Sub-MHz accuracy of IR transition frequencies in H_2

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The frequencies of infrared transitions in the electronic ground state of the hydrogen molecule have been obtained with sub-MHz accuracy. Calculations have been performed in the nonrelativistic quantum electrodynamics framework using a four-particle explicitly correlated wave function in the exponential basis. In consequence, the long-standing discrepancies—up to several megahertz—between high-precision measurements and previous theoretical predictions have been resolved.

The rovibrational ladder of energy levels and the infrared (IR) spectrum of the hydrogen molecule is widely used in astronomy [1–5], plasma physics [6], physical chemistry [7, 8], and metrology [9, 10]. The long lifetimes of rovibrational states, counted in days [11], make H_2 an attractive subject for highly precise spectroscopic measurements. On the other hand, the structural simplicity of this four-particle molecule enables ultra-high-precision calculations that fully account for interparticle correlation, finite-nuclear-mass, relativistic, and QED effects. Just a decade ago, the theoretical predictions and measurements of the energy of rovibrational transitions in H_2 isotopologues agreed to within 10 MHz [12–32]. This precision opened the possibility for testing quantum electrodynamics (QED) effects on rotational transitions [33], setting bounds on a hypothetical fifth force [34], and on the number of extra spatial dimensions [35, 36]. Recently, advancements in spectroscopic techniques have allowed measurements to reach an accuracy of the order of 10 kHz [37–53]. As a result, discrepancies between theory and experiment at the level of several megahertz have been revealed. It was suspected that the incomplete treatment of relativistic and QED recoil effects could be the main reason for these discrepancies.

In this Letter, we present the results of our calculations performed using a nonadiabatic exponential wave function. Such functions possess correct asymptotic properties, but are extremely rarely used in molecular calculations, due to difficulties in evaluating corresponding integrals. We have overcome these difficulties and developed a method applicable to arbitrary rovibrational excitation levels. We show that for the rovibrational transitions in H_2, the discrepancy between theory and experiment has been reduced to a fraction of a megahertz, which is about three parts per billion (ppb). This achievement indicates that our calculations predict up to 10 significant digits of transition frequencies. There are not many instances of physical systems where such a level of agreement between molecular or atomic spectroscopy and first-principles calculations has been reached. Examples include the transitions in hydrogen [54, 55] and helium atoms [56], as well as those in the hydrogen molecular ion [57–60].

Our calculations are based on the nonrelativistic quantum electrodynamic (NRQED) theory, where the energy of a bound rovibrational level of a light molecule is expressed as the expansion in powers of the fine-structure constant α

$$E(\alpha) = \alpha^2 m\, E^{(2)} + \alpha^4 m\, E^{(4)} + \alpha^5 m\, E^{(5)} + \alpha^6 m\, E^{(6)} + \alpha^7 m\, E^{(7)} + \ldots . \tag{1}$$

Subsequent terms of this expansion can be identified as the nonrelativistic energy, the relativistic correction, the QED correction, and higher-order corrections. An important feature of NRQED is that the coefficients $E^{(n)}$ of this expansion can be expressed as expectation values of some effective Hamiltonians $H^{(n)}$ with the nonrelativistic wave function Ψ. These expectation values can be evaluated using a fully four-body wave function or, if this is unfeasible, using approximations involving the separation of nuclear and electronic variables. Of course, the first approach is preferable because it fully accounts for the finite-nuclear-mass effects.

Such a wave function must reflect the rotational and electronic degrees of freedom present in the hydrogen molecule. Ψ should also account for the coupling between the rotational angular momentum of nuclei and orbital angular momentum of electrons $\vec{L}$. Having this in mind, we construct the wave function Ψ as follows

$$\Psi^{J,M} = \sum_{\Lambda} \Psi^{J,M}_{\Lambda}\,, \tag{2}$$

where J and M are the total rotational and magnetic quantum numbers. The summation index Λ is an eigenvalue of the projection of $\vec{L}$ on the internuclear axis and runs over subsequent electronic states $\Sigma_g, \Sigma_u, \Pi_g, \Pi_u, \Delta_g, \Delta_u, \ldots$, which corresponds to $|\Lambda| = 0, 1, 2, \ldots$. The functions $\Psi^{J,M}_{\Lambda}$ are represented as the linear combination

$$\Psi^{J,M}_{\Lambda} = \sum_{\{k\}} c_{\{k\}} \mathcal{A}_{12}\, \psi^{J,M}_{\{k\},\Lambda} \tag{3}$$

of four-particle basis functions

$$\psi^{J,M}_{\{k\},\Lambda} = \mathcal{Q}_\Lambda\, e^{-\alpha_\Lambda R-\beta_\Lambda(\zeta_1+\zeta_2)}\, R^{k_0}\, r_{12}^{k_1}\, \eta_1^{k_2}\, \eta_2^{k_3}\, \zeta_1^{k_4}\, \zeta_2^{k_5} \quad (4)$$

with elliptic-like coordinates $\zeta_1 = r_{1A} + r_{1B}$, $\eta_1 = r_{1A} - r_{1B}$, $\zeta_2 = r_{2A} + r_{2B}$, $\eta_2 = r_{2A} - r_{2B}$, and $\vec{R} = \vec{r}_{AB}$. The operator $\mathcal{A}_{12}$ imposes antisymmetry for electrons, whereas the factor $\mathcal{Q}_\Lambda$ describes the angular couplings. This basis function (4) was named *the nonadiabatic James-Coolidge* (naJC) function for its resemblance to the classic two-electron function introduced by James and Coolidge [61], who got the idea from Hylleraas' function designed in 1929 for the helium atom [62].

