PHYSICAL REVIEW A **104**, 032806 (2021)

Rovibrational spin-averaged transitions in the hydrogen molecular ions

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(Received 30 July 2021; accepted 26 August 2021; published 7 September 2021)

We reconsider the calculation of rovibrational transition frequencies in hydrogen molecular ions. Some previously neglected contributions, such as the deuteron polarizability, are included into consideration in comparison with our previous work. In particular, one-loop and two-loop QED corrections at $m\alpha^7$ and $m\alpha^8$ orders are recalculated in the framework of the adiabatic approximation, with systematic inclusion of corrections associated with vibrational motion. Improved theoretical transition frequencies are obtained and found to be in very good agreement with recent high-precision spectroscopy experiments in HD$^+$. New values for the m_p/m_e and m_d/m_p mass ratios are determined.

DOI: 10.1103/PhysRevA.104.032806

I. INTRODUCTION

Considerable progress has been recently achieved in the spectroscopy of hydrogen molecular ions. Several rovibrational transitions in HD$^+$ have been measured with relative uncertainties in the 10^{-11}–10^{-12} range through Doppler-free spectroscopy of ultracold trapped ions in the Lamb-Dicke regime [1–3], approaching or even exceeding the precision of theoretical predictions [4]. This has allowed one to get improved determinations of the proton-to-electron mass ratio, and to perform tests of QED constraining hypothetical "fifth forces" between hadrons [1,5]. These results, as well as other ongoing projects [6,7], and perspectives of reaching higher precision [8,9], e.g., using quantum-logic spectroscopy schemes [10–12], provide strong motivation to improve the theory further.

In our paper [4], we calculated the frequencies of fundamental vibrational transitions in the nonrelativistic QED approach, including corrections up to the $m\alpha^8$ order. Since then, several new advances in the theory of hydrogenlike atoms have been achieved [13–15], which allows one to get improved results for the corresponding correction terms in the hydrogen molecular ions. In addition, we found that several contributions that had been neglected in our previous consideration were of comparable magnitude to the estimated error bar, and thus should be included. Finally, changes in the recommended values of fundamental constants, the nucleus-to-electron mass ratios but also the Rydberg constant, proton and deuteron radii, between the previous (2014) CODATA adjustment [16] and the most recent one (2018) [17] (see Table I) also affect our theoretical predictions and their uncertainties.

The aim of this work is to reanalyze the theory, with particular emphasis on the evaluation of QED corrections at orders $m\alpha^7$ and $m\alpha^8$ in the framework of the adiabatic approximation, where we systematically include "vibrational" corrections, i.e., the second-order perturbation terms due to perturbation of the vibrational wave function. Improved theoretical rovibrational transition frequencies are given for experimentally relevant transitions, and the impact of these new results on the determination of the proton-to-electron mass ratio is illustrated.

We use atomic units throughout this paper ($\hbar = m_e = e = 1$). Other constants used in calculations are taken from the CODATA18 adjustment [17] (see Table I), including the fine-structure constant, $\alpha = 7.297\,352\,5693(11)\times 10^{-3}$.

II. NUCLEAR SIZE AND POLARIZABILITY CORRECTIONS

In our previous calculations [4,18], we only included the leading-order nuclear finite-size correction [see Eq. (6) in [18]]. Some higher-order nuclear corrections are not negligible at the current level of theoretical accuracy, in particular the deuteron polarizability [19]. Here, we follow the notations used in [16]. According to Eq. (34) of [16], we write the $m\alpha^5$ deuteron polarizability contribution as

$$E^{(5)}_{\rm pol}({\rm D}) = [-21.37(8)]\langle \pi\delta(\mathbf{r}_d)\rangle \;({\rm kHz}). \qquad (1)$$

For example, this results in a 0.33 kHz shift for the frequency of the fundamental vibrational transition $(L=0, v=0) \to (0,1)$, which is comparable to the overall theoretical uncertainty of 0.5 kHz for this transition (see Table II).

