The determination of the dissociation energy of the hydrogen molecule (H\textsubscript{2}) and its deuterated isotopomers (HD and D\textsubscript{2}) has played an important role in the development of molecular quantum mechanics.\textsuperscript{1} Classical physics and even the old quantum theory of Bohr and Sommerfeld proved inadequate to explain the existence of H\textsubscript{2} and of chemical bonds in general. The first qualitatively correct theoretical description of chemical bonds was achieved in 1927 by Heitler and London\textsuperscript{2} in their celebrated application of the new quantum theory to the H\textsubscript{2} molecule.

Although Heitler and London’s estimate of the dissociation energy of H\textsubscript{2} (2.9 eV) was smaller than the experimental value of Wittmer [4.15 eV (Ref. 3)] by about 30\%, their work marked the beginning of a still ongoing series of theoretical studies aimed at accurately describing the chemical bond in H\textsubscript{2} in first-principles calculations. The observable quantity used to assess the accuracy of the calculations is the dissociation energy \(D_0\), i.e., the energy difference between the onset of the H\textsubscript{(1s)}+H\textsubscript{(1s)} (or H+D, or D+D) dissociation continuum and the ground rovibronic level of H\textsubscript{2} (or HD, or D\textsubscript{2}). Consequently, precise and accurate measurements of the dissociation energy of the hydrogen molecule and its deuterated isotopomers have played an essential role in the validation of the theoretical results. To illustrate this point, we refer to the extensive work published during the past 50 years on the dissociation energy of HD\textsuperscript{4–18} which is the subject of this communication. More many articles have been published on the dissociation energy of H\textsubscript{2} and D\textsubscript{2} (see Refs. 19–21 and references therein).

During the 83 years that have elapsed since Heitler and London’s work, there were periods during which experimental and theoretical results appeared to be in conflict, but these conflicts were invariably resolved by the next generation of more accurate experiments or calculations, so that today nobody seriously thinks of questioning the ability of the quantum theory to accurately describe chemical bonds. Instead, the interest in comparing ever more precise theoretical and experimental values of the dissociation energy of the hydrogen molecule is motivated by the necessity, at each new generation of experiments, to include and quantify effects neglected in the previous theoretical treatments. The challenge consists of fully accounting for electron correlation effects, properly treating nonadiabatic and relativistic effects, and including quantum electrodynamics (QED) corrections of sufficiently high order in the fine-structure constant \(\alpha\) (see, e.g., Refs. 17 and 21).

To account for the most recent experimental value of the dissociation energy of H\textsubscript{2} \([D_0(\text{H}_2) =36\ 118.069\ 62(37)\ \text{cm}^{-1}\) (Ref. 19)], Piszczatowski et al.\textsuperscript{21} had to calculate relativistic and QED corrections at the adiabatic level of theory by including all contributions of the order of \(\alpha^2\) and \(\alpha^3\) and the major (one-loop) \(\alpha^4\) term. Their result \([D_0(\text{H}_2) =36\ 118.0695(10)\ \text{cm}^{-1}]\) is in agreement with experiment. In the same study, a similar calculation for D\textsubscript{2} \([D_0(\text{D}_2) =36\ 748.3633(9)\ \text{cm}^{-1}]\) pointed at a small discrepancy (by two standard deviations) with experimental results,\textsuperscript{18} which was resolved in a very recent measurement yielding a value \(D_0(\text{D}_2) =36\ 748.362\ 86(68)\ \text{cm}^{-1}\).\textsuperscript{20} No similarly accurate values have been reported for HD. The purpose of this communication is to present a new determination of the dissociation energy of HD that can be used as a test of a calculation by Pachucki and Komasa\textsuperscript{22} carried out in parallel to the experiments described here.

The experimental setup and procedure were described in detail in our equivalent studies on H\textsubscript{2} (Ref. 19) and D\textsubscript{2}.\textsuperscript{20} In brief, members of the singlet \(np\) Rydberg series converging to the \(X^+\ \Sigma^+_g\) electronic ground state of HD\textsuperscript{+} were produced in a (2+1)’ three-photon excitation scheme starting

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Communication: The ionization and dissociation energies of HD

