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Author(s):
Liu, Jinjun; Sprecher, Daniel; Jungen, Christian; Ubachs, Wim; Merkt, Frédéric

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Determination of the ionization and dissociation energies of the hydrogen molecule
Determination of the ionization and dissociation energies of the deuterium molecule (D$_2$)

Jinjun Liu,† Daniel Sprecher,† Christian Jungen,‡ Wim Ubachs,§ and Frédéric Merkt$^*$$^a$

$^1$Laboratorium für Physikalische Chemie, ETH-Zürich, 8093 Zürich, Switzerland
$^2$Laboratoire Aimé Cotton, CNRS II, Bâtiment 505, Campus d’Orsay, 91405 Orsay Cedex, France
$^3$Department of Physics and Astronomy, Laser Centre, Vrije Universiteit, De Boelelaan 1081, 1081 HV Amsterdam, The Netherlands

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The transition wave numbers from selected rovibrational levels of the EF $^1\Sigma^+_g(v=0)$ state to selected $np$ Rydberg states of ortho- and para-D$_2$ located below the adiabatic ionization threshold have been measured at a precision better than $10^{-3}$ cm$^{-1}$. Adding these wave numbers to the previously determined transition wave numbers from the $X^1\Sigma^+_g(v=0, N=0,1)$ states of D$_2$ and to the binding energies of the Rydberg states calculated by multichannel quantum defect theory, the ionization energies of ortho- and para-D$_2$ are determined to be $124\,745.394\,07\,(58)$ cm$^{-1}$ and $124\,715.003\,77\,(75)$ cm$^{-1}$, respectively. After re-evaluation of the dissociation energy of D$_2^+$ and using the known ionization energy of D, the dissociation energy of D$_2$ is determined to be $36\,748.362\,86\,(68)$ cm$^{-1}$. This result is more precise than previous experimental results by more than one order of magnitude and is in excellent agreement with the most recent theoretical value $36\,748.363\,3$ cm$^{-1}$ [K. Piszczałkowski, G. Lach, M. Przybyłek et al., J. Chem. Theory Comput. 5, 3039 (2009)]. The ortho-para separation of D$_2$, i.e., the energy difference between the $N=0$ and $N=1$ rotational levels of the $X^1\Sigma^+_g(v=0)$ ground state, has been determined to be $59.781\,30\,(95)$ cm$^{-1}$. © 2010 American Institute of Physics. [doi:10.1063/1.3374426]

I. INTRODUCTION

The ionization and dissociation energies of the hydrogen molecule (H$_2$) and its isotopomers (D$_2$ and HD) are benchmark quantities in molecular quantum mechanics. Recently, we measured the transition wave number from the EF state of ortho-H$_2$ to a selected Rydberg state below the ground state of ortho-H$_2^+$ with a precision of 0.000 29 cm$^{-1}$. Combining this measurement with previous experimental and theoretical results for other energy intervals, the ionization and dissociation energies of the hydrogen molecule have been determined to be $124\,417.491\,13\,(37)$ and $36\,118.069\,62\,(37)$ cm$^{-1}$, respectively. Most recently, Piszczałkowski et al. made a new theoretical calculation of the dissociation energy of H$_2$ and D$_2$ by including nonadiabatic, relativistic, and quantum electrodynamics (QED) corrections. The relativistic and QED corrections were obtained at the adiabatic level of theory by including all contributions of the order $\alpha^2$ and $\alpha^3$ as well as the major (one-loop) $\alpha^4$ term, where $\alpha$ is the fine-structure constant. The theoretical value they obtained for the dissociation energy of H$_2$, $36\,118.0695\,(10)$ cm$^{-1}$, is in excellent agreement with our value. For the D$_2$ molecule, however, Piszczałkowski et al. pointed out a small discrepancy (at the level of two standard deviations of the experimental value) between their theoretical value [36 748.3633(9) cm$^{-1}$] and the most recent experimental result [36 748.343(10) cm$^{-1}$, Ref. 4]. A new experimental determination of the dissociation energy of D$_2$ with a similar precision to that reached for H$_2$ would therefore be desirable to resolve this discrepancy and would provide another quantity with which future theoretical calculations can be compared.

We report here on a new determination of the ionization energies of both ortho- and para-D$_2$ $E_i(\text{ortho-D}_2)=E_i(\text{D}_2)$ and $E_i(\text{para-D}_2)$ from which we derive a new experimental value of the dissociation energy of D$_2$. The ionization energies are obtained in each case as a sum of three energy intervals (see Fig. 1). In the case of ortho-D$_2$, the first energy interval is between the $X^1\Sigma^+_g(v=0, N=0)$ and the $EF\,^1\Sigma^+_g(v=0, N=0)$ levels, the transition wave number of which was measured with high precision previously ($99\,461.449\,08\,(11)$ cm$^{-1}$, Ref. 5), the second between the $EF\,^1\Sigma^+_g(v=0, N=0)$ and the $29p2\,(0)$ Rydberg state belonging to a series converging on the $X^1\Sigma^+_g(u^+=0, N^+=2)$ level of ortho-D$_2^+$, and the third between the $29p2\,(0)$ Rydberg state and the $X^1\Sigma^+_g(u^+=0, N^+=0)$ ionic level. In the case of para-D$_2$, the first energy interval is between the $X^1\Sigma^+_g(v=0, N=1)$ and the $EF\,^1\Sigma^+_g(v=0, N=1)$ levels ($99\,433.716\,38\,(11)$ cm$^{-1}$, Ref. 5), the second between the $EF\,^1\Sigma^+_g(v=0, N=1)$ and the $52p1\,(0)$ Rydberg state belonging to a series converging on the $X^1\Sigma^+_g(u^+=0, N^+=1)$ level of para-D$_2^+$, and the third the binding energy of the $52p1\,(0)$ Rydberg state. The transition wave numbers between the selected rovibrational levels of the $EF$ state and the Rydberg states were measured using a $2(1')$ resonant three-photon excitation sequence followed by delayed pulsed-field ionization (PFI) of the Rydberg states as in our study of H$_2$. The binding energies of the Rydberg states were calculated by multichannel quantum defect theory (MQDT). The accuracy

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$^a$Electronic mail: feme@xuv.phys.chem.ethz.ch.
of the MQDT calculations for D\textsubscript{2} has been verified independently in a comparison with a high-resolution measurement of the \textit{nf} Rydberg spectra of D\textsubscript{2} by millimeter-wave spectroscopy\textsuperscript{6} and also with high-resolution laser spectra of the \textit{np} Rydberg states (see below).

