

Improved ionization and dissociation energies of the deuterium molecule

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The ionization energy of D_2 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 D_2 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 it was found to be in good agreement (at 1.6σ) with recent *ab initio* calculations of the four-particle nonadiabatic relativistic energy and of quantum-electrodynamic corrections up to order $m\alpha^6$. This result constitutes a test of quantum electrodynamics in the molecular domain, while a perspective is opened to determine nuclear charge radii from molecules.

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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 photoexcitation 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 Zürich-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 four-particle variational calculations, developed independently by different groups [15–17]. A very accurate theoretical value for the dissociation energy of D_2 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 H_2 , 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. First, 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 H_2 , both for ortho- H_2 [20] and para- H_2 [21]. Second, the technique of Ramsey-comb spectroscopy utilizing frequency comb lasers for direct excitation of the EF $^1\Sigma_g^+$ 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 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

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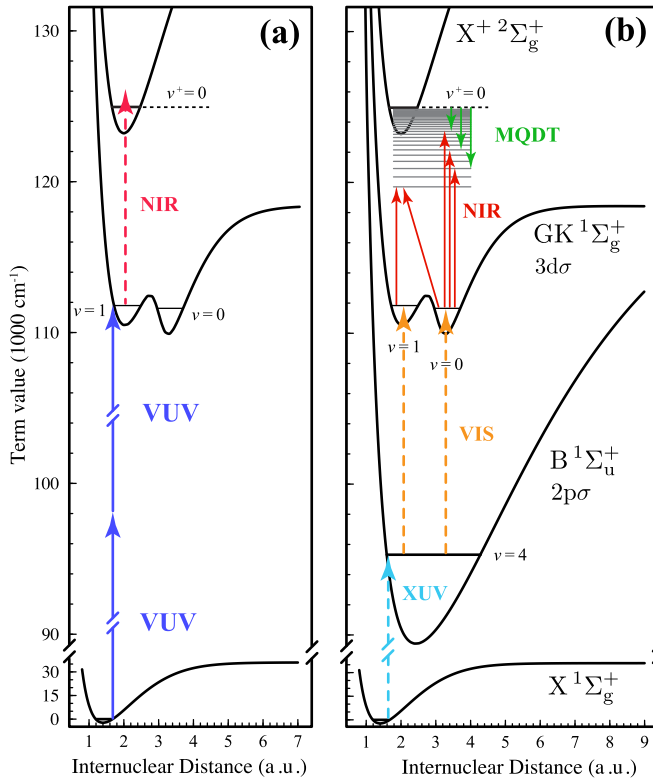


FIG. 1. Potential-energy curves of the electronic states of the hydrogen molecule relevant to this study. The level positions of the Rydberg states (gray) are not to scale. (a) In Amsterdam, the $\text{GK}(v = 1, N = 2) \leftarrow \text{X}(v = 0, N = 0)$ two-photon transition, indicated in dark blue, 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 Zürich, 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 $\text{B}(v = 4, N = 1)$ 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 multichannel quantum defect theory for the binding energies of the measured nf levels, forming an extrapolation to the ionization limit $E_1(\text{D}_2)$.

carried out in the Amsterdam and Zürich laboratories and their results combined. The excitation schemes are represented in a level diagram of the molecule in Fig. 1.

II. GK-STATE SPECTROSCOPY IN AMSTERDAM

In the Amsterdam laboratory, the $\text{GK}^1\Sigma_g^+(v = 1, J = 2) \leftarrow \text{X}^1\Sigma_g^+(v = 0, J = 0)$ 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. 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 $\beta\text{-BaB}_2\text{O}_4$ (BBO) and a $\text{KBe}_2\text{BO}_3\text{F}_2$ (KBBF) crystal. The main improvement of the setup in comparison

