Experimental and Theoretical Evidence for Long-Lived Molecular Hydrogen Anions ${H_2}^-$ and ${D_2}^-$

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The existence of (metastable) molecular hydrogen anions ${H_2}^-$, ${D_2}^-$, and ${H_3}^-$ is demonstrated. These anion species were produced by sputtering of TiH_2 and TiD_2 targets with Cs^+ ions and were identified by accelerator mass spectrometry. From the respective flight times through the spectrometer, lifetimes for ${H_2}^-$ and ${D_2}^-$ of at least 3 μs and 4 μs, respectively, can be inferred. Theoretical calculations within the nonlocal resonance model predict the existence of highly rotationally excited anions with lifetimes in the μs range. It is proposed that in sputtering molecular hydrogen species with high rotational and vibrational excitation are formed that are stable on the time scale of the experiment.

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Given the ubiquitousness of the hydrogen molecule H_2, the negative ${H_2}^-$ species may easily qualify for being one of the most fundamental and important molecular *anions*. Commonly considered [1,2] too short lived (lifetime $\tau \sim 10^{-15}$ s) to be detected directly, it is nonetheless believed to be rather crucial in various collision processes like dissociative attachment (DA: $e^- + H_2 \rightarrow H + H^-$), associative detachment (AD: $H + H^- \rightarrow H_2 + e^-$), or collision detachment ($H + H^- \rightarrow H + H + e^-$). Apart from their basic importance, these reactions are relevant also in many applications; for example, DA is probably the primary source of H^- ions in hydrogen (deuterium) plasmas from which intense $H^-(D^-)$ ion beams are extracted for use in heating fusion plasmas [3–5]. In astrophysics, it was suggested [6] that AD is responsible for the creation of H_2 in the early stages of the development of the Universe.

Despite several experimental efforts during the past three decades [7–10], the possible existence and the lifetime of the molecular hydrogen anions (${H_2}^-$ and ${D_2}^-$) remained uncertain. The first experimental attempt to detect ${H_2}^-$ was published by Hurley *et al.* [7], using a discharge ion source. Surprisingly, the ${H_2}^-$ ion was reported to be about 5.5 times more abundant than the stable H^- ion, an observation that could not be reproduced later. Aberth *et al.* [8] reported the observation of metastable ($\tau > 10$ μs) HD^-, ${D_2}^-$, D_3^-, and HD_2^- anions at very low intensity levels, but they were unable to detect ${H_2}^-$, ${H_3}^-$, and H_2D^- because of mass interferences; in that work, the anion species were produced in a hollow-cathode duoplasmatron source and analyzed in a combination of a Wien filter and 90° magnetic sector (with a resolution of $m/\Delta m \sim 500$). Later, Bae *et al.* [9] searched for ${H_2}^-$ and ${H_3}^-$ employing a two-step electron capture process, albeit with negative results. Very recently, Wang *et al.* [10] observed ${H_3}^-$ produced in a dielectric-barrier discharge plasma; a three-body collision process was proposed as the dominant formation mechanism. The rather moderate mass resolution of the quadrupole mass analyzer did not allow for an explicit identification of ${H_2}^-$ or ${D_2}^-$ in that experiment.

Theoretical work [2,11] indicated that ${H_2}^-$ is unstable for internuclear separations R close to the equilibrium distance of H_2, $1.4a_0$ (a_0 is the Bohr radius, 0.53 Å) and decays within a few femtoseconds. $H + H^-$ is stable electronically for $R > 3a_0$, but the nuclei can move freely due to an attractive polarization force towards smaller internuclear distances. On the other hand, signatures of narrow resonances were found in calculated $H + H^-$ cross sections for nonzero (high) angular momentum J [11]. No conclusive information on the existence of long-lived quartet spin states is available to our knowledge.

