

Communication: The ionization and dissociation energies of HD

Journal Article**Author(s):**

Sprecher, Daniel; Liu, Jinjun; Jungen, Christian; Ubachs, Wim; Merkt, Frédéric

Publication date:

2010-09

Permanent link:

<https://doi.org/10.3929/ethz-a-010781913>

Rights / license:

[In Copyright - Non-Commercial Use Permitted](#)

Originally published in:

The Journal of Chemical Physics 133(11), <https://doi.org/10.1063/1.3483462>

This article may be downloaded for personal use only. Any other use requires prior permission of the author and AIP Publishing.

The following article appeared in *J. Chem. Phys.* **133**, 111102 (2010) and may be found at <http://dx.doi.org/10.1063/1.3483462>.

Communication: The ionization and dissociation energies of HD

Daniel Sprecher, Jinjun Liu, Christian Jungen, Wim Ubachs, and Frédéric Merkt

Citation: *The Journal of Chemical Physics* **133**, 111102 (2010); doi: 10.1063/1.3483462

View online: <http://dx.doi.org/10.1063/1.3483462>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/133/11?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Determination of the ionization and dissociation energies of H₂ and He₂](#)

AIP Conf. Proc. **1504**, 495 (2012); 10.1063/1.4771748

[High-level ab initio predictions for the ionization energy, bond dissociation energies, and heats of formation of nickel carbide \(NiC\) and its cation \(NiC⁺\)](#)

J. Chem. Phys. **133**, 114304 (2010); 10.1063/1.3479759

[Determination of the ionization and dissociation energies of the deuterium molecule \(D₂\)](#)

J. Chem. Phys. **132**, 154301 (2010); 10.1063/1.3374426

[Electronically excited and ionized states of the CH₂ OH radical: A theoretical study](#)

J. Chem. Phys. **132**, 114308 (2010); 10.1063/1.3354975

[Determination of the ionization and dissociation energies of the hydrogen molecule](#)

J. Chem. Phys. **130**, 174306 (2009); 10.1063/1.3120443



NEW Special Topic Sections

NOW ONLINE
Lithium Niobate Properties and Applications:
Reviews of Emerging Trends

AIP | Applied Physics
Reviews

Communication: The ionization and dissociation energies of HD

Daniel Sprecher,¹ Jinjun Liu,¹ Christian Jungen,^{2,3} Wim Ubachs,⁴ and Frédéric Merkt^{1,2,a)}

¹Laboratorium für Physikalische Chemie, ETH-Zürich, 8093 Zürich, Switzerland

²Laboratoire Aimé Cotton du CNRS, Université de Paris-Sud, 91405 Orsay, France

³Department of Physics and Astronomy, University College London, London WC1E 6BT, United Kingdom

⁴Department of Physics and Astronomy, Laser Centre, Vrije Universiteit, De Boelelaan 1081, 1081 HV Amsterdam, The Netherlands

(Received 9 July 2010; accepted 4 August 2010; published online 15 September 2010)

The adiabatic ionization energy [in units of hc , $E_i=124\,568.485\,81(36)\text{ cm}^{-1}$] and the dissociation energy [$D_0=36\,405.783\,66(36)\text{ cm}^{-1}$] of HD have been determined using a hybrid experimental-theoretical method. Experimentally, the wave numbers of the $EF(v=0, N=0) \rightarrow np[X^+(v^+=0 \text{ and } 1, N^+=0)]$ and $EF(v=0, N=1) \rightarrow np[X^+(v^+=0, N^+=1)]$ transitions to singlet Rydberg states were measured by laser spectroscopy and used to validate predictions of the electron binding energies by multichannel quantum defect theory. Adding the transition energies, the electron binding energies and previously reported term energies of the EF state led to a determination of the adiabatic ionization energy of HD and of rovibrational energy spacings in HD^+ . Combining these measurements with highly accurate theoretical values of the ionization energies of the one-electron systems H, D, and HD^+ further enabled a new determination of the dissociation energy of HD. © 2010 American Institute of Physics. [doi:10.1063/1.3483462]

