Improved Ionization and Dissociation Energies of the Deuterium Molecule

J. Hussels,1 N. Hölsch,2 C.-F. Cheng,1,3 E. J. Salumbides,1 H. L. Bethlem,1 K. S. E. Eikema,1 Ch. Jungen,4 M. Beyer,1 F. Merkt,2,* and W. Ubachs1,†

1Department of Physics and Astronomy, LaserLaB, Vrije Universiteit Amsterdam, de Boelelaan 1081, 1081 HV Amsterdam, The Netherlands
2Laboratorium für Physikalische Chemie, ETH Zürich, 8093 Zürich, Switzerland
3Department of Chemical Physics, University of Science and Technology of China, Hefei, 230026 China
4Department of Physics and Astronomy, University College London, London WC1E 6BT, United Kingdom

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The ionization energy of D2 has been determined experimentally from measurements involving two-photon Doppler-free vacuum-ultraviolet pulsed laser excitation and near-infrared continuous-wave laser excitation to yield \( E_1(D_2) = 124\,745.393\,739(26) \text{ cm}^{-1} \). From this value, the dissociation energy of D2 is deduced to be \( D_0(D_2) = 36\,748.362\,282(26) \text{ cm}^{-1} \), representing a 25-fold improvement over previous values, and found in good agreement (at 1.6σ) with recent ab initio calculations of the 4-particle nonadiabatic relativistic energy and of quantum-electrodynamic corrections up to order \( m a^6 \). This result constitutes a test of quantum electrodynamics in the molecular domain, while a perspective is opened to determine nuclear charge radii from molecules.

I. INTRODUCTION

The hydrogen molecule and its isotopologues have become target species for testing quantum theories of molecular structure including quantum electrodynamics (QED), even to the extent of testing the Standard Model of physics in the low energy domain [1]. The dissociation energy \( D_0 \) of the molecule is a benchmark for confronting theory and experiment and developments in both areas have mutually stimulated progress. In the 1960s, an experimental value of \( D_0(D_2) \) was determined by photo-excitation to the \( n = 2 \) limit in the molecule, first by Herzberg and collaborators [2, 3], trying to verify agreement with theories in that period [4, 5]. The results were later improved by Stoicheff and collaborators, who measured vacuum-ultraviolet laser-induced fluorescence [6], and by Eyler and collaborators, who performed double-resonance laser excitation [7, 8]. Near-threshold spectral structures and the smooth onset of dissociation at \( n = 2 \), however, formed a bottleneck for further progress.

The Zurich-Amsterdam collaboration proposed an alternative scheme for approaching the problem by targeting the ionization energy \( E_1 \) of the molecule, in which case very narrow levels in Rydberg series can be measured at extreme precision and extrapolated to their limit. \( E_1 \) is determined by stepwise laser excitation and \( D_0 \) is obtained via the thermochemical cycle:

\[
D_0(D_2) = E_1(D_2) + E_1(D_2^+) - 2E_1(D),
\]

using the accurate values for the ionization energy of the atom, \( E_1(D) \), and the ionization energy of the molecular ion, \( E_1(D_2^+) \). A combination of experiments by our collaboration led to a much improved value of \( D_0(D_2) \) at \( 6.8 \times 10^{-4} \text{ cm}^{-1} \) accuracy over a decade ago [9]. At the same time an improved theoretical approach led to a similarly accurate value for \( D_0(D_2) \) in agreement with experiment [10].

This agreement prompted improved calculations of the Born-Oppenheimer (BO) potential [11] and leading-order effects of the nonadiabatic corrections [12]. A highly accurate treatment to solve the Schrödinger equation [13] was developed, but progress in theory was halted by unexpected difficulties in the treatment of the relativistic corrections [14]. A breakthrough was achieved through non-BO or 4-particle variational calculations, developed independently by different groups [15–17]. A very accurate theoretical value for the dissociation energy of D2 is now available \( (D_0(D_2) = 36\,748.362\,342(26) \text{ cm}^{-1} \) [18]), over an order of magnitude more accurate than the prevailing experimental value [9].

