



Anionic Hydrogen Cluster Ions as a New Form of Condensed Hydrogen

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We report the first experimental observation of negatively charged hydrogen and deuterium cluster ions, H_n^- and D_n^- , where $n \geq 5$. These anions are formed by an electron addition to liquid helium nanodroplets doped with molecular hydrogen or deuterium. The ions are stable for at least the lifetime of the experiment, which is several tens of microseconds. Only anions with odd values of n are detected, and some specific ions show anomalously high abundances. The sizes of these “magic number” ions suggest an icosahedral framework of H_2 (D_2) molecules in solvent shells around a central H^- (D^-) ion. The first three shells, which contain a total of 44 H_2 or D_2 molecules, appear to be solidlike, but thereafter a more liquidlike arrangement of the H_2 (D_2) molecules is adopted.

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The simplest polyatomic anion is H_3^- . Theoretical studies of this ion go back as far as 1937 [1], but it is only through relatively recent high-quality electronic structure calculations that this ion has been shown to be stable [2–4]. The latest calculations reveal a shallow potential energy well which can contain a small number of bound vibrational levels. The dissociation energy from the zero point level of H_3^- is calculated to be only ~ 70 cm^{-1} [4]. The H_3^- ground state is mainly electronically bound, whereas the first excited state of H_3^- is quasistationary [5]. In some regions of the nuclear coordinate space, these two states are coupled nonadiabatically.

Experimental studies of H_3^- have proved challenging. Although the detection of this ion was first reported more than 40 years ago [6,7], the signals were weak, leading to questions about the reliability of the claims [8]. It is only more recently, via experiments in dielectric discharge plasmas, that H_3^- has been observed at an abundance that made firm identification possible [3]. Weak signals from H_3^- and D_3^- have also been detected in secondary-ion mass spectrometry experiments by the sputtering of solid HfH₂ and TiD₂ targets [9].

H_3^- is the smallest member of the group of polyatomic H_n^- cluster anions containing an odd number of hydrogen atoms. The first theoretical study for ions with $n \geq 5$ was carried out by Sapse *et al.* [10], who were partly motivated by the possibility that these ions might be present in the interstellar medium. Sapse *et al.* performed Hartree-Fock calculations with a small basis set. The largest cluster considered was H_{13}^- , and this and all smaller clusters were found to adopt highly symmetric arrangements of H_2 around a central H^- ion. Thus, H_7^- , H_9^- , H_{11}^- , and H_{13}^- showed planar trigonal, tetrahedral, pentagonal bipyramidal, and octahedral arrangements of H_2 molecules around the H^- ion, respectively, whereas H_5^- was calculated to be

linear. In a subsequent study, Hirao and Yamabe [11] employed the configuration interaction method and obtained similar cluster structures to Sapse *et al.* However, in more recent calculations, Huang and Matta have combined density functional theory with harmonic vibrational frequency calculations and found that the highly symmetric structures reported previously were not true minima on their potential energy surfaces [12]. For example, Huang and Matta determined H_5^- to be strongly bent rather than linear. Consequently, there are real doubts about the basic structures of H_n^- ions that need to be resolved, and given that there are no reliable estimates of the actual dissociation energies (D_0) of these clusters, it is not even clear if anions with $n > 3$ are stable.

Here we report the first experimental detection of anionic hydrogen and deuterium clusters larger than H_3^-/D_3^- and have done so for a wide range of cluster sizes. The experimental procedure involved the formation of the corresponding neutral $(H_2)_N$ and $(D_2)_N$ clusters by adding H_2 or D_2 gas to liquid helium nanodroplets. The neutral clusters were cooled to the ambient temperature of the helium nanodroplets, 0.38 K [13], prior to an impact by a beam of electrons with a controlled energy. H_2 and D_2 are heliophilic (have a negative chemical potential when immersed in liquid helium [13]) and so will reside inside the helium droplets rather than on the surface. The helium droplets were then exposed to a beam of electrons, which generated anionic products in the gas phase that were detected by mass spectrometry. The transfer of negative charge to the $(H_2)_n$ and $(D_2)_N$ clusters occurs via a mobile electron bubble, whose formation has a threshold energy in excess of 1 eV in order to inject the electron into the helium conduction band [14]. The droplets used in the present work were relatively large ($\sim 10^6$ helium atoms), and for droplets of this size the electron bubble, although