In view of the conflicting previous results, the aim of the present study was the unambiguous verification of the existence of (metastable) ${H_2}^-$ and ${D_2}^-$ anions. The atomic and molecular hydrogen anions were produced by Cs-beam sputtering of suitable target materials (TiH_2 and TiD_2) and detected by means of highly sensitive and selective mass-spectrometric techniques. The experiments were performed at VERA, the Vienna Environmental Research Accelerator. VERA is a facility for accelerator mass spectrometry (AMS) based upon a 3 MV tandem accelerator, manufactured by National Electrostatics Corporation (NEC). Essential to the efficient production of the molecular hydrogen anions seems to be the sputtering ion source. At VERA we use a Middleton-type sputter source [12], a so-called multi-cathode source for negative ions by cesium sputtering (MC-SNICS) in which the target to be sputtered (here TiH_2 or TiD_2) and the surface ionizer producing the Cs^+ sputtering beam (here up to ~0.5 mA with an impact energy of ~5.4 keV) are enclosed in a common chamber containing cesium vapor. Optimal neutral cesium coverage of the sputter target greatly enhances the yield of negative ions [13]. A simplified layout of the VERA AMS facility is shown in Fig. 1; for a more detailed description the reader is referred to [14,15]. AMS allows us to analyze mass-selected, negatively charged molecules by injecting them into a tandem accelerator and breaking them up into their atomic constituents during the stripping process in the high-voltage terminal. The positively charged atomic ions are further accelerated and are again mass analyzed after the accelerator; finally their energy is measured. If all atomic constituents due to the breakup of the same molecule arrive *simultaneously* in the energy detector, an unambiguous identification of the molecule is accomplished (see below). This was first demonstrated in [16]. A detailed description of this detection scheme for molecular anions is given in [17].

Figure 2 shows the spectra in the energy detector when *negative* ions with mass-to-charge ratio $m_0/q_0 \sim -2$ [Fig. 2(a)], $m_0/q_0 \sim -3$ [Fig. 2(b)], or $m_0/q_0 \sim -4$ [Fig. 2(c)] are injected at the low-energy side of the tandem accelerator and the high-energy side is set to detect *positively* charged ions with mass-to-charge ratio $m_1/q_1 \sim +1$ [Figs. 2(a) and 2(b)] or $m_1/q_1 \sim +2$ [Fig. 2(c)]. The significance of these results for proving the existence of H_2^- can be discussed by means of Fig. 2(a). Anions with mass m_0 and charge q_0 are produced from TiH_2 in a sputtering ion source at a voltage U_0 and are accelerated to a kinetic energy $E_0 = U_0 q_0 \sim 70$ keV. At the low-energy side (i.e., before the ions are injected into the tandem), a 45° electrostatic analyzer selects the energy-to-charge ratio, E_0/q_0, and a 90° injector magnet defines m_0/q_0 (actually it defines $E_0/q_0 \times m_0/q_0$, but E_0/q_0 is already fixed by the electrostatic analyzer); here, we cannot separate H_2^- with $m_0 = 2.0156$ amu from D^- with $m_0 = 2.0141$ amu which are both to be expected from regular TiH_2 (natural abundances are 99.9885% and 0.0115% for H and D, respectively). Ion current measurements before injection give about 1.7 nA for $m_0/q_0 \sim -2$ (H_2^- and D^-), compared to about 10 μA for H^-. When injected into the tandem accelerator, both H_2^- and D^- reach an energy $q_0(U_0 + U_T) \sim 1.57$ MeV at the terminal which is at voltage $U_T \sim 1.50$ MV. Here they interact with the stripper gas (O_2, thickness $\sim 10^{17}$ cm^{-2}), lose electrons, and become positively charged. Thus, H_2^- breaks apart into two independent H^+ ions with half the energy, i.e., $\sim$0.785 MeV (generally, a fragment with mass m_1 from a molecule with mass m_0 gets the energy $q_0(U_0 + U_T) \times (m_1/m_0)$ when we neglect Coulomb explosion, i.e., the release of the molecular binding energy). The subsequent acceleration by $U_T \sim 1.50$ MV towards the end of the tandem acts onto the individual H^+ ions with charge q_1, providing each of them the final energy $E_1 = q_0(U_0 + U_T)(m_1/m_0) + q_1 U_T$, i.e., $\sim$2.285 MeV. The D^- anions simply become D^+ in the stripper and thus arrive at $\sim$3.07 MeV. At the high-energy side, a 90° analyzing magnet and a 90° electrostatic analyzer work as the high-energy mass spectrometer that selects $(m_1/q_1) \times (E_1/q_1)$ and (E_1/q_1), respectively, where m_1, q_1, and E_1 denote the mass, the charge, and the energy, respectively, of the ions to be analyzed after the accelerator. So, by setting the high-energy side to the appropriate fields

