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Rovibrational levels of HD†

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The dissociation energies of all rotation–vibration states of the molecular HD in the ground electronic state are calculated to a high accuracy by including nonadiabatic, relativistic α^2, and quantum electrodynamic α^3 effects, with approximate treatment of small higher order α^4, and finite nuclear size corrections. The obtained result for the ground molecular state of 36 405.7828(10) cm^{-1} is in a small disagreement with the latest most precise experimental value.

I. Introduction

Since the beginning of quantum mechanics molecular hydrogen and its isotopomers have been a ground for testing and developing experimental techniques and theoretical models. In determination of the dissociation energy (D_0), experimental and theoretical measurements have diminished their individual uncertainties to below 10^{-3} cm^{-1} and are in good agreement. In particular, the latest theoretical $D_0 = 36\ 118.0695(10)$ cm^{-1} of H_2, obtained by Piszczatowski et al.,[1] agrees very well with $36\ 118.06962(37)$ cm^{-1} derived experimentally by Liu et al.[2] Analogous results obtained last year for D_2 are $36\ 748.3633(9)$ cm^{-1} from theory[1] and $36\ 748.36287(60)$ cm^{-1} from experiment.[3] The tiny difference of 0.0004 cm^{-1} fits well within both error estimates. To achieve this 10^{-3} cm^{-1} level of accuracy, the theory must have taken into account, with sufficient precision, not only the electron correlation but also the finite nuclear mass, relativistic, and quantum electrodynamics (QED) effects.

Particularly challenging is the accurate inclusion of nonadiabatic effects. One possible approach is to obtain a nonadiabatic wave function (depending explicitly on nuclear coordinates) by minimizing the nonrelativistic energy. For H_2 such calculations, using explicitly correlated James–Coolidge functions, were attempted by Kołos and Wolniewicz in 1963[4,5] and 15 years later by Bishop and Cheung.[6] The same authors performed purely nonadiabatic calculations for HD. Kołos and Wolniewicz obtained $D_0 = 36\ 402.4$ cm^{-1},[7] whereas Bishop and Cheung reported $D_0 = 36\ 405.97$ cm^{-1}.[8] Calculations in a similar spirit, but using extensively optimized explicitly correlated Gaussian functions, were performed by Stanke et al.[9] Their nonadiabatic wave function was further employed to compute perturbatively the relativistic correction to the nonadiabatic energy. An apparent drawback of these methods is their decreasing accuracy observed for the higher excited states, particularly those lying close to dissociation threshold. For such states the perturbative treatment of relativistic effects may be inadequate. As an example, the $v = 14$, $J = 4$ state of

H_2 becomes a resonance after the inclusion of relativistic effects on the level of the potential energy curve (PEC). Moreover, certain properties like the ortho–para mixing or the scattering length, are inaccessible within the direct nonadiabatic approach.

In contrast, the nonadiabatic perturbation theory (NAPT) approach employed here, relies on solving the radial, variable-mass Schrödinger equation with the PEC for the nuclei constructed from the adiabatic potential augmented by R-dependent nonadiabatic, relativistic and QED corrections. The theory of the nonadiabatic potentials has been developed in ref. 10 and 11, whereas the relativistic and QED corrections to the PEC are evaluated on the basis of the nonrelativistic quantum electrodynamics (NRQED).[12–14] These corrections are unambiguously identified by an expansion of a bound atomic or molecular state energy in powers of the fine structure constant α:

$$E = E^{(0)} + \alpha^2 E^{(2)} + \alpha^3 E^{(3)} + \alpha^4 E^{(4)} + \cdots, \qquad (1)$$

where $E^{(3)}$ and higher order terms may additionally depend on $\ln \alpha$. The first term of the expansion represents the nonrelativistic energy, $\alpha^2 E^{(2)}$ is the leading relativistic contribution, terms proportional to α^3 and α^4 describe the QED effects of the leading and higher order, respectively. In this paper we report on application of this approach to all rovibrational levels of the ground electronic state of HD molecule. Uncertainty of our results comes mainly from the neglect of the finite nuclear mass corrections of the order $\alpha^2 m/M$ to the relativistic contribution to the PEC, and from the approximate treatment of the α^4 correction. The neglect of higher order nonadiabatic terms proportional to $(m/M)^3$ also increases the overall uncertainty.