Nuclear finite-size corrections at the same order [20] are written as [see Eq. (59) in [16]]

$$\begin{aligned} E^{(5)}_{\rm fns}({\rm D}) &= -(2R_\infty c)\frac{2\pi}{3}C_\eta\left(\frac{R_d}{a_0}\right)^3\langle \pi\delta(\mathbf{r}_d)\rangle \\ &= [-0.57(3)]\langle \pi\delta(\mathbf{r}_d)\rangle \;({\rm kHz}), \end{aligned} \qquad (2)$$

TABLE I. Reevaluation of the fundamental constants of atomic physics by CODATA in 2018. CODATA14 (respectively, CODATA18) values are given in the upper (respectively, lower) line.

Quantity	Symbol	Value	Uncertainty
Proton charge radius	r_p	$0.8751(61)\times10^{-15}$ m	7.0×10^{-3}
		$0.8414(19)\times10^{-15}$ m	2.2×10^{-3}
Rydberg constant	$R_\infty=\alpha^2 m_e c/2h$	$10\,973\,731.568\,508(65)$ m^{-1}	5.9×10^{-12}
		$10\,973\,731.568\,160(21)$ m^{-1}	1.9×10^{-12}
Proton-to-electron Mass ratio	$\mu_p=m_p/m_e$	$1836.152\,673\,89(17)$	9.5×10^{-11}
		$1836.152\,673\,43(11)$	6.0×10^{-11}
Deuteron-to-electron Mass ratio	$\mu_d=m_d/m_e$	$3670.482\,967\,85(13)$	3.5×10^{-11}
		$3670.482\,967\,88(13)$	3.5×10^{-11}

where a_0 is the Bohr radius, $R_d=2.127\,99(74)$ the rms charge radius of the deuteron, and $C_\eta=2.0(1)$.

The contribution at the next order ($m\alpha^6$), as it is written in Ref. [16], Eq. (59), is "state-dependent" term proportional to the squared value of the electron wave function at the nucleus, and would require an independent calculation. However, this term can be estimated from its value for the hydrogen atom ground state by using the linear combination of atomic orbitals (LCAO) approximation for the electronic wave function:

$$\psi_{\rm LCAO}(\mathbf{r})=\frac{1}{\sqrt{2}}[\psi_{1s}(\mathbf{r}_p)+\psi_{1s}(\mathbf{r}_d)],$$

where ψ_{1s} is the hydrogen ground state wave function. Under this approximation, one gets from Eq. (59) of [16]

$$\begin{aligned}E^{(6)}_{\rm fns}({\rm D})&=-(2R_\infty c)\frac{2\pi}{3}\left(\frac{R_d}{a_0}\right)^2(Z\alpha)^2\left(C_\theta-\ln\frac{ZR_d}{a_0}\right)\langle\pi\delta(\mathbf{r}_d)\rangle\\&=[3.96(2)]\langle\pi\delta(\mathbf{r}_d)\rangle\ ({\rm kHz}),\end{aligned}\qquad(3)$$

with $C_\theta=0.38(4)$. Only the uncertainty from C_θ is indicated in this equation. Due to the employed LCAO approximation, one may estimate the uncertainty of $E^{(6)}_{\rm fns}(D)$ as equal to the nonlogarithmic term, which is still much smaller than the overall theoretical uncertainty.

TABLE II. Fundamental transition frequency ν_{01} for the HD$^+$ molecular ion (in kHz). CODATA14 recommended values of fundamental constants were used in [4], and the latest CODATA18 values are used in the present work. Nuclear size and polarizability corrections are included in ν_{α^2}, and "other" corrections correspond to the muonic and hadronic vacuum polarization. Theoretical uncertainties of contributions at each order in α, if not negligible, are indicated within parentheses. In the final value of the transition frequency, the first error is the theoretical uncertainty, and the second one is due to the uncertainty of fundamental constants.

	[4]	This work
ν_{nr}	57 349 439 952.4	57 349 439 955.1
ν_{α^2}	958 151.7	958 154.6
ν_{α^3}	−242 126.3	−242 126.3
ν_{α^4}	−1708.9(1)	−1708.9(1)
ν_{α^5}	106.4(1)	105.9(1)
ν_{α^6}	−2.0(5)	−0.8(5)
Other		0.25
$\nu_{\rm tot}$	57 350 154 373.4(0.5)(1.8)	57 350 154 379.8(0.5)(1.3)

In the proton case, all the corrections considered above are negligibly small at the current level of accuracy.

