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# LETTERS

## Identification of the $(H^-)(H_2)_{12}$ Hydride Anion Cluster in Solid Hydrogen

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Pulsed-laser ablation of metals with normal hydrogen [deuterium] condensing at 3.5 K produces a strong 3972.0 [2869.8] $cm^{-1}$ absorption the same as high energy irradiation of solid hydrogen [deuterium]. New experimental observations and quantum chemical calculations show that these charge centers are $(H^-)(H_2)_n$ $[(D^-)(D_2)_n]$ anion clusters, which have not been observed in the gas phase and are unique to solid hydrogen. First, doping our $H_2$ $[D_2]$ samples with $CCl_4$, a very efficient electron scavenger, replaces the above absorptions with new 4067.0 [2925.6] $cm^{-1}$ bands, which are due to the $(Cl^-)(H_2)_n$ $[(Cl^-)(D_2)_n]$ anion clusters. Second, $(H^-)(H_2)_n$ is destroyed by $\lambda > 290$ nm but restored with 193 nm radiation through photoionization of metal atoms to produce electrons for capture by H atoms. Third, model MP2 calculations for $(H^-)(H_2)_6$ with the $D_{6h}$ structure, which is a contracted portion of the solid hydrogen lattice, strongly supports these new assignments and suggests that the complex has the same coordination number 12 as the hydrogen lattice. Thus, $(H^-)(H_2)_{12}$ cluster anions are characterized in the solid hydrogen microcrystal.

Hydrogen is the most abundant element in the universe, and atomic hydrogen, namely, a bound proton and electron, is most fundamental to physics and chemistry.[1] In hydrogen discharges many $H_2$ molecules are broken apart, and the H atoms and $H^+$ and $e^-$ particles form the small proton cluster $H_3^+$ and the $H^-$ anion. Continuous absorption by the $H^-$ anion is thought to be responsible for opacity in the solar photosphere.[2] The important triangular $H_3^+$ cation has been observed in early laboratory studies and in the interstellar medium.[3−5] As the pressure increases $(H_3^+)(H_2)_n$ clusters are produced and mass spectra show particular stability for the $(H_3^+)(H_2)_3$ and $(H_3^+)(H_2)_6$ ions, but even mass number cations have much smaller intensities than odd masses.[6,7] The early $H_n^+$ mass spectroscopy has been reviewed, and structures have been calculated for the important protonated hydrogen clusters $H_3^+$, $H_5^+$, $H_7^+$, and $H_9^+$ (i.e., $(H_3^+)(H_2)_3$).[8] Several $(H_3^+)(H_2)_n$ cluster cations have been observed through infrared photodissociation spectroscopy,[9] but the negative $(H^-)(H_2)_n$ clusters have not been identified.

The $H_3^-$ anion has been observed very recently in a discharge plasma.[10] Computations have found $H_3^-$ to be thermodynamically stable with the 1.1 kcal/mol well depth and 0.2 kcal/mol anharmonic calculated zero-point dissociation energy.[11,12] Because the larger $(H^-)(H_2)_2$ anion is calculated to be bound by about 3 kcal/mol,[13] continued cluster growth is straightforward. Very recent B3LYP calculations show decreasing $H^-{-}H_2$ distances and increasing average binding energies for $(H^-)(H_2)_n$ clusters, $n = 2, 3, 4$.[14] Thus, $H^-$ can nucleate the growth of larger $(H^-)(H_2)_n$ clusters, which may be involved in interstellar chemistry, as the clustering of cold hydrogen gas to protons has been suggested in the interstellar medium.[15] What happens to these charged hydrogen clusters at even higher hydrogen densities such as found in solid hydrogen? This is best answered by subjecting solid hydrogen to ionizing radiation.