II. Nonrelativistic Hamiltonian

We consider a two-electron diatomic molecule in the reference frame attached to the geometrical center of the two nuclei. The total wave function ϕ is a solution of the stationary Schrödinger equation

$$H\phi = E\phi, \qquad (2)$$

with the Hamiltonian

$$H = H_{el} + H_n, \qquad (3)$$

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split into the electronic and nuclear parts. In the electronic Hamiltonian

$$H_{el} = -\sum_a \frac{\nabla_a^2}{2m_e} + V, \qquad (4)$$

where V is the Coulomb interaction

$$V = -\frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R}, \qquad (5)$$

the nuclei have fixed positions $\vec{R}_A$ (proton) and $\vec{R}_B$ (deuteron), and $\vec{R} = \vec{R}_A - \vec{R}_B$. The nuclear Hamiltonian is

$$H_n = -\frac{\nabla_R^2}{2\mu_n} - \frac{\nabla_{el}^2}{2\mu_n} - \left(\frac{1}{M_B} - \frac{1}{M_A}\right)\vec{\nabla}_R \cdot \vec{\nabla}_{el}$$

$$= H_n' + H_n'', \qquad (6)$$

where $\vec{\nabla}_{el} = \frac{1}{2}\sum_a \vec{\nabla}_a$, $\mu_n = (1/M_A + 1/M_B)^{-1}$ is the nuclear reduced mass, and H_n', H_n'' are even and odd parts with respect to the inversion.

In order to simplify the calculation of nonadiabatic corrections we introduce a unitary transformation

$$\tilde{H} = U^+ H U \qquad (7)$$

of the form

$$U = e^{\lambda \vec{r} \cdot \vec{\nabla}_R} \qquad (8)$$

with $\vec{r} = \sum_a \vec{r}_a$ and the nuclear mass asymmetry parameter

$$\lambda = -\frac{m_e}{2}\left(\frac{1}{M_B} - \frac{1}{M_A}\right). \qquad (9)$$

The transformed Hamiltonian is

$$\tilde{H} = H + \lambda[H, \vec{r} \cdot \vec{\nabla}_R] + \frac{\lambda^2}{2}[[H, \vec{r} \cdot \vec{\nabla}_R], \vec{r} \cdot \vec{\nabla}_R] + \mathcal{O}(\lambda^3), \qquad (10)$$

where the higher order terms in the electron–nuclear mass ratio $\mathcal{O}[(m_e/M_{A,B})^3]$ are neglected, so that

$$\tilde{H} = H_{el} + H_n' + \lambda[V, \vec{r} \cdot \vec{\nabla}_R]$$

$$+ 2\frac{\lambda^2}{m_e}[\vec{\nabla}_{el} \cdot \vec{\nabla}_R, \vec{r} \cdot \vec{\nabla}_R] + \frac{\lambda^2}{2}[[H_{el}, \vec{r} \cdot \vec{\nabla}_R], \vec{r} \cdot \vec{\nabla}_R], \qquad (11)$$

and the odd $\mathcal{O}[(m_e/M_{A,B})^2]$ terms are neglected as well. The internal commutator in the last term of eqn (11) is

$$[H_{el}, \vec{r} \cdot \vec{\nabla}_R] = -\vec{r} \cdot \vec{\nabla}_R(V) - \frac{2}{m_e}\vec{\nabla}_{el} \cdot \vec{\nabla}_R, \qquad (12)$$

so that the transformed Hamiltonian can be decomposed as

$$\tilde{H} = H_{el} + \tilde{H}_n' + \tilde{H}_n''. \qquad (13)$$

where

$$\tilde{H}_n' = H_n' + \lambda^2\left[\frac{1}{m_e}\vec{\nabla}_{el} \cdot \vec{\nabla}_R - \frac{1}{2}\vec{r} \cdot \vec{\nabla}_R(V), \vec{r} \cdot \vec{\nabla}_R\right]$$

