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# Communication: Heavy-Rydberg states of HD and the electron affinity of the deuterium atom

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The electron affinity of the deuterium atom has been determined to be 6086.81(27) $cm^{-1}$ from a measurement of the difference between the $D^+ + H^-$ and $H^+ + D^-$ ion-pair dissociation energies and a thermochemical cycle involving the electron affinity of H and the ionization energies of H and D. Heavy-Rydberg states and the ion-pair dissociation thresholds of HD were accessed with good efficiency using a three-photon excitation sequence through the B $^1\Sigma_u^+$ ($v = 22$, $N = 1$) and $\bar{H}$ $^1\Sigma_g^+$ ($v = 9$, $N = 0$) intermediate levels and the threshold positions were determined using the method of threshold-ion-pair-production spectroscopy. © *2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).* https://doi.org/10.1063/1.5043186

Measurements of the threshold energies $E_{IPF}$ for the formation of ion pairs from neutral molecules can be used to determine the electron affinity $E_{ea}$ of atoms and molecules using the thermodynamical cycle (illustrated here for the case of a diatomic molecule AB)

$$E_{ea}(B) = D_0(AB) + E_I(A) - E_{IPF}(A^+ + B^-). \quad (1)$$

In Eq. (1), $D_0(AB)$ is the dissociation energy of AB, $E_I(A)$ is the ionization energy of A, and $E_{ea}(B)$ is the electron affinity of B.

$E_{IPF}$ is the convergence limit of the infinite series of bound vibrational levels of the ion pair $A^+B^-$. At very high values of the vibrational quantum number $v$ and for a given value of the rotational angular-momentum quantum number $N$, these levels can be regarded as heavy-Rydberg states,[1] the Rydberg electron of a conventional Rydberg state being replaced by the much heavier anion $B^-$. Their term values $T(v, N)$ follow the Rydberg formula for heavy-Rydberg states[1,2]

$$T(v,N) = E_{IPF}/(hc) - \frac{\mathcal{R}_{A^+B^-}}{(v+N+1-\mu_N)^2}, \quad (2)$$

where $n_{IP} = v + N + 1$ replaces the principal quantum number $n$, the vibrational quantum defect $\mu_N$ replaces the electronic quantum defect $\mu_\ell$, and $\mathcal{R}_{A^+B^-} = \mathcal{R}_\infty \mu_{A^+B^-}/m_e$ ($\mathcal{R}_\infty$ is the Rydberg constant and $\mu_{A^+B^-}$ the reduced mass of $A^+$ and $B^-$; $\mathcal{R}_{A^+B^-}$ is at least three orders of magnitude larger than $\mathcal{R}_\infty$). This analogy is the consequence of the fact that the energy-level structures of Rydberg and heavy-Rydberg states are dictated, at high values of $n$ and $n_{IP}$, respectively, by the Coulomb interaction between the ion core and the Rydberg electron and between $A^+$ and $B^-$. In the following, we distinguish between heavy-Rydberg states, which behave according to Eq. (2) and have very high $n_{IP}$ values ($\gg$100), and ion-pair states, which are molecular states having dominant $A^+ - B^-$ character at large internuclear distances but which are in general not particularly accurately described by Eq. (2) because of significant contributions of valence or Rydberg states at short internuclear distances. Typical examples of ion-pair states of molecular hydrogen are the outer (F and $\bar{H}$) wells of the EF $^1\Sigma_g^+$ and $H\bar{H}$ $^1\Sigma_g^+$ states.

Measurements of $E_{IPF}$ can be carried out by photoionization spectroscopy, either by determining the appearance threshold of the fragments $A^+$ and $B^-$ as the frequency of a tunable source is scanned[3] or by monitoring the dissociation of very high (typically $n_{IP} \gg 1000$) heavy-Rydberg states induced by weak pulsed electric fields and correcting for the field-induced shift of the ion-pair dissociation threshold. This method, which is the heavy-Rydberg analog of pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy,[4] was introduced by Hepburn and his co-workers under the acronym of TIPPS (for threshold ion-pair-production spectroscopy).[5,6] A third method would consist of extrapolating the spectral positions of heavy-Rydberg states using Eq. (2) in the same way as Rydberg series are extrapolated to determine ionization energies.[7] This third method has not been used yet because of difficulties associated with the observation of unperturbed heavy-Rydberg series, as discussed below.