The dissociation energy of D\textsubscript{2} \([D_0(D_2)]\) can be derived using the relation (see Fig. 5 of Ref. 3)

\[
D_0(D_2) = E_i(D_2) + D_0(D_2^+) - E_i(D),
\]

from the dissociation energy of the molecular cation \([D_0(D_2^+)]\), which was re-evaluated using available literature data (see Appendix B), and the ionization energy of the atom \([E_i(D)]\), which is known very accurately.\textsuperscript{7}

In addition, the ortho-para separation of the neutral molecule \(\Delta E_{1-0}\), defined as the energy level separation between the \(N=0\) and \(N=1\) rotational energy levels of the \(1^\Sigma^+_g(v=0)\) state of D\textsubscript{2}, can be derived using the relation (see Fig. 1):

\[
\Delta E_{1-0} = E_i(\text{ortho-D}_2) + \Delta E^+_{1-0} - E_i(\text{para-D}_2),
\]

where \(\Delta E^+_{1-0}\) is the ortho-para separation of the cation, which is known very accurately from calculations.\textsuperscript{8}

**II. EXPERIMENT**

The experimental setup is the same as used in our previous study of H\textsubscript{2}.\textsuperscript{3} In brief, the third harmonic of a commercial dye laser \((\lambda \sim 201 \text{ nm, bandwidth} \sim 0.04 \text{ cm}^{-1})\) was used to excite the \(EF^+ 1\Sigma^+_g(v=0, N=0,1) \leftarrow X^1\Sigma^+_g(v=0, N=0,1)\) two-photon transitions. The second harmonic of the near-infrared (NIR) output of a pulsed titanium-doped sapphire (Ti:Sa) amplifier \((\lambda \sim 396 \text{ nm, bandwidth} \sim 20 \text{ MHz})\),\textsuperscript{9,10} seeded by a Ti:Sa cw ring laser, was then used to access \textit{np} Rydberg states belonging to series converging on the lowest two rotational levels \((N^*=0 \text{ or } 1)\) of the \(X^+ 2\Sigma^+_g(v=0)\) state of D\textsubscript{2} from the selected \(EF^+ 1\Sigma^+_g(v=0, N=0 \text{ or } 1)\) levels. The 396 nm laser beam was split into two components and introduced into the interaction region in a counterpropagating configuration, both components overlapping spatially with the 201 nm beam. The difference between the transition wave numbers measured using each of these two components represents twice the Doppler shift resulting from a possible nonorthogonality between the molecular beam and the 396 nm laser beams and can be eliminated by taking the average value of the two measurements. The transitions were detected by ionizing the Rydberg states created by the two-step process using a pulsed electric field applied with a time delay with respect to the laser pulses. The generated cations were extracted by the same field and accelerated toward a microchannel plate detector. Spectra were obtained by monitoring the D\textsubscript{2} ion signal as a function of the wave number of the second laser.

The absolute and relative calibration of the Ti:Sa-cw-ring-laser frequency was carried out by recording, simultaneously with the PFI spectra, the Doppler-free saturation absorption spectrum of I\textsubscript{2} \textsuperscript{3,5,11} and the transmission signal through a high-finesse Fabry–Pérot etalon locked to a polarization-stabilized He–Ne laser.\textsuperscript{12} The frequency shift arising in the multipass amplification in the Ti:Sa crystals (<10 MHz) was determined by monitoring the interference between the pulse-amplified laser beam with the cw NIR output of the ring laser and taking the Fourier transform of the beat-note signal recorded when the 396 nm laser was on resonance with the EF to Rydberg transitions.

**III. RESULTS**

**A. Survey spectra of Rydberg states and MQDT calculations**

In our previous work on H\textsubscript{2}, the binding energy of the selected 54\rho\textsubscript{1}i\textsubscript{1}(0) Rydberg state of ortho-H\textsubscript{2} was taken from the result of a millimeter-wave spectroscopic experiment analyzed by MQDT at submegahertz accuracy.\textsuperscript{14} In a similar millimeter-wave experiment carried out on para-D\textsubscript{2},\textsuperscript{6} transitions from \(n=51d–53d\) to \(n=54f–57f\) Rydberg states belonging to series converging on the ground state of para-D\textsubscript{2} could also be measured and extrapolated to their series limits using the same MQDT parameters as used for ortho-H\textsubscript{2} at the same accuracy. These results confirmed the expectation that isotopic substitution does not affect the eigenquantum defects and demonstrated the ability of MQDT to predict the binding energy of Rydberg states with submegahertz accuracy.

No millimeter-wave transitions to the \textit{np} states accessed in the present experiment were observed for para-D\textsubscript{2}. The binding energies of these \textit{np} states were therefore calculated by MQDT in the present work, as listed in the second column of Table I. These values correspond to energy level separations between the centers of gravity of the hyperfine structures of both the Rydberg states and the \(N^*=0 \text{ (} N^*=1 \text{)}\)
level of ortho-$D_2^+$ (para-$D_2^+$). The hyperfine structure of the Rydberg states of para-$D_2$ was determined by MQDT in a full calculation of the type described in Refs. 6 and 14 and the hyperfine structure of para-$D_2^+$ was taken from Ref. 6. The binding energies were found to be identical to within 1 MHz with the binding energies determined in MQDT calculations neglecting nuclear spins. These are also expected to be accurate within 1 MHz. One should note here that the hyperfine splittings of the $np$ ($S = 0$) states at $n < 60$ is extremely small (typically less than 5 MHz) because the exchange interaction is much larger than the hyperfine interaction. In the present calculation, the MQDT parameters are the same as those determined for $H_2$ in Ref. 14 and ionization channels associated with vibrational levels of the cation with $v^+ \leq 9$ were included. The energies of the ionic levels were taken from Ref. 8. The $p$ Rydberg states are labeled $n\ell N_\pi^p(S)$ with all quantum numbers having their usual meanings (see Ref. 14 for details). A strong interaction between the $N^+ = 0$ and $N^+ = 2$ channels of ortho-$D_2$ and between the $N^+ = 1$ and $N^+ = 3$ channels of para-$D_2$ leads to the observation, for instance, of the $29p2_1$ level in spectra of the $np0_1$ levels. This interaction is perfectly described by the MQDT calculations.

