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Lifetimes of the negative molecular hydrogen ions: H_2^-, D_2^-, and HD^-

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The lifetimes of three isotopologs of the molecular hydrogen anion have been measured using an electrostatic ion-beam trap. Much longer lifetimes (up to ~2 ms for D_2^-) than predicted by the most recent calculation are found, and it is proposed that more than one electronic state contributes to the overall lifetimes of these species.

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The negative molecular hydrogen ion is the simplest molecular anion. Apart from being of fundamental interest, the negative ion is of importance as an intermediate step in a number of collisional processes [1–3]. For example, associative detachment (AD) $H+H^- \rightarrow H_2+e^-$, dissociative attachment (DA) $H_2+e^- \rightarrow H+H^-$, and collisional detachment ($H+H^- \rightarrow H+H+e^-$) are central in the determination of the thermal equilibrium of H^- ions and H_2 molecules in various astrophysical plasmas [4]. Also, the DA process is probably a dominant mechanism for the production of H^- in ion sources, which are useful for the generation of neutral particle beams, for the injection of ions into controlled thermonuclear devices, or for ion propulsion [5,6].

Despite more than 40 years of experimental effort, the existence of the molecular hydrogen anion remained uncertain. The first mass spectroscopic detection of H_2^- was reported by Khvostenko and Dukel'skii [7] in 1958, followed by Hurley [8] in 1974. However, no isotopic confirmation of these measurements was made, so the results remained in doubt. Aberth *et al.* [9] reported the observation of metastable (>10 μs) HD^- and D_2^-, at very low intensities, but definite detection was hampered by mass interferences. Later, Bae *et al.* [10] searched for H_2^- employing a two-step electron capture process, but with no success. A very small H_2^- signal was noted by McKeegan *et al.* [11] in a high-resolution secondary-ion mass spectrometer. The authors did not, however, emphasize the potential relevance of this observation. Recently, Wang *et al.* [12] attributed mass peaks in dielectric-barrier discharge plasmas to H_2^- and D_2^-, but quantitative information could not be extracted due to the wide distribution of ion energies.

As a result of the mounting evidence for the existence of the anions, experiments were started around 1990 [1,13,14] to unravel their electronic structures. Because it was assumed, however, that they were too short lived to be observed directly, various collision processes were studied. Finally, in 2005, *long-lived* metastable molecular hydrogen anions (H_2^- and D_2^-) were definitively observed [15,16] using an accelerator mass spectrometer. The ions were produced by sputtering of TiH_2 and TiD_2 targets with Cs^+ ions. Based on the time of flight of the molecular ions through the accelerator system, it was estimated that the ions have lifetimes of at least a few microseconds, and are produced with high rotational and vibrational excitation.

On the theoretical side, early calculations [1,14] have indicated that H_2^- is unstable for internuclear separations close to the equilibrium distance of H_2, and should decay within a few femtoseconds. Calculations of the AD cross section, on the other hand, have shown that narrow resonances exist for high angular momenta J [1]. In a very recent calculation, it was demonstrated that the ground $^2\Sigma_u^+$ potential of H_2^- and D_2^- can support quasibound, high-angular-momentum states, with lifetimes in the microsecond range [15]. Because of the large angular momentum, the equilibrium internuclear distance of such states is predicted to be as large as 2.6 Å, making their production rather unlikely via standard collision processes. It was calculated that the longest-lived resonances, obtained with rotational quantum number $J=26$ (H_2^-) and 37 (D_2^-), would have lifetimes of 0.52 and 14 μs, respectively. These states have relatively long lifetimes because for high J, the adiabatic potential creates a repulsive barrier at small internuclear distance which reduces the amplitude of the nuclear wave function in the autodetachment region, and at large distance, the centrifugal barrier prevents the particles from escaping into the dissociative attachment channel. For both H_2^- and D_2^-, the energies of the states with the longest lifetimes have been calculated to be above the $H+H^-$ (or $D+D^-$) limit and are thus assumed to mainly decay via these channels, and not to H_2+e^- (or D_2+e^-).