The nonlinear $(\alpha_\Lambda, \beta_\Lambda)$ and linear $c_{\{k\}}$ parameters are determined variationally by solving the four-body Schrödinger equation $H^{(2)}\Psi^{J,M} = E^{(2)}\Psi^{J,M}$ with the nonrelativistic Hamiltonian

$$H^{(2)} = \left\langle \Psi \left| \sum_a \frac{p_a^2}{2\,m_a} + V \right| \Psi \right\rangle, \quad (5)$$

where V is the sum of Coulomb potentials, and the index a at particle momentum p and mass m runs through all four particles. A more detailed description of the Ansatz and results of such nonrelativistic calculations can be found in [63–66]. Here, we mention that nonrelativistic energy can be obtained with accuracy limited only by uncertainties of physical constants, such as the electron-proton mass ratio and the Rydberg constant $\mathcal{R}_\infty$.

This nonrelativistic wave function is then used to calculate the expectation value of operators contained in relativistic and QED Hamiltonians $H^{(n)}$. Namely, the relativistic correction is evaluated as an expectation value of the spin-independent Breit-Pauli Hamiltonian $H^{(4)}$ and consists of the mass velocity term

$$-\left\langle \Psi \left| \sum_a \frac{p_a^4}{8\,m_a^3} \right| \Psi \right\rangle, \quad (6)$$

the Breit orbit-orbit term

$$\left\langle \Psi \left| \sum_{a>b} \frac{1}{2\,m_a\,m_b} p_a^i \left(\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^i r_{ab}^j}{r_{ab}^3} \right) p_b^j \right| \Psi \right\rangle, \quad (7)$$

and the Darwin term

$$\frac{\pi}{2} \left\langle \Psi \left| \sum_{a>b} \left(\frac{1}{m_a} + \frac{1}{m_b} \right) \delta^{(3)}(r_{ab}) \right| \Psi \right\rangle. \quad (8)$$

Details of the newly developed integration methods for evaluation of the above expectation values, as well as their regularization and numerical convergence, are given in [67] and [68]. Preliminary results for the lowest rotational levels of H_2 are also shown therein.

Contributions from the coupling between the nuclear spin and rotation, as well as between nuclear spins, are small because they depend quadratically on the electron-to-nucleus mass ratio. These effects are usually invisible in IR spectroscopy. Nevertheless, they were measured by Ramsey in 1971 [69], which allowed us [9], using the four-body Gaussian wave function, to determine the quadrupole moment of the deuteron to an accuracy better than for any other element of the periodic table. In this work, the energy levels are averaged over the nuclear spin orientations, thus no hyperfine coupling is considered.

The next term of the α-expansion (1) is the leading quantum electrodynamic correction represented by the following expression

$$\begin{aligned} E^{(5)} &= -\frac{2}{3\,\pi}\,\mathcal{D}\,\ln k_0 - \frac{7}{6\,\pi}\left\langle \frac{1}{r_{12}^3} \right\rangle_\epsilon \quad (9) \\ &+ \frac{4}{3}\sum_{i,X}\left\{ \left(1 + \frac{m}{4m_X}\right)\ln(\alpha^{-2}) + \frac{19}{30} + \frac{m}{m_X}\,\frac{31}{6} \right\}\langle \delta^3(r_{iX})\rangle \\ &- \frac{7}{6\,\pi}\sum_{i,X}\frac{m}{m_X}\left\langle \frac{1}{r_{iX}^3}\right\rangle_\epsilon + \left(\frac{164}{15} + \frac{14}{3}\ln\alpha\right)\langle\delta^3(r_{12})\rangle, \end{aligned}$$

where indices i and X correspond to electrons and nuclei, respectively. Eq. (9) consists of five terms: the Bethe logarithm term, two Araki-Sucher terms, and two Dirac-delta terms. Currently, only the last two terms can be evaluated using the four-body naJC wave function. The first three lead to unknown integrals in this basis. Therefore, these terms were estimated using the Born-Oppenheimer (BO) approximation, resulting in frequency uncertainties dominating the overall error budget. The Bethe logarithm and the electron-electron Araki-Sucher terms were calculated in [70], while the electron-nucleus Araki-Sucher contribution is reported here.