The determination of the dissociation energy of the hydrogen molecule (H_2) and its deuterated isotopomers (HD and D_2) has played an important role in the development of molecular quantum mechanics.¹ Classical physics and even the old quantum theory of Bohr and Sommerfeld proved inadequate to explain the existence of H_2 and of chemical bonds in general. The first qualitatively correct theoretical description of chemical bonds was achieved in 1927 by Heitler and London² in their celebrated application of the new quantum theory to the H_2 molecule.

Although Heitler and London's estimate of the dissociation energy of H_2 (2.9 eV) was smaller than the experimental value of Witmer [4.15 eV (Ref. 3)] by about 30%, their work marked the beginning of a still ongoing series of theoretical studies aimed at accurately describing the chemical bond in H_2 in first-principles calculations. The observable quantity used to assess the accuracy of the calculations is the dissociation energy D_0 , i.e., the energy difference between the onset of the $H(1s)+H(1s)$ (or $H+D$, or $D+D$) dissociation continuum and the ground rovibronic level of H_2 (or HD , or D_2). Consequently, precise and accurate measurements of the dissociation energy of the hydrogen molecule and its deuterated isotopomers have played an essential role in the validation of the theoretical results. To illustrate this point, we refer to the extensive work published during the past 50 years on the dissociation energy of HD ,^{4–18} which is the subject of this communication. Many more articles have been published on the dissociation energy of H_2 and D_2 (see Refs. 19–21 and references therein).

During the 83 years that have elapsed since Heitler and London's work, there were periods during which experimental and theoretical results appeared to be in conflict, but these conflicts were invariably resolved by the next generation of

more accurate experiments or calculations, so that today nobody seriously thinks of questioning the ability of the quantum theory to accurately describe chemical bonds. Instead, the interest in comparing ever more precise theoretical and experimental values of the dissociation energy of the hydrogen molecule is motivated by the necessity, at each new generation of experiments, to include and quantify effects neglected in the previous theoretical treatments. The challenge consists of fully accounting for electron correlation effects, properly treating nonadiabatic and relativistic effects, and including quantum electrodynamics (QED) corrections of sufficiently high order in the fine-structure constant α (see, e.g., Refs. 17 and 21).

To account for the most recent experimental value of the dissociation energy of H_2 [$D_0(H_2)=36\,118.069\,62(37)\text{ cm}^{-1}$ (Ref. 19)], Piszczatowski *et al.*²¹ had to calculate relativistic and QED corrections at the adiabatic level of theory by including all contributions of the order of α^2 and α^3 and the major (one-loop) α^4 term. Their result [$D_0(H_2)=36\,118.0695(10)\text{ cm}^{-1}$] is in agreement with experiment. In the same study, a similar calculation for D_2 [$D_0(D_2)=36\,748.3633(9)\text{ cm}^{-1}$] pointed at a small discrepancy (by two standard deviations) with experimental results,¹⁸ which was resolved in a very recent measurement yielding a value $D_0(D_2)=36\,748.362\,86(68)\text{ cm}^{-1}$.²⁰ No similarly accurate values have been reported for HD . The purpose of this communication is to present a new determination of the dissociation energy of HD that can be used as a test of a calculation by Pachucki and Komasa²² carried out in parallel to the experiments described here.

The experimental setup and procedure were described in detail in our equivalent studies on H_2 (Ref. 19) and D_2 .²⁰ In brief, members of the singlet np Rydberg series converging to the $X^+ \ ^2\Sigma_g^+$ electronic ground state of HD^+ were produced in a $(2+1')$ three-photon excitation scheme starting

^{a)}Electronic mail: feme@xuv.phys.chem.ethz.ch.