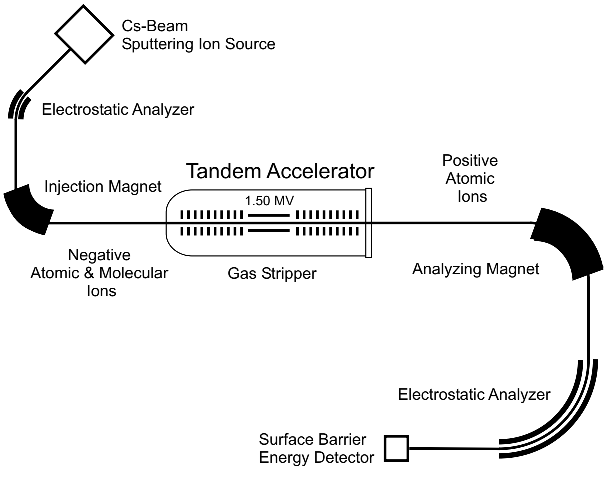

FIG. 1. Schematic layout of the facility for accelerator mass spectrometry. Mass-selected negative ions are injected into the tandem accelerator. After stripping, the emerging positive ions are further analyzed at the high-energy side.

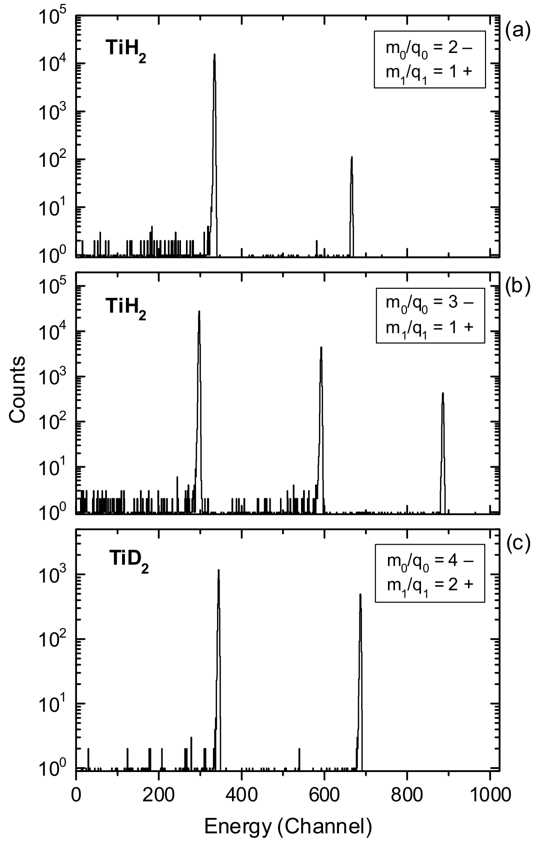

FIG. 2. Energy spectra measured in a surface barrier detector when negative ions with mass-to-charge ratio $m_0/q_0 \sim -2$, H_2^-, and D^- [Fig. 2(a)], or -3, H_3^-, HD^-, and T^- [Fig. 2(b)], or -4, mainly D_2^- [Fig. 2(c)] are injected into the tandem accelerator and the high-energy side is set to detect positively charged ions with mass-to-charge ratio $m_1/q_1 \sim +$, H^+ [Figs. 2(a) and 2(b)], or $+2$, D^+ [Fig. 2(c)].

(largely different for H^+ and D^+), we can easily distinguish what is originating from D^- and what from $H_2{}^-$. Ion current measurements after analysis yield $\sim$1.1 nA for $m_1/q_1 \sim +2$, i.e., D^+ from D^-, and $\sim$0.03 nA for $m_1/q_1 \sim +1$, i.e., H^+ from $H_2{}^-$. Finally, an unambiguous identification of these ions is provided by the energy spectra measured in a surface barrier detector. D^+ gives a single peak at 3.07 MeV. For H^+, however, two peaks appear: one at $E_1 \sim 2.285$ MeV and the second at exactly twice this energy, since there is a significant chance for both H^+ from the breakup of the very same $H_2{}^-$ to reach the detector *simultaneously*. From this data we conclude that at the location of the stripper we have a $H_2{}^-/H^-$ abundance ratio of the order of 10^{-5}. As this value has to be derived from currents measured at the low-energy side and the high-energy side, respectively, a transmission of 30% is assumed (the transmission depends on operating conditions).