These improvements on the theoretical side, obtained in a similar fashion also for H2, represent a challenge for experiment. Two strategies were developed to increase the experimental accuracy of the determination of the ionization and dissociation limits of the hydrogen molecules. Firstly, a pathway through the GK\(^1\Sigma_g^+\) state, based on two-photon VUV laser excitation, was suggested [19] and employed, leading to greatly improved threshold values for H2, both for ortho-H\(_2\) [20] and para-H\(_2\) [21]. Secondly, the technique of Ramsey-comb spectroscopy utilizing frequency comb lasers for direct excitation of the EF\(^1\Sigma_u^+\) state in H\(_2\) was explored [22] and combined with narrowband laser excitation of Rydberg states to yield the most accurate value for the dissociation and ionization energies in H\(_2\) [23].

Here, we present new results based on stepwise excitation through the high-lying GK\(^1\Sigma_g^+\) state in the D\(_2\) molecule. As in the previous studies on H\(_2\), the measurements were partly carried out in the Amsterdam and Zurich laboratories and their results combined. The excitation schemes are represented in a level diagram of the

* frederic.merkt@phys.chem.ethz.ch (F. Merkt)
† w.m.g.ubachs@vu.nl (W. Ubachs)
molecule in Fig. 1.

Figure 1. Potential-energy curves of the electronic states of the hydrogen molecule relevant to this study. The level positions of the Rydberg states (gray) are not to scale. (a) In Amsterdam, the $\text{GK}(v = 1, N = 2) \leftrightarrow X(v = 0, N = 0)$ two-photon transition, indicated in dark blue, was measured to determine the term value of the $\text{GK}(v = 1, N = 2)$ state. The excited molecules were detected through ionization with near-infrared (NIR) laser radiation. (b) In Zurich, both the $\text{GK}(v = 1, N = 2)$ and $\text{GK}(v = 0, N = 2)$ levels were populated from the ground state in stepwise two-photon excitation schemes via the B($v = 4, N = 1$) state and their relative positions obtained by measuring transitions to the same hyperfine component of a low-$n$ Rydberg state. Starting from the long-lived $\text{GK}(v = 0, N = 2)$ state, $nf$ Rydberg states belonging to series converging to the rovibrational ground state of the $D_2^+$ ion were measured for a range of $n$ values. The green arrows indicate the results from multi-channel quantum defect theory for the binding energies of the measured $nf$ levels, forming an extrapolation to the ionization limit $E_i(D_2)$.

II. GK-STATE SPECTROSCOPY IN AMSTERDAM

In the Amsterdam laboratory, the $\text{GK}^1\Sigma_g^+(v = 1, J = 2) - X^1\Sigma_g^+(v = 0, J = 0)$ energy interval in $D_2$, also referred to as the GK-X S(0) transition energy, is measured in a two-photon Doppler-free configuration. In order to generate the required narrowband 178 nm vacuum ultraviolet (VUV) laser light, near-infrared light from a continuous-wave (CW) titanium-sapphire (Ti:Sa) laser at 714 nm is pulse amplified in a Ti:Sa oscillator-amplifier system [24] and harmonically upconverted using a $\beta$-BaB$_2$O$_4$ (BBO) and a KBe$_2$BO$_3$F$_2$ (KBBF) crystal. The main improvement of the setup in comparison to the setup used in previous experiments [20, 21] is the implementation of a liquid-N$_2$-cooled valve for producing the pulsed molecular beam, which allows us to determine the molecule velocities more precisely for assessing the residual Doppler shift. Molecules in the $\text{GK}^1\Sigma_g^+(1,2)$ excited state are detected by selective ionization, employing autoionization resonances, excited with a single visible photon from an auxiliary pulsed dye laser. Two measurement campaigns were performed, the first one using an autoionization resonance at high energy, 125 899.0 (1.0) cm$^{-1}$, the second using a resonance near the ionization threshold, at 124 744.0 (1.0) cm$^{-1}$. In the former case, the ionization laser was delayed by 30 ns with respect to the VUV laser to reduce the AC-Stark effect caused by the ionization laser. In the latter case, the AC-Stark effect was sufficiently small at zero delay, so that the VUV and visible laser pulses were overlapped. Systematic studies were performed to estimate the contributions to the error budget by the AC-Stark effect (0.10 MHz from the visible laser and 0.24 MHz from the VUV laser inducing the two-photon transition). For details on these AC-Stark analyses we refer to a recent PhD Thesis [25].