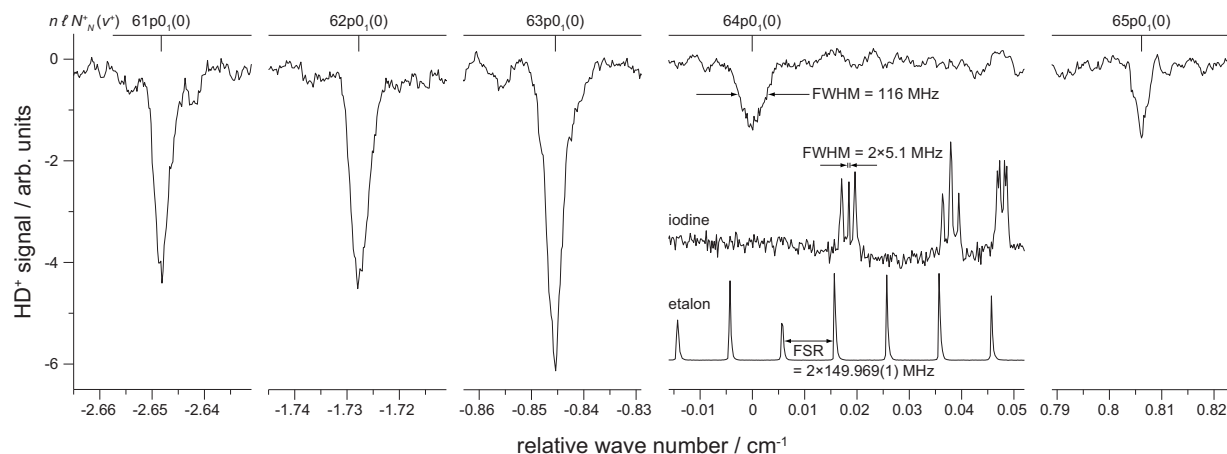


FIG. 1. Part of the survey spectrum of the $(v^+, N^+) = (0, 0)$ Rydberg series showing the 61–65 $p0_1(0)$ Rydberg states of HD recorded from the $EF(v=0, N=0)$ intermediate level. Etalon traces and iodine spectra were recorded simultaneously using the fundamental cw laser frequency for the relative and absolute frequency calibrations, respectively. The relative intensities are very sensitive to the experimental conditions and are not reliable.

from the $X^1\Sigma_g^+(v=0, N=0, 1)$ state of HD. The $EF^1\Sigma_g^+(v=0, N=0, 1)$ intermediate state was excited in a two-photon transition using the third harmonic of a commercial dye laser ($\lambda \sim 201$ nm, bandwidth ~ 1 GHz, referred to as $X \rightarrow EF$ laser). The second harmonic of a pulsed titanium-doped sapphire (Ti:Sa) amplifier (bandwidth ~ 20 MHz, referred to as $EF \rightarrow n$ laser),²³ seeded by a Ti:Sa cw ring laser, was then used to access the Rydberg states. For detection, the Rydberg states were ionized and the HD^+ ions accelerated toward a microchannel plate detector by a pulsed electric field. The spectra were obtained by monitoring the HD^+ ion signal as a function of the wave number of the $EF \rightarrow n$ laser.

Survey spectra of three Rydberg series were recorded [we use the notation $n\ell N_N^+(v^+)$; all quantum numbers have their usual meanings; see, e.g., Ref. 24]: the $np0_1(0)$ and $np0_1(1)$ series from the $EF(v=0, N=0)$ intermediate level, and the $np1_{1,2}(0)$ series from the $EF(v=0, N=1)$ intermediate level. As illustration, several sections of the survey spectrum of the $EF(v=0, N=0) \rightarrow np0_1(0)$ transitions are displayed in Fig. 1, and the second column of Table I lists the transition wave numbers with respect to the $64p0_1(0)$ level for all Rydberg states detected with a sufficient signal-to-noise ratio. The complete experimental data set, including the positions of the members of the $np1_{1,2}(0)$ and $np0_1(1)$ series with respect to the $69p1_2(0)$ and $55p0_1(1)$ levels, respectively, is given in the supplementary material.²⁵ The absolute positions of the reference levels are determined separately, as explained below.