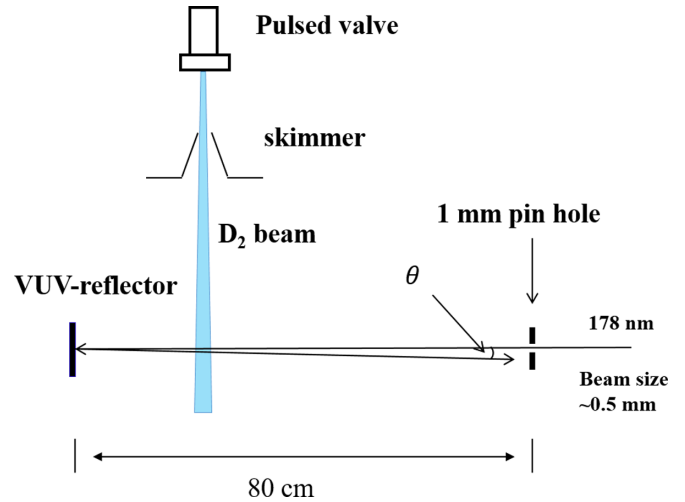


FIG. 2. Schematic overview of the interaction zone of the D_2 molecular beam with the VUV laser beam. A small residual Doppler shift may arise when the angle θ between the incoming and reflected beam is not exactly 180° .

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, $125\,899.0(1.0)\text{ cm}^{-1}$, the second using a resonance near the ionization threshold, at $124\,744.0(1.0)\text{ cm}^{-1}$. 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 the reader to Ref. [25].

Even though the experiment is Doppler-free, small residual Doppler shifts persist in case of slight misalignments from exact counterpropagation of the two VUV beams crossing the molecular D_2 beam. A small angle between the counterpropagating 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 between the counterpropagating 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 $\text{GK}^1\Sigma_g^+(1,2) \leftarrow \text{X}^1\Sigma_g^+(0,0)$ 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

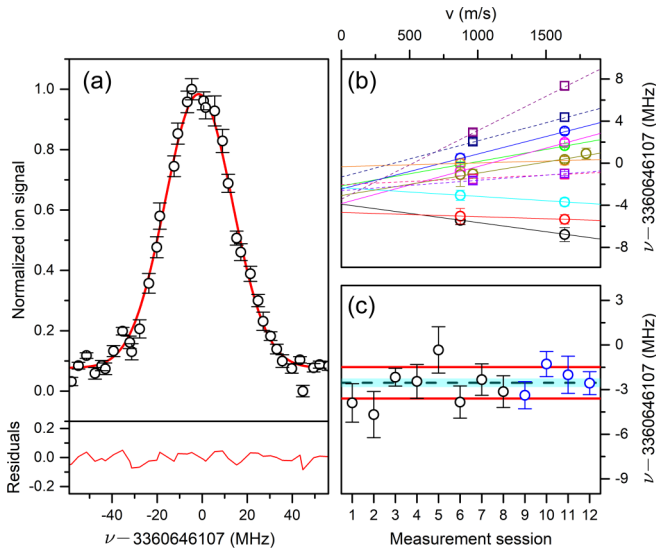


FIG. 3. (a) Example of a chirp-compensated scan of the GK $1\Sigma_g^+(1,2) \leftarrow X 1\Sigma_g^+(0,0)$ two-photon transition in D_2 , fitted with a Gaussian curve with residuals shown below. (b) Transition frequency as a function of central velocity of the D_2 beam with different colors representing different alignments of the VUV beam. Every data point results from five to ten ac-Stark and second-order Doppler compensated scans. For all alignments, a linear fit is used to extrapolate to a Doppler-free value. Solid and dashed lines result from the two separate measurement campaigns. (c) Extrapolated Doppler-free transition frequencies, resulting from 12 measurement sessions. Black and blue data points result from the two separate measurement campaigns. The red lines indicate the standard deviation (1 MHz). The dotted line at 3 360 646 104.46 MHz is the average value, and the blue bar is the standard error of the mean (0.35 MHz), which is the combined uncertainty due to the statistical error and the first-order Doppler shift.

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 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 2. 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 retroreflection of the VUV beam inside the vacuum, and it can be considered

TABLE I. Error budget of the measurement of the GK $1\Sigma_g^+(1,2) \leftarrow X 1\Sigma_g^+(0,0)$ transition in D_2 .

Measured frequency	3 360 646 104.46 MHz
Effect	Uncertainty
Residual first-order Doppler	(350 kHz) _{stat}
Second-order Doppler	30 kHz
ac-Stark ionization laser	100 kHz
ac-Stark VUV laser	240 kHz
Hyperfine structure	100 kHz
Final frequency	3 360 646 104.46(45) MHz

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 GK $1\Sigma_g^+(1,2) \leftarrow X 1\Sigma_g^+(0,0)$ transition frequency of D_2 is 0.45 MHz.