Even though the experiment is Doppler-free, small residual Doppler shifts persist in case of slight misalignments from exact counter-propagation of the two VUV beams crossing the molecular $D_2$ beam. A small angle between the counter-propagating beams deviating from 180°, will give rise to a first-order Doppler shift. To reduce this residual Doppler shift, we ascertain that the incoming and reflected VUV beams both pass through a 1 mm pinhole at a distance of 80 cm from the retroreflecting mirror, as shown in Fig. 2. In this way, the angle

![Figure 2](image-url)

Figur 2. Schematic overview of the interaction zone of the $D_2$ molecular beam with the VUV laser beam. A small residual Doppler shift may arise when the angle $\theta$ between the incoming and reflected beam is not exactly 180°.
between the counter-propagating beams is constrained to less than 0.6 mrad, limiting the residual Doppler shift to 6 MHz. This residual Doppler shift is compensated by measuring the $^{1}\Sigma_g^+(1,2) \leftarrow X^1\Sigma_g^+(0,0)$ transition frequency as a function of the mean velocity of the molecular beam. The velocity of the probed molecules was varied in a controlled manner by changing the temperature of the pulsed valve and by changing the delay time between the trigger that opens the valve and the trigger of the pulsed lasers. The average velocity of the beam decreases from about 1700 m/s to 850 m/s upon cooling the valve from room-temperature to liquid-N$_2$ temperature (77 K), while the intensity of the molecular beam increases by about a factor of two. Doppler-free transition frequencies are obtained from extrapolation to zero velocity for different alignments of the VUV beam. In this analysis each measurement point is corrected for the AC-Stark effect and for the small second-order Doppler effect.

In Fig. 3 a spectrum of the GK-X S(0) line is shown. The frequency is determined from a beat-note measurement of the CW Ti:Sa seed-laser output to a frequency-comb laser, while each pulse is first chirp-compensated and thereafter analyzed for residual chirp [24]. Twelve measurement sessions were carried out, each leading to a Doppler-extrapolated value at an uncertainty of 1-2 MHz (see full and dashed lines in Fig. 3(b)). This uncertainty includes statistics, chirp phenomena and residual first-order Doppler shifts, as well as the second-order Doppler effect. Note that in the experimental configuration there is no photon-recoil effect. Each measurement session involves a different alignment and retro-reflection of the VUV beam inside the vacuum, and can be considered to lead to independent results for which the average of the mean can be computed at an accuracy of 0.35 MHz (see Fig. 3(c)).

The error budget for the VUV part of the experiments is presented in Table I. The statistical error of 0.35 MHz includes the uncertainty of the first-order Doppler extrapolation, which itself includes the uncertainty caused by the chirp measurements. The uncertainty in the second-order Doppler effect as well as from the hyperfine structure both result from conservative estimates. The uncertainties of the AC-Stark shifts were different in the two measurement campaigns. The largest value of these two uncertainties is adopted. The final uncertainty in the $^{1}\Sigma_g^+(1,2) \leftarrow X^1\Sigma_g^+(0,0)$ transition frequency of D$_2$ is 0.45 MHz.

The symmetric lineshape of the GK-X S(0) transition fully hides the hyperfine structure of much less than 1 MHz within a linewidth of 30 MHz. This transition connects the center-of-gravity of the $F = 0, 2$ hyperfine levels of the ortho $N = 0$ ground state to the GK $N = 2$ excited state, with $F = 0, 2,$ and 4 hyperfine substates. We include a conservative 100 kHz estimate for the contribution of hyperfine effects associated with the unresolved VUV-transition to the error budget. In the subsequent step, the $F = 2$ component of the GK-state with $I = 0$ (see below) is further excited into the Rydberg manifold; this $F = 2$ level is not subject to a hyperfine interaction, which represents an advantage of the measurement scheme possible in D$_2$ over that used in ortho-H$_2$ [20, 23].