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

tional levels of HD^+ , which are needed as input to the MQDT calculations, were taken from *ab initio* calculations (Ref. 27 for $v^+=0-4$ and Ref. 28 for $v^+=5-21$). The hyperfine effects were included in the frame transformation connecting the close-coupling case [Hund's case (b)] and the long-range coupling case [Hund's case (e)], as explained in detail in Ref. 24. Because of the reduced symmetry of HD compared to H_2 and D_2 , the two nuclear spins are independent, and the close-coupling angular momentum coupling scheme had to be extended (details will be included in a future publication). For the long-range coupling case, the *ab initio* hyperfine Hamiltonian operator of HD^+ from Ref. 29 was used. The explicit inclusion of the hyperfine structure of the Rydberg states turned out to be necessary to properly account for the weak singlet-triplet mixing, and calculations

TABLE I. Experimental wave numbers of members of the $np0_1(0)$ Rydberg series relative to the $64p0_1(0)$ state and electron binding energies calculated by MQDT. The sum of these two quantities represents an experimental determination of the electron binding energy of the $64p0_1(0)$ state (all values in cm^{-1}).

Rydberg state $n\ell N_N^+(v^+)$	Relative experimental wave number ^a	MQDT binding energy	Sum related to mean value
56 $p0_1(0)$	-8.308 25	35.085 48	-0.000 45
57 $p0_1(0)$	-7.170 62	33.948 50	0.000 21
58 $p0_1(0)$	-6.207 10	32.985 51	0.000 73
26 $p2_1(0)$ ^b	-5.422 39	32.200 84	0.000 77
60 $p0_1(0)$	-3.598 05	30.375 18	-0.000 55
61 $p0_1(0)$	-2.648 18	29.424 91	-0.000 96
62 $p0_1(0)$	-1.727 58	28.505 35	0.000 10
63 $p0_1(0)$	-0.845 56	27.622 88	-0.000 36
64 $p0_1(0)$	0	26.778 44	0.000 76
65 $p0_1(0)$	0.806 12	25.971 30	-0.000 26
66 $p0_1(0)$	1.579 71	25.200 21	0.002 24
67 $p0_1(0)$	2.310 81	24.463 89	-0.002 97
68 $p0_1(0)$	3.014 34	23.761 27	-0.002 07
Standard deviation			0.000 61 ^c

^aThe estimated experimental uncertainty is 0.0008 cm^{-1} .

^bState with the largest contribution from the interacting 26 $p2_1(0)$ state.

^cThe Rydberg states 66–68 $p0_1(0)$ have not been taken into account because they are perturbed (see text for detail).

neglecting the hyperfine interaction led to binding energies which were too large by about 20 MHz.

The binding energies of the observed np Rydberg states (defined as the center of gravity of the electron binding energies of the relevant hyperfine components) resulting from the MQDT calculations are given in the third column of Table I for the $np0_1(0)$ series and in the supplementary material²⁵ for the other series. Adding the relative transition wave numbers from the second column to these values would ideally lead to the same value of the ionization energy for all members of a Rydberg series. With the exception of the states $66-68p0_1(0)$ the deviation is on the order of the experimental uncertainty of ~ 24 MHz. We believe that the $66-68p0_1(0)$ Rydberg states are subject to perturbations resulting from a g/u -mixing channel interaction with the $ns1_1$ and $nd1_1$ Rydberg series, potentially enhanced by the weak stray field present in the experimental volume. The results presented in Table I demonstrate that the MQDT calculations reproduce the experimentally observed positions well within the experimental uncertainty of the survey spectra, as might have been expected from our previous studies of H_2 and D_2 .^{24,26}