All three methods are severely limited by the vanishing overlap of the nuclear wavefunctions of the heavy-Rydberg states and the molecular state out of which photoexcitation is carried out, which is typically the ground electronic state or a low-lying (valence or Rydberg) electronically excited state. This vanishing overlap represents a significant difference to high Rydberg states, which can always be excited from the ground neutral state, with a probability scaling as $n^{-3}$ and reflecting the probability density of the Rydberg electron in the region of the valence orbitals of the neutral molecule. The difference originates from the fact that heavy-Rydberg states only exist when the distance between $A^+$ and $B^-$ greatly exceeds the size of the orbitals of $A^+$ and $B^-$. Such large internuclear distances are not directly accessible from low-lying electronic states of AB because of poor overlap of the nuclear

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wavefunctions. Transitions to heavy-Rydberg states are therefore only observed in a photoexcitation spectrum through interactions with valence or Rydberg states, which inevitably cause deviations from Eq. (2), as discussed, for instance, in Refs. 1, 6, and 8.

We present here a strategy to *directly* access heavy-Rydberg states and illustrate it with a determination of $E_{ea}(D)$. The strategy involves resonant multiphoton excitations through ion-pair states from which heavy-Rydberg states can be accessed as efficiently as Rydberg states can be excited from low-lying electronic states, i.e., with an absorption cross section that scales as $n_{IP}^{-3}$. Just below the ion-pair-dissociation thresholds, where the vibrational levels cannot be resolved anymore, the rapid decrease with increasing $n_{IP}$ of the absorption cross section to individual vibrational levels is exactly compensated by the increase of the vibrational-state density, which scales as $n_{IP}^{3}$. Specifically, we determined the energy interval $\Delta E_{IPF}$ between the $H^+ + D^-$ and $D^+ + H^-$ dissociation thresholds of HD, which is related to the difference in the ionization energies and electron affinities of hydrogen and deuterium by

$$\Delta E_{IPF} = E_I(D) - E_I(H) + E_{ea}(D) - E_{ea}(H). \quad (3)$$

The determination relies on the fact that $E_I(H)$,[9] $E_I(D)$,[10] and $E_{ea}(H)$[11] are all accurately known. $E_{ea}(H)$, corresponding to the energy interval between $^1S_0$ ground state of $H^-$ and the $F = 0$ lower hyperfine component of the $^2S_{1/2}$ ground state of H, has been determined to be 6082.99(15) $cm^{-1}$ in the classical investigation of Lykke, Murray, and Lineberger.[11] In the same study, Lykke *et al.* also reported $E_{ea}(D)$ [6086.2(6) $cm^{-1}$], however, less accurately.

The heavy-Rydberg states of molecular hydrogen have been observed previously. Ubachs and co-workers[12,13] used a two-photon excitation scheme via selected rovibrational levels of the B $^1\Sigma_u^+$ and C $^1\Pi_u$ states to record spectra of the *gerade* heavy-Rydberg states of $H_2$ with $n_{IP}$ in the range 140–230. The quantum defects derived from the experimental line positions were found to be strongly energy-dependent in agreement with calculations,[14,15] making the extrapolation to the ion-pair dissociation threshold difficult (see also Ref. 16). McCormack and co-workers observed *ungerade* heavy-Rydberg states of $H_2$ in the same $n_{IP}$ range from selected rovibrational levels of the EF intermediate state.[17] Shiell *et al.* have reported the TIPP spectra of $H_2$ and $D_2$ and determined the field-free ion-pair formation thresholds of $H_2$ and $D_2$ to be 139 714.8 ± 1.0 $cm^{-1}$ and 140 370.2 ± 1.0 $cm^{-1}$, respectively.