### III. RYDBERG SPECTROSCOPY IN ZURICH

The experiments carried out in Zurich are aimed at connecting the $^{1}\Sigma_g^+(1,2)$ level to $E_2$(D$_2$) via measurement of transitions to high-$n$ Rydberg states. Although
the final state of the GK-X S(0) transition measured in Amsterdam is located in the G inner well of the GK $1\Sigma^+_g$ state, we measured transitions to long-lived Rydberg states from a rovibrational level in the K outer well, the GK(0,2) level. This level is protected from radiative decay by smaller Franck-Condon factors to the lower-lying ungerade states, in particular the $1\Pi_u$ state. This effect is amplified in D$_2$ compared to H$_2$, because the twice larger reduced mass leads to lower rovibrational energies, thus increasing the tunneling barrier and enhancing the localization of the vibrational wavefunctions in the respective wells. We measured the relevant lifetimes using the pump-probe scheme described in Ref. [26] and found them to be 13.2(6) ns and 240(40) ns for the GK(1,2) and GK(0,2) states, respectively, with corresponding natural linewidths of $\approx 12$ MHz and below 1 MHz, respectively.

The relative position of the GK(1,2) and GK(0,2) states was determined with an accuracy of 210 kHz by repeatedly measuring the transition frequencies from these two states to the same final state, the $(F^+ = 3/2, G = 2)$ hyperfine component of the 50f0$_3$ Rydberg state. For the level scheme see Fig. 1.

$$n = 49, N^+ = 0$$

In the absence of rotational excitation of the ion core, $N^+ = 0$, the fine and hyperfine structure of the molecular Rydberg state results from coupling the Rydberg electron with orbital and electron-spin angular momentum, $\vec{l}$ and $\vec{s}$, respectively, to the D$_2^+$ hyperfine structure. The nuclear spin allowed in the rotational ground state is $I = 0, 2$, resulting in the total angular momentum of the ion core given by $\vec{F}^+ = \vec{G}^+ = \vec{I} + \vec{S}^+ = (3/2, 1/2, 5/2)$. For the rotationless molecular ion, only the Fermi-contact term in the hyperfine hamiltonian does not vanish and causes a splitting between $F^+ = 3/2$ and $5/2$, while leaving the $I = 0$ component $F^+ = 1/2$ unaffected. As can be seen from Fig. 4, the observed structure in the laser spectra of the 49f0$_3$ $\leftrightarrow$ GK(0,2) transition shows three lines, corresponding to the $F^+$ components indicated by orange bars. A multichannel-quantum-defect-theory (MQDT) calculation including spin [27] reveals a further splitting into a doublet for each $F^+$, which can be explained by the coupling of the Rydberg-electron spin, leading to $\vec{G} = \vec{G}^+ + \vec{s}$. The total angular momentum is then obtained through $\vec{F} = \vec{G} + \vec{l}$, which does not result in an observable splitting in Fig. 4.

The observed coupling scheme and intensity pattern result from the interplay of the following three interactions: i.) the Fermi-contact interaction in the ion core, ii.) the exchange interaction and iii.) the spin-orbit interaction of the Rydberg electron. Interaction (iii) is negligible, explaining the vanishing splitting of different $F$ levels for a given $G$. For states with $I = 0$, interaction (i) vanishes and only the exchange interaction (ii) is present, leading to a splitting between singlet and triplet states with $S = S^+ + s$ being a good quantum number and equal to $G$. The small singlet-triplet splitting for nonpenetrating f Rydberg states was calculated to be 2.4 MHz at $n = 49$ (corresponding to the splitting between $G = 0, 1$ for $I = 0$ in Fig. 4). In terms of the quantum defects, this represents a difference of $\approx 4 \times 10^{-5}$, which is consistent with the singlet-triplet splittings observed experimentally in the H$_2$ 4f state (cf. Table II of Ref. [28]). For $I = 2$, (i) dominates over (ii), leading to $G$ states with mixed singlet-triplet character. In Fig. 4, the stick spectra below each calculated hyperfine component indicate the corresponding singlet (green) and triplet (red) character and show good agreement with the observed spectrum, in which only the singlet character can be excited starting from the GK $1\Sigma^+_g$ state.