Although it has been proven that the same MQDT parameters can be used to describe the $nf$ levels of both ortho-$H_2$ and para-$D_2$ with submegahertz accuracy, we decided to independently verify the accuracy of the calculations of $np$ states of both ortho- and para-$D_2$. For this reason, we recorded the survey spectra of the $np$ Rydberg series of ortho- and para-$D_2$ in the region close to the $nd$ and $nf$ states that were accessed in the previous millimeter-wave experiments. The spectra of ortho- and para-$D_2$ are displayed in Figs. 2(a) and 2(b), respectively, and consist each of one series of strong transitions from the $EF^1\Sigma_g^+(v = 0, N = 0)$ and $2p$ Rydberg states belonging to series converging on the $X^+ \Sigma_g^+(v^+ = 0, N^+ = 0)$ level of ortho-$D_2^+$ and on the $X^+ \Sigma_g^+(v^+ = 0, N^+ = 1)$ level of para-$D_2^+$, respectively. The third column of Table I gives their positions (in $cm^{-1}$) relative to the $29p2_1$ and the $52p1_2$ states in the case of ortho- and para-$D_2$, respectively. These two states are those that were chosen in the measurements using counterpropagating laser beams to determine the ionization energies (see Sec. III B). Adding up the MQDT binding energy and the relative wave number of each Rydberg state measured experimentally yields independent values of the binding energies of the $29p2_1$ and the $52p1_2$ states, which are listed in the last column of Table I. The uncertainties (one standard deviation) of the binding energies determined in this way are

<table>
<thead>
<tr>
<th>Rydberg state</th>
<th>MQDT binding energy (cm$^{-1}$)</th>
<th>Experimental wave number (cm$^{-1}$) relative to $29p2_1$</th>
<th>Experimental binding energy of $29p2_1$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$50p0_1$</td>
<td>44,193.51</td>
<td>$-0.961$ 90(80)</td>
<td>43,231.61</td>
</tr>
<tr>
<td>$29p2_1^a$</td>
<td>43,232.89</td>
<td>0</td>
<td>43,232.89</td>
</tr>
<tr>
<td>$51p0_1$</td>
<td>42,014.44</td>
<td>1.217 20(80)</td>
<td>43,231.64</td>
</tr>
<tr>
<td>$52p0_1$</td>
<td>40,517.04</td>
<td>2.715 88(80)</td>
<td>43,232.92</td>
</tr>
<tr>
<td>$53p0_1$</td>
<td>39,051.17</td>
<td>4.181 28(80)</td>
<td>43,232.45</td>
</tr>
<tr>
<td>$54p0_1$</td>
<td>37,661.24</td>
<td>5.571 52(80)</td>
<td>43,232.76</td>
</tr>
<tr>
<td>$55p0_1$</td>
<td>36,370.53</td>
<td>6.862 34(80)</td>
<td>43,232.87</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Rydberg state</th>
<th>MQDT binding energy (cm$^{-1}$)</th>
<th>Experimental wave number (cm$^{-1}$) relative to $52p1_2$</th>
<th>Experimental binding energy of $52p1_2$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$24p3_2^b$</td>
<td>45,104.08</td>
<td>$-4.550$ 18(80)</td>
<td>40,553.90</td>
</tr>
<tr>
<td>$50p1_2$</td>
<td>43,666.74</td>
<td>$-3.114$ 74(80)</td>
<td>40,552.00</td>
</tr>
<tr>
<td>$51p1_2$</td>
<td>42,096.42</td>
<td>$-1.543$ 32(80)</td>
<td>40,553.10</td>
</tr>
<tr>
<td>$52p1_2$</td>
<td>40,552.23</td>
<td>0</td>
<td>40,552.23</td>
</tr>
<tr>
<td>$53p1_2$</td>
<td>39,073.74</td>
<td>1.487 74(80)</td>
<td>40,552.48</td>
</tr>
<tr>
<td>$54p1_2$</td>
<td>37,669.40</td>
<td>2.884 40(80)</td>
<td>40,553.80</td>
</tr>
<tr>
<td>$55p1_2$</td>
<td>36,339.05</td>
<td>4.213 60(80)</td>
<td>40,552.65</td>
</tr>
<tr>
<td>$56p1_2$</td>
<td>35,081.98</td>
<td>5.471 70(80)</td>
<td>40,553.68</td>
</tr>
<tr>
<td>$57p1_2$</td>
<td>33,898.69</td>
<td>6.655 06(80)</td>
<td>40,553.75</td>
</tr>
</tbody>
</table>

$^a$Calculated by adding up the MQDT binding energy of each Rydberg state and its relative position (in cm$^{-1}$) with respect to the $29p2_1$ ($52p1_2$) state of ortho-$D_2$ (para-$D_2$) determined in the survey spectra.

$^b$State with the largest contribution from the $29p2_1$ ($24p3_2$) zero-order state. Because of the strong interaction between the $np0_1$ and $np2_1$ ($np1_2$ and $np3_2$) channels of ortho-$D_2$ (para-$D_2$), all Rydberg states are mixed.
0.000 58 cm\(^{-1}\) and 0.000 74 cm\(^{-1}\) for the 29p2\(_{1}\) state of ortho-D\(_2\) and the 52p1\(_{2}\) state of para-D\(_2\), respectively, and implicitly include the uncertainties of the MQDT calculation and of the relative frequency calibration of the spectra. The estimated experimental uncertainty is 0.000 80 cm\(^{-1}\), and the standard deviations of the binding energy calculation originate entirely from the experimental uncertainty, which consequently validates the accuracy of the MQDT calculation for the np states: errors in the binding energies calculated by MQDT of the order of 10 MHz would have been detected, and we believe that the MQDT calculations of the np Rydberg states of D\(_2\) are as accurate as those of H\(_2\), i.e., better than 1 MHz.\(^{14}\) Note that other weaker transitions were also observed and assigned to transitions to other Rydberg states but were not included into the analysis because of their poor signal-to-noise ratio.

