Metastable states of diatomic hydrogen anions

Holger Kreckel¹, Philipp Herwig¹, Dirk Schwalm¹,², M. Čížek³, Robin Golser⁴, Oded Heber², Brandon Jordon-Thaden¹, Andreas Wolf¹

¹Max-Planck-Institut für Kernphysik, 69117 Heidelberg, Germany
²Department of Particle Physics, Weizmann Institute of Science, Rehovot 76100, Israel
³Charles University Prague, Faculty of Mathematics and Physics, Institute of Theoretical Physics, 180 00 Praha 8, Czech Republic
⁴Universität Wien, Fakultät für Physik - Isotopenforschung, 1090 Wien, Austria

E-mail: holger.kreckel@mpi-hd.mpg.de

Abstract. Transient states of the negative hydrogen molecule H⁻₂ have drawn attention as intermediate reaction complexes in important molecular reactions like associative detachment (AD: H⁻ + H → H⁻₂ → H₂ + e⁻) and dissociative attachment (DA: e⁻ + H₂ → H⁻₂ → H + H⁺). Recently it has been shown that metastable states of hydrogen molecular anions exist that defy both autodetachment and spontaneous dissociation for several microseconds (in the case of H⁻₂) and even milliseconds (in the case of D⁻₂). Here we present Coulomb explosion measurements for H⁻₂ and D⁻₂ that provide detailed information on the shape of the molecular wave function. We compare these experimental results with calculated wave functions obtained using a non-local resonance model. Our measurements confirm the predicted stabilization of H⁻₂ and D⁻₂ in states of high angular momentum.

1. Introduction

Neutral and positively charged hydrogen molecules H₂ and H²⁺ are much-studied systems that overall can be considered well understood. Negative hydrogen molecules are much more elusive, their existence has been debated in the literature since the first detections were claimed in the late 1950s [1]. In 1963 Taylor and Harris could show that the lowest electronic state H⁻²Σ⁺ is unstable with respect to electron autodetachment at typical internuclear distances for diatomic molecules [2]. Subsequent calculations yielded lifetimes of < 10⁻¹⁵ s [3], which would render experimental observation virtually impossible. Nevertheless, the first clear-cut experimental evidence for the existence of long-lived states of H⁻₂ and D⁻₂ was achieved by Golser et al. in 2005 [4] employing the Vienna Environmental Research Accelerator (VERA). For their study H⁻₂ (and D⁻₂) ions were produced by a sputter ion source and detected by accelerator mass spectrometry. In subsequent ion beam trap measurements at the Weizmann Institute of Science, Heber et al. [5] determined the lifetimes of the most long-lived states of H⁻₂ and D⁻₂ to be 8.2 µs and 1.89 ms, respectively.

The theoretical description of H⁻₂ has often been motivated by related physical processes. A large body of work exists, e.g., for electron scattering of H₂. A review of the early experimental results is given in [6], for a more recent theoretical study the reader is referred to [7]. The description of metastable H⁻₂ states, however, has been driven by its role as an intermediate complex in associative detachment (H⁻ + H → H₂ → H₂ + e⁻) and dissociative attachment.
\((e^- + H_2 \rightarrow H^-_2 \rightarrow H + H^-)\) reactions. Čížek et al. presented a non-local resonance model to calculate rate coefficients for these fundamental processes in 1998 [8]. A revised version of the same model [9] was used to calculate the lifetimes of the long-lived states of \(H^-_2\) and \(D^-_2\) that were observed in the ion beam trap measurements of Heber et al. [5]. In the theoretical description, the rotational barrier that is introduced in high angular momentum states inhibits the ion to enter the zone of rapid autodetachment at short internuclear distances \(R\). A shallow potential minimum forms for \(J = 27\) (\(H^-_2\)) or \(J = 37 - 38\) (\(D^-_2\)) at large distances around \(R \approx 5a_0\) that can support one (for \(H^-_2\)) or two metastable vibrational states (for \(D^-_2\)).