Whereas the different hyperfine components of the Rydberg state cannot be resolved for $I = 2$, the line in Fig. 4 (middle) arises solely from the transition to the Rydberg hyperfine component corresponding to $N^+ = 0, I = 0, F^+ = 1/2, S = G = 0, \ell = 3, F = 3$. The following discussion and analysis focuses on these states because a comparison between experimental and calculated line positions can be made at the highest precision.

The transitions between the GK(0,2) state and eight members of the $n$0f0$_3 (I = 0, S = 0)$ Rydberg series with $n$ values between 49 and 69 were recorded in a pulsed skimmed supersonic beam of pure D$_2$ emanating from a cryogenic pulsed valve ($T_{\text{valve}} = 60$ K) using single-mode CW NIR radiation from a Ti:Sa laser. The laser fre-

Figure 4. Spectra of the three $F^+ = (3/2, 1/2, 5/2)$ hyperfine components of the 49f0$_3$ state of D$_2$ recorded from GK(0,2) with only the forward propagating laser beam. The normalization of the ion signal was performed for each spectrum individually and the fitted Voigt profiles are shown in blue. All three spectra were recorded without changing the geometry of the laser beam paths. $\nu_0$ was chosen as the center-of-gravity of the calculated hyperfine structure (orange) and the spectra were shifted to match the $(I = 0, G = 0)$ component. The summed squared coefficients from all MQDT eigenvectors belonging to singlet (green) and triplet (red) basis states in Hund’s case (a) are shown below the spectrum for each hyperfine component. The last coupling step to form the total angular momentum $\vec{F} = \vec{G} + \vec{l}$ is omitted because the splitting is not resolved on the scale of the figure.
frequency was stabilized to a frequency comb which was referenced to a Rb GPS standard. The first-order Doppler shift was cancelled by taking the average of two Doppler components generated in an optical setup in which the laser beam is retro-reflected and carefully overlapped with the forward propagating beam. We refer to Ref. [29] for further details on the apparatus and measurement procedures.

A representative frequency-comb-calibrated spectrum of the resulting Doppler-doublet of the 62f0(I = 0, S = 0) ← GK(0,2) transition is depicted in the upper panel of Fig. 5(a), where the fitted spectrum is displayed in blue. Stray electric fields were compensated in three dimensions, limiting the uncertainty of the transition frequencies from the DC-Stark effect to between 12 kHz at n = 49 and 130 kHz at n = 69. The increase of the uncertainty with n results from the n^7 scaling of the polarizability of Rydberg states [30]. These uncertainties were added in quadrature to the respective statistical uncertainties resulting from independent sets of measurement series carried out after full realignment of the lasers to determine the total uncertainties of the Doppler-free transition frequencies. All frequencies were corrected for the photon-recoil shift and the second-order Doppler shift.

The error budget for the laser excitation of nf-Rydberg states from the GK 1^1Σ^+_g(0, 2) state is compiled in Table II and includes contributions from the DC and AC-Stark shifts, Zeeman shift, pressure shift, Doppler shift and the lineshape model. The photon-recoil shift was subtracted from the observed frequencies. Our procedure to estimate all uncertainties is described in Ref. [29] and we only present here the procedure followed to determine the uncertainties from the DC Stark and the first-order Doppler effects, and the lineshape model.

**DC Stark effect:** The transition to the 62f0(I = 0, S = 0) state is taken as illustration because this is the transition with which the three-dimensional field compensation was performed. The combined uncertainty of the fit of the quadratic DC-Stark shift in all three spatial dimensions amounted to 60 kHz and was scaled with n^7 for the other states of the series, resulting in uncertainties between 12 kHz at n = 49 and 130 kHz at n = 69.