**B. Measurements using counterpropagating laser beams**

In order to eliminate possible Doppler shifts of the EF to Rydberg transition frequencies and determine the ionization energies with better accuracy, the transition wave numbers from the \(N=0\) (\(N=1\)) levels of the EF \(1\Sigma^+_g(v=0)\) state to the 29p2\(_{1}(0)\) Rydberg state of ortho-D\(_2\), \(52p1\(_{2}(0)\) state of para-D\(_2\)) were determined in separate high-precision measurements using counterpropagating laser beams. These two transitions were selected because their fundamental wave numbers are in the vicinity of an I\(_2\) line, the frequency of which had previously been determined to a precision better than 100 kHz using a frequency comb.\(^{5}\) An example illustrating the calibration of the transition frequency to the 52p1\(_{2}(0)\) state of para-D\(_2\) is displayed in Fig. 3.

For each transition, ten measurements were carried out on different days, each measurement consisting of two spectra, one recorded with the 396 nm laser beam propagating parallel, and the other with the 396 nm laser propagating antiparallel to the 201 nm laser beam. The fundamental transition wave numbers determined from these measurements are plotted with their uncertainties in Fig. 4. The center wave

![Fig. 2. PFI spectra of Rydberg states of (a) ortho- \(D_2\) and (b) para-\(D_2\). The relative intensities are very sensitive to experimental conditions and are not reliable.](image-url)

![Fig. 3. (a) Spectrum of the transition from the EF \(1\Sigma^+_g(v=0), N=1\) level to the 52p1\(_{2}(S=0)\) level of para-D\(_2\), [b] and (c) \(I_2\) calibration and etalon traces, respectively. The position of the \(a_2\) hyperfine component of the P181, \(R-X\) (0-14) rovibronic transition of \(I_2\) was determined to be 378 342 844.89(3) MHz using a frequency comb (Ref. 5) and used for the absolute frequency calibration.](image-url)
D. Ionization energies, dissociation energy, and the ortho-para separation

Figure 1 illustrates the energy level diagram used in the determination of the ionization energies of ortho- and para-D$_2$. The numerical values of all relevant energy intervals are listed in Table III and lead to values of the ionization energies of ortho- and para-D$_2$ of 124 745.394 07(58) cm$^{-1}$ and 124 715.003 77(75) cm$^{-1}$, respectively. These values correspond to the energy separations between the centers of gravity of the hyperfine structure of the N$^0$ (1) level of ortho-D$_2$ (para-D$_2$) and the N$^0$ (0) level of ortho-D$_2^+$ (para-D$_2^+$).

Using the ionization energy of D$_2$ [$E_i(D_2) = E_i(\text{ortho-D}_2)$] determined in the present work and the previously calculated values of $D_0(D_2^+)$ [21 711.583 34(35) cm$^{-1}$, slightly modified from Ref. 8 to take account of higher relativistic and radiative corrections as described in Appendix B)] and $E_i(D)$ [109 708.614 552 99(10) cm$^{-1}$, from Ref. 15], the dissociation energy of D$_2$ is determined from Eq. (1) to be 36 748.362 86(68) cm$^{-1}$ (see Table III). It is important to note that calculations on one-electron systems are much more accurate than on systems with more than one electron. A possible error in the value of $D_0(D_2^+)$ used here would directly influence the present value of $D_0(D_2)$.

The ortho-para separation of D$_2^+$, i.e., the spacing between the N$^0$=0 and N$^0$=1 levels of the X$^+$ $^1\Sigma^+_g$(v$^*$$^=$0) ground state of D$_2^+$, was previously determined by ab initio calculation to be 29.3910(1) cm$^{-1}$. Combining this result with the ionization energies of ortho- and para-D$_2$, the ortho-para separation of D$_2$ can be calculated using Eq. (2) to be 59.781 30(95) cm$^{-1}$ (see Table III). This value is in excellent agreement with, but more accurate than the value [59.7805(16) cm$^{-1}$] which is calculated using the molecular constants previously derived from an electric quadrupole vibration-rotation spectrum of the fundamental vibrational band of D$_2$. 16

The overall uncertainties in the ionization energies, the dissociation energy, and the ortho-para separation are determined as quadrature summation of the uncertainties of all energy intervals. The estimated uncertainty of the binding energies of the Rydberg states by MQDT (1 MHz) are based on the previous work on ortho-H$_2$. 14

IV. DISCUSSION AND CONCLUSIONS

In the present work, the ionization energies of ortho- and para-D$_2$ have been determined with a precision of 17 and 22 MHz, respectively. These values, derived as combinations of experimentally measured transition frequencies and binding energies of the experimentally accessed Rydberg states calculated based on an MQDT analysis, are confirmed in three different ways:

C. Error budget for the EF to Rydberg transition wave numbers

The same calibration procedure as used in the previous work on H$_2$ (Ref. 3) was used for D$_2$ and its details are not repeated in the body of the article but are presented in Appendix A. Here only the resulting error budget is presented in Table II.

As in our previous investigation of H$_2$ we evaluated statistical and systematic uncertainties separately. All uncertainties were assumed to be independent of each other and are summarized in Table II. The total statistical and systematic uncertainties were calculated as quadrature summations of all respective contributions. The calibrated EF to Rydberg transition wave numbers from the measurements displayed in Fig. 4 are given as contributions (2) and (6) in Table III. Their uncertainties are taken as the linear summation of the statistical and systematic uncertainties.
TABLE III. Energy intervals and determination of the ionization energies, dissociation energy and the ortho-para separation of D₂ in cm⁻¹. The labelling of the energy intervals corresponds to Fig. 1.