The same principles were employed to detect $D_2{}^-$ by sputtering a TiD_2 target highly enriched in D; cf. Fig. 2(c). In this case, the low-energy side is set to $m_0/q_0 \sim -4$, while positive ions with $m_1/q_1 \sim +2$ are detected at the high-energy side. The two peaks seen in the energy spectrum of the surface barrier detector [Fig. 2(c)] prove the arrival of $D_2{}^-$ molecular anions at the stripper. For the injected current at the low-energy side we measure $\sim$0.11 nA, the analyzed current at the high-energy side, a mixture of $1 \times D^+$ and $2 \times D^+$, is $\sim$0.13 nA. As the injected current is mostly $D_2{}^-$, we can calculate the $D_2{}^-/D^-$ ratio from the measured low-energy data: $D_2{}^-/D^-$ is of the order of 2×10^{-5} at the entrance to the accelerator ($D^- \sim 6\ \mu$A).

These experiments demonstrate conclusively that both $H_2{}^-$ and $D_2{}^-$ are formed in the sputtering process; from the respective flight times from the ion source to the tandem terminal stripper, we infer lifetimes of at least 3 μs and 4 μs, respectively. Note that due to the high-energy mass spectrometer, a molecular anion must have reached the stripper *intact* if a positive fragment has passed through to the detector. The flight times include the various stages of acceleration except the very first step after sputtering. Independent from the AMS measurements, $H_2{}^-$ and $D_2{}^-$ anions were recently also detected by one of the authors (H. G.) in a conventional secondary-ion mass spectrometer operated at sufficiently high mass resolution ($m/\Delta m \sim 1500$) to separate $H_2{}^-$ from D^-. This will enable us to do further studies on abundance ratios, lifetimes, etc.

In the course of the measurements, other diatomic and triatomic molecular hydrogen anions, e.g., HD^-, $H_3{}^-$, H_2D^-, and D_3^- were observed, too. While details of these results will not be discussed here, one spectrum is shown in Fig. 2(b). Setting the low-energy side to $m_0/q_0 \sim -3$ (which might be $H_3{}^-$, HD^-, or T^-) and selecting $m_1/q_1 \sim +1$, i.e., H^+ for detection, we clearly get three peaks due to the three H^+ ions originating from $H_3{}^-$ anions.

In the following we discuss theoretical results related to the origin of $H_2{}^-$ ions. It is well known that the interaction of low-energy electrons with the H_2 molecule is dominated by a so-called shape resonance of ${}^2\Sigma_u^+$ symmetry [18] which is of a very short lifetime of the order of 10^{-15} s. To substantiate the obtained experimental results we will show here that for highly rotationally excited hydrogen molecules this resonance generates a series of states with a lifetime of the order of 10^{-6} s. In the nonlocal resonance model [2,11] the nuclear dynamics of the transient anion is governed by the effective Hamiltonian

$$H_{\mathrm{eff}} = T_N + V_d(R) + \int V_{d\varepsilon}(R) \times [E - \varepsilon - T_N - V_0(R) + i0]^{-1} V^*_{d\varepsilon}(R) d\varepsilon, \qquad (1)$$

where $V_d(R)$ is the potential-energy function of the transient state, $V_0(R)$ is the potential of the neutral molecule, and T_N is the kinetic energy of nuclei. The integral term is the non-Hermitian nonlocal potential responsible for autodetachment of the transient anion. The magnitude of the autodetachment width $\Gamma \equiv 2\pi|V_{d\varepsilon}(R)|^2$ is of the order of eV for $R < 3a_0$. Since the potential $V_d(R)$ is attractive for $R > 2a_0$ (see, e.g., [11]), the nuclear wave function has a large amplitude in the autodetachment region, which leads to a fast decay of the anion state. If the anion has nonzero angular momentum $J > 0$, the effective Hamiltonian, Eq. (1), is modified by an additional term $J(J + 1)/(2\ \mu R^2)$. The potentials $V_0^J(R)$ for D_2, $V_d^J(R)$, and the real part $V_{\mathrm{ad}}(R)$ of the local complex approximation [2] for $D_2{}^-$ with $J = 36$ are shown in Fig. 3. For $R > 3a_0 V_{\mathrm{ad}}(R)$ gives the adiabatic potential for the electronically bound anionic state (for $R < 3a_0$ it is the pole of the fixed nuclei scattering K matrix). It is worthwhile to note that for high J the anion potential $V_d(R)$ as well as the adiabatic potential $V_{\mathrm{ad}}(R)$ build a repulsive barrier which reduces the amplitude of the nuclear wave function in the autodetachment region, increasing thus the autoionization lifetime. At large