The higher-order QED contribution $E^{(6,0)}$ is calculated within the BO approximation and is expressed by the potential [71]

$$\begin{aligned} \mathcal{E}^{(6,0)}(R) &= \left\langle \phi \left| H^{(6,0)} \right| \phi \right\rangle \\ &+ \left\langle \phi \left| H^{(4,0)} \frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'} H^{(4,0)} \right| \phi \right\rangle, \quad (10) \end{aligned}$$

where $H^{(4,0)}$ is the leading-order relativistic (Breit-Pauli) Hamiltonian in the nonrecoil limit, and $H^{(6,0)}$ is the higher-order relativistic Hamiltonian. $H_{\rm el}$ and $H_{\rm n}$ are the electronic and the nuclear parts, respectively, of the nonrelativistic Hamiltonian $H^{(2)}$. The explicit formulas for $\mathcal{E}^{(6,0)}(R)$ are far too extensive to be presented here—they can be found in [71]. The total correction is

$$\begin{aligned} E^{(6,0)} &= \left\langle \chi \left| \mathcal{E}^{(6,0)}(R) \right| \chi \right\rangle \\ &+ \left\langle \chi \left| \mathcal{E}^{(4,0)}(R) \frac{1}{(E^{(2,0)} - H_{\rm n})'} \mathcal{E}^{(4,0)}(R) \right| \chi \right\rangle, \end{aligned} \quad (11)$$

where χ is the nuclear wave function obtained by solving the radial Schrödinger equation.

The α^7 term is a very problematic correction because its complete form is still unknown. It is therefore estimated by a dominating term inferred from the atomic hydrogen theory [72]

$$E^{(7)} \approx \pi \left\langle \Psi \left| \sum_{a,X} \delta^3(r_{aX}) \right| \Psi \right\rangle \left\{ \frac{1}{\pi} \left[A_{60} + A_{61} \, \ln \alpha^{-2} + A_{62} \, \ln^2 \alpha^{-2} \right] + \frac{1}{\pi^2} \, B_{50} + \frac{1}{\pi^3} \, C_{40} \right\}. \tag{12}$$

This correction gives another significant contribution to the error budget.

The leading correction from the finite nuclear size effect was accounted for by

$$E^{(4)}_{\text{fs}} = \frac{2\pi}{3} \left\langle \Psi \left| \sum_{a,X} \delta^3(r_{aX}) \right| \Psi \right\rangle \frac{r^2_{C,p}}{\lambda^2} \,, \tag{13}$$

where $r_{C,p} = 0.84075(64)$ fm is the root mean square charge radius of the proton [72], and λ is the reduced electron Compton wavelength.

Calculations were performed using CODATA 2022 recommended physical constants, in particular the proton-to-electron mass ratio $m_p/m = 1836.152\,673\,426(32)$, the inverse fine structure constant $1/\alpha = 137.035\,999\,177(21)$, the Rydberg constant $\mathcal{R}_\infty = 10\,973\,731.568\,157(12)$ m^{-1}, and the speed of light in vacuum $c = 299\,792\,458$ m s^{-1} [72]. Results of calculations are presented in Table I, which contains numerical values of the dissociation energy $D_{v,J} = 2\,E(\text{H}) - E(\text{H}_2)$ for the lowest vibrational ($v = 0, 1, 2$) and rotational ($J = 0, \ldots 4$) quantum numbers. The range of quantum numbers is sufficiently wide to cover all levels involved in measured infrared transitions of sub-MHz accuracy reported in the literature. The uncertainties assigned to theoretically predicted dissociation energy are also of sub-MHz accuracy (1 MHz $\approx 0.000\,033\,\text{cm}^{-1}$), where the dominant source of these uncertainties is the incomplete calculation of the α^7 term.

Establishing reliable uncertainty for each transition frequency ν is challenging, due to the partial error cancellation between two rovibrational levels. The overall uncertainty u is a root-mean-square of the individual uncertainties u_n originating from subsequent terms $\nu^{(n)} = \Delta E^{(n)}$ of the α-expansion. To determine the u_n, we have applied distinct approaches depending on the method by which the $\nu^{(n)}$ term was evaluated. For $\nu^{(n)}$ obtained with the DNA approach (as $\nu^{(2)}$ and $\nu^{(4)}$), the uncertainty was estimated as a maximum uncertainty of both levels. For $\nu^{(n)}$ obtained with the adiabatic approximation (as $\nu^{(5)}$ and $\nu^{(6)}$), the uncertainty was estimated by $\nu^{(n)} m/\mu_\text{n}$, where μ_n is the nuclear reduced mass. As the complete $\nu^{(7)}$ is currently unknown, and its dominant term from the atomic hydrogen theory provides just an estimate, a conservative 25% error is assumed.

Having determined uncertainties, we can now compare our results to experimental values. Among many measurements of IR transitions in H_2, just nine claim sub-MHz accuracy. These measurements were taken within the last two years [49–51, 53], and they concern purely rotational transitions as well as the transitions belonging to the fundamental vibrational band and the first overtone band. Table II combines these experimental and corresponding theoretical frequencies. Each panel is dedicated to a single transition line and contains all components comprising the final theoretical frequency, along with their individual error bars. The bottom row of each panel shows the difference between the theoretical and experimental frequency, accompanied by the combined uncertainty, σ. An agreement is found for all nine lines, with the most considerable difference of $1.4\,\sigma$ for the $Q_1(1)$ line. The differences are also depicted in Fig. 1 against the ±1 MHz band. This figure vividly shows that theoretical predictions and spectroscopic measurements reached sub-MHz agreement. For some lines, the experimental accuracy is an order of magnitude higher than the theoretical one, which motivates further development of computational methods, particularly that for $\nu^{(7)}$.