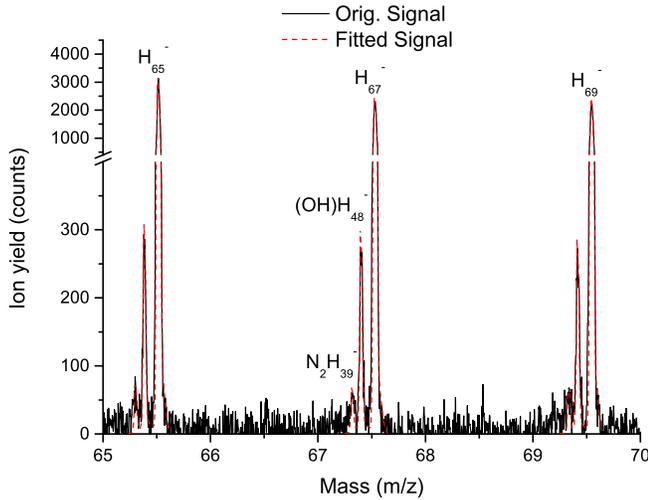
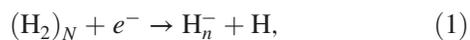


FIG. 1. Section of the mass spectrum recorded for hydrogen cluster anions. The dominant series of ions seen here are from H_n^- , but small quantities of $(H_n)OH^-$ and $(H_n)N_2^-$ are also detected because of trace quantities of water and air in the apparatus. Also shown is a simulation derived from *IsotopeFit* [24], which is used to deconvolute overlapping contributions from different sized clusters and from different isotope combinations. The agreement between the fitted and experimental data is essentially perfect in this region.

metastable, is relatively long-lived and the electron can find and transfer onto the molecular cluster [15].

The anions detected by mass spectrometry consisted of bare H_n^- and D_n^- ions, as seen in the representative mass spectrum for H_n^- shown in Fig. 1. In Figs. 2(a) and 2(b), we show how the abundances of H_n^- and D_n^- vary as a function of n following the addition of electrons at a kinetic energy of 11 eV (the dependence of the cluster ion production on electron energy will be discussed in a subsequent publication). Cluster ions can be observed with n extending well beyond 100. Crucially, only anions with odd n are seen, suggesting that these are produced by dissociative electron attachment to an H_2 or D_2 molecule, which is a well-known process in the gas phase [16–18]. Having formed H^- , this can then combine with the other H_2 molecules in the cluster either by a three-body collision association [3] or via radiative association [4,19]. The latter might lead to the formation of H_3^- anions in the interstellar medium, where a third body is not available, but in a helium droplet a three-body collisional association mechanism is far more likely. The net effect is the formation of a cluster anion via the process



where $n = 2N - 1$. Also possible, but not shown in reaction (1), is the loss of one or more intact H_2 molecules from the cluster as the anion is formed. The observation of only odd n anions shows that the surrounding helium is

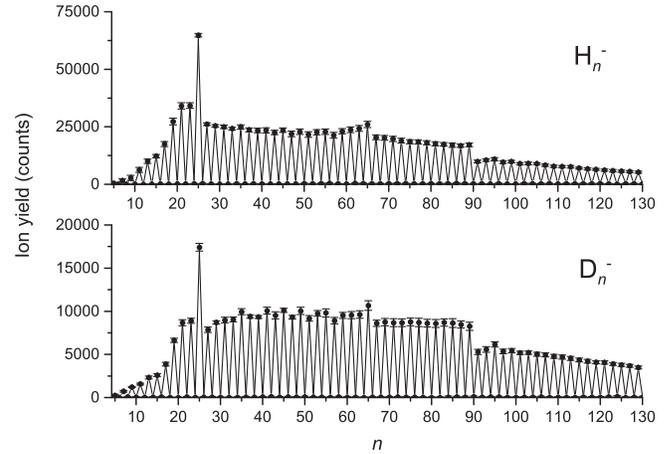


FIG. 2. Plots of the measured ion signal levels for (a) H_n^- and (b) D_n^- as a function of n . The signal levels are expressed as integrated ion counts for a given mass spectral peak.