III. $m\alpha^7$- AND $m\alpha^8$-ORDER CORRECTIONS IN THE ADIABATIC APPROXIMATION

Relativistic and QED corrections at the orders $m\alpha^4$ to $m\alpha^6$ have been evaluated in a full three-body approach using precise variational wave functions [18,21], except for the $m\alpha^6$ relativistic correction [4,22]. For calculation of $m\alpha^7$ and higher-order one- and two-loop corrections we use the Born-Oppenheimer approach, where the states of the molecule are taken in the form

$$\Psi^{\rm BO}=\phi_{\rm el}(\mathbf{r};R)\chi_{\rm BO}(R).\qquad(4)$$

The electronic wave function obeys the clamped nuclei Schrödinger equation for a bound electron

$$[H_{\rm el}-\mathcal{E}_{\rm el}(R)]\phi_{\rm el}=0,\qquad(5)$$

where

$$H_{\rm el}=\frac{p^2}{2m}+V+\frac{Z_1Z_2}{R},\qquad V=-\frac{Z_1}{r_1}-\frac{Z_2}{r_2}.$$

Here $H_{\rm el}$ is the electronic Hamiltonian, Z_1 and Z_2 are the charges of the nuclei, and r_1,r_2 are the distances from the electron to nuclei 1 and 2, respectively. The wave function $\chi_{\rm BO}(R)$ describes the relative nuclear motion, and is a solution of

$$(H_{vb}-E_0)\chi_{\rm BO}=\left[-\frac{\nabla^2_R}{2\mu_N}+\mathcal{E}_{\rm el}(R)-E_0\right]\chi_{\rm BO}=0,\qquad(6)$$

where $\mu_N=M_1M_2/(M_1+M_2)$ is the reduced mass of the nuclei.

Instead of the Born-Oppenheimer solution $\chi_{\rm BO}(R)$ we use the adiabatic solution $\chi_{\rm ad}(R)$, which includes as well the adiabatic corrections

$$\mathcal{E}_{\rm ad}(R)=\mathcal{E}_{\rm el}+\int d\mathbf{r}\langle\phi_{\rm el}|\frac{\mathbf{p}^2}{8\mu_N}+\frac{\mathbf{P}^2}{2\mu_N}-\frac{\kappa}{2\mu_N}\mathbf{pP}|\phi_{\rm el}\rangle,\qquad(7)$$

where $\mathbf{p}$ is the electron impulse in the center-of-mass frame, $\mathbf{P}$ the relative impulse of the two nuclei, and $\kappa=(M_1-M_2)/(M_1+M_2)$ is the asymmetry parameter. See Ref. [23], or a review by Carrington *et al.* [24] for more details.

The one-loop self-energy correction of order $m\alpha^7$ to the energy of a bound electron in the two-center problem (nonrecoil limit) has been determined in [25–29]. The electronic part of the correction can be calculated using the effective Hamiltonian of Eq. (6) from Ref. [29]:

$$\Delta E^{(7)}_{\text{el-SE}} = \langle \chi_{\text{ad}} | \mathcal{E}^{(7)}_{\text{1 loop-SE}}(R) | \chi_{\text{ad}} \rangle, \tag{8}$$

numerical data for the $\mathcal{E}^{(7)}_{\text{1 loop-SE}}(R)$ effective potential may be found in the Supplemental Material to [27].

The one-loop vacuum polarization (Uehling potential) contribution has been considered in [30]. The adiabatic approximation was also compared with full three-body calculations, confirming that it is accurate to $O(m/M)$ (where m/M is the electron-to-nucleus mass ratio). The electronic part of the correction can be written as

$$\Delta E^{(7+)}_{\text{el-VP}} = \langle \chi_{\text{ad}} | \mathcal{E}^{(7+)}_{\text{1 loop-VP}}(R) | \chi_{\text{ad}} \rangle, \tag{9}$$

where $\mathcal{E}^{(7+)}_{\text{1 loop-VP}}(R)$ is given by Eq. (16) of [30].