Unlike earlier calculations [73] that estimated the relativistic and quantum electrodynamic corrections using the Born-Oppenheimer approximation, the current DNA results include the finite-nuclear-mass effects. For frequencies in the first overtone the difference between current and previous calculations reaches 3 MHz, in the fundamental band it is approximately 1.5 MHz, and for purely rotational transitions it is about 0.1 MHz. The small third value demonstrates effective cancellation of recoil effects within a single oscillation band. The change in the total recoil effect is primarily due to relativistic and the leading QED components of the frequency.

As well as the nine transition frequencies displayed in Table II, other energy gaps can be evaluated by taking the difference of dissociation energies from Table I. An upper bound to the uncertainty for such a transition can be inferred from Table II, i.e., 0.1 MHz for a rotational transition, 0.4 MHz for the fundamental band, and 0.8 MHz for the first overtone.

The results obtained demonstrate that finite-nuclear-mass effects significantly impact not only nonrelativistic energy but also relativistic and quantum electrodynamics (QED) corrections. By incorporating these effects, the theoretical predictions matched the experimental results with sub-MHz accuracy. Further improvements will require a fully nonadiabatic calculation of the Bethe logarithm for excited rovibrational levels. We believe this task is feasible since it has already been accomplished at the ground level [74]. The same nonadiabatic effects might be responsible for the discrepancy observed between theoretical predictions and experimental results

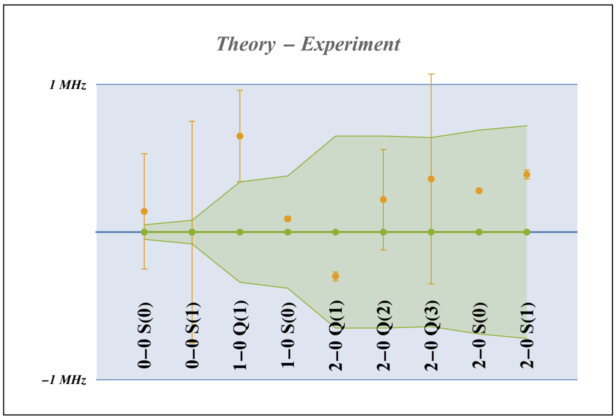

FIG. 1. Difference between theoretically predicted and experimental line position shown against the ±1 MHz error band (in blue) and the theoretical error band (in green). The error bars around the dots come from the experiment.

for the J spin-spin coupling in the nuclear magnetic resonance (NMR) spectra of HD [75]. This J-coupling is quite small, about 43 Hz, making it particularly sensitive to long-range spin-spin interactions between hadrons [76, 77]. In conclusion, relativistic and QED nonadiabatic effects are indispensable for achieving the required level of accuracy in testing QED in molecular systems and for interpreting any discrepancies in terms of yet unknown forces.

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[1] J. Margolis and G. Hunt, On the level of H_2 quadrupole absorption in the Jovian atmosphere, Icarus **18**, 593 (1973).

[2] E. Roueff, H. Abgrall, P. Czachorowski, K. Pachucki, M. Puchalski, and J. Komasa, The full infrared spectrum of molecular hydrogen, Astron. Astrophys. **630**, A58 (2019).

[3] K. Tchernyshyov, A Detection of H_2 in a High-velocity Cloud toward the Large Magellanic Cloud, Astrophys. J. **931**, 78 (2022).

[4] A. Jacob, Small molecules, big impact: a tale of hydrides past, present, and future, Astrophys. Space Sci. **368**, 76 (2023).

[5] J. Tennyson *et al.*, The 2024 release of the ExoMol database: Molecular line lists for exoplanet and other hot atmospheres, J. Quant. Spectrosc. Radiat. Transfer **326**, 109083 (2024).

[6] D. Bruno, Uncertainty quantification of a collisional-radiative model for hydrogen plasmas, Phys. Scr. **100**, 035611 (2025).

[7] J. Zúñiga, A. Bastida, A. Requena, and J. Cerezo, Ab initio partition functions and thermodynamic quantities for the molecular hydrogen isotopologues, J. Phys. Chem. A **125**, 9226 (2021).

[8] J. W. Leachman, Ø. Wilhelmsen, and K. I. Matveev, Thermophysical properties, in *Cool Fuel: The Science and Engineering of Cryogenic Hydrogen* (Oxford University Press, 2025).

[9] M. Puchalski, J. Komasa, and K. Pachucki, Hyperfine Structure of the First Rotational Level in H_2, D_2 and HD Molecules and the Deuteron Quadrupole Moment, Phys. Rev. Lett. **125**, 253001 (2020).

[10] M. Puchalski, J. Komasa, A. Spyszkiewicz, and K. Pachucki, Nuclear magnetic shielding in HD and HT, Phys. Rev. A **105**, 042802 (2022).

[11] K. Pachucki and J. Komasa, Magnetic dipole transitions in the hydrogen molecule, Phys. Rev. A **83**, 032501 (2011).