unable to prevent dissociation of the initially formed transient anion. This is in marked contrast to helium droplet experiments focusing on the cationic clusters, H_n^+ , formed by electron ionization. Although odd n ions overwhelmingly dominate in the gas phase [20], even n ions become significant positively charged products when experiments are carried out in helium nanodroplets [21]. This is presumably because of partial quenching of the initially “hot” ions by the surrounding helium, which thereby stabilizes the even n ions. The absence of even n clusters for the anions is consistent with the very short lifetimes expected for H_2^- and D_2^- (on the order of 10^{-15} s) following an electron attachment to the cold neutral molecule [22,23], although the lifetimes extend into the microsecond regime when the anions are highly rotationally excited [23].

Particularly striking in Fig. 2 are anomalously intense signals at $n = 25, 65,$ and 89 , which are seen equally clearly for hydrogen and deuterium. We associate each of these peaks with cluster ions of increased stability relative to the cluster ions with one additional H_2 or D_2 molecule. These “magic number” ions correspond to 12, 32, and 44 H_2 (D_2) molecules in combination with a hydride (deuteride) anion. In what follows, we explicitly mention only hydrogen, but the same general conclusions also apply to deuterium. The smallest magic anion is consistent with an icosahedral arrangement of 12 H_2 molecules in the first shell around a central H^- core. The larger magic cluster anions can also be interpreted in terms of icosahedral-like structures by analogy with cationic clusters between atomic ions and helium atoms [25]. Thus, the $n = 65$ magic anion can be explained by a second shell of 20 H_2 molecules occupying the 20 triangular faces of a regular icosahedron, generating a dodecahedral arrangement. This is a layer often referred to as an anti-Mackay structure [26,27]. For the $n = 89$ anion, there are a further 12 H_2 molecules

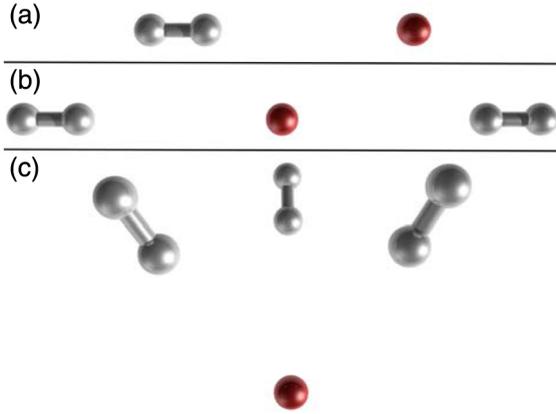


FIG. 3. Calculated equilibrium structures for H_3^- , H_5^- , and H_7^- , which are found to be linear for H_3^- and H_5^- and trigonal pyramidal for H_7^- (C_{3v} point group symmetry). The gray spheres indicate the positions of the nuclei in the hydrogen molecules, whereas the red sphere indicates the position of the nucleus of the atomic hydrogen anion. Detailed information about the structures, including those of the neutral clusters, can be found in Supplemental Material [30], along with other information such as the charge density distributions in the highest occupied molecular orbitals of the anions.

occupying the vertices of the inner shell icosahedron, giving a rhombic tricontahedron structure. This effectively completes a well-defined third solvation shell.