The first such investigation with solid deuterium containing tritium revealed a new 2867 $cm^{-1}$ absorption produced by $\beta$ emission from tritium.[16] Subsequent work with proton irradiated solid deuterium gave the same infrared band.[17,18] Later Oka and co-workers irradiated solid p-$H_2$ with 3 MeV electrons and $\gamma$-rays and produced several sharp new absorptions near the 4152 $cm^{-1}$ H−H fundamental and stronger bands at 3959 and

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3971 cm$^{-1}$.[19,20] These workers proposed that positive and negative charges formed by irradiation are stabilized as $(H_3^+)(H_2)_n$ cation clusters and $(H^-)(H_2)_n$ anion clusters in the solid p-$H_2$ microcrystal host. The stronger bands were attributed to the stretching vibration of p-$H_2$ at the nearest neighbor position to the $H_3^+$ and $H^-$ charges formed by the ionizing radiation, but no isotopic hydrogen experiments were done nor any attempts made to characterize the particular charge centers.

We have performed extensive laser-ablated metal experiments with normal hydrogen condensing into the solid at 3.5 K and observed a photosensitive metal independent absorption at 3972.0 cm$^{-1}$. The laser-ablation plume contains metal atoms, cations, and electrons and sufficient vacuum ultraviolet radiation to produce H, $H^+$, and $e^-$ in these solid hydrogen samples: Similar argon matrix experiments with Cu and $H_2$ produce CuH, $Ar_nH^+$, and $CuH_2^-$ and attest to the initial formation of the fundamental atomic H, $H^+$, and $e^-$ species.[21] We report here new experiments with solid hydrogen and MP2 quantum chemical calculations that identify the 3972.0 cm$^{-1}$ absorption as $(H^-)(H_2)_n$ ($n$ is most likely 12 in the $H_2$ lattice) and provide the first experimental evidence for a hydride anion−dihydrogen cluster. We also offer the new $(Cl^-)(H_2)_n$ cluster absorption at 4067.0 cm$^{-1}$ as a chemical substituent for $(H^-)(H_2)_n$ because the $Cl^-$ anion ($r = 1.81$ Å) is only slightly larger than the $H^-$ anion ($r = 1.54$ Å).[22] The smaller $Cl^-$−HH dimer complex has recently been characterized by a 4004.8 cm$^{-1}$ H−H stretching frequency.[23]

Our basic laser-ablated metal and solid hydrogen experiment has been described previously.[24,25] Briefly laser-ablated metal atoms, cations, electrons, and photons in the vacuum ultraviolet through infrared ranges are co-deposited with normal hydrogen (also $D_2$ and HD) onto a 3.5 K window for transmission infrared spectroscopic examination. The samples are subjected to further irradiation from a filtered medium-pressure mercury arc lamp or an ArF laser and to annealing cycles until the solid evaporates, and more spectra are recorded at each stage in the experiment.

First, the 3972.0 ± 0.5 cm$^{-1}$ absorption has been observed in 30 transition and main group metal laser-ablation experiments with normal hydrogen. Hence, the particular metal has nothing to do with the 3972.0 cm$^{-1}$ absorption, but ablated electrons and ionizing radiation are common to all of these experiments. Second, exposure of these samples to filtered mercury arc radiation revealed a 50% decrease in the 3972.0 cm$^{-1}$ band with $\lambda > 380$ nm, and destruction with $\lambda > 290$ nm radiation. Third, analogous experiments with pure deuterium gave a 2869.8 ± 0.2 cm$^{-1}$ counterpart, which was stable to $\lambda > 380$ nm radiation but destroyed by $\lambda > 290$ nm light from the mercury arc. Fourth, investigations with mixtures of $H_2$ and $D_2$ yielded broader bands at nearly the same frequencies, and pure HD produced an intermediate band at 3478.7 ± 0.3 cm$^{-1}$. Figure 1 compares infrared spectra from four isotopic hydrogen experiments using an aluminum target, which gave the highest product yields. Aluminum has the lowest ionization energy of the metals co-deposited with $H_2$ to date. The observed $H_2/D_2$ frequency ratio, 1.3841, and the intermediate HD frequency, demonstrate that these absorptions are due to H−H [D−D] stretching vibrations. Finally, no other absorptions were observed in these experiments that track photochemically with the above product bands. Hence, the 3972.0 cm$^{-1}$ absorption is due to a species produced by ionizing radiation that has only one type of strong infrared absorbing chromophore.