[12] S. Kassi and A. Campargue, Electric quadrupole and dipole transitions of the first overtone band of HD by CRDS between 1.45 and 1.33 μm, J. Mol. Spectrosc. **267**, 36 (2011).

[13] A. Campargue, S. Kassi, K. Pachucki, and J. Komasa, The absorption spectrum of H_2: CRDS measurements of the (2-0) band, review of the literature data and accurate ab initio line list up to 35000 cm^{-1}, Phys. Chem. Chem. Phys. **14**, 802 (2012).

[14] S. Kassi, A. Campargue, K. Pachucki, and J. Komasa, The absorption spectrum of D_2: Ultrasensitive cavity ring down spectroscopy of the (2-0) band near 1.7 μm and accurate ab initio line list up to 24 000 cm^{-1}, J. Chem. Phys. **136**, 184309 (2012).

[15] C.-F. Cheng, Y. R. Sun, H. Pan, J. Wang, A.-W. Liu, A. Campargue, and S.-M. Hu, Electric-quadrupole transition of H_2 determined to 10^{-9} precision, Phys. Rev. A **85**, 024501 (2012).

[16] G. D. Dickenson, M. L. Niu, E. J. Salumbides, J. Komasa, K. S. E. Eikema, K. Pachucki, and W. Ubachs, Fundamental vibration of molecular hydrogen, Phys. Rev. Lett. **110**, 193601 (2013).

[17] M. Niu, E. Salumbides, G. Dickenson, K. Eikema, and W. Ubachs, Precision spectroscopy of the rovibrational splittings in H_2, HD and D_2, J. Mol. Spectrosc. **300**, 44 (2014).

[18] Y. Tan, J. Wang, C.-F. Cheng, X.-Q. Zhao, A.-W. Liu, and S.-M. Hu, Cavity ring-down spectroscopy of the electric quadrupole transitions of in the 784-852 nm region, J. Mol. Spectrosc. **300**, 60 (2014).

[19] S. Kassi and A. Campargue, Electric quadrupole transitions and collision-induced absorption in the region of the first overtone band of H_2 near 1.25μm, Journal of Molecular Spectroscopy **300**, 55 (2014).

[20] D. Mondelain, S. Kassi, T. Sala, D. Romanini, D. Gatti, and A. Campargue, Sub-MHz accuracy measurement of the S(2) 2-0 transition frequency of D_2 by Comb-Assisted Cavity Ring Down spectroscopy, J. Mol. Spectrosc. **326**, 5 (2016).

[21] P. Wcisło, F. Thibault, M. Zaborowski, S. Wójtewicz, A. Cygan, G. Kowzan, P. Masłowski, J. Komasa, M. Puchalski, K. Pachucki, R. Ciuryło, and D. Lisak, Accurate deuterium spectroscopy for fundamental studies, J. Quant. Spectrosc. Radiat. Transfer **213**, 41 (2018).

[22] T. M. Trivikram, M. Schlösser, W. Ubachs, and E. J. Salumbides, Relativistic and QED Effects in the Funda-

TABLE I. Dissociation energy $D_{v,J}$ for the five lowest rotational levels in the vibrational states $v = 0, 1, 2$ of H_2 [cm^{-1}].

(v, J)	$D_{v,J}$	(v, J)	$D_{v,J}$	(v, J)	$D_{v,J}$
(0,0)	36 118.069 630(26)	(1,0)	31 956.903 458(26)	(2,0)	28 031.066 922(29)
(0,1)	35 999.582 816(26)	(1,1)	31 844.329 004(25)	(2,1)	27 924.275 245(29)
(0,2)	35 763.696 497(26)	(1,2)	31 620.231 155(26)	(2,2)	27 711.708 670(29)
(0,3)	35 412.550 787(25)	(1,3)	31 286.678 128(26)	(2,3)	27 395.367 529(30)
(0,4)	34 949.272 190(25)	(1,4)	30 846.690 132(26)	(2,4)	26 978.171 929(31)

TABLE II. Transition frequency components [MHz] in H_2. The total theoretical frequency is compared with experimental data. CODATA recommended physical constants were used [72]; in particular, the proton root mean square charge radius $r_{C,p} = 0.84075(64)$ fm.