As shown in [4,30], beyond the above electronic contributions one also needs to include vibrational corrections. The latter are second-order perturbation terms stemming from perturbation of the vibrational wave function by the leading relativistic and radiative corrections to the adiabatic potential $\mathcal{E}_{\text{ad}}(R)$, namely,

$$\begin{aligned}
\mathcal{E}^{(4)}_{\text{BP}}(R) &= \alpha^2 \left\langle -\frac{p^4}{8m^3} + \frac{\pi\rho}{2m^3} + H_{\text{so}} \right\rangle_{|R}, \\
\mathcal{E}^{(5)}_{\text{SE}}(R) &= \alpha^3 \frac{4}{3}\left[\ln\frac{1}{\alpha^2} - \beta(R) + \frac{5}{6}\right] \langle Z_1\delta(\mathbf{r}_1) + Z_2\delta(\mathbf{r}_2)\rangle_{|R}, \\
\mathcal{E}^{(5)}_{\text{VP}}(R) &= -\alpha^3 \frac{4}{15} \langle Z_1\delta(\mathbf{r}_1) + Z_2\delta(\mathbf{r}_2)\rangle_{|R}.
\end{aligned} \tag{10}$$

Here $\rho = \nabla^2 V/(4\pi)$, H_{so} is the electron spin-orbit Hamiltonian (see [22] for details), and $\beta(R)$ is the nonrelativistic Bethe logarithm for the bound electron in the two-center problem, whose values as a function of R may be found in the Supplemental Material to Ref. [27] or in [31].

The $m\alpha^7$-order vibrational correction from one-loop self-energy and vacuum polarization is then obtained via the second-order perturbation formalism as

$$\begin{aligned}
\Delta E^{(7)}_{\text{vb}} &= 2\langle \chi_{\text{ad}} | \mathcal{E}^{(4)}_{\text{BP}}(R) Q' (E_0 - H_{\text{vb}})^{-1} Q' \\
&\quad \times \left[\mathcal{E}^{(5)}_{\text{SE}}(R) + \mathcal{E}^{(5)}_{\text{VP}}(R)\right] | \chi_{\text{ad}} \rangle;
\end{aligned} \tag{11}$$

here Q' is a projection operator onto a subspace orthogonal to $\chi_{\text{ad}}(R)$ from Eq. (5). The difference with respect to our previous calculations is that $\mathcal{E}^{(5)}_{\text{SE}}(R)$ in Eq. (10) includes the contribution from the electron anomalous magnetic moment, which was missed in Eq. (10) of [4].

We now turn to the $m\alpha^8$ order, starting with the one-loop self-energy correction. The higher-order remainder ($m\alpha^8$ and above) for this contribution can be estimated from the hydrogen $1S$ state results by using the LCAO approximation:

$$\begin{aligned}
\Delta E^{(8+)}_{\text{el-1 loop}} &= \alpha^5 \langle \chi_{\text{ad}} | (G_{\text{SE}}(1S) - A_{60}) \\
&\quad \times \left\langle Z_1^3\delta(\mathbf{r}_1) + Z_2^3\delta(\mathbf{r}_2) \right\rangle | \chi_{\text{ad}} \rangle,
\end{aligned} \tag{12}$$

where $G_{\text{SE}}(1S) = -30.290\,24(2)$ is the higher-order remainder and $A_{60} = -30.924\,149$. Both numbers are taken from Table II of [13]. This is more accurate than the treatment of Ref. [4], where only the $m\alpha^8$-order term was estimated. The theoretical uncertainty is estimated as equal to $|\Delta E^{(8+)}_{\text{el-1 loop}} - \Delta E^{(8\,\log)}_{\text{el-1 loop}}|$, where $\Delta E^{(8\,\log)}_{\text{el-1 loop}}$ is the known $m\alpha^8$-order logarithmic term [first term of Eq. (14) in [4]].