The symmetric line shape 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 ZÜRICH

The experiments carried out in Zürich are aimed at connecting the GK $1\Sigma_g^+(1,2)$ level to $E_1(D_2)$ 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 $C 1\Pi_u$ 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 wave functions 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) and 240(40) ns for the GK(1,2) and GK(0,2)

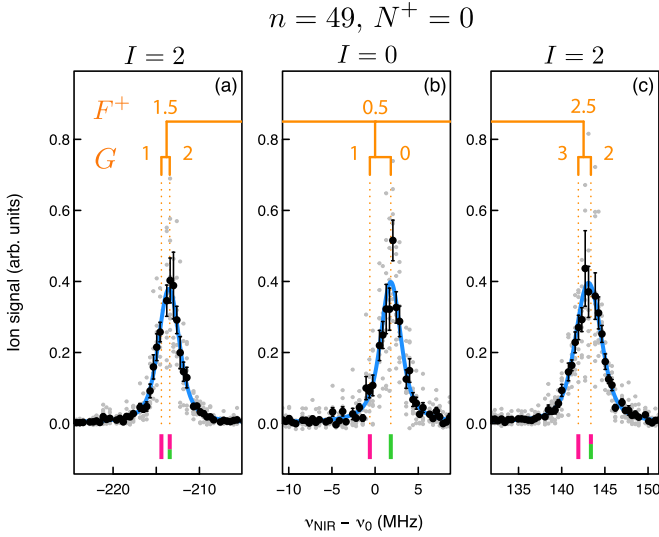


FIG. 4. Spectra of the three $F^+ = (3/2, 1/2, 5/2)$ hyperfine components of the $49f_0_3$ state of D_2 recorded from GK(0,2) with only the forward propagating laser beam. The normalization of the ion signal was performed for each spectrum individually, and the fitted Voigt profiles are shown in blue. All three spectra were recorded without changing the geometry of the laser beam paths. ν_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 $\vec{F} = \vec{G} + \vec{\ell}$ is omitted because the splitting is not resolved on the scale of the figure.

states, respectively, with corresponding natural linewidths of ≈ 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 $50f_0_3$ Rydberg state. For the level scheme, see Fig. 1.

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, $\vec{\ell}$ 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 $49f_0_3 \leftarrow$ 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 $\vec{F} = \vec{G} + \vec{\ell}$, 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 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 $\sim 4 \times 10^{-5}$, 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 $1^1\Sigma_g^+$ 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 focus 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 $nf_0_3(I = 0, S = 0)$ 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 frequency was stabilized to a frequency comb which was referenced to a Rb GPS standard. The first-order Doppler shift was canceled by taking the average of two Doppler components generated in an optical setup in which the laser beam is retroreflected 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 $62f_0_3(I = 0, S = 0) \leftarrow$ 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.