After recording the survey spectra, the transitions to the states $64p0_1(0)$, $69p1_2(0)$, and $55p0_1(1)$ were chosen for measurements of absolute transition wave numbers. These wave numbers were obtained by measuring the difference between the fundamental frequency of the $EF \rightarrow n$ laser and the positions of selected $^{127}I_2$ absorption lines, as illustrated in Fig. 1 for the transition to the $64p0_1(0)$ Rydberg state. For the $64p0_1(0)$ and $69p1_2(0)$ states, the a_2 hyperfine component of the $P181, B-X(0-14)$ transition at $12\,620.158\,873(1)\text{ cm}^{-1}$,²⁰ and for the $55p0_1(1)$ state, the a_{10} hyperfine component of the $P124, B-X(2-11)$ transition at $13\,571.8944(5)\text{ cm}^{-1}$ (Ref. 30) were chosen. In order to eliminate possible Doppler shifts, the $EF \rightarrow n$ laser beam was split into two components and introduced into the interaction region in a counterpropagating configuration. The measurements were carried out in independent pairs by blocking one and then the other beam component. The individual transition wave numbers determined from these measurements are plotted as squares and triangles in Fig. 2. The final results were obtained by taking the average of all measurements, considering the shifts and uncertainties given in the supplementary material.²⁵

Table II summarizes all energy intervals used to determine the positions $E_i^{(v^+,N^+)}$ of the energy levels of HD^+ with respect to the $X^1\Sigma_g^+(v=0, N=0)$ ground state of HD. Rovibrational energy spacings of HD^+ derived from these quantities are given in Table III and are in agreement with the *ab initio* values of Korobov,²⁷ the experimental uncertainty being, however, more than three orders of magnitude larger than the 0.3 ppb (parts per 10^9) accuracy of the calculations. By subtracting the highly accurate HD^+ rovibrational energies calculated *ab initio* by Korobov²⁷ from $E_i^{(0,1)}$ and $E_i^{(1,0)}$, two more independent values of the adiabatic ionization energy are obtained (in addition to $E_i^{(0,0)}$). All three values are consistent within their uncertainties, and, when combined in a statistical analysis, they lead to the final result

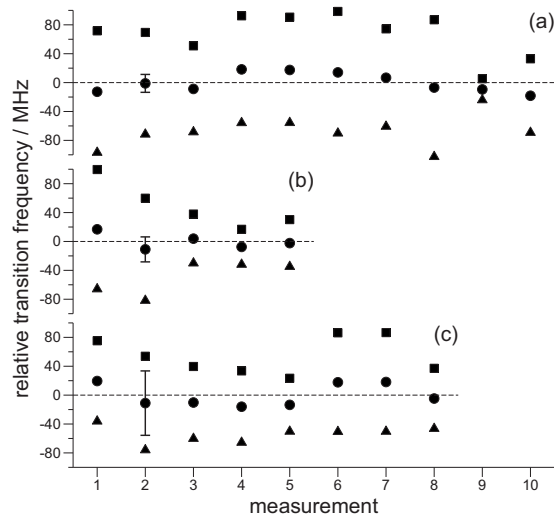


FIG. 2. Distribution of the measured transition frequencies of (a) $EF(v=0, N=0) \rightarrow 64p0_1(0)$, (b) $EF(v=0, N=1) \rightarrow 69p1_2(0)$, and (c) $EF(v=0, N=0) \rightarrow 55p0_1(1)$ relative to the final state indicated by the dashed lines. Triangles and squares represent independent measurements with each of the two counterpropagating laser beams. Closed circles are the mean values of pairs of measurements. Vertical bars indicate the uncertainties (one standard deviation).