<table>
<thead>
<tr>
<th>Energy interval</th>
<th>Wave number (cm⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>EF ¹Σ⁺(v=0, N=0)—X ¹Σ⁺(v=0, N=0)</td>
<td>99 461.449 08(11)</td>
<td>5</td>
</tr>
<tr>
<td>29p₂⁺(0)—EF ¹Σ⁺(v=0, N=0)</td>
<td>25 240.712 10(57)</td>
<td>This work</td>
</tr>
<tr>
<td>X ²Σ⁺(v=0, N=0)—29p₂⁺(0) (binding energy)</td>
<td>43.232 89(3)</td>
<td>This work</td>
</tr>
<tr>
<td>E₁(ortho-D₂) = [X ²Σ⁺(v=0, N=0)—X ¹Σ⁺(v=0, N=0)]</td>
<td>124 745.394 07(58)</td>
<td>This work</td>
</tr>
<tr>
<td>EF ¹Σ⁺(v=0, N=1)—X ¹Σ⁺(v=0, N=1)</td>
<td>99 433.716 38(11)</td>
<td>5</td>
</tr>
<tr>
<td>52p₁⁺(0)—EF ¹Σ⁺(v=0, N=1)</td>
<td>25 240.735 16(74)</td>
<td>This work</td>
</tr>
<tr>
<td>X ²Σ⁺(v=0, N=1)—52p₁⁺(0) (binding energy)</td>
<td>40.552 23(3)</td>
<td>This work</td>
</tr>
<tr>
<td>E₁(ortho-D₂) = [X ²Σ⁺(v=0, N=1)—X ¹Σ⁺(v=0, N=1)]</td>
<td>124 715.003 77(75)</td>
<td>This work</td>
</tr>
<tr>
<td>D₀(D₂)</td>
<td>21 711.583 34(35)¹</td>
<td>8</td>
</tr>
<tr>
<td>E₀(D)</td>
<td>109 708.614 552 99(10)</td>
<td>15</td>
</tr>
<tr>
<td>D₀(D₂) = E₁(D₀,D₂) + D₂(D₂) — E₁(D)</td>
<td>36 748.362 86(68)</td>
<td>This work</td>
</tr>
<tr>
<td>X ²Σ⁺(v=0, N=1—0) (ortho-para separation of D₂)</td>
<td>29.3910(1)</td>
<td>8</td>
</tr>
<tr>
<td>X ¹Σ⁺(v=0, N=1—0) (ortho-para separation of D₂)</td>
<td>59.781 30(95)</td>
<td>This work</td>
</tr>
</tbody>
</table>

¹Slightly modified to take into account of higher relativistic and radiative corrections (see Appendix B).

(1) Survey spectra of np Rydberg states were recorded. The binding energies of selected Rydberg states of ortho-D₂ [29p₂⁺(0)] and para-D₂ [52p₁⁺(0)] were determined as sums of the experimental relative transition wave numbers and the MQDT binding energies corresponding to all Rydberg states observed in the spectra (see Table I). The precision of the calculation (one standard deviation) corresponds to the uncertainty of the frequency calibration, which validates the MQDT calculations (Sec. III A).

(2) Combining the ionization energies of both ortho- and para-D₂ determined in the present work with previously calculated ortho-para separation of D₂, the ortho-para separation of D₂ was determined and found to be consistent with the previous experimental value of McKellar and Oka.¹⁶

(3) Control measurements of the transition frequencies from the EF state to lower n Rydberg states (n=39, binding energy ~72 cm⁻¹) of both ortho- and para-D₂ were also carried out.¹⁷ At n=39 the uncertainties resulting from the stray fields are much reduced, but possible errors in the estimation of the binding energies by MQDT increase. The ionization energies derived as sums of the experimentally measured level energies of the Rydberg states and their binding energies calculated by MQDT agree with those reported in the previous paper within the estimated uncertainty. The quantum defects used in the calculations are effective ones, deter-
FIG. 5. Values for the ionization energy of D₂ as determined in various studies or combinations thereof. The theoretical values were reported without uncertainties. The inset represents an enlargement of the area surrounded by the dashed line. The numerical values and the references are listed in Table IV.

Figure 5 summarizes the results of determinations, by various methods, of the ionization energy of D₂ over the past 35 years. The numerical values are also listed in Table IV. Because of the relationship between the dissociation and ionization energies of D₂ [Eq. (1)], the recommended value of the dissociation energy evolved in a very similar manner. The dissociation energy of D₂ was determined in the present work as a hybrid experimental-theoretical value. Comparing with the most recent experimental result [36 748.343(10) cm⁻¹, Ref. 4], the present value for the dissociation energy of D₂ [36 748.362 86(68) cm⁻¹] is more precise by more than one order of magnitude but differs by two standard deviations of the previous measurement. Our new value is in remarkable agreement with the most recent theoretical value [36 748.3633(9) cm⁻¹, Ref. 2]. The same excellent agreement was found between our value of the dissociation energy of H₂ [36 118.069 62(37) cm⁻¹, Ref. 3] and the value derived ab initio [36 118.0695(10) cm⁻¹, Ref. 2].

TABLE IV. $E_i(D_2)$ as determined in various experimental and theoretical studies or combinations thereof, in cm⁻¹.

<table>
<thead>
<tr>
<th>Year</th>
<th>Expt.</th>
<th>Theor.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1975</td>
<td>124 745.6(6)⁴</td>
<td></td>
<td>28</td>
</tr>
<tr>
<td>1990</td>
<td>124 745.49(11)</td>
<td></td>
<td>29</td>
</tr>
<tr>
<td>1991</td>
<td>124 745.382</td>
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<td>30,31</td>
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<td>1992</td>
<td>124 745.353(24)</td>
<td></td>
<td>32,33</td>
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<tr>
<td>1993</td>
<td>124 745.353(24)</td>
<td></td>
<td>34</td>
</tr>
<tr>
<td>1993</td>
<td>124 745.377</td>
<td></td>
<td>35</td>
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<tr>
<td>1993</td>
<td>124 745.387</td>
<td></td>
<td>36</td>
</tr>
<tr>
<td>1994</td>
<td>124 745.401</td>
<td></td>
<td>37</td>
</tr>
<tr>
<td>1995</td>
<td>124 745.395</td>
<td></td>
<td>38</td>
</tr>
<tr>
<td>2010</td>
<td>124 745.394 07(58)</td>
<td></td>
<td>This work</td>
</tr>
</tbody>
</table>

¹A correction of −1.0 cm⁻¹ was included to account for the pressure shift (see Ref. 33).