In this work, we present the first measurements of the lifetimes of H_2^-, D_2^-, and HD^-. The experiments were carried out in an electrostatic ion-beam trap at the Weizmann Institute molecular physics laboratory. The ions were produced in a cesium sputter ion source, similar to the one described in [15], in which the target to be sputtered was made of TiH_2 (for the production of H_2^-), TiD_2 (for D_2^-), or an equal mixture of both (for HD^-). The ions were extracted from the ion source, accelerated to a kinetic energy of 4.2 keV, and chopped using a set of deflection plates, located ~1 m after the source, in order to produce relatively short (few microsecond) bunches. After a further 1.2 m, the ions were mass selected by a 90° deflection magnet that bent the

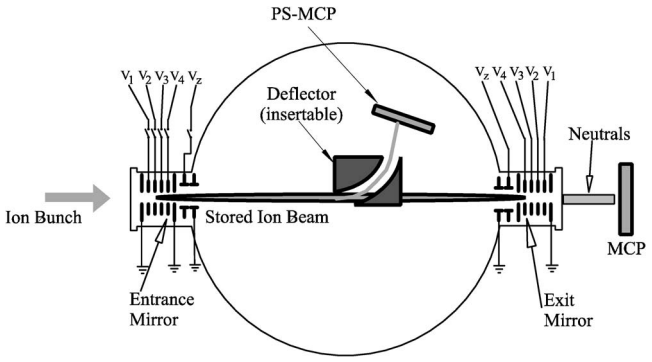

FIG. 1. The electrostatic ion-beam trap. The beam is injected through the left mirror, while the electrode voltages are off, and switched on once the bunch is located in the trap. The insertable deflector can be lowered into the beam path, to deflect the beam and charged fragments toward the position-sensitive MCP.

beam toward the ion trap, located about 3.6 m downstream.

The electrostatic ion-beam trap [17,18] (see Fig. 1) comprises two identical mirrors, each with eight electrodes, as described in Ref. [19]. The distance between the innermost electrodes is 490 mm (see Fig. 1). The mirrors are installed in a cylindrical vacuum chamber with inner diameter of 451 mm, pumped to below 7×10^{-12} Torr. By applying appropriate voltages to the mirror electrodes, one can achieve stable trapping, where the ions oscillate between the two mirrors. Ions are injected into the trap by grounding the entrance electrodes (left mirror in Fig. 1); once the bunch is inside, it is trapped by rapidly switching on ($\sim$100 ns) the input voltages. A microchannel plate (MCP) detector is located after the exit mirror, at a distance of 1.02 m from the center of the trap. More details about the operation of the trap and its characteristics can be found in Refs. [17,18,20]. With the aid of a linear manipulator, a 31° electrostatic spherical deflector [21] can be inserted between the mirrors in order to bend the injected beam toward a 40-mm-diam position-sensitive microchannel plate (PS MCP), fitted with a resistive anode readout, located at a distance of 78 mm from the center of the trap (when the deflector is inserted, the voltages on the mirrors are switched off, and the beam is not trapped). The deflector is surrounded by a grounded shield with a 10 mm wide $\times$5 mm high entrance aperture.

While the ions are trapped, neutral particles escaping from the trap in the exit direction are detected by the external MCP. They can be produced either by collision of the stored ions with the residual gas [18,20], or via the natural decay of the stored molecular anions, which can decay either by autodetachment ($H_2^-\rightarrow H_2+e^-$), dissociation ($H_2^-\rightarrow H+H^-$), or dissociative autodetachment ($H_2^-\rightarrow H+H+e^-$). Since all these processes produce at least one neutral particle, the rate measured by the MCP is directly proportional to the decay rate of the ions in the trap. One of the advantages of the electrostatic trap is that no tuning is required when changing the mass of the ion. This ensures that the ion loss due to inherent instabilities (such as misalignment of the mirrors) is identical for all species. For reference, the trap lifetimes of H^- and D^- under similar conditions as in this experiment were measured to be of the order of 50 ms.

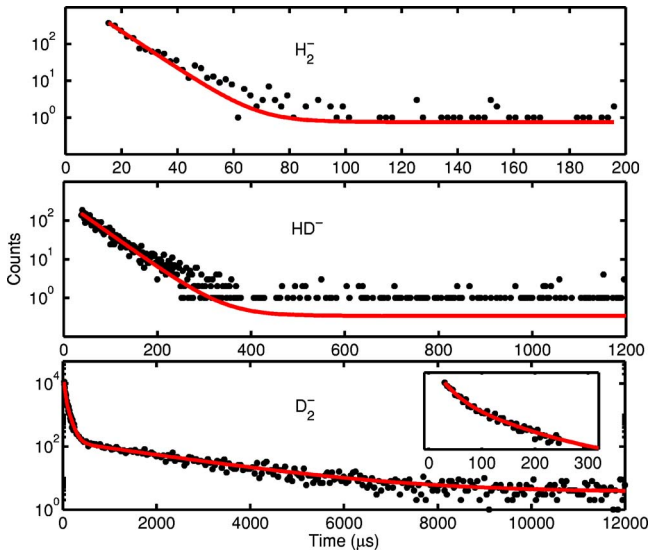

FIG. 2. (Color online) Measured rate of neutral particles exiting the trap for H_2^- (top), HD^- (middle), and D_2^- (bottom). The full lines, representing the best fit to the data points, include the contribution from the "zero counts" which cannot be displayed on the logarithmic scale. The inset shows in more detail the two short lifetimes of D_2^-.