$E_i(HD) = 124\,568.485\,81(36)\text{ cm}^{-1}$. The dissociation energy D_0 of HD can be derived using the relation (see Fig. 5 of Ref. 19)

$$D_0(HD) = E_i(HD) + E_i(HD^+) - E_i(H) - E_i(D), \quad (1)$$

where $E_i(HD^+) = 131\,224.684\,15(6)\text{ cm}^{-1}$ is taken from *ab initio* calculations²⁷ and $E_i(H) = 109\,678.771\,743\,07(10)\text{ cm}^{-1}$ and $E_i(D) = 109\,708.614\,552\,99(10)\text{ cm}^{-1}$ from the most recent determination of the Rydberg constant.³¹ The resulting value is $D_0(HD) = 36\,405.783\,66(36)\text{ cm}^{-1}$, where the uncertainty is dominated by the experimental uncertainty of the ionization energy of HD.

TABLE II. Energy intervals used in the determination of the positions (labeled $E_i^{(v^+,N^+)}$) of the levels $(v^+, N^+) = (0,0)$, $(0,1)$, and $(1,0)$ of HD^+ with respect to the rovibronic ground state of HD.

Label	Energy interval	Wave number (cm ⁻¹)	Reference
(1)	$X(0,0) - X(0,1)$	89 227 950(5)	34
(2)	$X(0,0) - EF(0,0)$	99 301.346 62(20)	35
(3)	$X(0,1) - EF(0,1)$	99 259.917 93(20)	35
(4)	$EF(0,0) - 64p0_1(0)$	25 240.360 96(42)	This work
(5)	$EF(0,1) - 69p1_2(0)$	25 240.152 51(58)	This work
(6)	$EF(0,0) - 55p0_1(1)$	27 143.988 30(148)	This work
(7)	$64p0_1(0) - X^+(0,0)^a$	26.778 44(3)	This work
(8)	$69p1_2(0) - X^+(0,1)^a$	23.048 34(3)	This work
(9)	$55p0_1(1) - X^+(1,0)^a$	36.145 65(3)	This work
$E_i^{(0,0)} = (2) + (4) + (7)$		124 568.486 02(47)	
$E_i^{(0,1)} = (1) + (3) + (5) + (8)$		124 612.346 73(61)	
$E_i^{(1,0)} = (2) + (6) + (9)$		126 481.480 57(149)	

^a $X^+(v^+, N^+)$ labels the center of gravity of all fine and hyperfine components of the $X^+ 2\Sigma_g^+(v^+, N^+)$ state of HD^+ .

TABLE III. Summary of the energy intervals determined in this work and comparison to the most recent literature data. The notation $E_i^{(v^+,N^+)}$ is used.

Label	Wave number (cm^{-1})	Reference
$E_i^{(0,1)} - E_i^{(0,0)}$	43.860 71(77)	This work ^a
(A)	43.861 201 86(2)	27
$E_i^{(1,0)} - E_i^{(0,0)}$	1912.994 55(154)	This work ^a
(B)	1912.995 234 7(7)	27
$E_i^{(0,0)}$	124 568.486 02(47)	This work ^a
$E_i^{(0,1)} - (A)$	124 568.485 53(61)	This work ^a
$E_i^{(1,0)} - (B)$	124 568.485 34(149)	This work ^a
Combined $E_i(\text{HD})^b$	124 568.485 81(36)	This work ^a
	124 568.491(17)	32
$D_0(\text{HD})$	36 405.783 66(36)	This work ^a
	36 405.828(16)	18
	36 405.7828(10)	22

^aThe values in parentheses represent one standard deviation in units of the last digit.

^bThe final result for the adiabatic ionization energy was obtained by a weighted average of the three values above. The uncertainty of $0.000\,36\text{ cm}^{-1}$ (11 MHz) assumes that the systematic uncertainties of the three measurements are independent.