**Lineshape model:** The statistical uncertainty for a single measurement results from the uncertainty of the nonlinear weighted fit of the lineshape of the two Doppler components (see Fig. 5a) and was found to be of the order of 50-100 kHz. We observed Voigt profiles with linewidths (FWHM) of 2.5-3.5 MHz and in general determined the line centers to at best 1/50 of the FWHM. We observed Voigt profiles with linewidths (FWHM) of 2.5-3.5 MHz and in general determined the line centers to at best 1/50 of the FWHM.

**Table II. Error budget for the transition between the GK(0,2) state of D2 and the 62f0(I = 0, S = 0) Rydberg state, resulting from a series of independent measurements. All systematic uncertainties are the same for the other measured transitions except the uncertainty in the DC Stark shift which is n-dependent (see text).**

| Uncertainty Source | Correction | Final Frequency |
|--------------------|------------|----------------|
| DC Stark shift     | 60 kHz     | 388 255 115.129(16) MHz |
| AC Stark shift     | ~5 kHz     | 388 255 115.048(82) MHz |
| Zeeman shift       | ~10 kHz    |                |
| Pressure shift     | ~1 kHz     |                |
| Residual 1st-order Doppler shift | (<200 kHz) |                |
| 2nd-order Doppler shift | +2 kHz |                |
| Line-shape model   | 50 kHz     |                |
| Photon-recoil shift| ~83 kHz    |                |
| Systematic uncertainty | 80 kHz |                |

**Final frequency:** 388 255 115.048(82) MHz
measured transition was obtained as the standard error of the weighted mean of the transition frequencies from all independent measurements.

Table III lists the wave numbers of all transitions $nlN^+_N(I=0, S=0) \leftrightarrow GK^1\Sigma^+_g(0,2)$ recorded in the present study. The statistical uncertainties determined from sequences of independent measurements are given as $\sigma_{stat}$ in MHz. The systematic uncertainties were added in quadrature to obtain the final experimental uncertainties $\sigma_{tot}$ shown in Fig. 5(b), which were used in the determination of the ionization energy of the GK$^1\Sigma^+_g(0,2)$ state. Table III also lists the Rydberg-state binding energies calculated by MQDT. By taking the weighted average of the sums of measured transition frequencies and MQDT binding energies, we determine the ionization energy of the GK(0,2) level to be $12979.3448024(53) \text{ cm}^{-1}$ excluding the systematic uncertainty originating from the incomplete set of quantum defects. The second-last column gives the transition wave numbers $\nu_{calc}$ obtained by subtracting the calculated Rydberg-state binding energies from this mean ionization energy. These values can be directly compared to the experimental transition wave numbers $\nu_{obs}$. The differences, which are shown in the last column of Table III as well as in Fig. 5(b), are all smaller than 250 kHz and do not exhibit a systematic trend.

The $l = 3$ quantum-defect functions used for the MQDT calculations were extracted from available ab initio BO potential-energy curves for low-$n$ singlet and triplet states [31, 32]. No adjustment of the quantum defects to experimental data was performed. We estimated the maximum possible error in the extrapolation to the ionization threshold to be 600 kHz, including 160 kHz originating from the residuals (root mean squared error, given by the dashed red lines in Fig. 5(b)) and the rest from the systematic uncertainty associated with the narrow range of binding energies probed experimentally. States of lower principal quantum number could not be used in this analysis because of vibrational channel interactions. As an additional verification, the extrapolation result could be confirmed within the given uncertainty using quantum defects obtained previously using a polarization model based on ab initio data of the multipole moments of the molecular ion [33].

### IV. DISCUSSION AND CONCLUSION

![Figure 6](image-url)

Figure 6. Comparison between experimental [2, 3, 6–9, 37, 38] and theoretical [5, 10, 17, 18, 39–44] results for $D_0(D_2)$ in a historical perspective. Note the improvement of 10,000 over the plotted time span and the factor of 25 improvement over the previous experimental round.