In the next sections we report on foil-induced Coulomb Explosion Imaging (CEI) experiments [10] that aim at a comprehensive test of the theoretical description and shed light on the structure and stability of these fundamental molecular anions. The original publications of the experimental results can be found in reference [11] for \(H^-_2\) and reference [12] for \(D^-_2\).

In CEI experiments fast molecular ions traverse an ultrathin foil where they are stripped of all their binding electrons. This leads to strong Coulomb repulsion among the remaining positively charged atoms and their mutual potential energy is converted to kinetic energy. The resulting energy release is recorded in all three dimensions to infer detailed information on the initial molecular configuration.

2. Experiment: Coulomb Explosion Imaging

We used two different ion sources to produce \(H^-_2\) and \(D^-_2\). While the initial \(H^-_2\) experiments were carried out with a sputter ion source, we later found that a duoplasmatron ion source delivered stronger and more stable beams of \(D^-_2\). Typical currents for \(H^-_2\) and \(D^-_2\) were on the order of several pico-Ampere, while up to \(10 \mu\text{A}\) of the corresponding atomic anions \(H^-\) and \(D^-\) could be extracted under the same source conditions. In both cases the ions were mass-selected (in the case of \(H^-_2\), the majority of the mass 2 beam actually consisted of \(D^-\), which was contained in the source material in natural abundance) and accelerated by a linear radio frequency quadrupole accelerator to 0.97 MeV and 1.92 MeV for \(H^-_2\) and \(D^-_2\), respectively. The

![Figure 1](image.png)

**Figure 1.** Sketch of the CEI beamline (distances not to scale). The molecular ions enter the beamline with energies of 0.97 MeV and 1.92 MeV for \(H^-_2\) and \(D^-_2\), respectively. Circular apertures are used to collimate the beam before the ions hit the diamond-like-carbon stripping foil. After electron stripping the Coulomb repulsion sets in and the ions are drifting apart until they are detected by a three-dimensional imaging system [10]. A magnetic separation field behind the stripping foil is used to select only \(H^+\) or \(D^+\) fragments for experiments with \(H^-_2\) and \(D^-_2\), respectively. A second auxiliary magnetic field before the stripping foil can be used to divert all charged particles in order to examine neutral decay products that are created along the straight flight path upstream of the stripping region.
ions were then magnetically guided into the CEI beamline (shown in Figure 1) where they were collimated by two sets of circular apertures and directed at an ultrathin diamond-like-carbon foil. At their respective energies, the distance from ion source to CEI setup corresponds to a flight time of $\sim 10\,\mu s$. Upon entry in the foil all the binding electrons are stripped off. Following the electron stripping, the mutual Coulomb repulsion sets in and rapidly converts potential energy into kinetic energy. After a flight distance of several meters the atomic fragments have gained distances of several centimeters, which were recorded by a time and position sensitive detector [10]. A magnetic separation field behind the stripping foil is used to suppress unwanted background events by selecting only fragments of the desired charge/mass ratio. A fast high voltage chopper at the beginning of the CEI beamline blocks the beam once a particle impact has been recorded at the detector, thus ensuring the measurement of single molecule breakups.

An illustration of the Coulomb explosion principle for $\text{H}_2^-$ and $\text{H}_2$ is shown in Figure 2. Since the electrons are removed within the first $10^{-16}\,\text{s}$ upon impact on the foil, the nuclei can be considered frozen during the stripping process. This corresponds to a vertical projection of

![Figure 2](image-url)

**Figure 2.** Illustration of the CEI principle. The fast electron stripping process can be described as a vertical projection of the initial molecular wave function onto the repulsive Coulomb and centrifugal potential. The resulting kinetic energy release is effectively a mirror image of the initial molecular wave function. Depicted are potentials and distributions for neutral $\text{H}_2$ ($v = 0, J = 26$) and $\text{H}_2^-$ ($v = 0, J = 27$) anions.
the molecular wave function onto the bare repulsive Coulomb potential. Once the protons find
themselves on the repulsive curve, they begin to dissociate. The CEI method measures the
kinetic energy release (KER) distribution, which effectively is a mirror image of the square of
the wave function of the initial molecule or molecular ion.