In conclusion, the positions of the energy levels $(v^+, N^+) = (0, 0)$, $(0, 1)$, and $(1, 0)$ of the $X^+ 2\Sigma_g^+$ ground state of HD^+ with respect to the $X^+ 1\Sigma_g^+(v=0, N=0)$ rovibronic ground state of HD have been determined with accuracies of 14, 18, and 45 MHz, respectively. The measurements have been confirmed by (i) comparing the relative positions of 37 *np* Rydberg states with the predictions of MQDT calculations (see Table I and the supplementary material²⁵) and (ii) verifying the consistency of the three values with highly accurate *ab initio* calculations of rovibrational levels of HD^+ (see Table III). Combining the experimental values with *ab initio* calculations of the one-electron systems H, D, and HD^+ enabled the determination of the ionization and dissociation energies of HD with an uncertainty of 11 MHz. The present value for the adiabatic ionization energy [$E_i = 124\,568.485\,81(36)\text{ cm}^{-1}$] is in agreement with the most recent previous experimental value [$E_i = 124\,568.491(17)\text{ cm}^{-1}$ (Ref. 32)]. The dissociation energy [$D_0 = 36\,405.783\,66(36)\text{ cm}^{-1}$] deviates by three standard deviations from the result of Zhang *et al.* [$D_0 = 36\,405.828(16)\text{ cm}^{-1}$ (Ref. 18)]. Comparison to the result of a theoretical investigation by Pachucki and Komasa [$D_0 = 36\,405.7828(10)\text{ cm}^{-1}$ (Ref. 22)] shows agreement between the calculated value and our result within the uncertainty limits.

HD represents a more stringent test of the theoretical predictions than H_2 and D_2 because of its lower symmetry and the necessity to include a “heteronuclear” term in the Hamiltonian operator, as discussed earlier by Wolniewicz³³ [see also Eq. (24) of Ref. 22]. HD also posed additional difficulties in our determination: It necessitated the inclusion of a more complex frame transformation and forced us to avoid spectral regions where *ns* and *nd* Rydberg states lie very close to the *np* Rydberg states. These difficulties might explain why the theoretical and experimental results agree only at the side of the error margins. Nevertheless, we be-

lieve that the present determination of the dissociation energy of HD provides strong support for the validity of the latest calculations.²² An agreement between theoretical and experimental values of the dissociation energy of molecular hydrogen at the level of 10^{-3} cm^{-1} , indeed, is well beyond what the pioneers in this field might have considered achievable.

D.S. thanks the Laboratoire Aimé Cotton for the hospitality during his repeated visits in 2008–2010. This work was financially supported by the European Research Council (ERC) (advanced Grant No. 228286) and the Swiss National Science Foundation under Project No. 200020-125030.

¹H. Primas and U. Müller-Herold, *Elementare Quantenchemie* (Teubner Studienbücher, Stuttgart, 1984).

²W. Heitler and F. London, *Z. Phys.* **44**, 455 (1927).

³E. E. Witmer, *Phys. Rev.* **28**, 1223 (1926).

⁴G. Herzberg and A. Monfils, *J. Mol. Spectrosc.* **5**, 482 (1961).

⁵W. Kołos and L. Wolniewicz, *J. Chem. Phys.* **41**, 3674 (1964).

⁶L. Wolniewicz, *J. Chem. Phys.* **45**, 515 (1966).

⁷W. Kołos and L. Wolniewicz, *J. Chem. Phys.* **49**, 404 (1968).

⁸G. Herzberg, *Phys. Rev. Lett.* **23**, 1081 (1969).

⁹S. Takezawa and Y. Tanaka, *J. Chem. Phys.* **56**, 6125 (1972).

¹⁰D. M. Bishop and L. M. Cheung, *Chem. Phys. Lett.* **55**, 593 (1978).

¹¹L. Wolniewicz, *J. Chem. Phys.* **78**, 6173 (1983).

¹²W. Kołos, K. Szalewicz, and H. J. Monkhorst, *J. Chem. Phys.* **84**, 3278 (1986).