$$= H_n' + \frac{\lambda^2}{m_e}\nabla_R^2 + \frac{\lambda^2}{2}r^i r^j \nabla_R^i \nabla_R^j(V) \qquad (14)$$

$$\tilde{H}_n'' = -\lambda \vec{r} \cdot \vec{\nabla}_R(V). \qquad (15)$$

Both the nuclear Hamiltonians involve the derivative of the Coulomb operator V, which is

$$\vec{\nabla}_R(V) = \frac{1}{2}\left(-\frac{\vec{r}_{1A}}{r_{1A}^3} + \frac{\vec{r}_{1B}}{r_{1B}^3} - \frac{\vec{r}_{2A}}{r_{2A}^3} + \frac{\vec{r}_{2B}}{r_{2B}^3}\right) - \frac{\vec{n}}{R^2} \qquad (16)$$

with $\vec{n} = \vec{R}/R$, while the second derivative of V is further transformed in eqn (47)–(49).

III. Adiabatic approximation

In the adiabatic approximation the total wave function of the molecule

$$\phi_a(\vec{r}, \vec{R}) = \phi_{el}(\vec{r})\chi(\vec{R}) \qquad (17)$$

is represented as a product of the electronic wave function ϕ_{el} and the nuclear wave function χ. The electronic wave function obeys the clamped nuclei electronic Schrödinger equation

$$[H_{el} - \mathscr{E}_{el}(R)]|\phi_{el}\rangle = 0, \qquad (18)$$

while the wave function χ is a solution to the nuclear Schrödinger equation with the effective potential generated by electrons

$$\left[-\frac{\nabla_R^2}{2\mu_n} + \mathscr{E}_a(R) + \mathscr{E}_{el}(R) - E_a\right]|\chi\rangle = 0, \qquad (19)$$

where $\mathscr{E}_a(R)$ is the so-called adiabatic (or diagonal) correction defined as

$$\mathscr{E}_a(R) = \langle\phi_{el}|H_n'|\phi_{el}\rangle_{el}$$

$$= \frac{1}{2\mu_n}(\langle\vec{\nabla}_R\phi_{el}|\vec{\nabla}_R\phi_{el}\rangle_{el} - \langle\phi_{el}|\vec{\nabla}_{el}^2|\phi_{el}\rangle_{el}). \qquad (20)$$

Separation of the angular variables in eqn (19) leads to the well-known radial nuclear equation

$$\left[-\frac{1}{R^2}\frac{\partial}{\partial R}\frac{R^2}{2\mu_n}\frac{\partial}{\partial R} + \frac{J(J+1)}{2\mu_n R^2} + \mathscr{E}_{el}(R) + \mathscr{E}_a(R)\right]\chi_J(R)$$

$$= E_a\chi_J(R). \qquad (21)$$

Solving this equation gives an adiabatic energy level E_a and an adiabatic radial nuclear wave function χ_J.

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IV. Nonadiabatic nuclear Schrödinger equation

Following the NAPT formalism introduced recently,[10,11] we can obtain energy levels E including leading nonadiabatic corrections by solving the following nonadiabatic version of the radial Schrödinger equation

$$\left[-\frac{1}{R^2}\frac{\partial}{\partial R}\frac{R^2}{2\mu_{\parallel}(R)}\frac{\partial}{\partial R} + \frac{J(J+1)}{2\mu_{\perp}(R)R^2} + \mathscr{Y}(R) \right]\chi_J(R) = E\chi_J(R),$$

(22)

where $\mathscr{Y}(R)$ is a nonadiabatic potential energy function. In the nonrelativistic limit

$$\mathscr{Y}(R) = \mathscr{E}_{\text{el}}(R) + \mathscr{E}_{\text{a}}(R) + \delta\mathscr{E}_{\text{na}}(R) + \delta\mathscr{E}_{\text{na}}'(R),$$