To access the heavy-Rydberg states of HD with $n_{IP} \geq 200$ and the region of the $H^+ + D^-$ and $D^+ + H^-$ dissociation thresholds, we used the resonant excitation sequence

$$\begin{aligned} X(v = 0, N = 0) &\xrightarrow{\text{VUV}} B(v = 22, N = 1) \\ &\xrightarrow{\text{VIS-1}} \bar{H}(v = 9, N = 0) \\ &\xrightarrow{\text{VIS-2}} D^+ + H^- \text{ and } H^+ + D^- \end{aligned} \quad (4)$$

depicted in Fig. 1. This figure also depicts the potential-energy function of the X (lowest blue line) and $X^+$ (red line) ground states of HD and $HD^+$ and of several ion-pair states of

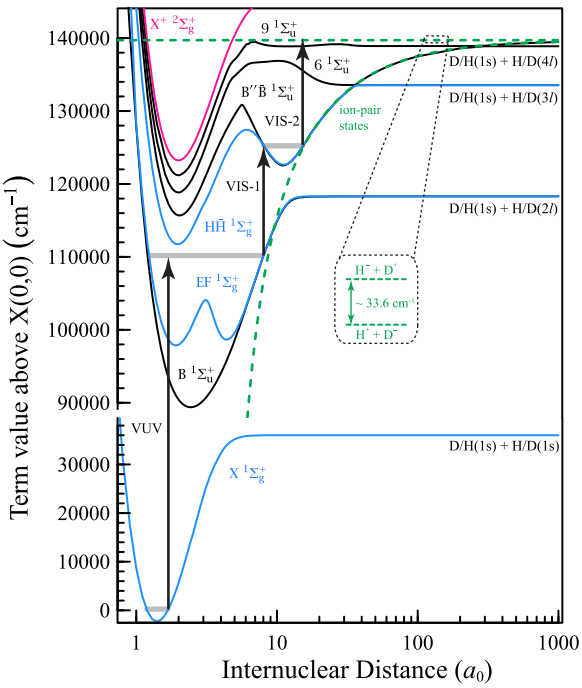



FIG. 1. Potential-energy curves and excitation scheme used for the observation of heavy-Rydberg states of HD beyond $n_{IP} = 200$ (see the text for details).

*gerade* (blue) and *ungerade* (black) symmetry (from Refs. 18 and 19) and the $-1/R$ Coulomb potential (dashed green line) characteristic of ion-pair states. The HH̄ and B″B̄ states are the lowest electronic states of molecular hydrogen having long-range attractive walls that almost exactly match the Coulomb potential. The B and HH̄ ion-pair states chosen as intermediate levels in Eq. (4) are correlated adiabatically to the H/D(1s) + D/H($n\ell$) dissociation thresholds with $n = 2$ and 3, respectively. The excitation sequence selects the $N = 0$ rotational level of the $\bar{H}(v = 9)$ state so that the heavy-Rydberg states observed here have a total angular momentum (excluding spins) of $N = 1$.

The experiments were carried out using the spectrometer described in Ref. 20. The pulsed tunable vacuum-ultraviolet (VUV) and visible (VIS-1 and VIS-2) lasers employed in this sequence have been described in detail in Refs. 21 and 22, where a similar excitation sequence was used to access the shape resonances of $H_2^+$ from the ground state of $H_2$. The lasers crossed a skimmed supersonic beam of HD at right angles on the axis of a cylindrically symmetric electrode stack consisting of six resistively coupled metallic plates. The ions generated by photoionization or electric field ionization were extracted by applying a pulsed electric potential across the stack and accelerated toward a microchannel-plate detector located at the end of a time-of-flight mass spectrometer. All spectra were recorded by monitoring the ion signals as a function of the wavenumber of the VIS-2 laser. The spectra of the heavy-Rydberg states of HD were obtained by simultaneously collecting the $HD^+$ ion signal produced by autoionization and the $H^+$ and $D^+$ ion signals resulting from predissociation into H($n$ = 3, 4) and D($n$ = 3, 4) fragments followed by photoionization of these excited fragments with the VIS-2 laser. H/D($n$ = 2) fragments could not be detected because the

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frequency of the VIS-2 laser was not high enough to ionize them. The thresholds for dissociation into H($n \geq 5$) and D($n \geq 5$) fragments are located energetically above $E_{\mathrm{IPF}}$. The VIS-2 laser wavenumber was calibrated at an accuracy of 0.03 $\mathrm{cm}^{-1}$ using a commercial wavemeter.