Our present work on D₂ hence serves as an independent verification of the theoretical calculations in Ref. 2. Because the experimental uncertainties in the values of the dissociation energies of H₂ and D₂ are smaller than those of the best ab initio calculations, they represent a benchmark for future calculations.

ACKNOWLEDGMENTS

This work was financially supported by the European Research Council (ERC Grant No. 228286) and the Swiss National Science Foundation under project No. 200020-116245. Additional support from the Swiss Academy of Technical Sciences, Program PHC Germaine de Staël Nr. 2008-35 is also acknowledged.

APPENDIX A: EXPERIMENTAL ERRORS AND UNCERTAINTIES

This appendix provides the information on the different contributions to the uncertainties in the determination of the frequencies of the transitions from the $EF^1Σ_g^+ (v=0, N =0,1)$ states to the $np$ Rydberg states of ortho- and para-D₂ located below the $X^+ 2Σ_g^+(v^*=0, N^*=0,1)$ ionization thresholds.

1. Statistical uncertainties

Determination of the line centers. The central wave numbers of the I₂ calibration lines were determined by fitting Lorentzian line shapes to the recorded line profiles. The central wave numbers of the $EF$ to Rydberg transitions of D₂ were obtained by fitting Gaussian line shapes. The averaged uncertainties (one standard deviation) in determining the center frequencies are $2 \times 0.35$ MHz ($2 \times 0.37$ MHz) and $2 \times 2.8$ MHz ($2 \times 3.5$ MHz) for I₂ and D₂ transitions in the case of ortho-D₂ (para-D₂), respectively. The larger uncertainty in the case of para-D₂ results from the weaker nature of the transitions as discussed in Sec. III B.

Nonlinearity of the ring laser. The maximum deviation of the NIR readout frequency of the Ti:Sapphire laser from the actual frequency resulting from the nonlinearity of the scans occurs at the midpoint between two neighboring monitor etalon fringes. From the maximal relative error of $\sim 1.5\%$ over...
one free spectral range (FSR) of the monitor etalon, we conclude
that the frequency uncertainty resulting from the non-
linearity is always smaller than \((1/2)\text{FSR} \times 1.5\% = 1.1\) MHz in the NIR and smaller than 2.2 MHz in the UV.

**Doppler shift.** Although the method of counterpropa-
gating laser beams was employed (see Sec. III B), there still
could be a small residual Doppler shift caused by an imper-
fect alignment of the two 396 nm laser beams. The common
beam path of the two beams is \(L \approx 3.5\) m. If two beams
deviate by \(\delta = 0.5\) mm (which is still easily resolvable by
eye) at the extremity of the common path, the Doppler shift
\(\Delta v_{\text{Doppler}}\) is

\[
\Delta v_{\text{Doppler}} = \frac{1}{2} \frac{v_{\text{D}}}{c} \frac{\delta}{L}, \quad v_0 = 0.23\ \text{MHz},
\]

where \(v_{\text{D}} = 1260\ \text{m/s}\) is the speed of \(\text{D}_2\) in the jet expansion
and \(v_0\) is the transition frequency. The Doppler shift is there-
fore smaller than 0.23 MHz.

### 2. Systematic errors and uncertainties

**Uncertainty of the FSR.** The FSR of the etalon was
determined to be 149.9691(13) MHz in nine measurements
 carried out on nine days. Multiplying the uncertainty of the FSR
by the number of FSRs separating the \(I_2\) line that was used
for calibration [the \(a_2\) hyperfine component of the P181, \(B
+X\) \((0-14)\) rovibrionic transition at \(12\ 620.158\ 873(1)\ \text{cm}^{-1}\)]
from the position of the Rydberg transitions gives uncertain-
ties of \(2 \times 0.043\) and \(2 \times 0.046\) MHz in the transition fre-
cuencies of ortho- and para-\(\text{D}_2\), respectively.

**\(I_2\) calibration by frequency comb.** This uncertainty is less
than 0.1 MHz in the NIR as explained in Ref. 5.

**Frequency shifts occurring in the Ti:Sa amplifier.** The frequency shifts occurring in the Ti:Sa amplifier, \(-4.736(38)\)
MHz for ortho-\(\text{D}_2\) measurements and \(-6.901(75)\) MHz for para-\(\text{D}_2\) measurements, were determined simultaneously
with the measurements described in Sec. III B and have al-
ready been corrected for in the transition wave numbers
presented in Fig. 4. The larger frequency shift for the para-\(\text{D}_2\)
measurements and its larger uncertainty result from the fact
that a higher 396 nm laser power had to be used to compen-
sate for the weaker signal, which could only be achieved by
pumping the Ti:Sa crystals with higher Nd:YAG laser intensi-
ties.

**Frequency shifts in the doubling crystal.** The frequency
shifts arising in frequency doubling have been estimated to be
less than 0.35 MHz in our previous study.\(^3\)

**Ac stark shifts caused by the 396 nm laser power.** To estimate the ac Stark shift, the \(D_2\) spectra were recorded at
different laser powers and hence different intensities of the
396 nm laser and zero-intensity positions were estimated in a
linear extrapolation. The uncertainties associated with the ex-
trapolations are estimated as the product of the slope and the
laser powers used in the measurements.