(23)

with the nonadiabatic correction constructed from the homonuclear part $\delta\mathscr{E}_{\text{na}}(R)$, defined in our previous work on H_2,[10,11] and the heteronuclear part proportional to λ^2

$$\delta\mathscr{E}_{\text{na}}' = \lambda^2\left[\left\langle \phi_{\text{el}} \left| \frac{1}{m_{\text{e}}}\nabla_R^2 + \frac{1}{2}r^i r^j \nabla_R^i \nabla_R^j(V) \right| \phi_{\text{el}} \right\rangle_{\text{el}} \right.$$
$$\left. + \left\langle \phi_{\text{el}} \left| \vec{r}\cdot\vec{\nabla}_R(V)\frac{1}{(\mathscr{E}_{\text{el}} - H_{\text{el}})'}\vec{r}\cdot\vec{\nabla}_R(V) \right| \phi_{\text{el}} \right\rangle_{\text{el}} \right],$$

(24)

which is obtained from eqn (14) and (15). Apart from the nonadiabatic potential $\mathscr{Y}(R)$, the difference between eqn (22) and (21) lies in the effective masses used. In the adiabatic eqn (21) the reduced nuclear mass μ_n appearing in both translational and rotational kinetic terms is a constant, while in the nonadiabatic eqn (22) it is given by two different functions of the internuclear distance. These two effective reduced mass functions

$$\frac{1}{2\mu_{\parallel}(R)} \equiv \frac{1}{2\mu_n} + \mathscr{W}_{\parallel}(R) - \frac{\lambda^2}{m_e}$$

(25)

$$\frac{1}{2\mu_{\perp}(R)} \equiv \frac{1}{2\mu_n} + \mathscr{W}_{\perp}(R) - \frac{\lambda^2}{m_e}$$

(26)

are defined with the help of additional radial functions

$$\mathscr{W}_{\parallel}(R) = \frac{1}{\mu_n^2}\left\langle \vec{n}\cdot\vec{\nabla}_R\phi_{\text{el}} \left| \frac{1}{(\mathscr{E}_{\text{el}} - H_{\text{el}})'} \right| \vec{n}\cdot\vec{\nabla}_R\phi_{\text{el}} \right\rangle_{\text{el}}$$

(27)

and

$$\mathscr{W}_{\perp}(R) = \frac{1}{\mu_n^2}\frac{(\delta^{ij} - n^i n^j)}{2}\left\langle \nabla_R^i\phi_{\text{el}} \left| \frac{1}{\mathscr{E}_{\text{el}} - H_{\text{el}}} \right| \nabla_R^j\phi_{\text{el}} \right\rangle_{\text{el}}.$$

(28)

In total, three radial functions are needed to construct the nonadiabatic radial Schrödinger eqn (22) for diatomic molecules: two functions, defined by eqn (27) and (28), to describe the variable effective reduced masses of eqn (25) and (26), and the nonadiabatic potential $\mathscr{Y}$. This potential, in turn, is expressed by another four functions: BO energy $\mathscr{E}_{\text{el}}$, adiabatic $\mathscr{E}_{\text{a}}$, nonadiabatic homonuclear $\delta\mathscr{E}_{\text{na}}'$ and heteronuclear $\delta\mathscr{E}_{\text{na}}'$ corrections (see eqn (23)).

V. Separated atoms limit

At large internuclear distances the effective reduced mass functions (25) and (26) are expected to approach a value corresponding to the reduced mass of separate H and D atoms

$$\frac{1}{\mu_A} = \frac{1}{m_{\text{p}} + m_{\text{e}}} + \frac{1}{m_{\text{d}} + m_{\text{e}}}.$$

(29)

Because $\mathscr{W}_{\parallel}(R)$ and $\mathscr{W}_{\perp}(R)$ tend to $-m_{\text{e}}(4\mu_n^2)$, when $R \to \infty$, we have

$$\frac{1}{2\mu_{\parallel}(\infty)} = \frac{1}{2\mu_{\perp}(\infty)} = \frac{1}{2\mu_n} - \frac{m_{\text{e}}}{4\mu_n^2} - \frac{\lambda^2}{m_{\text{e}}}$$