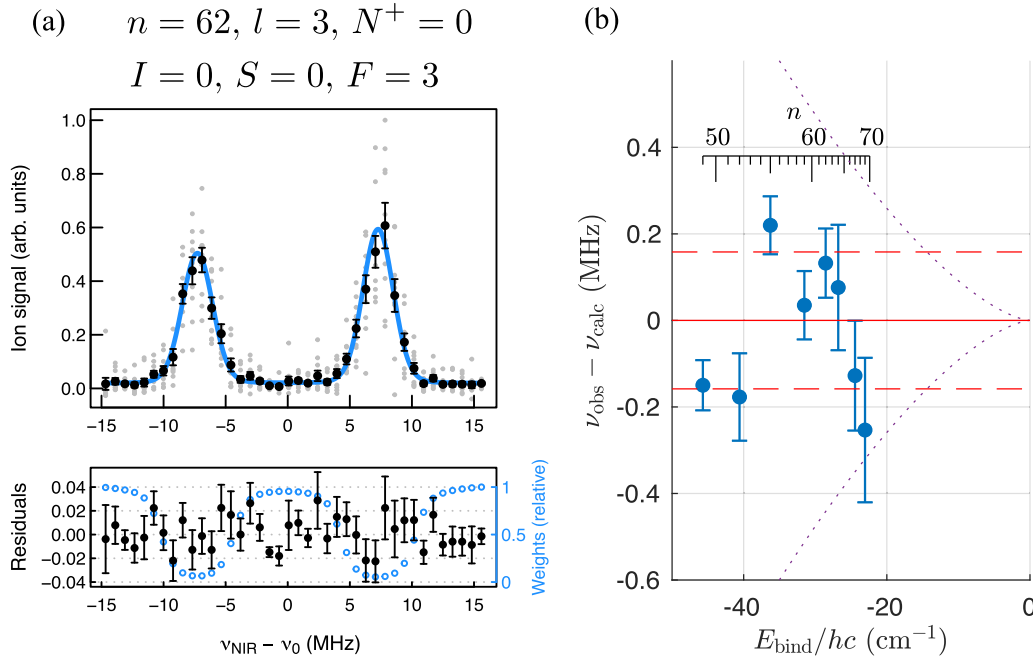


FIG. 5. (a) Top: Determination of the Doppler-free position of the $I = 0$ component from a fit of two Voigt profiles (blue) to the two Doppler components obtained with the forward and backward propagating laser beams (gray, averages in black). Bottom: corresponding relative weights (blue) and weighted average residuals (black). (b) Residuals of the binding energies of the GK(0,2) state determined from $nf_0_3(I = 0, S = 0)$ Rydberg states measured for a range of selected n -values. The resulting statistical uncertainty of the binding energy of the GK(0,2) state is indicated by red dashed lines, and the estimated uncertainty of the Rydberg-state binding energies from the MQDT treatment is indicated by the purple dotted lines.

The error budget for the laser excitation of nf -Rydberg states from the GK $^1\Sigma_g^+(0, 2)$ state is compiled in Table II and includes contributions from the dc and ac-Stark shifts, Zeeman shift, pressure shift, Doppler shift, and the line-shape 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 line-shape model.

dc Stark effect: The transition to the $62f_0_3(I = 0, S = 0)$ state is taken as illustration because this is the transition

TABLE II. Error budget for the transition between the GK(0,2) state of D_2 and the $62f_0_3(I = 0, S = 0)$ 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).

Measured frequency	388 255 115.129(16) MHz	
	Correction	Uncertainty
dc Stark shift		60 kHz
ac Stark shift		~ 5 kHz
Zeeman shift		~ 10 kHz
Pressure shift		~ 1 kHz
Residual first-order Doppler shift		$(<200 \text{ kHz})_{\text{stat}}$
Second-order Doppler shift	+2 kHz	0.5 kHz
Line-shape model		50 kHz
Photon-recoil shift	-83 kHz	
Systematic uncertainty		80 kHz
Final frequency	388 255 115.048(82) MHz	

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 $n = 69$.

Line-shape model: The statistical uncertainty for a single measurement results from the uncertainty of the nonlinear weighted fit of the line shape of the two Doppler components [see Fig. 5(a)] 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 found the nonlinear fits of Voigt line profiles to be more sensitive to the starting parameters than the fits of Lorentzian line profiles which we used in our previous studies in H_2 [23,29]. This difference is most likely caused by having two fit parameters for the width instead of one. Deviations of the fitted line centers caused by fit convergence issues were observed to be of the order of 50 kHz and we cautiously took this value as additional systematic uncertainty.

Doppler effect: The counterpropagating laser beams used to cancel the first-order Doppler shift were realigned for each independent set of measurements. This transfers the systematic error resulting from a beam misalignment, which was found to be better than 200 kHz, into a statistical error of the sample of independent measurements after recording each transition at least 4 and up to 14 times. The final statistical uncertainty for a measured transition was obtained as the standard error of the weighted mean of the transition frequencies from all independent measurements.

TABLE III. Experimental wave numbers of the measured $nf(N^+ = 0, I = 0, S = 0, F = 3)$ Rydberg states (ungerade symmetry) of ortho- D_2 relative to the GK $^1\Sigma_g^+(0, 2)$ state, their statistical and combined uncertainties (in MHz), their binding energies calculated by MQDT, the predicted transition energies, and the deviation between experiment and theory.

n	$\tilde{\nu}_{\text{obs}}/\text{cm}^{-1}$	$\sigma_{\text{stat}}/\text{MHz}$	$\sigma_{\text{tot}}/\text{MHz}$	$E_{\text{bind}}^{\text{calc}}/\text{cm}^{-1}$	$\tilde{\nu}_{\text{calc}}/\text{cm}^{-1}$	$\nu_{\text{obs-calc}}/\text{MHz}$
49	12933.6376366	0.028	0.058	45.7071608	12933.6376416	-0.149
52	12938.7605655	0.086	0.101	40.5842310	12938.7605714	-0.176
55	12943.0666421	0.037	0.067	36.2781676	12943.0666348	+0.220
59	12947.8198070	0.044	0.079	31.5249965	12947.8198059	+0.034
62	12950.7966157	0.016	0.082	28.5481911	12950.7966113	+0.133
64	12952.5524111	0.114	0.145	26.7923938	12952.5524086	+0.076
67	12954.8992025	0.055	0.127	24.4455956	12954.8992068	-0.128
69	12956.2956976	0.096	0.167	23.0490963	12956.2957061	-0.254
weighted standard error:						0.160