The results of the present measurements and their uncertainties are compiled in Table IV. The resulting value for $D_0(D_2)$ represents the dissociation energy of the center of gravity [45] of the $N = 0$ ground state. The final outcomes are the ionization energy of the D$_2$ molecule $E_1(D_2) = 124745.393739(26) \text{ cm}^{-1}$, and its dissociation energy $D_0(D_2)= 36748.362282(26) \text{ cm}^{-1}$, which are 25 times more accurate than previous experimental results [9]. Part of this improvement derives from the renewed calculation of $E_1(D_2^+)$, which was published in Ref. [35] and subsequently updated [36]. Putting this aside, the experimental improvement of $D_0(D_2)$ would be 22-fold. This major improvement is included in an overview of the development of this benchmark value over the past 60 years starting with the work of Herzberg [2, 3], displayed in Fig. 6. A comparison is made...
with the development in accuracy on the theory side, demonstrating that progress on both sides goes hand-in-hand. The experimental accuracy has improved by a factor of more than ten thousand times during this period. A comparison with the most recent theoretical value for $D_0(D_2)$, which is of the same accuracy, yields agreement within 1.6σ.

Precision measurements in $D_2$ are important for testing the QED framework in molecules, even though precision tests have been carried out for the $H_2$ species [20, 21, 23]. Inspection of the various contributions to the binding energy of the ground state of $H_2$ and $D_2$ in the most recent calculations, where nonadiabatic effects were computed in a non-BO variational approach, shows that the various terms in the QED expansion have different contributions for the isotopologues, and hence those are tested in different combinations. These calculations further reveal that the finite-nuclear-size (FNS) effect strongly differs between the $H_2$ and $D_2$ isotopic species. Whereas the FNS effect in $H_2$ contributes by only $-930$ kHz to the binding energy of the molecule [46], the most accurate measurement of the binding energy is at the level of $340$ kHz [23], so verifying the calculations at the level of 36%. In $D_2$ the FNS effect amounts to $6.1$ MHz [18] because of the much larger nuclear charge radius of the deuteron (CODATA-2018 value of $r_d = 2.12799(74)$ fm [47]). With the current experimental precision of $780$ kHz, the measured dissociation energy is sensitive to the FNS-effect below the 13% accuracy level. This converts to a 6% accuracy level on $r_d$, a level indicated by the orange area in Fig. 6.

The present accuracy for $r_d$ (in CODATA-2018 [47]) is entirely based on a measurement in the muonic deuteron atom ($\mu D$) [48], where the overlap with the nucleus gives a FNS effect that is larger by several orders of magnitude. It might be interesting to derive values of nuclear charge radii, without including results from muonic systems, and so pursue a derivation from measurements constrained to the first family of particles in the Standard Model of physics. A combination of accurate results on the $1S-2S$ transition in atomic hydrogen [49] and deuterium [50] and results on hydrogen and deuteron neutral molecules, including also results from the recent accurate measurements on the HD$^+$ ion [51, 52] and planned experiments on the $H^+_2$ ion [53], open the perspective to determine accurate values of the correlated physical parameters ($r_d, R_\infty$) and ($r_p, R_\infty$), where $R_\infty$ is the Rydberg constant, from non-muonic purely electronic spectroscopy. A comparison with results of these parameters on $r_p$ and $r_d$ from $\mu H$ [54] and $\mu D$ [48] may then be interpreted as a test of lepton universality.

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state of the hydrogen molecule, J. Mol. Spectrosc. **54**, 303 (1975).

[40] L. Wolniewicz, The $^3\Sigma^+_g$ state vibration-rotational energies of the $\text{H}_2$, HD, and $\text{D}_2$ molecules, J. Chem. Phys. **78**, 6173 (1983).

[41] W. Kołos, K. Szalewicz, and H. Monkhorst, New Born-Oppenheimer potential energy curve and vibrational energies for the electronic ground state of the hydrogen molecule, J. Chem. Phys. **84**, 3278 (1986).

[42] W. Kołos and J. Rychlewski, Improved theoretical dissociation energy and ionization potential for the ground state of the hydrogen molecule, J. Chem. Phys. **98**, 3960 (1993).

[43] L. Wolniewicz, Relativistic energies of the ground state of the hydrogen molecule, J. Chem. Phys. **99**, 1851 (1993).

[44] L. Wolniewicz, Nonadiabatic energies of the ground state of the hydrogen molecule, J. Chem. Phys. **103**, 1792 (1995).