For a strict quantum mechanical treatment of the Coulomb explosion process, one would
have to project the molecular wave function $|\Psi(R)|^2$ onto the continuum wave function of the
repulsive Coulomb and centrifugal potential (the so-called Coulomb functions). However, in
detailed model calculations we have shown that a simplified treatment using properly normalized
position eigenstates

$$\Psi^C(R, E_{kin}) \approx \sqrt{|dR(E_{kin})/dE_{kin}|} \delta(R - R(E_{kin})),$$

yields a very good approximation [12]. This semi-classical approximation results in the following
description of the KER distribution

$$P(E_{kin}) dE_{kin} \approx |\Psi(R)|^2 \left|\frac{dR}{dE_{kin}}\right| dE_{kin},$$

which is the basis for a well-established Monte Carlo simulation code [13, 14] that is employed
for the analysis of most CEI experiments. The simulation also includes effects that occur during
the ions passage through the foil, notably charge exchange and multiple scattering, as well as
detector efficiencies and the magnetic deflection field. In a typical CEI analysis, calculated wave
functions are forward simulated with the Monte-Carlo code and the resulting distributions are
compared to the measured KER distributions.

In Figure 2 two simulated KER distributions are plotted. The first one shows the expected
outcome for the Coulomb explosion of neutral $H_2$, which is centered around $\sim 16$ eV, a typical
value for a diatomic molecule. The distribution for $H_2^-$, on the other hand, is centered around
$\sim 5$ eV. This small KER value is a manifestation of a very soft explosion, reflecting the unusually
large average internuclear distance of $H_2^-$ anions.

3. Results

In Figure 3 the measured CEI distribution for $H_2^-$ without experimental cuts is shown by the
black dots. The bell-shaped curve that peaks around $\sim 5$ eV immediately reveals the large
internuclear distance of metastable $H_2^-$ and the fact that the ions do not have significant
vibrational excitation – as expected. A more surprising feature was observed in the form of
a shallow peak at larger KER values. By introduction of an auxiliary magnetic field before the
stripping region, it was possible to divert all charged particles and record only neutral fragments
that are created along the beam path. The measured distribution (green squares) coincides
with the shallow peak at higher energies, and can thus be attributed to $H_2$ molecules which are
resulting from autodetachment occurring in the beam upstream of the stripping foil. By careful
analysis of the respective count rates, it was possible to estimate a partial decay time constant
due to autodetachment of $5 \pm 2 \mu$s [11]. This time constant is somewhat shorter – but consistent
within the error margins – than the measured lifetime of the longest state of $H_2^-$, which was
found to be $8.2 \pm 1.5 \mu$s in previous ion beam trap experiments [5]. This finding suggests that
autodetachment is the main decay pathway for this state.

Due to the influence of the Earth’s magnetic field on the charged particle beam, the center-
of-mass position of $H_2^-$ breakup events was slightly different from the center-of-mass of neutral
$H_2$ events, as the latter trajectories are unaffected by external fields. This allowed us to separate
$H_2^-$ and $H_2$ events using a simple center-of-mass cut. Figure 4 shows the extracted $H_2^-$ KER
distribution without contamination by neutral $H_2$. The measured distribution is compared with
the simulated KER distributions of the two most long-lived \( \text{H}_2^- \) states, as predicted by theory [9]. Very good agreement is found for \( \text{H}_2^- \) in \( v = 0, J = 27 \). However, it should be noted that the CEI results are mainly sensitive to the shape of the wave function, but not on the exact angular momentum, as only a small fraction of the KER stems from rotational excitation. Therefore, the present results confirm the shape of the initial wave function of the molecular ion, but they do not allow for a serious constraint on the angular momentum quantum number \( J \).