Component	$S_0(0):\ (0,2) \to (0,0)$	$S_0(1):\ (0,3) \to (0,1)$	$Q_1(1):\ (1,1) \to (0,1)$
$\nu^{(2)}$	10 623 700.7825(3)	17 598 550.7339(4)	124 571 317.1657(4)
$\nu^{(4)}$	230.555(11)	378.562(11)	699.881(11)
$\nu^{(5)}$	−91.335(47)	−150.565(77)	−636.16(33)
$\nu^{(6)}$	−0.793(3)	−1.308(4)	−5.719(18)
$\nu^{(7)}$	0.040(10)	0.070(17)	0.310(78)
$\nu^{(4)}_{\rm fs}$	−0.01346(2)	−0.02219(3)	−0.0943(1)
Theory	10 623 839.229(49)	17 598 777.469(80)	124 571 375.38(34)
Experiment	10 623 839.09(39)[a]	17 598 777.46(75)[a]	124 571 374.73(31)[b]
Difference	0.14(39)	0.01(75)	0.65(46)
Component	$S_1(0):\ (1,2) \to (0,0)$	$Q_2(1):\ (2,1) \to (0,1)$	$Q_2(2):\ (2,2) \to (0,2)$
$\nu^{(2)}$	134 841 618.0297(4)	242 091 633.7378(5)	241 392 544.6686(5)
$\nu^{(4)}$	917.267(11)	1235.957(12)	1209.546(12)
$\nu^{(5)}$	−723.86(37)	−1228.46(63)	−1221.38(63)
$\nu^{(6)}$	−6.482(21)	−11.089(36)	−11.031(35)
$\nu^{(7)}$	0.340(85)	0.59(15)	0.59(15)
$\nu^{(4)}_{\rm fs}$	−0.1072(2)	−0.1824(3)	−0.1814(3)
Theory	134 841 805.19(38)	242 091 630.55(65)	241 392 522.22(65)
Experiment	134 841 805.102(15)[c]	242 091 630.851(30)[a]	241 392 522.00(34)[a]
Difference	0.09(38)	−0.30(65)	0.22(73)
Component	$Q_2(3):\ (2,3) \to (0,3)$	$S_2(0):\ (2,2) \to (0,0)$	$S_2(1):\ (2,3) \to (0,1)$
$\nu^{(2)}$	240 349 158.6533(5)	252 016 245.4511(5)	257 947 709.3872(5)
$\nu^{(4)}$	1170.245(12)	1440.101(12)	1548.807(12)
$\nu^{(5)}$	−1210.85(62)	−1312.71(68)	−1361.42(70)
$\nu^{(6)}$	−10.945(35)	−11.824(38)	−12.253(39)
$\nu^{(7)}$	0.59(15)	0.63(16)	0.66(17)
$\nu^{(4)}_{\rm fs}$	−0.1799(3)	−0.1949(3)	−0.2021(3)
Theory	240 349 107.52(64)	252 016 361.45(69)	257 947 884.98(72)
Experiment	240 349 107.15(71)[a]	252 016 361.164(8)[d]	257 947 884.597(30)[a]
Difference	0.36(96)	0.28(69)	0.39(72)

[a]Fleurbaey *et al.*, 2023 [49]; [b]Lamperti *et al.*, 2023 [50]; [c]Stankiewicz *et al.*, 2025 [53]; [d]Cozijn *et al.*, 2023 [51];

mental Vibration of T_2, Phys. Rev. Lett. **120**, 163002 (2018).

[23] L.-G. Tao, A.-W. Liu, K. Pachucki, J. Komasa, Y. R. Sun, J. Wang, and S.-M. Hu, Toward a determination of the proton-electron mass ratio from the lamb-dip measurement of HD, Phys. Rev. Lett. **120**, 153001 (2018).

[24] E. Fasci, A. Castrillo, H. Dinesan, S. Gravina, L. Moretti, and L. Gianfrani, Precision spectroscopy of HD at 1.38 μm, Phys. Rev. A **98**, 022516 (2018).

[25] R. Z. Martinez, D. Bermejo, P. Wcisło, and F. Thibault, Accurate wavenumber measurements for the $S_0(0)$, $S_0(1)$, and $S_0(2)$ pure rotational Raman lines of D_2, J. Raman Spectrosc. **50**, 127 (2019).

[26] N. Hölsch, M. Beyer, E. J. Salumbides, K. S. E. Eikema, W. Ubachs, C. Jungen, and F. Merkt, Benchmarking Theory with an Improved Measurement of the Ionization and Dissociation Energies of H_2, Phys. Rev. Lett. **122**, 103002 (2019).

[27] M. Beyer, N. Hölsch, J. Hussels, C.-F. Cheng, E. J. Salumbides, K. S. E. Eikema, W. Ubachs, C. Jungen, and F. Merkt, Determination of the Interval between the Ground States of Para- and Ortho-H_2, Phys. Rev. Lett. **123**, 163002 (2019).

[28] K.-F. Lai, P. Czachorowski, M. Schlösser, M. Puchalski, J. Komasa, K. Pachucki, W. Ubachs, and E. J. Salumbides, Precision tests of nonadiabatic perturbation

theory with measurements on the dt molecule, Phys. Rev. Research **1**, 033124 (2019).

[29] K.-F. Lai, V. Hermann, M. Trivikram, M. Diouf, M. Schlösser, W. Ubachs, and E. Salumbides, Precision measurement of the fundamental vibrational frequencies of tritium-bearing hydrogen molecules: T_2, DT, HT, Phys. Chem. Chem. Phys. , (2020).

[30] D. Mondelain, S. Kassi, and A. Campargue, Transition frequencies in the (2-0) band of D_2 with MHz accuracy, J. Quant. Spectrosc. Radiat. Transfer **253**, 107020 (2020).

[31] H. Jóźwiak, H. Cybulski, and P. Wcisło, Hyperfine structure of quadrupole rovibrational transitions in tritium-bearing hydrogen isotopologues, J. Quant. Spectrosc. Radiat. Transfer **256**, 107255 (2020).