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The adiabatic ionization energy [in units of \(\hbar c\), \(E_i =124\ 568.485\ 81(36)\ \text{cm}^{-1}\)] and the dissociation energy \([D_0(\text{H}_2) =36\ 405.783\ 66(36)\ \text{cm}^{-1}]\) of HD have been determined using a hybrid experimental-theoretical method. Experimentally, the wave numbers of the \(EF(v=0,N=0)\rightarrow np[X^+(v^*=0\text{ and } N^*=0)\text{ and } EF(v=0,N=1)\rightarrow np[X^+(v^*=0\text{, } N^*=1)\text{]}\) transitions to singlet Rydberg states were measured by laser spectroscopy and used to validate predictions of the electron binding energies by multichannel quantum defect theory. Adding the transition energies, the electron binding energies and previously reported term energies of the \(EF\) state led to a determination of the adiabatic ionization energy of HD and of rovibrational energy spacings in HD\textsuperscript{+}. Combining these measurements with highly accurate theoretical values of the ionization energies of the one-electron systems H, D, and HD\textsuperscript{+} further enabled a new determination of the dissociation energy of HD. © 2010 American Institute of Physics. [doi:10.1063/1.3483462]
from the $X^1 \Sigma^+_g(v=0,N=0,1)$ state of HD. The $EF^1 \Sigma^+_u(v=0,N=0,1)$ intermediate state was excited in a two-photon transition using the third harmonic of a commercial dye laser ($\lambda \sim 201$ nm, bandwidth $\sim 1$ GHz, referred to as $X \rightarrow EF$ laser). The second harmonic of a pulsed titanium-doped sapphire (Ti:Sa) amplifier (bandwidth $\sim 20$ MHz, referred to as $EF \rightarrow n$ laser),$^{23}$ seeded by a Ti:Sa cw ring laser, was then used to access the Rydberg states. For detection, the Rydberg states were ionized and the HD$^+$ ions accelerated toward a microchannel plate detector by a pulsed electric field. The spectra were obtained by monitoring the HD$^+$ ion signal as a function of the wave number of the $EF \rightarrow n$ laser.

Survey spectra of three Rydberg series were recorded [we use the notation $n\ell N_p(v^*)$; all quantum numbers have their usual meanings; see, e.g., Ref. 24]: the $np_0(0)$ and $np_0(1)$ series from the $EF(v=0,N=0)$ intermediate level, and the $np_{11,2}(0)$ series from the $EF(v=0,N=1)$ intermediate level. As illustration, several sections of the survey spectrum of the $EF(v=0,N=0) \rightarrow np_0(0)$ transitions are displayed in Fig. 1, and the second column of Table I lists the transition wave numbers with respect to the $64p_0(0)$ level for all Rydberg states detected with a sufficient signal-to-noise ratio. The complete experimental data set, including the positions of the members of the $np_{11,2}(0)$ and $np_0(1)$ series with respect to the $69p_{12}(0)$ and $55p_0(1)$ levels, respectively, is given in the supplementary material. The absolute positions of the reference levels are determined separately, as explained below.

Multichannel quantum defect theory (MQDT) extended to the treatment of hyperfine effects, as described in Ref. 24, was used to determine the electron binding energies of the $np$ Rydberg states. The quantum defects used in the MQDT calculations have been adjusted to very high-resolution experimental data, are independent of isotopic substitution, and can be used to determine the electron binding energies of high-$n$ Rydberg states with an accuracy better than 1 MHz, as explained in Refs. 20, 24, and 26. A sufficient number of vibrational channels (up to $v^*=9$) was included to ensure convergence, as verified in separate calculations of singlet and triplet Rydberg manifolds. The positions of the rovibra-

tional levels of HD$^+$, which are needed as input to the MQDT calculations, were taken from $ab$ initio calculations (Ref. 27 for $v^*=0$–4 and Ref. 28 for $v^*=5$–21). The hyperfine effects were included in the frame transformation connecting the close-coupling case [Hund’s case (b)] and the long-range coupling case [Hund’s case (c)], as explained in detail in Ref. 24. Because of the reduced symmetry of HD compared to H$_2$ and D$_2$, the two nuclear spins are independent, and the close-coupling angular momentum coupling scheme had to be extended (details will be included in a future publication). For the long-range coupling case, the $ab$ initio hyperfine Hamiltonian operator of HD$^+$ from Ref. 29 was used. The explicit inclusion of the hyperfine structure of the Rydberg states turned out to be necessary to properly account for the weak singlet-triplet mixing, and calculations

![Figure 1](image-url)
neglecting the hyperfine interaction led to binding energies which were too large by about 20 MHz.