The second-order vibrational contribution is expressed as

$$\begin{aligned}
\Delta E^{(8)}_{\text{vb-1 loop}} &= 2\langle \chi_{\text{ad}} | \mathcal{E}^{(4)}_{\text{BP}}(R) Q' (E_0 - H_{\text{vb}})^{-1} Q' \\
&\quad \times \left[\mathcal{E}^{(6)}_{\text{SE}}(R) + \mathcal{E}^{(6)}_{\text{VP}}(R)\right] | \chi_{\text{ad}} \rangle,
\end{aligned} \tag{13}$$

where

$$\begin{aligned}
\mathcal{E}^{(6)}_{\text{SE}}(R) &= \alpha^4 \left[\frac{139}{32} - 2\ln 2\right] \pi \left\langle Z_1^2\delta(\mathbf{r}_1) + Z_2^2\delta(\mathbf{r}_2) \right\rangle_{|R}, \\
\mathcal{E}^{(6)}_{\text{VP}}(R) &= \alpha^4 \frac{5}{48} \pi \left\langle Z_1^2\delta(\mathbf{r}_1) + Z_2^2\delta(\mathbf{r}_2) \right\rangle_{|R}.
\end{aligned}$$

Finally, we consider two-loop $m\alpha^8$-order corrections. For hydrogenlike atoms, the two-loop correction at orders $m\alpha^8$ and higher is generally expressed in the form [13,17]

$$\begin{aligned}
E^{(8+)}_{\text{2 loop}} &= \frac{(Z\alpha)^6}{\pi^2 n^3} [B_{63} \ln^3 (Z\alpha)^{-2} + B_{62} \ln^2 (Z\alpha)^{-2} \\
&\quad + B_{61} \ln (Z\alpha)^{-2} + G^{\text{2 loop}}(Z\alpha)]
\end{aligned} \tag{14}$$

where $G^{\text{2 loop}}(Z\alpha)$ is the higher-order remainder calculated in [32,33]. We adopt similar notations for hydrogen molecular ions:

$$\begin{aligned}
E^{(8+)}_{\text{2 loop}} &= \frac{\alpha^6}{\pi} \langle \chi_{\text{ad}} | \mathcal{B}_{63}(R) \ln^3(\alpha^{-2}) + \mathcal{B}_{62}(R) \ln^2(\alpha^{-2}) \\
&\quad + \mathcal{B}_{61}(R) \ln(\alpha)^{-2} + G^{\text{2 loop}}(1S) \left\langle Z_1^3\delta(\mathbf{r}_1) \right. \\
&\quad \left. + Z_2^3\delta(\mathbf{r}_2) \right\rangle | \chi_{\text{ad}} \rangle.
\end{aligned} \tag{15}$$

Again, the higher-order remainder is estimated using the LCAO approximation. In our calculations, we adopted the value $G^{\text{2 loop}}(1S) = -94.5(6.6)$ from [15]. This is more accurate than our previous treatment [4], where only the $m\alpha^8$-order correction was estimated using $B_{60}(1S)$ instead of $G^{\text{2 loop}}(1S)$. The theoretical uncertainty is estimated as equal to the term proportional to $G^{\text{2 loop}}(1S)$, after subtraction of the known term of order $m\alpha^9 \ln^2(\alpha)$ [Eq. (26) of [13]].

Calculation of the $\mathcal{B}_{6k}(R)$ effective potentials for the two-center problem is described in [4]. Since then, a new contribution to the B_{61} coefficient in hydrogenlike atoms from light-by-light (LbL) scattering diagrams has been found, yielding a correction $B_{61}^{\text{LbL}} = 0.830\,309$ for S states [14]. For the two-center problem we thus add the following term to $\mathcal{B}_{61}(R)$:

$$\mathcal{B}^{\text{LbL}}_{61}(R) = B^{\text{LbL}}_{61} \left\langle Z_1^3\delta(\mathbf{r}_1) + Z_2^3\delta(\mathbf{r}_2) \right\rangle_{|R}. \tag{16}$$