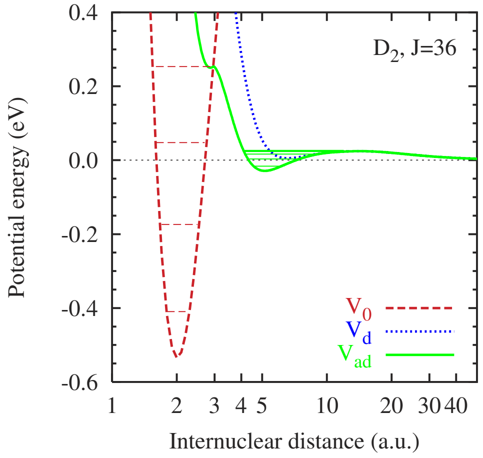

FIG. 3 (color online). Potential-energy curves of D_2 and $D_2{}^-$ for $J = 36$. Dashed line (red): potential-energy function of D_2, dotted line (blue): potential-energy function of the discrete state of $D_2{}^-$, solid line (green): adiabatic potential function of the shape resonance and bound electronic states of $D_2{}^-$.

TABLE I. Parameters of the most long-lived resonances for each rotational quantum number J. Resonance energies relative to DA threshold are given in meV.

$H_2{}^-$ resonances			$D_2{}^-$ resonances		
J	E_{res}	τ	J	E_{res}	τ
21	-136	2.4 ps	31	-118	0.13 ns
22	-105	12 ps	32	-97	0.70 ns
23	-75	0.11 ns	33	-76	6 ns
24	-47	0.9 ns	34	-55	39 ns
25	-20	12 ns	35	-35	0.51 μs
26	5	0.52 μs	36	-16	5.7 μs
27	28	2 ns	37	2	14 μs
			38	19	7.2 μs
			39	34	41 ps

internuclear distances the centrifugal barrier $J(J+1)/(2\,\mu R^2)$ prevents the particles to escape into the dissociative attachment channel. Hence, it is plausible that long-lived states exist between the two barriers.

To verify this hypothesis, we calculated the cross sections for electron impact vibrational excitation and dissociative attachment of H_2 and D_2 molecules using the method described in [11] over a broad range of rotational quantum states J and in the range of energies corresponding to expected states in the outer potential well. We found several very narrow resonances with energies close (within 0.1 meV) to the bound states in $V_{\mathrm{ad}}(R)$. The energies of the bound states for $J = 36$ in $D_2{}^-$ are indicated in Fig. 3. Widths and positions of the resonances have been analyzed using the Fano formula. The widths spread over a broad region of 10^{-10}–10^{-3} eV. Cross sections for vibrational excitation attain values up to hundreds of square Ångstroms at the resonances. The calculated energies and lifetimes of the lowest resonances are collected in Table I. The calculations were carried out for all (even and odd) accessible values of the angular dependence J; i.e., we considered both parahydrogen and ortho-hydrogen. The J dependence of the resonance parameters is consistent with the increasing repulsion and decreasing well depth for growing J. The resonances in $D_2{}^-$ live longer than for $H_2{}^-$ as expected because of the tunneling mechanism for the decay.

We have thus demonstrated that the ground $^2\Sigma_u^+$ potential of $H_2{}^-$ can support quasibound, high angular momentum states with lifetimes in the microseconds range. For $H_2{}^-$ the longest lifetime is predicted as $\tau = 0.52\ \mu$s for $J = 26$, and for $D_2{}^-$ we find $\tau = 14\ \mu$s for $J = 37$. These long-lived states may survive from the sputtering ion source to the stripper (3–5 μs). This explanation is supported by the well known fact that highly excited rotational and vibrational states have been frequently observed in neutral and ionized molecules formed by sputtering (see, e.g., [13]), but no data appear to exist for $H_2{}^-$. Considerable evidence both from experiments and simulations indicate that highly excited molecules (both charged and neutral ones) tend to fragment upon having escaped from the sample; depending on the degree of excitation (and, of course, the stability of the molecule), these decay reactions may occur over a wide time scale, ranging from pico to microseconds. Clearly, many molecular hydrogen species produced originally in the ion source may have decomposed by the time they could reach the tandem accelerator. Hence, the number of $H_2{}^-$ and $D_2{}^-$ detected constitutes only a lower limit in terms of the abundance of these species as compared to H^- or D^-.

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