Photoionization spectra were recorded by carrying out the photoexcitation under field-free conditions and extracting the $H^+$, $D^+$, and $HD^+$ ions with a single delayed pulsed extraction field of 3 V/cm. TIPP spectra were recorded using a pulse sequence consisting of a 3-$\mu$s-long −2 V/cm discrimination pulse immediately followed by a 1.5 V/cm field-dissociation pulse. The discrimination pulse served the purpose of field dissociating the highest-lying heavy-Rydberg states and of removing the resulting ions as well as prompt ions from the ion-extraction region. The long-lived heavy-Rydberg molecules were then field dissociated and extracted by the field-dissociation pulse and the $H^+$ and $D^+$ fragments collected in separate time-of-flight windows. This pulse sequence enabled us to record TIPP spectra at a resolution of 1 $\mathrm{cm}^{-1}$ by monitoring the field dissociation of long-lived heavy-Rydberg states, yielding $H^+$ and $D^+$ ions just below the $H^+ + D^-$ and $D^+ + H^-$ thresholds, respectively (see Fig. 3).

Figure 2 depicts photoionization spectra of HD in the region of heavy-Rydberg states with $n_{\mathrm{IP}} \approx 400$ obtained by monitoring the $HD^+$ (top trace), $D^+$ (middle trace), and $H^+$ (bottom trace) signals. Heavy-Rydberg states are clearly visible in all three spectra and are resolved over the entire spectral range. They can be grouped into two series, one converging on the lower ($H^+ + D^-$) and the other on the upper ($D^+ + H^-$) ion-pair dissociation thresholds, as indicated by the lower and upper assignment bars, respectively. The energy-level structure is well described by Eq. (2), indicating that the quantum defects are to a good approximation energy independent and that the Coulomb-dominated regime is reached. The observation of signals of comparable signal-to-noise ratio in all three spectra indicate that the two $N = 1$ heavy-Rydberg channels of HD are strongly coupled to the $n = 3$, 4 dissociation continua and to the electronic Rydberg channels of HD.

The line shapes of the individual resonances rapidly evolve along the series. In certain regions, the resonances have Lorentzian profiles, in others they appear as windows, and in others still they have asymmetric Fano-type profiles. Most resonances overlap and are subject to interference effects such as those described by Mies[23] so that it is often not possible to determine their exact positions, which prevented the extrapolation of the series limits using Eq. (2). The spectra presented in Fig. 2 represent the first observation of heavy-Rydberg states in HD and also the first observation of heavy-Rydberg states of molecular hydrogen with $n_{\mathrm{IP}} \gg 200$, a region where nonadiabatic interactions with Rydberg states at short range become less important (see Fig. 1).

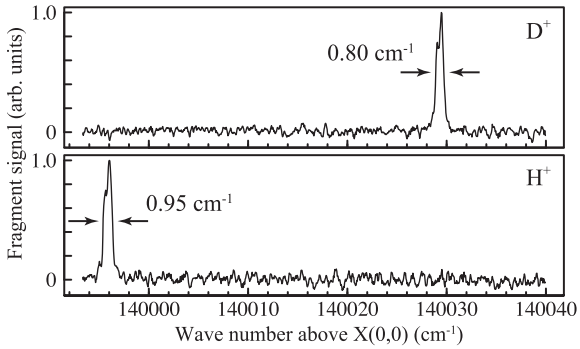



FIG. 3. TIPP spectrum of HD in the vicinity of the $D^+ + H^-$ and $H^+ + D^-$ dissociation thresholds obtained by monitoring the $D^+$ (upper spectrum) and $H^+$ (lower spectrum) ions produced by delayed pulsed field dissociation.