In an independent step we analyzed the CEI results of the \( \text{H}_2 \) autodetachment product [11]. By comparison of the measured KER distribution to the well-known \( \text{H}_2 \) wave functions for various values of \( J \), we were able to place a limit of \( J = 25 \pm 2 \) on the angular momentum of the \( \text{H}_2 \) resulting from autodetachment. Assuming that the detached electron does not carry away a significant amount of the nuclear angular momentum, this result is consistent with the best fit to the wave function of metastable \( \text{H}_2^- \) which resulted in \( v = 0, J = 27 \).

The CEI results for the deuterated \( \text{D}_2^- \) anion are shown in Figure 5. According to theoretical

**Figure 3.** Measured KER distributions obtained by CEI of \( \text{H}_2^- \) (black dots). The second distribution (green squares), which is centered at higher KER values, is the result of a measurement that employed an auxiliary magnetic field before the stripping region, thus diverting all charged particles. This distribution corresponds to the breakup of neutral \( \text{H}_2 \) molecules that are the result of electron autodetachment along the straight beam path upstream of the stripping foil.

**Figure 4.** Measured KER distributions obtained by CEI of \( \text{H}_2^- \) (black dots). Contributions from neutral \( \text{H}_2 \) have been removed by a center-of-mass cut (see text). The error bars are inferred from the counting statistics for each bin. The uncertainty on the horizontal energy scale is on the order of the size of the symbols. Also shown are the fits of the two most long-lived states of \( \text{H}_2^- \), as predicted by theory [9]. The best agreement is found for \( \text{H}_2^- \) in \( v = 0, J = 27 \).
predictions three states have long enough lifetimes to reach the CEI beamline, namely \((v = 1, J = 37)\), \((v = 0, J = 37)\), and \((v = 0, J = 38)\), with lifetimes of 16 \(\mu\)s, 61 \(\mu\)s, and 2.1 ms, respectively. These lifetimes are in fair agreement with the decay times observed in the experiment of Heber et al. [5], which were found to be \((23 \pm 3) \mu\text{s}\), \((84 \pm 3) \mu\text{s}\), and \((1.89 \pm 0.08) \text{ms}\), respectively. Also shown in Figure 5 is the best fit to the experimental distribution using the wave functions for all three predicted long-lived states. As can be seen, good agreement between experiment and theory is found, with individual populations of the three states ranging from 26% to 38%.

The CEI results for \(\text{D}_2^-\) showed no neutral contamination in the KER spectrum and measurements using the auxiliary magnetic field yielded just an unspecified broad background with very low count rate. The absence of neutral \(\text{D}_2\) from the beam could either be due to the fact that only the very long-lived states are reaching the CEI beamline, or – less likely – because metastable \(\text{D}_2^-\) decays predominantly by dissociation, which the present experiment is not sensitive to.

4. Summary and Discussion

We have used the CEI method to analyze the nuclear wave functions of metastable states of \(\text{H}_2^-\) and \(\text{D}_2^-\). The measured distributions show very good agreement with calculated wave functions for the most long-lived states of both ions [9]. In the case of \(\text{H}_2^-\) we observed neutral \(\text{H}_2\) molecules that were created in the ion beam due to electron autodetachment. The analysis of these \(\text{H}_2\) fragments allowed us to constrain their angular momentum to \(J = 25 \pm 2\) [11], in good agreement with the predicted angular momentum of the longest-lived \(\text{H}_2^-\) state of \(J = 27\).

For \(\text{D}_2^-\) we can achieve a good fit to the measured distribution if we use wave functions of all three metastable states with predicted lifetimes >10 \(\mu\)s. There was no detectable contribution from neutral \(\text{D}_2\) found in the beam.

The deuterated hydrogen anion \(\text{D}_2^-\) has been the subject of a complementary experimental study published by Lammich at al. [15]. In their work \(\text{D}_2^-\) ions were dissociated by a short laser pulse and the fragments were recorded by a time and position sensitive detector. From the resulting KER distribution the authors extracted information on the initial angular momentum of the metastable \(\text{D}_2^-\) ions. They concluded from their measured data that theory underestimates the angular momentum of the most long-lived states by several \(\hbar\). However, a recent re-evaluation
of these data explains the discrepancy and in fact shows good agreement with the theoretical predictions [12].