¹³W. Kołos and J. Rychlewski, *J. Chem. Phys.* **98**, 3960 (1993).

¹⁴L. Wolniewicz, *J. Chem. Phys.* **99**, 1851 (1993).

¹⁵E. E. Eyler and N. Melikechi, *Phys. Rev. A* **48**, R18 (1993).

¹⁶A. Balakrishnan, M. Vallet, and B. P. Stoicheff, *J. Mol. Spectrosc.* **162**, 168 (1993).

¹⁷L. Wolniewicz, *J. Chem. Phys.* **103**, 1792 (1995).

¹⁸Y. P. Zhang, C. H. Cheng, J. T. Kim, J. Stanojevic, and E. E. Eyler, *Phys. Rev. Lett.* **92**, 203003 (2004).

¹⁹J. Liu, E. J. Salumbides, U. Hollenstein, J. C. J. Koelemeij, K. S. E. Eikema, W. Ubachs, and F. Merkt, *J. Chem. Phys.* **130**, 174306 (2009).

²⁰J. Liu, D. Sprecher, Ch. Jungen, W. Ubachs, and F. Merkt, *J. Chem. Phys.* **132**, 154301 (2010).

²¹K. Piszczatowski, G. Łach, M. Przybytek, J. Komasa, K. Pachucki, and B. Jeziorski, *J. Chem. Theory Comput.* **5**, 3039 (2009).

²²K. Pachucki and J. Komasa, *Phys. Chem. Chem. Phys.* **12**, 9188 (2010), the present work was carried out in parallel to this theoretical investigation without exchanging information until both results were final.

²³R. Seiler, Th. Paul, M. Andrist, and F. Merkt, *Rev. Sci. Instrum.* **76**, 103103 (2005).

²⁴A. Osterwalder, A. Wüest, F. Merkt, and Ch. Jungen, *J. Chem. Phys.* **121**, 11810 (2004).

²⁵See supplementary material at <http://dx.doi.org/10.1063/1.3483462> for the positions of all Rydberg states of HD measured in the realm of this investigation and for a table containing all shifts and uncertainties in the positions of the $64p0_1(0)$, $69p1_2(0)$, and $55p0_1(1)$ Rydberg states of HD.

²⁶H. A. Cruse, Ch. Jungen, and F. Merkt, *Phys. Rev. A* **77**, 042502 (2008).

²⁷V. I. Korobov, *Phys. Rev. A* **77**, 022509 (2008) (and references therein).

²⁸L. Wolniewicz and J. D. Poll, *Mol. Phys.* **59**, 953 (1986).

²⁹D. Bakalov, V. I. Korobov, and S. Schiller, *Phys. Rev. Lett.* **97**, 243001 (2006).

³⁰H. Knöckel, B. Bodermann, and E. Tiemann, *Eur. Phys. J. D* **28**, 199 (2004). The transition wave number was calculated using the IODINESPEC software.

³¹P. J. Mohr, B. N. Taylor, and D. B. Newell, *Rev. Mod. Phys.* **80**, 633 (2008); see <http://physics.nist.gov/hdel> for numerical values.

³²G. M. Greetham, U. Hollenstein, R. Seiler, W. Ubachs, and F. Merkt, *Phys. Chem. Chem. Phys.* **5**, 2528 (2003).

³³L. Wolniewicz, *Can. J. Phys.* **53**, 1207 (1975).

³⁴K. M. Evenson, D. A. Jennings, J. M. Brown, L. R. Zink, K. R. Leopold, M. D. Vanek, and I. G. Nolt, *Astrophys. J.* **330**, L135 (1988).

³⁵S. Hannemann, E. J. Salumbides, S. Witte, R. T. Zinkstok, E.-J. van Duijn, K. S. E. Eikema, and W. Ubachs, *Phys. Rev. A* **74**, 062514 (2006).