The second-order contribution due to vibrational motion is expressed as

$$\begin{aligned}
\Delta E^{(8)}_{\text{vb-2 loop}} &= 2\langle \chi_{\text{ad}} | \mathcal{E}^{(4)}_{\text{BP}}(R) Q' (E_0 - H_{\text{vb}})^{-1} Q' \mathcal{E}^{(6)}_{\text{2 loop}}(R) | \chi_{\text{ad}} \rangle \\
&\quad + \langle \chi_{\text{ad}} | \left[\mathcal{E}^{(5)}_{\text{SE}}(R) + \mathcal{E}^{(5)}_{\text{VP}}(R)\right] Q' (E_0 - H_{\text{vb}})^{-1} Q' \\
&\quad \times \left[\mathcal{E}^{(5)}_{\text{SE}}(R) + \mathcal{E}^{(5)}_{\text{VP}}(R)\right] | \chi_{\text{ad}} \rangle,
\end{aligned} \tag{17}$$

with

$$\mathcal{E}^{(6)}_{\text{2 loop}}(R) = \frac{\alpha^4}{\pi^2} [0.538\,941] \pi \langle Z_1\delta(\mathbf{r}_1) + Z_2\delta(\mathbf{r}_2) \rangle_{|R}.$$

TABLE III. Theoretical and experimental spin-averaged transition frequencies (in kHz). CODATA18 values of fundamental constants were used in the calculations. For theoretical values, the first uncertainty is due to yet uncalculated terms and used approximations in theory, while the second uncertainty is due to inaccuracy in the CODATA18 recommended mass values.

$(L, v) \to (L', v')$	Theory	Experiment
$(0, 0) \to (1, 0)$	1 314 925 752.932(19)(61)	1 314 925 752.910(17)
$(0, 0) \to (1, 1)$	58 605 052 163.9(0.5)(1.3)	58 605 052 164.24(86)
$(3, 0) \to (3, 9)$	415 264 925 502.8(3.3)(6.7)	415 264 925 501.8(1.3)

Due to the presence of a logarithmic term in $\mathcal{E}^{(5)}_{\rm SE}(R)$, the vibrational correction is enhanced by a factor of $\ln^2(\alpha^{-2})$ and contributes to the $\mathcal{B}_{62}$, $\mathcal{B}_{61}$, and nonlogarithmic terms. It results in a 1.14 kHz shift for the fundamental vibrational transition, thus the neglect of this term in [4] was not justified.

The last corrections requiring new consideration are the muonic and hadronic vacuum polarization corrections. The muonic term is [see Eq. (14) of [13]]

$$\mathcal{E}_{\mu{\rm VP}}(R) = \left(\frac{m_e}{m_\mu}\right)^2 \mathcal{E}^{(5)}_{\rm VP}(R), \tag{18}$$

and the hadronic term may be written as [Eq. (15) of [13]]

$$\mathcal{E}_{\rm hadVP}(R) = 0.671(15)\, \mathcal{E}_{\mu{\rm VP}}(R). \tag{19}$$

The sum of these two contributions shifts the fundamental transition frequency by 0.25 kHz.

IV. RESULTS

Our results for the frequency of the fundamental transition $(L = 0, v = 0) \to (0, 1)$ in HD$^+$ are presented in Table II and compared with previous results from Ref. [4]. The change in the nonrelativistic transition frequency ν_{nr} is mainly due to those of the nucleus-to-electron mass ratios (mostly μ_p) and Rydberg constant between the 2014 and 2018 CODATA adjustments. The shift in ν_{α^2} is due to the nuclear corrections; it stems from the CODATA18 values of the proton and deuteron radii, and from the inclusion of higher-order finite-size and polarizability corrections described in Sec. II. The change in ν_{α^5} comes from the correction of the vibrational contribution [Eq. (11)]. Finally, several improvements have been made in the calculation of ν_{α^6} as detailed in Sec. III: inclusion of vibrational contributions, estimate of the all-order remainder both in one-loop and too-loop corrections, as well as the inclusion of light-by-light scattering diagrams in the two-loop correction. The total shift of the transition frequency is +6.4 kHz, of which +5.4 kHz is due to the shifts in the fundamental constants (+2.7 kHz for ν_{nr}, and +2.7 kHz for the leading-order finite-size correction in ν_{α^2}), and +1.0 kHz comes from the new contributions discussed in Secs. II and III.

The theoretical uncertainty is dominated by the one-loop [Eq. (12)] and two-loop [term proportional to $G^{2\,\rm loop}(1S)$ in Eq. (15)] higher-order remainders (see discussion in [4]). In the uncertainty from fundamental constants, the largest contribution by far is that of the proton-to-electron mass ratio μ_p (1.7 kHz and 1.1 kHz using 2014 and 2018 CODATA values, respectively).