The ion currents extracted from the source were very weak, being $\sim$1 pA for D_2^-. For H_2^- and HD^- the currents were too small to measure with a Faraday cup. With the mirror electrodes grounded, the currents of H_2^- and HD^- reaching the trap could be measured with the MCP after the exit mirror. Both were about 30 times smaller than for D_2^-.

The data acquisition was triggered by the chopper control signal. The trapping cycle was repeated every two seconds, and the results presented here are the sum of several thousand cycles. The time of flight from the source to the center of the trap is 13, 16, and 18 μs for H_2^-, HD^-, and D_2^-, respectively. It was found that electronic noise due to the switching of the entrance mirror, plus the neutral particles produced along the injection beamline, saturated the amplifier connected to the MCP and paralyzed the data acquisition for an additional 2–3 μs. Hence, only neutral particles leaving the trap after this time were counted as real events. This initial dead time of 15–20 μs defines also the order of magnitude of the lower limit for lifetimes that can be measured with such a setup: For example, the population of metastable states with $<$5 μs would have decreased by at least a factor of 20 prior to starting the measurement.

Figure 2 shows the measured lifetimes for H_2^-, HD^-, and D_2^-. Because these species were created in an unknown distribution of states with different lifetimes, the number of exponential decays needed to fit the data was not known *a priori*. For each isotopolog we chose the minimum number of exponential decays which faithfully reproduced the data with reasonable error bars. For both H_2^- and HD^-, the data points were fitted using a combination of a single-exponential decay and a constant background, while the D_2^- spectrum required three exponential decays and a constant background to faithfully represent the data. Although the quality of the fit for H_2^- using a single decay is relatively

TABLE I. Measured and calculated [15] lifetimes. There are no theoretical values available for HD^-. For H_2^- and D_2^-, only the longest calculated lifetimes for the $^2\Sigma_u^+$ states are shown.

Species	Expt. (μs)	Theory (μs)
H_2^-	8.2 ± 1.5	0.52
HD^-	50.7 ± 1.0	
D_2^-	$\tau_1=23\pm3$	
	$\tau_2=84\pm3$	14
	$\tau_3=1890\pm80$	

poor, the longest lifetime comes out clearly. Adding more decays yields lifetimes with relatively large and overlapping error bars. The lifetimes obtained from these fits for each of the three species are given in Table I. The uncertainties include both statistical and systematic errors based on previous works where lifetimes of the same order of magnitude have been measured and compared to other results [22].

Two mass contaminations need to be considered: H_3^- could be mistaken for HD^- and D^- for H_2^-. A search for H_3^- (with a TiH_2 target) was performed, and only very small traces could be found (in agreement with Refs. [15,16] which show that H_3^- is produced in such ion sources with intensities that are about 5×10^{-3} weaker than for H_2^-). On the other hand, given the natural relative abundance of deuterium ($\sim1\times10^{-4}$) and the H^- current obtained from TiH_2, the ratio of D^- to H_2^- can be estimated to be ~30. However, this does not represent a problem for the H_2^- lifetime measurement shown in Fig. 2 since the trap lifetime of D^- was measured to be 55 ms; therefore the overall contribution of neutral D atoms exiting the trap and recorded by the MCP during the first 50 μs is below 0.1%.

To get some information on the decay channels, we made use of the fact that for each of these species, at least one of the measured lifetimes is of the same order of magnitude as the time of flight from the ion source to the trap. Thus, substantial decay must occur after the 90ø magnet, and if charged fragments (H^- or D^-) are produced in such decays (dissociation channel) along the path, they should be observable. We have attempted to detect such particles by converting the trap into a crude (31°) spherical energy analyzer [21]. This was done by switching off the mirror voltages and moving the electrostatic deflector into the beam path. Because of the relatively narrow aperture in the deflector shield, only the main ion beam and atomic fragments produced after the last steering and focusing quadrupoles (located ~2 m upstream) can enter the deflector.