**Frequency shifts caused by the 201 nm laser power.** The transition frequencies were found to be dependent on the 201
nm laser power. When the average laser power is low
\((< 4.5\ \text{mW})\), corresponding to average pulse energies of
180 \(\mu\text{J}\); the estimated beam waist in the interaction region is

\(~1\ \text{mm}^2\), the transition frequencies remain constant, but
they start increasing at laser powers beyond 4.5 mW. Be-
cause we also observed these frequency shifts in experiments
in which the 396 nm laser was delayed with respect to the
201 nm laser, they cannot arise from an ac Stark shift in-
duced by the 201 nm laser. Instead, we attribute them to
the stray electric fields caused by the ions generated by the 201
nm laser in a \((2+1)\) resonance-enhanced multiphoton ioniza-
tion process. The measurements using counterpropagating la-
sor beams presented in Fig. 4 were carried out at low 201 nm
laser power (~1.5 mW for ortho-\(\text{D}_2\) and ~2.0 mW for para-\(\text{D}_2\) so that no frequency corrections needed to be made.
Nevertheless, it was necessary to include additional uncertain-
ties of 3.5 MHz for ortho-\(\text{D}_2\) and 10.8 MHz for para-\(\text{D}_2\),
determined in the same way as for the ac Stark shift caused by
the 396 nm laser power.

**Dc Stark shifts caused by stray electric fields.** The effects of dc electric fields of different magnitudes and polarities
were investigated by applying dc voltages across the 7.8-cm-
long stack of cylindrical plates surrounding the ionization
region. Figure 6 shows the effect of these dc voltages on the
spectrum of para-\(\text{D}_2\). The transition to the \(52d_1\) state is
always observable and its intensity increases with increasing
electric field. The linewidth increases as well, presumably
TABLE V. Re-evaluation of the dissociation energy of D\(_2\) including all relativistic and radiative corrections up to order R\(_{\alpha^4}\) and the leading two terms of order R\(_{\alpha^5}\). In this treatment one assumes that the perturbation series is convergent. The estimation is based on calculations of Moss (Refs. 8, 24, 25, and 39) on H\(_2^+\), HD\(^+\), and D\(_2^+\) of Korobov (Refs. 26 and 27) on H\(_2^+\) and HD\(^+\), and of CODATA (Ref. 7) on H and D. The upper part of the table gives the ground state energy of the respective species and their corrections. All values are in units of cm\(^{-1}\). The correction terms are listed in Refs. 26 and 27. The corrections are: RR=relativistic and recoil, NS=nuclear size, SAV=self-energy, anomalous magnetic moment, and vacuum polarization, and TP=transverse photon exchange.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Nonrel. energy</th>
<th>R(_{\alpha^4})</th>
<th>R(_{\alpha^5})</th>
<th>total correction</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td>RR</td>
<td>NS</td>
<td>SAV</td>
</tr>
<tr>
<td>E(H)</td>
<td>7</td>
<td>-109 677.583 41</td>
<td>-1.460 95</td>
<td>0.000 04</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>-109 707.426 59</td>
<td>-1.460 92</td>
<td>0.000 00</td>
</tr>
<tr>
<td>E(D)</td>
<td>7</td>
<td>-109 707.426 59</td>
<td>-1.460 95</td>
<td>0.000 24</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>-109 707.426 59</td>
<td>-1.460 92</td>
<td>0.000 00</td>
</tr>
<tr>
<td>E((H_2^+))</td>
<td>26, 27</td>
<td>-131 056.875 75</td>
<td>-1.599 55</td>
<td>0.000 05</td>
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<tr>
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<td>24</td>
<td>-131 056.875 75</td>
<td>-1.598 82</td>
<td>0.000 00</td>
</tr>
<tr>
<td>Deviations</td>
<td>26, 27</td>
<td>-131 223.436 26</td>
<td>-1.602 10</td>
<td>0.000 18</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>-131 223.436 26</td>
<td>-1.601 52</td>
<td>0.000 00</td>
</tr>
<tr>
<td>Deviations</td>
<td>39</td>
<td>-131 418.947 71</td>
<td>-0.000 58</td>
<td>0.000 00</td>
</tr>
<tr>
<td>E((D_2^+))</td>
<td>8</td>
<td>-131 418.947 71</td>
<td>-1.604 82</td>
<td>0.000 00</td>
</tr>
<tr>
<td>Estimated deviations</td>
<td>8</td>
<td>-131 418.947 71</td>
<td>-0.000 58(30)(^a)</td>
<td>0.000 02(10)(^a)</td>
</tr>
<tr>
<td>Estimated corrections</td>
<td>26, 27</td>
<td>-131 223.436 26</td>
<td>-1.605 40(32)(^b)</td>
<td>0.000 33(5)(^c)</td>
</tr>
<tr>
<td>D(_7)((H_2^+))</td>
<td>24</td>
<td>21 379.292 28</td>
<td>0.1379</td>
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<tr>
<td>=E(H)−E((H_2^+))</td>
<td>7, 26, 27</td>
<td>21 379.292 34</td>
<td>0.138 60</td>
<td>-0.000 01</td>
</tr>
<tr>
<td>D(_7)((HD^+))</td>
<td>25</td>
<td>21 516.009 96</td>
<td>0.1406</td>
<td>-0.080 7</td>
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<tr>
<td>=E(D)−E((HD^+))</td>
<td>7, 26, 27</td>
<td>21 516.009 67</td>
<td>0.141 14</td>
<td>0.000 06</td>
</tr>
<tr>
<td>D(_7)((D_2^+))</td>
<td>8</td>
<td>21 711.521 05</td>
<td>0.1439</td>
<td>-0.081 6</td>
</tr>
<tr>
<td>Estimated (D_7)((D_2^+))</td>
<td>8</td>
<td>21 711.521 12</td>
<td>0.144 45(32)</td>
<td>-0.000 07(5)</td>
</tr>
</tbody>
</table>

\(^a\)Taken to be the same as for HD\(^+\) but including an uncertainty larger than the difference between the H\(_2^+\) and HD\(^+\) values.

\(^b\)Sum of the value from Ref. 8 and the estimated deviation.

\(^c\)Extrapolated linearly from the values of H\(_2^+\) and HD\(^+\).