Table III lists the wave numbers of all transitions $nN_N^+(I = 0, S = 0) \leftarrow \text{GK } ^1\Sigma_g^+(0, 2)$ recorded in the present study. The statistical uncertainties determined from sequences of independent measurements are given as σ_{stat} in MHz. The systematic uncertainties were added in quadrature to obtain the final experimental uncertainties σ_{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 $12\,979.344\,802\,4(53)\text{ cm}^{-1}$ excluding the systematic uncertainty originating from the incomplete set of quantum defects. The second-to-last column gives the transition wave numbers $\tilde{\nu}_{\text{calc}}$ 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 $\tilde{\nu}_{\text{obs}}$. 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

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 $E_1(D_2) = 124\,745.393\,739(26)\text{ cm}^{-1}$, and its dissociation energy $D_0(D_2) = 36\,748.362\,282(26)\text{ cm}^{-1}$, 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

TABLE IV. Ionization and dissociation energies of D_2 from the present measurements, and comparison with previous results and with theory.

	Energy level interval	Value (cm^{-1})	Uncertainty (MHz)	Ref.
(1)	$X(v = 0, N = 0) \rightarrow \text{GK}(v = 1, N = 2)$	112099.087712(15)	0.45	This work
(2)	$\text{GK}(v = 0, N = 2) \rightarrow \text{GK}(v = 1, N = 2)$	333.038775(7)	0.21	This work
(3)	$\text{GK}(v = 0, N = 2) \rightarrow X^+(v^+ = 0, N^+ = 0)$	12979.344802(20)	0.60	This work
(4)=(1)-(2)+(3)	$E_1(\text{ortho-}D_2)$	124745.393739(26)	0.78	This work
(5)	$E_1(\text{ortho-}D_2)$	124745.39407(58)	17	[9]
(6)	$E_1(D)$	109708.61455294(17)	0.005	[34]
(7)	$E_1(D_2^+)$	131420.1976492(8)	0.024	[35,36]
(8)=(4)+(7)-2×(6)	$D_0(D_2)$	36748.362282(26)	0.78	This work
(9)	$D_0(D_2)$	36748.36286(68)	20	[9]
(10)	$D_0(D_2)$	36748.362342(26)	0.80	Theory [18]
(8)-(10)	obs.-calc. $D_0(D_2)$	-0.000060(37)	1.1	

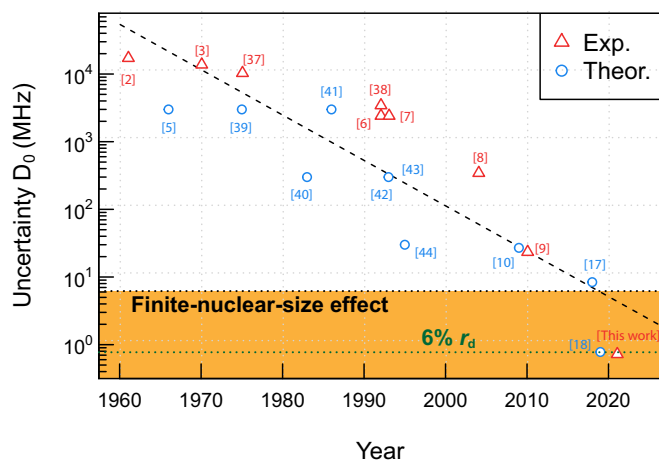


FIG. 6. Comparison between experimental [2,3,6–9,37,38] and theoretical [5,10,17,18,39–44] results for $D_0(D_2)$ in a historical perspective. Note the improvement of 10 000 over the plotted time span and the factor of 25 improvement over the previous experimental round.

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 10 000 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 deuterium atom (μD) [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 deuterium 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_∞) and (r_p, R_∞), where R_∞ is the Rydberg constant, from nonmuonic purely electronic spectroscopy. A comparison with results of these parameters on r_p and r_d from μH [54] and μD [48] may then be interpreted as a test of lepton universality.

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