In lieu of the detector slit that is common in a hemispherical energy analyzer, only the particles hitting the PS MCP in a specific 2-mm-wide vertical slice were counted. The number of counts in a fixed time as a function of deflector voltage for HD^- and D_2^- is shown in Fig. 3. The trajectories of the charged particles through the deflector were calculated using SIMION [23] and it was found that particles carrying the full beam energy (i.e., the molecular anions that did not decay) would hit the chosen slice for a deflection voltage $V_{defl}\sim1420$ V. As seen in Fig. 3, a peak is indeed observed around this voltage for both species (the minor difference in

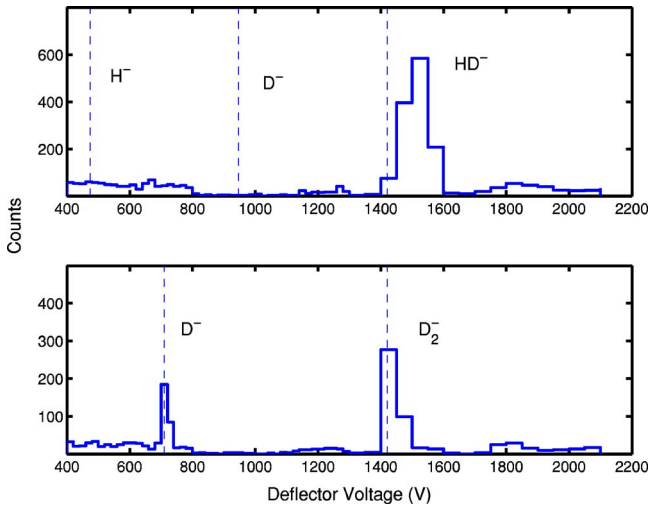

FIG. 3. (Color online) Measured number of ions hitting the PS MCP in a vertical slice 2 mm wide as a function of the voltage on the electrostatic deflector for HD^- (top) and D_2^- (bottom). The expected position of the main beam and the negative atomic fragments are shown as vertical dashed lines.

peak positions is probably due to slightly different angles of the beams entering the deflector).

Since the fragments produced by the decay of the molecular anions carry a kinetic energy which is approximately proportional to their mass, an additional peak is expected at $\frac{1}{2}V_{defl}$ for D^- produced by the decay of D_2^-, while two additional peaks are expected for HD^-: at $\frac{1}{3}V_{defl}$ (H^-) and $\frac{2}{3}V_{defl}$ (D^-). The results in Fig. 3 show clearly that peaks are only observed for the D_2^- case, implying that for HD^-, either states that decay by dissociation are not populated in the ion sources or, more likely, these states have lifetimes short compared to the time of flight from the source to the trap (~16 μs). The lifetime for the dissociation into D^- can be estimated from the peak intensity ratio $I(D_2^-)/I(D^-)\approx4$ (Fig. 3). The time of flight of D_2^- from the last set of quadrupoles to the trap is about 6 μs; since 20% of the bunch dissociates during this time, the lifetime for this process is ~28 μs. This is in good agreement with τ_1 in Table I; thus it is highly probable that this short lifetime is correlated with dissociation.

A similar measurement performed for H_2^- shows no peak above the background at $\frac{1}{2}V_{defl}$ (for the H^- fragment), but this is to be expected since it is essentially only D^- that is counted at V_{defl}. (See discussion of mass contamination, above.) If there are equivalent states to τ_1 and τ_2 for HD^-, they are too short lived ($\leqslant5$ μs) to be measured by the present apparatus. This last conclusion is also valid for H_2^-, but as pointed out above, could not be reliably checked due to the large expected D^- contamination.

Although τ_1 and τ_2 are longer than the calculated values for the most long-lived resonances belonging to the $^2\Sigma_u^+$ states [15], they are of the same order of magnitude (see Table I) and it is not unlikely that at least one of them is due to the decay of this state, an assumption which is reinforced

by the observation of the dissociation as a decay channel for D_2^- (see above) in the present experiment.

If the decay of HD^- seen in Fig. 2 were due to dissociation, then negative fragments should have been observable in our energy analyzer (Fig. 3). We therefore conclude that these states decay either by autodetachment or by dissociative autodetachment. These states might also be the same ones responsible for the very long lifetime observed for D_2^-.

We have thus demonstrated that the negative hydrogen molecular ions have lifetimes that are much longer than predicted by the current theory, more than two orders of magnitude for D_2^- and more than one order of magnitude for H_2^-. Hence, new theoretical concepts will be required in order to explain the measured data We propose that an additional electronic state is responsible for this long lifetime. As suggested by Aberth *et al.* [9], metastable H_2^- (and its isotopologs) could also exist in a quartet state such as He^- [24,25]. As reported by Bae *et al.* [10], the most probable configuration would be a $^4\Sigma_g$ state, with at least the ground vibrational level lying below the neutral $H_2(c\,^3\Pi_u)$. However, to our knowledge, no calculations have yet been done on quartet states for negative molecular hydrogen ions. It is worth pointing out that high-spin states have also been proposed as long-lived states for small molecular anions such as CO^- and N_2^- [26].

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