[32] S. Kassi, H. Fleurbaey, and A. Campargue, First detection and absolute transition frequencies in the (3–0) band of D_2, J. Chem. Phys. **160**, 094306 (2024).

[33] E. J. Salumbides, G. D. Dickenson, T. I. Ivanov, and W. Ubachs, QED effects in molecules: Test on rotational quantum states of H_2, Phys. Rev. Lett. **107**, 043005 (2011).

[34] E. J. Salumbides, J. C. J. Koelemeij, J. Komasa, K. Pachucki, K. S. E. Eikema, and W. Ubachs, Bounds on fifth forces from precision measurements on molecules, Phys. Rev. D **87**, 112008 (2013).

[35] E. J. Salumbides, A. N. Schellekens, B. Gato-Rivera, and W. Ubachs, Constraints on extra dimensions from precision molecular spectroscopy, New J. Phys. **17**, 033015 (2015).

[36] W. Ubachs, J. Koelemeij, K. Eikema, and E. Salumbides, Physics beyond the standard model from hydrogen spectroscopy, J. Mol. Spectrosc. **320**, 1 (2016).

[37] B. J. Drouin, S. Yu, J. C. Pearson, and H. Gupta, Terahertz spectroscopy for space applications: 2.5-2.7 THz spectra of HD, H_2O and NH_3, J. Mol. Spectrosc. **1006**, 2 (2011).

[38] F. M. J. Cozijn, P. Dupré, E. J. Salumbides, K. S. E. Eikema, and W. Ubachs, Sub-Doppler Frequency Metrology in HD for Tests of Fundamental Physics, Phys. Rev. Lett. **120**, 153002 (2018).

[39] M. L. Diouf, F. M. J. Cozijn, B. Darquié, E. J. Salumbides, and W. Ubachs, Lamb-dips and Lamb-peaks in the saturation spectrum of HD, Opt. Lett. **44**, 4733 (2019).

[40] M. L. Diouf, F. M. J. Cozijn, K.-F. Lai, E. J. Salumbides, and W. Ubachs, Lamb-peak spectrum of the HD (2-0) $P(1)$ line, Phys. Rev. Research **2**, 023209 (2020).

[41] T.-P. Hua, Y. R. Sun, and S.-M. Hu, Dispersion-like lineshape observed in cavity-enhanced saturation spectroscopy of hd at 1.4 μm, Opt. Lett. **45**, 4863 (2020).

[42] S. Wójtewicz, R. Gotti, D. Gatti, M. Lamperti, P. Laporta, H. Jóźwiak, F. Thibault, P. Wcisło, and M. Marangoni, Accurate deuterium spectroscopy and comparison with ab initio calculations, Phys. Rev. A **101**, 052504 (2020).

[43] A. Fast and S. A. Meek, Sub-ppb Measurement of a Fundamental Band Rovibrational Transition in HD, Phys. Rev. Lett. **125**, 023001 (2020).

[44] A. Castrillo, E. Fasci, and L. Gianfrani, Doppler-limited precision spectroscopy of HD at 1.4 μm: An improved determination of the $R(1)$ center frequency, Phys. Rev. A **103**, 022828 (2021).

[45] A. Fast and S. A. Meek, Precise measurement of the D_2 $S_1(0)$ vibrational transition frequency, Mol. Phys. **120**, e1999520 (2022).

[46] S. Kassi, C. Lauzin, J. Chaillot, and A. Campargue, The (2-0) $R(0)$ and $R(1)$ transition frequencies of HD determined to a 10^{-10} relative accuracy by Doppler spectroscopy at 80 K, Phys. Chem. Chem. Phys. **24**, 23164 (2022).

[47] F. M. J. Cozijn, M. L. Diouf, V. Hermann, E. J. Salumbides, M. Schlösser, and W. Ubachs, Rotational level spacings in HD from vibrational saturation spectroscopy, Phys. Rev. A **105**, 062823 (2022).

[48] F. M. J. Cozijn, M. L. Diouf, and W. Ubachs, Saturation spectroscopy of R(0), R(2) and P(2) lines in the (2-0) band of HD, Eur. Phys. J. D **76**, 220 (2022).

[49] H. Fleurbaey, A. O. Koroleva, S. Kassi, and A. Campargue, The high-accuracy spectroscopy of H_2 rovibrational transitions in the (2-0) band near 1.2 μm, Phys. Chem. Chem. Phys. **25**, 14749 (2023).

[50] M. Lamperti, L. Rutkowski, D. Ronchetti, D. Gatti, R. Gotti, G. Cerullo, F. Thibault, H. Jóźwiak, S. Wójtewicz, P. Masłowski, P. Wcisło, D. Polli, and M. Marangoni1, Stimulated Raman scattering metrology of molecular hydrogen, Commun. Phys. **6**, 67 (2023).

[51] F. M. J. Cozijn, M. L. Diouf, and W. Ubachs, Lamb Dip of a Quadrupole Transition in H_2, Phys. Rev. Lett. **131**, 073001 (2023).

[52] F. M. J. Cozijn, M. L. Diouf, W. Ubachs, V. Hermann, and M. Schlösser, Precision measurement of vibrational quanta in tritium hydride, Phys. Rev. Lett. **132**, 113002 (2024).