The binding energies of the observed np Rydberg states (defined as the center of gravity of the electron binding energies of the relevant hyperfine components) resulting from the MQDT calculations are given in the third column of Table I for the np0(0) series and in the supplementary material\textsuperscript{25} for the other series. Adding the relative transition wave numbers from the second column to these values would ideally lead to the same value of the ionization energy for all members of a Rydberg series. With the exception of the states 66–68p0(0) the deviation is on the order of the experimental uncertainty of \(\sim 24\) MHz. We believe that the 66–68p0(0) Rydberg states are subject to perturbations resulting from a g/u-mixing channel interaction with the ns1\(_1\) and nd1\(_1\) Rydberg series, potentially enhanced by the weak stray field present in the experimental volume. The results presented in Table I demonstrate that the MQDT calculations reproduce the experimentally observed positions well within the experimental uncertainty of the survey spectra, as might have been expected from our previous studies of H\(_2\) and D\(_2\)\textsuperscript{24,26}.

After recording the survey spectra, the transitions to the states 64p0(0), 69p1(0), and 55p0(1) were chosen for measurements of absolute transition wave numbers. These wave numbers were obtained by measuring the difference between the fundamental frequency of the \(E\rightarrow n\) laser and the positions of selected \(^{127}\)I\(_2\) absorption lines, as illustrated in Fig. 1, for the transition to the 64p0(0) Rydberg state. For the 64p0(0) and 69p1(0) states, the \(a_\text{10}\) hyperfine component of the P181, \(B\rightarrow X(0–14)\) transition at 12 620.158 873(1) cm\(^{-1}\),\textsuperscript{20} and for the 55p0(1) state, the \(a_\text{10}\) hyperfine component of the P124, \(B\rightarrow X(2–11)\) transition at 13 571.89445(5) cm\(^{-1}\) (Ref. 30) were chosen. In order to eliminate possible Doppler shifts, the \(E\rightarrow n\) laser beam was split into two components and introduced into the interaction region in a counterpropagating configuration. The measurements were carried out in independent pairs by blocking one and then the other beam component. The individual transition wave numbers determined from these measurements are plotted as squares and triangles in Fig. 2. The final results were obtained by taking the average of all measurements, considering the shifts and uncertainties given in the supplementary material.\textsuperscript{25}

Table II summarizes all energy intervals used to determine the positions \(E\_i^{(a,N)}\) of the energy levels of HD\(^+\) with respect to the \(X^+ \Sigma^+_1(v=0,N=0)\) ground state of HD. Rovibrational energy spacings of HD\(^+\) derived from these quantities are given in Table III and are in agreement with the \textit{ab initio} values of Korobov,\textsuperscript{27} the experimental uncertainty being, however, more than three orders of magnitude larger than the 0.3 ppb (parts per 10\(^6\)) accuracy of the calculations. By subtracting the highly accurate HD\(^+\) rovibrational energies calculated \textit{ab initio} by Korobov,\textsuperscript{27} from \(E\_i^{(1,0)}\) and \(E\_i^{(1,1)}\), two more independent values of the adiabatic ionization energy are obtained (in addition to \(E\_i^{(0,0)}\)). All three values are consistent within their uncertainties, and, when combined in a statistical analysis, they lead to the final result

\[
E_i^{(1)}(HD^+) = 124 568.485 81(36) \text{ cm}^{-1},
\]

which is the dissociation energy \(D_0\) of HD can be derived using the relation (see Fig. 5 of Ref. 19)

\[
D_0(\text{HD}) = E_i(\text{HD}) + E_i(\text{HD}^+) - E_i(\text{H}) - E_i(\text{D}),
\]

where \(E_i(\text{HD}^+) = 131 224.684 15(6) \text{ cm}^{-1}\) is taken from \textit{ab initio} calculations\textsuperscript{27} and \(E_i(\text{H}) = 109 678.771 743 07(10) \text{ cm}^{-1}\), and \(E_i(\text{D}) = 109 708.614 552 99(10) \text{ cm}^{-1}\) from the most recent determination of the Rydberg constant.\textsuperscript{31} The resulting value is \(D_0(\text{HD}) = 36 405.783 66(36) \text{ cm}^{-1}\), where the uncertainty is dominated by the experimental uncertainty of the ionization energy of HD.