Despite the weak ion-induced dipole binding expected in these anions and the quantum effects that might be derived from the zero point vibrational energy given the light atoms, the observed magic numbers indicate solidlike shell structures that extend out to three complete shells. Bartl *et al.* [25] have recently reported equivalent shells for He_nAr^+ and draw an analogy between icosahedral $He_{12}Ar^+$ and C_{60}^+ , where the coating of the latter by helium leads to a rigid helium layer [28]. It is the corrugations on the C_{60}^+ surface that lead to a rigid helium layer, and the same applies to the helium coating of $He_{12}Ar^+$. $(H_2)_{12}H^-$ presumably behaves in a similar way, and the corrugations on the surface of the cluster may even be enhanced by the anisotropy of the H_2 molecules. Having completed the first three shells around the hydride ion, the addition of further H_2 molecules leads to no other observable magic number features, suggesting that H_2 molecules beyond the third solvation shell have a more liquidlike arrangement.

We can compare our findings for anions with magic number data extracted from a Raman spectroscopic study of neutral $(H_2)_N$ clusters in a free jet expansion [29]. Very weak intermolecular forces are expected between the hydrogen molecules in $(H_2)_N$ clusters, and yet the Raman data seem to imply approximate magic numbers through maxima in the signal levels. These are broad maxima as a function of the cluster size, rather than the sharp features seen in the current study, but they nevertheless seemed to peak near $N = 13$ and 33, with tentative evidence for a third magic

TABLE I. Calculated adiabatic and vertical electron affinities of H, H_3 , H_5 , and H_7 .

Species	AEA/eV	VEA/eV
H^a	0.74	
H_3	0.78	0.77
H_5	0.81	0.81
H_7	0.87	0.69

^aThe experimental value for the electron affinity of atomic hydrogen is 0.75420 ± 0.0002 eV [32].

number near 55. Again, the suggestion is that semirigid structures might form for $(H_2)_N$ clusters, and for the first two shells the magic numbers match our findings for the anions. A magic number of 55 would correspond to the completion of the second layer of an icosahedral structure, but we see no evidence for such a structure in the case of the cluster anions.

The H_n^- and D_n^- must be stable for at least tens of microseconds in order to reach the detector in our experiments. This is consistent with the observations made by Wang *et al.* for H_5^- , whose lifetime was found to be $>8 \mu s$ [3]. The stabilities of these anions must be a reflection of the significant electron affinities of the corresponding neutral clusters. To explore this, we have performed *ab initio* calculations on the three smallest neutral clusters, H_3 , H_5 , and H_7 , and the corresponding anions. Calculations were performed using the MP2 method for full geometry optimization and the CCSD method for the evaluation of the total electronic energies: In both cases, large Gaussian basis sets of quadruple zeta quality were employed, as detailed in Supplemental Material [30,31]. Structures found for the anions are shown in Fig. 3. A number of conclusions can be reached from these calculations. First, H_5^- is found to be linear, which is different from a recent DFT study of small H_n^+ ions [12] but in good agreement with earlier *ab initio* studies of these ions [10,11]. In contrast, we find a trigonal pyramidal structure for H_7^- , which agrees with the aforementioned DFT study and disagrees with the planar trigonal structures predicted in the earlier theoretical work. Second, a simple Mulliken analysis shows that the negative charge is mainly on a single hydrogen atom in all three cluster anions. Finally, we have determined electron affinities of H_3 , H_5 , and H_7 and summarize the findings in Table I. Also shown is the electron affinity of the H atom, which is well known experimentally and provides a confirmation of the good quality of the calculations. The calculated electron affinities of H_3 , H_5 , and H_7 are comparable and significant, suggesting that the corresponding anions would be stable against autodetachment.

In summary, we have made the first observation of H_n^- and D_n^- cluster ions with $n \geq 5$. These anions, which are held together by weak induction forces, can be seen across a wide range of sizes and extend to well beyond $n = 100$ when formed in helium nanodroplets. Furthermore, magic numbers reveal symmetrical, rigid structures for the clusters

extending out to three solvation shells. These experimental observations now open the way to further studies of these rather fundamental cluster anions. Among the things in need of further investigation are the structures of these ions and an assessment of the role of any quantum effects, such as vibrational delocalization and bosonic exchange, on their properties.

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