Theoretical frequencies for the rovibrational transitions measured in recent experiments are presented in Table III. They are in very good agreement with experimental results in all cases. For the $(0, 0) \to (1, 1)$ transition the combined uncertainty $u = 0.86$ kHz ($u^{\rm expt.} = 0.16$ kHz and $u^{\rm theor,spin} = 0.85$ kHz) is given; for the $v = (3, 0) \to (3, 9)$ transition, the revised experimental value from [5] is used. Numerical results of calculations for all the contributions considered in Sec. III (with the $m\alpha^6$-order relativistic correction as well) for a wide range of rovibrational states are given in the Supplemental Material [34].

Using these improved theoretical predictions, we give in Table IV some updated determinations of the proton-to-electron mass ratio from HD$^+$ spectroscopy. We follow the least-squares fitting procedure used in the CODATA adjustments and described in Appendix E of [35]. The dependence of HD$^+$ transition frequencies on fundamental constants is linearized using a first-order Taylor expansion around their starting (CODATA18) values; first-derivative coefficients are obtained by the methods described in [36,37]. Following the CODATA approach, we adjust the individual particle masses rather than mass ratios. In more detail, we use CODATA18 values of m_d, R_∞, r_d, r_p; include as an additional data point the latest measurement of the electron mass [38]; and solve for the electron and proton masses. m_p/m_e and its uncertainty are then deduced from the adjusted values of m_p and m_e, taking the correlation between them into account. The covariance matrix of the HD$^+$ input data (see [35] for definition) is built including the three (uncorrelated) sources of uncertainties: experimental, theoretical, and parametric; the latter stemming from uncertainties of fundamental constants that are not directly involved in the adjustment (m_d, R_∞, r_d, r_p). When several HD$^+$ measurements are combined, the following assumptions are made regarding correlations: (i) uncorrelated experimental uncertainties, (ii) fully correlated theoretical uncertainties, and (iii) correlations between parametric uncertainties are included taking into account the

TABLE IV. Determinations of mass ratios using HD$^+$ spectroscopy.

Data	m_p/m_e	m_d/m_p
$(0, 0) \to (1, 0)$	1836.152 673 480(63)	
$(0, 0) \to (1, 1)$	1836.152 673 40(10)	
$(3, 0) \to (3, 9)$	1836.152 673 457(73)	
HD$^+$	1846.152 673 466(61)	
HD$^+$/Penning	1836.152 673 454(33)	1.999 007 501 243(31)

correlation coefficients between fundamental constants available from [39].

Values obtained in this way from each single HD$^+$ experiment are given in the first three lines of Table IV, and the combined result from the three measurements in the fourth line. Note that its uncertainty is only slightly reduced with respect to that of individual lines due to strong correlation between them. The latter value, although slightly higher (by 1.4 combined standard deviations), is in good agreement with that obtained from recent high-precision mass spectroscopy measurements of m_p [40], m_d [41], $m(\mathrm{HD}^+)$ [41], and m_d/m_p [42] in Penning traps: $m_p/m_e = 1836.152\,673\,343(60)$ [38,41].

Finally, the HD$^+$ data can be combined with the mass spectrometry measurements and the CODATA18 values of R_∞, r_d, and r_p to simultaneously determine the three particle masses, m_e, m_p, and m_d. The mass ratios m_p/m_e and m_d/m_p deduced from this adjustment are shown in the last line of Table IV. Relative uncertainties of 1.8×10^{-11} (for m_p/m_e) and 1.6×10^{-11} (for m_d/m_p) are obtained, improved by factors of 3.3 and 3.5 with respect to CODATA18.

In conclusion, we have presented a revised and improved theory of spin-averaged transition frequencies in hydrogen molecular ions. Further progress in precision now requires calculations of nonlogarithmic $m\alpha^8$-order one- and two-loop corrections.

ACKNOWLEDGMENTS

The authors thank J. C. J. Koelemeij for his help with the least-squares adjustments of fundamental constants. V.I.K. acknowledges support of the Russian Foundation for Basic Research under Grant No. 19-02-00058-a.

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