_2^{\delta-}$  of CaH<sub>4</sub> is more negatively charged than that in BaH<sub>4</sub>. Consequently, the experimentally observed longest H-H bond of BaH<sub>4</sub> cannot just be explained by the charge transfer from the metal to the  $\sigma^*$  orbital of H<sub>2</sub><sup> $\delta$ -</sup>.

The topological analysis of the ELF can offer further insight into the chemical origin of the  $H_2^{\delta-}$  frequency downshift and associated bond elongation.<sup>51</sup> In particular, we explore the ELF basin radius of the  $H_2^{\delta-}$  molecule along the line joining its middle point and the alkaline-earth atoms (see Figure 5, parts b and c). The I4/mmm structures have two ELF  $H_2^{\delta-}$  radii to consider because of the pseudo-octahedral metallic coordination, one along the ab plane and one along the c axis (see Figure S10). The  $R\overline{3}m$  (used to model the experimental  $Fm\overline{3}m$  BaH<sub>4</sub>, Figure S10) has only one Ba-to-H<sub>2</sub><sup> $\delta$ -</sup> and therefore only one radius of the ELF basin of the  $H_2^{\delta-}$  molecule along the line joining its middle point in the pseudo-octahedral metallic coordination. This  $R\overline{3}m$  BaH<sub>4</sub> Ba-to-H<sub>2</sub><sup> $\delta$ </sup> distance is longer than the Ba-to- $H_2^{\delta-}$  distance in the I4/mmm ab plane, but shorter than that in the I4/mmm c axis. Consequently, the resultant compression of the  $H_2^{\delta-}$  radius for the six equidistant  $R\overline{3}m$  Ba atoms is longer, justifying the similar Raman downshift of the vibron observed in  $Fm\overline{3}m$  compared to I4/ mmm BaH<sub>4</sub>. Upon compression of the I4/mmm structure, the  $H_2^{\delta-}$  ELF basin radius in the *ab* plane decreases as the alkalineearth atomic number increases (Figure 5b). Similarly, the ELF basin radius of the  $H_2^{\delta-}$  along the *c* axis also decreases upon compression, Figure 5c. We notice that, along the c axis, this distance is longer in  $BaH_4$  than in  $CaH_4$  and  $SrH_4$  (Figure 5b). As shown by the c/a ratio, c axis is not as compressible as a(Figure 1). The shorter  $H_2^{\delta-}$  radius on the *ab* plane can be associated with a higher compression of the metals on that plane. As a result, there is an elongation of the  $H_2^{\delta-}$  bond along the c axis which increases with the atomic number. This correlates with the greater vibron downshift in BaH<sub>4</sub> than for CaH<sub>4</sub>. Within the I4/mmm structures the  $H_2^{\delta-}$  unit lies along the *c* axis. Therefore, the upshift of the libron can be related to the increase in the c/a ratio in compression and with the atomic number of the cation. The larger the steric effect of the metal toward the  $H_2^{\delta-}$ , the more hindered the libration and the more upshifted the libron is.

In summary, our synchrotron X-ray diffraction measurements identify I4/mmm as a common structure adopted by the alkaline earth tetrahydrides, and all contain quasi-molecular hydrogen units within octahedral interstices. Comparison between the Raman spectra of the I4/mmm tetrahydrides demonstrates that the heavier alkaline earth cation causes a more pronounced downshift of the vibron Raman frequency, associated with a lengthening of the molecular hydrogen bond. Through the topological analysis of the ELF we find that the steric effect of the metal on the H-H bond is the dominating factor triggering the H-H bond lengthening. Although BaH<sub>4</sub> has the largest lattice parameters, its  $H_2^{\delta-}$  ELF basin radius toward the alkaline-earth metal is the smallest along the ab plane, so the H<sub>2</sub> is more strongly confined than in Ca or Sr. We propose that the H<sub>2</sub> bond elongation is caused by H<sub>2</sub> confinement in interstitial sites of the metals tearing apart the enclosed  $H_2$  molecule.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.2c02157.

Experimental and theoretical methods, characterization data for all new compounds, including unit-cell parameters, band structures, X-ray diffraction patterns, Raman of  $Fm\overline{3}m$  BaH<sub>4</sub>, and theoretical Raman frequencies, and Bader and ELF topological analyses (PDF)

Transparent Peer Review report available (PDF)

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# Notes

The authors declare no competing financial interest.

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