Identical experiments with gallium in $H_2$ [$D_2$] gave the same strong 3972.0 [2869.8] cm$^{-1}$ absorptions. After complete photobleaching by $\lambda > 290$ and 240 nm radiation, exposure to 193 nm ArF laser radiation formed a weak, broad 3957 cm$^{-1}$ absorption, reproduced 20% of the 2869.8 cm$^{-1}$ absorbance, and restored gallium hydride anion absorptions.[26] Infrared spectra for the Ga and $D_2$ sample are shown in Figure 2. The 2869.8 cm$^{-1}$ band was photobleached with $\lambda > 320$ nm and restored again with 193 nm radiation along with $GaD_4^-$ and $GaD_2^-$ absorptions.[26] However, irradiation of pure solid $D_2$ at 193 nm produced no change in the $D_2$ spectrum and no new absorptions (Figure 2h).

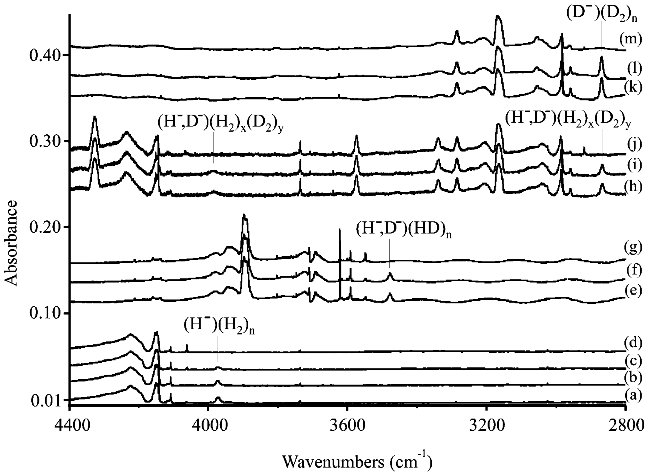

**Figure 1.** Infrared spectra in the 4400−2800 cm$^{-1}$ region for laser-ablated Al codeposited with normal and isotopic hydrogen at 3.5 K: (a) pure $H_2$ and Al deposited; (b) after annealing to 6.2 K; (c) after $\lambda > 380$ nm irradiation; (d) after $\lambda > 290$ nm irradiation; (e) pure HD and Al deposited; (f) after annealing to 6.8 K; (g) after $\lambda > 290$ nm irradiation; (h) $H_2 + D_2$ and Al deposited; (i) after annealing to 6 K; (j) after $\lambda > 380$ nm irradiation; (k) pure $D_2$ and Al deposited; (l) after annealing to 7 K; (m) after $\lambda > 290$ nm irradiation.

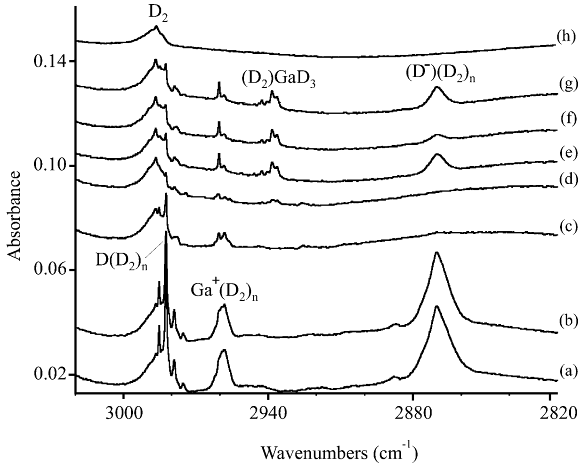

**Figure 2.** Infrared spectra in the 3020−2820 cm$^{-1}$ range for laser-ablated Ga codeposited with deuterium at 3.5 K: (a) pure $D_2$ and Ga deposited; (b) after $\lambda > 380$ nm irradiation; (c) after $\lambda > 290$ nm irradiation; (d) after $\lambda > 240$ irradiation; (e) after 193 nm radiation, 50 mW, 20 min; (f) after $\lambda > 320$ nm irradiation; (g) after second 193 nm irradiation; (h) pure $D_2$ deposited and irradiated by 50 mW at 193 nm for 20 min.