The TIPP spectra of HD in the vicinity of the ion-pair dissociation thresholds are depicted in Fig. 3. The lines corresponding to the lower and upper ion-pair dissociation thresholds are detected in the $H^+$ (lower trace) and $D^+$ (upper trace) signal channels. The heavy-Rydberg states contributing to the field-dissociation signals have $n_{\mathrm{IP}}$ values between about 8500 and 12 000. The line observed at the lower threshold is slightly broader [full width at half maximum (FWHM) of 0.95 $\mathrm{cm}^{-1}$] than that observed at the upper threshold (FWHM = 0.8 $\mathrm{cm}^{-1}$). These different widths indicate that the heavy-Rydberg states with $n_{\mathrm{IP}} \leq 9000$ located just below the upper threshold have shorter lifetimes than the corresponding states located below the lower threshold and are thus not detected. This observation suggests that the $H^-D^+$ heavy-Rydberg states may predissociate into the $H^+ + D^-$ ion-pair continuum. This process, however, would involve the transfer of *both* electrons.

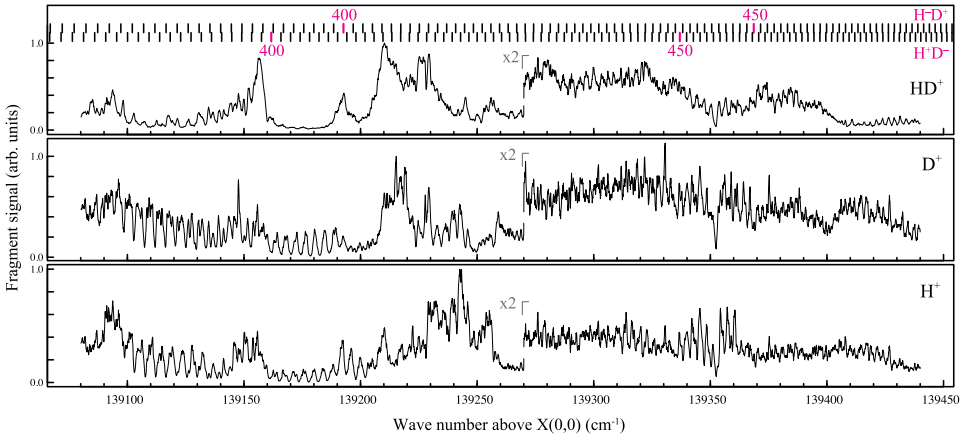



FIG. 2. Spectra, with a normalized intensity scale, of heavy-Rydberg states of HD obtained via the $\bar{H}(9,0)$ intermediate state. The assignment bars and numbers give the positions of the $H^+D^-$ and $H^-D^+$ heavy-Rydberg states calculated with the Rydberg formula for heavy-Rydberg states and the values of $n_{\mathrm{IP}}$, respectively.

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After correcting for the field-induced shifts of the ion-pair dissociation thresholds, we derive from the TIPP spectra values of 139 997.4(5) $cm^{-1}$ and 140 030.8(5) $cm^{-1}$ for the $H^+ + D^-$ and $D^+ + H^-$ dissociation thresholds, respectively. Using Eq. (1), values of 6087.2(5) $cm^{-1}$ and 6083.6(5) $cm^{-1}$ are derived for the electron affinities of D and H, respectively, with an uncertainty of 0.5 $cm^{-1}$ resulting from the determination of the field-induced shift of the thresholds. Both values agree within the experimental uncertainties with the electron affinities reported by Lykke *et al.*,[11] with $E_{ea}(H)$ being four times less, and $E_{ea}(D)$ being slightly more, precise than their values (see Table I).

The highest heavy-Rydberg states observed at both thresholds survive the 3 $\mu$s delay time between photoexcitation and the application of the field-dissociation pulse. The interval between the sharp high-energy edges of the two TIPP lines in Fig. 3 thus corresponds to the energy separation $\Delta E_{IPF}$ between the two thresholds and can be used to determine the electron affinity of D using Eq. (3). Because the effect of the pulsed dissociation field is the same for both lines of the TIPP spectra, this procedure to determine $E_{ea}(D)$ has the advantage that its accuracy is not limited by the uncertainty in the determination of the field-induced shift. By determining the half-maximum position of the high-energy edge of the two lines observed in 12 different recordings of the TIPP spectra of HD, we determined the interval between the two ion-pair dissociation thresholds of HD to be