Moreover, recent energy-resolved merged beams measurements of the associative detachment reaction \((H^- + H \rightarrow H_2 \rightarrow H_2 + e^-)\), where \(H_2^-\) acts as an intermediate complex, have shown very good agreement with theory over a wide range of energies, both for \(H^-\) on \(H\) [16, 17, 18] and \(D^-\) on \(D\) collisions [19]. In the light of the accumulated experimental evidence from both CEI and merged beams experiments that are in accord with theory, it appears that a good understanding of the most simple molecular anion has been reached.

Acknowledgement

We thank the accelerator staff at the Max-Planck-Institute for Nuclear Physics. We acknowledge support from the Max-Planck-Society. H.K. was supported by the European Research Council under Grant Agreement No. StG 307163, M.C. was supported by the grant agency of the Czech Republic project No. GACR 208/10/1281. D. S. acknowledges support by the Weizmann Institute through the Joseph Meyerhoff program.

References

[1] Khvostenko V I and Dukel’Skii V M 1958 Sov. Phys. JETP 7 709–710
[2] Taylor H S and Harris F E 1963 J. Chem. Phys. 39 1012–1016
[3] Bardesley J N, Herzenberg A and Mandl F 1966 Proceedings of the Physical Society 89 305–319
[4] Golser R, Gnaser H, Kutschera W, Priller A, Steier P, Wallner A, Čížek M, Horáček J and Domcke W 2005 Phys. Rev. Lett. 94 223003
[5] Heber O, Golser R, Gnaser H, Berkovits D, Toker Y, Eritt M, Rappaport M L and Zajfman D 2006 Phys. Rev. A 73 060501
[6] Trajmar S, Chutjian A and Register D F 1983 Phys. Rep. 97 220–356
[7] Telega S and Gianturco F A 2005 Eur. Phys. J D 36 271–280
[8] Čížek M, Horáček J and Domcke W 1998 J. Phys. B: At. Mol. Opt. Phys. 31 2571–2583
[9] Čížek M, Horáček J and Domcke W 2007 Phys. Rev. A 75 012507
[10] Wester R, Albrecht F, Grieser M, Knoll L, Repnow R, Schwalm D, Wolf A, Baer A, Levin J, Vager Z and Zajfman D 1998 Nucl. Instr. and Meth. in Phys. Res. A 413 379 – 396
[11] Jordan-Thaden B, Kreckel H, Golser R, Schwalb D, Berg M H, Buhr H, Gnaser H, Grieser M, Heber O, Lange M, Novotný O, Novotný S, Pedersen H B, Petignani A, Repnow R, Rubinstein H, Shafir D, Wolf A and Zajfman D 2011 Phys. Rev. Lett. 107 195003
[12] Herwig P, Schwalb D, Čížek M, Golser R, Grieser M, Heber O, Repnow R, Wolf A and Kreckel H 2013 Phys. Rev. A 87 062513
[13] Zajfman D, Both G, Kanter E P and Vager Z 1990 Phys. Rev. A 41 2482–2488
[14] Zajfman D, Graber T, Kanter E P and Vager Z 1992 Phys. Rev. A 46 194–200
[15] Lammich L, Andersen L H, Aravin G and Pedersen H B 2009 Phys. Rev. A 80 023413
[16] Kreckel H, Bruhns H, Čížek M, Glover S C O, Miller K A, Urbain X and Savin D W 2010 Science 329 69
[17] Bruhns H, Kreckel H, Miller K A, Urbain X and Savin D W 2010 Phys. Rev. A 82 042708
[18] Miller K A, Bruhns H, Eliášek J, Čížek M, Kreckel H, Urbain X and Savin D W 2011 Phys. Rev. A 84 052709 (Preprint 1110.0683)
[19] Miller K A, Bruhns H, Čížek M, Eliášek J, Cabrera-Trujillo R, Kreckel H, O’Connor A P, Urbain X and Savin D W 2012 Phys. Rev. A 86 032714