Next, experiments were done with 0.1% $CCl_4$ added to the $H_2$ [$D_2$] samples to serve as an electron trap.[27−29] The 3972.0 [2869.8] cm$^{-1}$ bands are replaced by new 4067.0 [2925.6] cm$^{-1}$ absorptions, which are less photosensitive but ultimately decrease with $\lambda > 240$ nm radiation. The latter $H_2/D_2$ frequency ratio, 1.3901, also characterizes an H−H [D−D] ligand vibration. The same bands were observed with 0.1% $CH_3Cl$ added. Infrared spectra are shown in Figure 3 comparing $D_2$ without

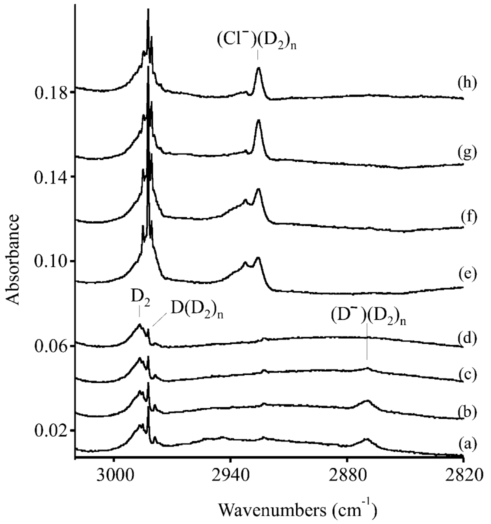

**Figure 3.** Infrared spectra in the 3020−2820 $cm^{-1}$ range for laser-ablated Fe codeposited with deuterium at 3.5 K: (a) pure $D_2$ and Fe deposited; (b) after $\lambda > 380$ nm irradiation; (c) after $\lambda > 320$ nm irradiation; (d) after $\lambda > 290$ irradiation; (e) $D_2$ with 0.1% $CCl_4$ and Fe deposited; (f) after $\lambda > 380$ nm irradiation; (g) after $\lambda > 240$ nm irradiation; (h) after annealing to 8 K.

and with $CCl_4$ using an iron target for the laser ablation. The 2869.8 and 2925.6 $cm^{-1}$ product bands are both stable to $\lambda > 380$ nm radiation, but $\lambda > 290$ nm light destroys the band in pure $D_2$ and increases the band with $CCl_4$ present, and $\lambda > 240$ nm radiation increases, then decreases, and ultimately destroys the latter band. Bands observed in very recent vibrational predissociation spectra of mass-selected $Cl^-$−HH [$Cl^-$−DD] clusters at 4004.8 [2878.5] $cm^{-1}$ ($H_2/D_2$ ratio 1.3913),[23] and the larger clusters[30] $Cl^-{-}(D_2)_2$ at 2887 $cm^{-1}$ and $Cl^-{-}(D_2)_3$ at 2891 $cm^{-1}$, substantiate the assignment of our new 4067.0 [2925.6] $cm^{-1}$ absorptions to the still larger $(Cl^-)(H_2)_n$ [$(Cl^-)(D_2)_n$] anion clusters in solid $H_2$ [$D_2$].

Further experiments were done with aluminum and 0.1% $CH_3Br$ or $CBr_4$ added to the $H_2$ [$D_2$] sample. In this case the above bands are replaced by new absorptions at 4076.0 [2931.5] $cm^{-1}$ for the analogous $(Br^-)(H_2)_n$ [$(Br^-)(D_2)_n$] cluster anions, which are more photosensitive than the chloride complexes. The $H_2/D_2$ frequency ratio 1.3904 also indicates an H−H [D−D] stretching mode. This follows the identification of absorptions by the $Br^-$−HH [$Br^-$−DD] dimers at 4044.5 [2906.9] $cm^{-1}$ in the gas phase.[31]

The restoration of 3972.0 [2869.8] $cm^{-1}$ absorptions in solid $H_2$ [$D_2$] with Ga present using 193 nm radiation provides strong evidence for their identification as anionic species. Following the resonance absorption of Ga in matrix samples,[32] the photoionization of Ga is expected to blue shift in solid hydrogen about 0.4 eV from the 6.0 eV gas-phase value: This makes photoionization of Ga efficient at 193 nm in solid hydrogen and provides electrons for attachment processes. However, 193 nm radiation is not sufficient to ionize hydrogen. In addition, a weak solid $D_2$ absorption is observed at 2986.8 $cm^{-1}$, a strong, sharp 2982.4 $cm^{-1}$ metal independent band is probably due to D atom perturbed $D_2$ in the solid, and the 2960.4 $cm^{-1}$ band, which is photobleached by UV light and restored as a sharp band by 193 nm radiation (Figure 2), is due to a $Ga^+(D_2)_n$ complex. Solid hydrogen counterparts of the latter are observed at 4152.6, 4143.4, and 4108.9 $cm^{-1}$, respectively.