$$\Delta E_{IPF}/(hc) = 33.62(23)\ cm^{-1}, \quad (5)$$

which, using Eq. (3) and the ionization energies of the atoms[9] and the (hyperfine-free, see below) electron affinity of the hydrogen atom [$E_{ea}(H) = 6083.03(15)\ cm^{-1}$[11]], results in

$$E_{ea}(D)/(hc) = 6086.81(27)\ cm^{-1}. \quad (6)$$

This value, which is compared with earlier experimental and theoretical results in Table I, is in agreement with, but more accurate than, the value of 6086.2(6) $cm^{-1}$ obtained by Lykke *et al.*[11] For the comparison with the theoretical calculations, which ignored the hyperfine structure, we added 3/4 of the splitting between the $F = 0$ and 1 hyperfine levels of H (i.e., 3 × 1422.807 58 MHz/4 = 0.0356 $cm^{-1}$) to the value $E_{ea}(H) = 6082.99(15)\ cm^{-1}$ determined for the $F = 0$ component by Lykke *et al.*. The hyperfine structure of D is negligible compared to the uncertainty of 0.6 $cm^{-1}$ of the value $E_{ea}(D) = 6086.2(6)\ cm^{-1}$ determined by Lykke *et al.*[11] Our new value of the electron affinity of D [6086.81(27) $cm^{-1}$] is in excellent agreement with the value calculated by Kinghorn and Adamowicz[24] in calculations including relativistic and quantum-electrodynamic corrections.

TABLE I. Electron affinities $E_{ea}$ of H and D. All values are in $cm^{-1}$ and are for the center of gravity of the two hyperfine components of H(1s) and D(1s). The values in parentheses correspond to one standard deviation in units of the last figure.

| | $E_{ea}(H)$ | $E_{ea}(D)$ | References |
|---|---|---|---|
| Experiment | 6083.03(15)[a] | 6086.2(6) | Lykke *et al.*[11] |
| | | 6086.81(27) | This work, TIPPS, and Eq. (3) |
| | 6083.6(5) | 6087.2(5) | This work, TIPPS, and Eq. (1) |
| Theory | 6083.096[b] | | Pekeris[25] |
| | 6083.099 414[c] | | Drake[26] |
| | 6083.099 4[c] | 6086.7137 | Kinghorn and Adamowicz[24] |

[a]This value corresponds to the center of gravity of the hyperfine structure (see the text).
[b]Including mass-polarization and relativistic corrections, but not the Lamb shift.
[c]Including mass-polarization, relativistic corrections, and the Lamb shift.

In this article, we have described a strategy, based on resonant multiphoton excitations through ion-pair states, to directly access heavy-Rydberg states and have illustrated it with the first observation of heavy Rydberg states of HD. Two heavy-Rydberg series converging on the $D^+ + H^-$ and the $H^+ + D^-$ ion-pair dissociation thresholds were studied from principal quantum numbers around 350 all the way to the series limit following excitation from the $\bar{H}(v = 9, N = 0)$ intermediate level. The heavy-Rydberg states of HD exhibit complex dynamics and decay through predissociation into the H/D(1s) + D/H($n\ell$) continua with $n \leq 4$ and through autoionization. The spectra are characterized by complex line shapes, which rapidly change with increasing $n_{IP}$ values, indicating interactions between electronic and heavy Rydberg states, the $HD^+ + e^-$ ionization, and the H/D(1s) +D/H($n \leq 4$, $\ell$) dissociation continua. High-resolution pulsed-field dissociation spectra of HD at the $H^+ + D^-$ and $H^- + D^+$ dissociation thresholds were also recorded and revealed long-lived heavy-Rydberg states in the range of principal quantum numbers beyond 8500. The analysis of these spectra led to the determination of an improved value of the electron affinity of the deuterium atom [6086.81(27) $cm^{-1}$]. A higher accuracy should be possible based on the extrapolation of the heavy-Rydberg-series. To reach this goal, a better understanding of their decay dynamics and of the line shapes is necessary.

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