\(^d\)Determined using the value of E(\(D_2^+\)) from Ref. 39 and the most recent value of E(D) (Ref. 7).
because of Stark splittings and mixing with Stark manifolds of high-\(\ell\) states. Because of the \(\Delta \ell = \pm 1\) selection rule of \(\ell\)-mixing by electric fields, the 52\(p\) state mixes first with the 52d state, and then with high-\(\ell\) states via the 52d state. The zero-field positions of high-\(\ell\) states (with quantum defect \(\delta_\ell = 0\)) and the extreme red- and blueshifted Stark levels are indicated by the dotted and dashed lines in Fig. 6. The Stark shifts of these levels are calculated using the formula \(\Delta E_\ell = \pm (3/2)F n^2\) (in atomic units), where \(F\) is the electric field. At a dc voltage of 2 V, the 52\(p\) and 52d levels are completely immersed in the high-\(\ell\) manifold of Stark states and the Stark spectra are dominated by a broad asymmetric line. Two new peaks appear at dc offsets beyond 0.25 V and can be assigned to the transitions from the \(EF\) state to the 52d1\(_1\)\((G=1/2)\) and 52d1\(_3\)\((G=3/2)\) Rydberg states based on the results of a previous laser experiment.\(^{18}\) For transitions to \(np\) levels of both ortho- and para-\(D_2\), no dependence of the transition frequencies on the electric field was observable at low electric fields. [A quadratic frequency shift with respect to the offset voltage\(^{19,20}\) was observed for the transitions to the 52d1\(_2\)\((G=1/2,3/2)\) states.] Consequently, no correction was needed for the dc Stark shift, but an uncertainty of 2 \(\times\) 5 MHz at 10 MHz was included to account for the shift at a field of \(\pm 250\) mV/7.8 cm. It is, however, certain that the stray electric field present during the measurements using counterpropagating laser beams summarized in Fig. 4 was smaller.

**Pressure shift.** Herzberg and Jungen\(^{21}\) determined the magnitude of the pressure shift for high-\(n\) Rydberg states of \(H_2\) to be 5.7 \(\pm 0.5\) cm\(^{-1}\)/amagat, which is expected to be the same for \(D_2\). From the estimate of \(\sim 10^{13}\) cm\(^{-3}\) for the \(D_2\) number density, we determine the pressure shift to be less than \(+0.1\) MHz with an uncertainty of \(\pm 0.05\) MHz. This pressure shift thus makes a close to negligible contribution to the error budget.

**APPENDIX B: RE-EVALUATION OF THE DISSOCIATION ENERGY OF \(D_2^+\)**

In our derivation of the dissociation energy of \(D_2\) we rely on the dissociation energy of \(D_2^+\) [see Eq. (1)]. This quantity has been calculated in 1993 by Moss to be 21 711.5833 cm\(^{-1}\).\(^{8}\) In his calculations, Moss included relativistic corrections of order \(R_s \alpha^2\) (taken from Ref. 22) and radiative corrections of order \(R_s \alpha^3\) (using the Bethe logarithm evaluated in Ref. 23). In similar calculations he also determined the dissociation energies of other rovibrionic states of \(H_2^+\), \(HD^+\), and \(D_2^+\), derived transition frequencies and compared his results with available experimental data.\(^{8,24,25}\) The agreement was in most cases better than the estimated experimental uncertainty of 0.001 cm\(^{-1}\).

A re-evaluation of the dissociation energy of \(D_2^+\) was carried out based on the recent work of Korobov on \(H_2^+\) and \(HD^+\), in which relativistic and radiative corrections of order up to \(R_s \alpha^3\) (including also the leading \(R_s \alpha^2\) terms) were calculated.\(^{26,27}\) The results of this reevaluation are summarized in Table V, where relativistic and radiative corrections to the energies of \(H, D, H_2^+, HD^+\), and \(D_2^+\) and the dissociation energies of \(H_2^+, HD^+,\) and \(D_2^+\) are given. While the radiative corrections of order \(R_s \alpha^3\) are in good agreement with those used by Moss,\(^{8,24,25}\) there is a discrepancy of \(-0.0007\) cm\(^{-1}\) and \(-0.0005\) cm\(^{-1}\) in the sum of the relativistic and the recoil corrections of order \(R_s \alpha^2\) in the dissociation energies of \(H_2^+\) and \(HD^+\), respectively. This discrepancy is almost fully compensated by the radiative corrections of order \(R_s \alpha^4\),\(^{26,27}\) leading to an excellent but coincidental agreement in the value of the overall correction. Based on the corrections needed for \(H_2^+\) and \(HD^+\), we estimated the corrections for the dissociation energy of \(D_2^+\) as detailed in Table V. The resulting dissociation energy for \(D_2^+\) is 21 711.583 34\(_{25}\) cm\(^{-1}\), which is almost identical to the value reported by Moss.\(^{8}\) As for \(H_2^+\) and \(HD^+\) the agreement results from an almost exact but coincidental compensation.

The rotational energy level structure of the vibronic ground state of \(D_2^+\) was also taken from Ref. 8 and used in the MQDT calculations (see Sec. III A) and in the determination of the ortho-para separation of \(D_2\) [see Eq. (2)]. Relativistic and radiative corrections are almost an order of magnitude smaller for the rotational energies than they are for the dissociation energy so that the values of Moss\(^{8,24,25}\) and Korobov\(^{26,27}\) for \(H_2^+\) and \(HD^+\) are in perfect agreement. The positions of the rotational energy levels of \(D_2^+\) were therefore taken without change from Ref. 8.

---

\(^{1}\)H. Primas and U. Müller-Herold, *Elementare Quantenchemie* (Teubner Studienbücher, Stuttgart, 1984). Section 5.3 ("Fakten und Zahlen: Die Geschichte des Wasserstoff-Moleküls") gives a complete account of the early efforts invested in the quantitative comparison of experimental and theoretical values of the dissociation energy of \(H_2\) and explains in detail how studies of molecular hydrogen contributed to establish the validity of molecular quantum mechanics and to understand chemical bonds physically.


\(^{15}\)See: http://physics.nist.gov/hdbel (The energy levels of hydrogen and deuterium in this database include all corrections detailed in Ref. 7. The fundamental constants used in the calculations are taken from CODATA 2002).


\(^{17}\)D. Sprecher, J. Liu, and F. Merkt (unpublished).