Complementary discharge experiments were performed: Pure hydrogen deposited through a quartz tube and subjected to tesla coil discharge revealed the same 3972 $cm^{-1}$ and sharp 4143.4 $cm^{-1}$ absorptions, and a like treatment of pure deuterium produced the same strong 2870 $cm^{-1}$ and sharp 2982.4 $cm^{-1}$ bands. These observations confirm the absence of metal in the absorbing species.

The significance of replacement of the 3972.0 $cm^{-1}$ hydride band by 4067.0 $cm^{-1}$ absorption for $Cl^-(H_2)_n$ and 4076.0 $cm^{-1}$ absorption for $(Br^-)(H_2)_n$ with added halocarbons is conclusive identification of the 3972.0 $cm^{-1}$ band in the pure $H_2$ system as an anion cluster. We propose that the ablated electrons formerly captured as $H^-$ to make the $(H^-)(H_2)_n$ cluster are preferentially captured as $Cl^-$ to form the $(Cl^-)(H_2)_n$ cluster and as $Br^-$ to form $(Br^-)(H_2)_n$ in solid hydrogen. In aluminum experiments with hydrogen, the $AlH_4^-$ hydride anion is also observed,[25] but with $CCl_4$ present no $AlH_4^-$ is formed because the ablated electrons are captured by $CCl_4$, the $Cl^-$ anion results,[27−29] and the $(Cl^-)(H_2)_n$ complex is formed and trapped. The $Cl^-$−HH and $Cl^-$−DD dimers are observed to photodetach with 299 nm laser radiation,[33] which is in accord with 240 nm photobleaching of our $(Cl^-)(H_2)_n$ [$(Cl^-)(D_2)_n$] clusters.

The 3971 [2867] $cm^{-1}$ absorption from radiation induced centers has consistently been attributed to $H_3^+$ [$D_3^+$] cation centered clusters. Oka et al. associated the 3971 $cm^{-1}$ band to the H−H stretching vibration at the nearest neighbor position to the charges[19] and compare this to the $H_2$ vibrations observed at 3980 $cm^{-1}$ for $H_7^+$ and 4020 $cm^{-1}$ for $H_9^+$ in the gas phase.[9] Poll and co-workers assign their 2867 $cm^{-1}$ absorption to $D_9^+$ where $D_3^+$ Stark shifts the three D−D ligand frequencies,[16−18,34] although $D^-$ anions are probably formed in these solid $D_2$ samples.[35] In both cases the stable $H_9^+$ [$D_9^+$] and higher odd $H_n^+$ [$D_n^+$] cations incorporate the stable $H_3^+$ [$D_3^+$] core following the gas-phase precedent,[8] and this triangular core is a much stronger infrared chromophore than the homonuclear $H_2$ [$D_2$] ligand. Accordingly, if the ligand infrared absorption is observed, then the stronger core absorption must also be observed. But such is not the case.

We believe that $(H_3^+)(H_2)_3$ is a good model for cation centers in solid hydrogen. Our MP2 calculations using the 6-311++G-(3dp, 3df) basis set[36] find structural parameters for this $D_{3h}$ ion comparable to other calculations and predict e′ stretching frequencies at 2495 $cm^{-1}$ ($H_3^+$ core) and 4403 $cm^{-1}$ ($H_2$ ligand) near values from other calculations.[8,37−39] However, the infrared intensity of the antisymmetric $H_3^+$ core mode is 8 times greater than that for the H−H ligand. Earlier SCF and CISD/TZP and recent DFT calculations using the B3(H) functional designed especially for hydrogen systems also compute 8-fold greater infrared intensities for the $H_3^+$ core over the $H_2$ ligands for the odd cations $H_9^+$ through $H_{21}^+$.[37,38] It therefore follows that the 3971 [2867] $cm^{-1}$ bands cannot be assigned to $H_2$ [$D_2$] ligand vibrations in $(H_3^+)(H_2)_n$ [$(D_3^+)(D_2)_n$] clusters because the much stronger $H_3^+$ [$D_3^+$] core absorptions expected in the 2200−2350 [1600−1700] $cm^{-1}$ region were not observed. We find no associated core absorptions for the $H_2$ [$D_2$] ligand bands observed here.