[45] H. Jóźwiak, H. Cybulski, and P. Wcisło, Hyperfine components of all rovibrational quadrupole transitions in the $\text{H}_2$ and $\text{D}_2$ molecules, J. Quant. Spectr. Rad. Transfer **253**, 107186 (2020).

[46] M. Puchalski, J. Komasa, P. Czachorowski, and K. Pachucki, Nonadiabatic QED Correction to the Dissociation Energy of the Hydrogen Molecule, Phys. Rev. Lett. **122**, 103003 (2019).

[47] E. Tiesinga, P. J. Mohr, D. B. Newell, and B. N. Taylor, CODATA Recommended Values of the Fundamental Physical Constants: 2018, J. Phys. Chem. Ref. Data **50**, 033105 (2021).

[48] R. Pohl, F. Nez, L. M. P. Fernandes, F. D. Amaro, F. Biraben, J. M. R. Cardoso, D. S. Covita, A. Dax, S. Dhawan, M. Diepold, A. Giesen, A. L. Gouveia, T. Graf, T. W. Hänsch, P. Indelicato, L. Julien, P. Knowles, F. Kottmann, E.-O. L. Bigot, Y.-W. Liu, J. A. M. Lopes, L. Ludhova, C. M. B. Monteiro, F. Mulhauser, T. Nebel, P. Rabinowitz, J. M. F. dos Santos, L. A. Schaller, K. Schuhmann, C. Schwob, D. Taquq, J. F. C. A. Veloso, and A. Antognini, Laser spectroscopy of muonic deuterium, Science **353**, 669 (2016).

[49] C. G. Parthay, A. Matveev, J. Alnis, B. Bernhardt, A. Beyer, R. Holzwarth, A. Maistrou, R. Pohl, K. Predehl, T. Udem, T. Wilken, N. Kolachevsky, M. Abgrall, D. Rovera, C. Salomon, P. Laurent, and T. W. Hänsch, Improved measurement of the hydrogen 1S−2S transition frequency, Phys. Rev. Lett. **107**, 203001 (2011).

[50] C. G. Parthay, A. Matveev, J. Alnis, R. Pohl, T. Udem, U. D. Jentschura, N. Kolachevsky, and T. W. Hänsch, Precision measurement of the hydrogen-deuterium 1S−2S isotope shift, Phys. Rev. Lett. **104**, 233001 (2010).

[51] S. Alighanbari, G. S. Giri, F. L. Constantin, V. I. Korobov, and S. Schiller, Precise test of quantum electrodynamics and determination of fundamental constants with HD$^+$ ions, Nature **581**, 152−158 (2020).

[52] S. Patra, M. Germann, J.-P. Karr, M. Haidar, L. Hilico, V. I. Korobov, F. M. J. Cozijn, K. S. E. Eikema, W. Ubachs, and J. C. Koelemeijer, Proton-electron mass ratio from laser spectroscopy of HD$^+$ at the part-per-trillion level, Science **369**, 1238 (2020).

[53] J. Schmidt, T. Louvradoux, J. Heinrich, N. Sillitoe, M. Simpson, J.-P. Karr, and L. Hilico, Trapping, cooling, and photodissociation analysis of state-selected $\text{H}_2^+$ ions produced by (3 + 1) multiphoton ionization, Phys. Rev. Appl. **14**, 024053 (2020).

[54] R. Pohl, A. Antognini, F. Nez, F. D. Amaro, F. Biraben, J. M. R. Cardoso, D. S. Covita, A. Dax, S. Dhawan, L. M. P. Fernandes, A. Giesen, T. Graf, T. W. Hänsch, P. Indelicato, L. Julien, C. Y. Kao, P. Knowles, E.-O. L. Bigot, Y.-W. Liu, J. A. M. Lopes, L. Ludhova, C. M. B. Monteiro, F. Mulhauser, T. Nebel, P. Rabinowitz, J. M. F. dos Santos, L. A. Schaller, K. Schuhmann, C. Schwob, D. Taquq, J. F. C. A. Veloso, and F. Kottmann, The size of the proton, Nature **466**, 213 (2010).