<table>
<thead>
<tr>
<th>Label</th>
<th>Energy interval</th>
<th>Wave number (cm(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>(X(0,0))–(X(0,1))</td>
<td>89.227 950(5)</td>
<td>34</td>
</tr>
<tr>
<td>(2)</td>
<td>(X(0,0))–(EF(0,0))</td>
<td>99 301.346 62(20)</td>
<td>35</td>
</tr>
<tr>
<td>(3)</td>
<td>(X(0,1))–(EF(0,1))</td>
<td>99 259.917 93(20)</td>
<td>35</td>
</tr>
<tr>
<td>(4)</td>
<td>(EF(0,0))–64p0(0)</td>
<td>25 240.360 96(42)</td>
<td>This work</td>
</tr>
<tr>
<td>(5)</td>
<td>(EF(0,1))–69p1(0)</td>
<td>25 240.152 51(58)</td>
<td>This work</td>
</tr>
<tr>
<td>(6)</td>
<td>(EF(0,0))–55p0(1)</td>
<td>27 143.988 30(48)</td>
<td>This work</td>
</tr>
<tr>
<td>(7)</td>
<td>64p0(0)–(X^+(0,0))</td>
<td>26 778 44(3)</td>
<td>This work</td>
</tr>
<tr>
<td>(8)</td>
<td>69p1(0)–(X^+(0,1))</td>
<td>23 048 34(3)</td>
<td>This work</td>
</tr>
<tr>
<td>(9)</td>
<td>55p0(1)–(X^+(1,0))</td>
<td>36 145 65(3)</td>
<td>This work</td>
</tr>
</tbody>
</table>

\(^{\text{3}}\)X^+(v^+,N^+)\) labels the center of gravity of all fine and hyperfine components of the \(X^+ \Sigma^+_1(v^+,N^+)\) state of HD\(^+\).
In conclusion, the positions of the energy levels \((v^+ , N^+) = (0, 0), (0, 1), \) and \((1, 0)\) of the \(X^+ \Sigma_g^+ \) ground state of HD\(^+\) with respect to the \(X^+ \Sigma_g^+ (v = 0, N = 0)\) rovibrionic ground state of HD have been determined with accuracies of 14, 18, and 45 MHz, respectively. The measurements have been confirmed by (i) comparing the relative positions of 37 \(np\) Rydberg states with the predictions of MQDT calculations (see Table I and the supplementary material\(^3\)) and (ii) verifying the consistency of the three values with highly accurate \textit{ab initio} calculations of rovibrational levels of HD\(^+\) (see Table III). Combining the experimental values with \textit{ab initio} calculations of the one-electron systems \(H, D,\) and HD\(^+\) enabled the determination of the ionization and dissociation energies of HD with an uncertainty of 11 MHz. The present value for the adiabatic ionization energy \([E_i=124 \text{ 568.485 81(36) cm}^{-1}]\) is in agreement with the most recent previous experimental value \([E_i=124 \text{ 568.491(17) cm}^{-1}\) (Ref. 32)]. The dissociation energy \([D_0=36 \text{ 405.783 66(36) cm}^{-1}]\) deviates by three standard deviations from the result of Zhang \textit{et al.} \([D_0=36 \text{ 405.828(16) cm}^{-1}\) (Ref. 18)]. Comparison to the result of a theoretical investigation by Pachucki and Komasa \([D_0=36 \text{ 405.7828(10) cm}^{-1}\) (Ref. 22)] shows agreement between the calculated value and our result within the uncertainty limits.

HD represents a more stringent test of the theoretical predictions than \(H_2\) and \(D_2\) because of its lower symmetry and the necessity to include a “heteronuclear” term in the Hamiltonian operator, as discussed earlier by Wolniewicz\(^33\) [see also Eq. (24) of Ref. 22]. HD also posed additional difficulties in our determination: It necessitated the inclusion of a more complex frame transformation and forced us to avoid spectral regions where \(ns\) and \(nd\) Rydberg states lie very close to the \(np\) Rydberg states. These difficulties might explain why the theoretical and experimental results agree only at the side of the error margins. Nevertheless, we believe that the present determination of the dissociation energy of HD provides strong support for the validity of the latest calculations.\(^2\) An agreement between theoretical and experimental values of the dissociation energy of molecular hydrogen at the level of \(10^{-3} \text{ cm}^{-1}\), indeed, is well beyond what the pioneers in this field might have considered achievable.

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\(^{8}\)K. Pachucki and J. Komasa, \textit{Phys. Chem. Chem. Phys.} \textbf{12}, 9188 (2010), the present work was carried out in parallel to this theoretical investigation without exchanging information until both results were final.


\(^{11}\)See supplementary material at \url{http://dx.doi.org/10.1063/1.3483462} for the positions of all Rydberg states of HD measured in the realm of this investigation and for a table containing all shifts and uncertainties in the positions of the 64p\(\ell_0(0), 69p\(\ell_1(0),\) and 55p\(\ell_0(1)\) Rydberg states of HD.