The hydride anion is of appropriate size to occupy a substitutional site in the solid hydrogen hexagonal closest packed (hcp) lattice with a 12 coordination number.[40,41] A good model anion cluster structure is hexagonal $(H^-)(H_2)_6$ with H−H ligands pointing out like the spokes of a wheel. Our MP2 calculation shows that the attraction of six equivalent H−H ligands to $H^-$ in the hexagonal plane is stable by 0.3 kcal/mol with harmonic zero point energy correction. We calculate a very strong $e_{1u}$ H−H stretching mode at 4331 $cm^{-1}$ for $(H^-)(H_2)_6$, which is 192 $cm^{-1}$ below our calculated value for free $H_2$. The 3972 $cm^{-1}$ $(H^-)(H_2)_n$ cluster absorption is a similar 180 $cm^{-1}$ below the induced 4152 $cm^{-1}$ $H_2$ fundamental in solid hydrogen. The

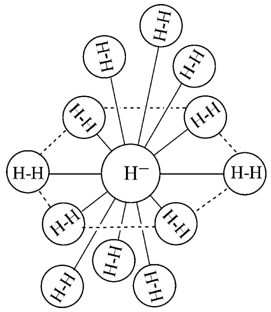

**Figure 4.** Structure proposed for the anion centered $(H^-)(H_2)_n$, $(Cl^-)(H_2)_n$, and $(Br^-)(H_2)_n$ clusters in solid hydrogen.

addition of single $H_2$ molecule caps, $(H^-)(H_2)_6(H_2')_2$, increases the binding energy to 0.5 kcal/mol and shifts the strong ligand mode only 9 $cm^{-1}$ to 4322 $cm^{-1}$. These MP2 calculations support our identification of the $(H^-)(H_2)_n$ cluster. Two $H_2$ molecule trios are needed to complete the hydrogen-lattice type structure, and two orientations of these trios are possible: identical as in the hcp lattice or rotated by 60° as in the cubic lattice. Our calculations cannot discriminate between these two structures, which have $D_{3h}$ and $O_h$ symmetries, respectively. Figure 4 shows the structure proposed for $(H^-)(H_2)_{12}$, which contains the hexagonal $(H^-)(H_2)_6$ "wheel" core and the hcp orientation of six additional H$-$H ligands. This structure fits comfortably into the solid hydrogen lattice, and the $H^- - H_2$ distance decreases about 0.8 Å from the $H_2$ lattice constant. It appears that the guest anion ($H^-$, $Cl^-$, or $Br^-$) is effectively solvated in a substitutional site by the solid hydrogen lattice.

Although hcp crystal structures are common, twelve ligands are uncommon in inorganic chemistry. Cotton et al. illustrate the icosahedral and cuboctahedral structures found in boron chemistry.[42] Here the $(H^-)$ anion coordinates to the $\sigma^*$ orbital of twelve HH ligands in a $D_{3h}$ or $O_h$ complex, which is stabilized by the anion-induced dipole interaction. The continuous near-infrared absorption[2] of gaseous $H^-$ is thus shifted into the near-ultraviolet in the $(H^-)(H_2)_{12}$ complex.

Our laser-ablated metal experiments with solid hydrogen produce a high concentration of H atoms by dissociation. These experiments also produce a much larger number of electrons for capture by H atoms to form $H^-$ than the number of $H^+$ cations from direct photoionization of H atoms owing to the much lower ionization energies of the ablated metal atoms compared to atomic hydrogen. Accordingly, metal cations are the major positive charge and the yield of $H^+$ (and $H_3^+$) cations is much less than the yield of hydride anions in these experiments. Investigations are in progress to prepare and trap the $(H_3^+)(H_2)_n$ cation cluster in solid hydrogen.

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