[53] K. Stankiewicz, M. Makowski, M. Słowiński, K. L. Sołtys, B. Bednarski, H. Jóźwiak, N. Stolarczyk, M. Narożnik, D. Kierski, S. Wójtewicz, A. Cygan, G. Kowzan, P. Masłowski, M. Piwiński, D. Lisak, and P. Wcisło, Cavity-enhanced spectroscopy in the deep cryogenic regime – new hydrogen technologies for quantum sensing, preprint arXiv:2502.12703 (2025).

[54] C. G. Parthey, 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).

[55] K. Pachucki and U. D. Jentschura, Two-Loop Bethe-Logarithm Correction in Hydrogenlike Atoms, Phys. Rev. Lett. **91**, 113005 (2003).

[56] G. Clausen, S. Scheidegger, J. A. Agner, H. Schmutz, and F. Merkt, Imaging-assisted single-photon doppler-free laser spectroscopy and the ionization energy of metastable triplet helium, Phys. Rev. Lett. **131**, 103001 (2023).

[57] U. Bressel, A. Borodin, J. Shen, M. Hansen, I. Ernsting, and S. Schiller, Manipulation of individual hyperfine states in cold trapped molecular ions and application to hd^+ frequency metrology, Phys. Rev. Lett. **108**, 183003 (2012).

[58] V. I. Korobov, L. Hilico, and J.-P. Karr, $m\alpha^7$-order corrections in the hydrogen molecular ions and antiprotonic helium, Phys. Rev. Lett. **112**, 103003 (2014).

[59] V. I. Korobov, L. Hilico, and J.-P. Karr, Fundamental transitions and ionization energies of the hydrogen molecular ions with few ppt uncertainty, Phys. Rev. Lett. **118**, 233001 (2017).

[60] M. R. Schenkel, S. Alighanbari, and S. Schiller, Laser spectroscopy of a rovibrational transition in the molecu-

lar hydrogen ion H_2^+, Nat. Phys. **20**, 383 (2024).

[61] H. M. James and A. S. Coolidge, The ground state of the hydrogen molecule, J. Chem. Phys. **1**, 825 (1933).

[62] E. Hylleraas, Neue Berechnung der Energie des Heliums im Grundzustande, sowie des tiefsten Terms von Ortho-Helium, Z. Physik **54**, 347–366 (1929).

[63] K. Pachucki and J. Komasa, Schrödinger equation solved for the hydrogen molecule with unprecedented accuracy, J. Chem. Phys. **144**, 164306 (2016).

[64] K. Pachucki and J. Komasa, Nonadiabatic rotational states of the hydrogen molecule, Phys. Chem. Chem. Phys. **20**, 247 (2018).

[65] K. Pachucki and J. Komasa, Nonrelativistic energy levels of HD, Phys. Chem. Chem. Phys. **20**, 26297 (2018).

[66] K. Pachucki and J. Komasa, Nonrelativistic energy levels of D_2, Phys. Chem. Chem. Phys. **21**, 10272 (2019).

[67] K. Pachucki and J. Komasa, Integrals for relativistic nonadiabatic energies of H_2 in an exponential basis, Phys. Rev. A **109**, 032822 (2024).

[68] K. Pachucki and J. Komasa, Relativistic correction from the four-body nonadiabatic exponential wave function, J. Chem. Theory Comput. **20**, 8644 (2024).

[69] R. F. Code and N. F. Ramsey, Molecular-Beam Magnetic Resonance Studies of HD and D_2, Phys. Rev. A **4**, 1945 (1971).

[70] M. Siłkowski, K. Pachucki, J. Komasa, and M. Puchalski, Leading-order QED effects in the ground electronic state of molecular hydrogen, Phys. Rev. A **107**, 032807 (2023).

[71] M. Puchalski, J. Komasa, P. Czachorowski, and K. Pachucki, Complete $\alpha^6 m$ corrections to the ground state of H_2, Phys. Rev. Lett. **117**, 263002 (2016).

[72] P. J. Mohr, D. B. Newell, B. N. Taylor, and E. Tiesinga, CODATA recommended values of the fundamental physical constants: 2022, Rev. Mod. Phys. **97**, 025002 (2025).

[73] H2Spectre ver. 7.4 Fortran source code, (2022), `https://qcg.home.amu.edu.pl/H2Spectre.html`.

[74] 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).

[75] M. Puchalski, J. Komasa, and K. Pachucki, Nuclear Spin-Spin Coupling in HD, HT, and DT, Phys. Rev. Lett. **120**, 083001 (2018).

[76] M. P. Ledbetter, M. V. Romalis, and D. F. J. Kimball, Constraints on short-range spin-dependent interactions from scalar spin-spin coupling in deuterated molecular hydrogen, Phys. Rev. Lett. **110**, 040402 (2013).

[77] L. Cong, W. Ji, P. Fadeev, F. Ficek, M. Jiang, V. V. Flambaum, H. Guan, D. F. Jackson Kimball, M. G. Kozlov, Y. V. Stadnik, and D. Budker, Spin-dependent exotic interactions, Rev. Mod. Phys. **97**, 025005 (2025).