(30)

$$= \frac{1}{2}\left[\frac{1}{m_{\text{p}}}\left(1 - \frac{m_{\text{e}}}{m_{\text{p}}}\right) + \frac{1}{m_{\text{d}}}\left(1 - \frac{m_{\text{e}}}{m_{\text{d}}}\right) \right],$$

(31)

which are exactly the leading terms of the expansion of the atomic reduced mass (29) in the electron–nuclear mass ratio

$$\frac{1}{2\mu_A} = \frac{1}{2}\left[\frac{1}{m_{\text{p}}}\left(1 - \frac{m_{\text{e}}}{m_{\text{p}}} + \left(\frac{m_{\text{e}}}{m_{\text{p}}}\right)^2 - \cdots\right) \right.$$

(32)

$$\left. + \frac{1}{m_{\text{d}}}\left(1 - \frac{m_{\text{e}}}{m_{\text{d}}} + \left(\frac{m_{\text{e}}}{m_{\text{d}}}\right)^2 - \cdots\right) \right].$$

(33)

In the separated atoms limit, the nonrelativistic energy of the system (the dissociation threshold) $\mathscr{E}(\infty)$ is simply a sum of the energies of hydrogen and deuterium atoms expressed by their reduced masses

$$\mathscr{E}(\infty) = -\frac{\mu_{\text{H}}}{2} - \frac{\mu_{\text{D}}}{2}.$$

(34)

The expansion of $\mathscr{E}(\infty)$ in the electron to nucleus mass ratio is of the form

$$\mathscr{E}(\infty) = -1 + \frac{1}{2}\left(\frac{m_{\text{e}}}{m_{\text{p}}} + \frac{m_{\text{e}}}{m_{\text{d}}}\right) - \frac{1}{2}\left(\frac{m_{\text{e}}^2}{m_{\text{p}}^2} + \frac{m_{\text{e}}^2}{m_{\text{d}}^2}\right) + \cdots.$$

(35)

Subsequent terms of this expansion coincide with the $R \to \infty$ limits of corresponding components of the nonadiabatic potential $\mathscr{Y}(R)$ of eqn (23),

$$\mathscr{E}_{\text{el}}(\infty) = -1,$$

(36)

$$\mathscr{E}_{\text{a}}(\infty) = \frac{m_{\text{e}}}{2\mu_n},$$

(37)

$$\delta\mathscr{E}_{\text{na}}(\infty) = -\left(\frac{m_{\text{e}}}{2\mu_n}\right)^2,$$

(38)

$$\delta\mathscr{E}_{\text{na}}'(\infty) = -\lambda^2.$$

(39)

In particular, the sum of eqn (38) and (39) is equal to the third term in the expansion (35).

VI. Relativistic and radiative corrections

The relativistic correction to the adiabatic potential for a singlet state is given by the expectation value with the

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nonrelativistic wave function of the Breit–Pauli Hamiltonian[15]

$$\alpha^{-2}\hat{H}_{BP} = -\frac{1}{8}\sum_a p_a^4 + \frac{\pi}{2}\sum_A\sum_a Z_A\delta(\vec{r}_{aA}) + \pi\sum_{a<b}\delta(\vec{r}_{ab})$$
$$-\frac{1}{2}\sum_{a<b}\left(\vec{p}_a\frac{1}{r_{ab}}\vec{p}_b + \vec{p}_a\cdot\vec{r}_{ab}\frac{1}{r_{ab}^3}\vec{r}_{ab}\cdot\vec{p}_b\right). \quad (40)$$

The expectation value $\mathscr{E}^{(2)}(R) = \langle\phi_{el}|\hat{H}_{BP}|\phi_{el}\rangle_{el}$ as a function of R, was computed for H_2 to a high accuracy by Wolniewicz[16] in 1993 and has recently been recalculated in ref. 1. In the present calculations, as in all the previous ones, we have omitted the small relativistic recoil corrections, namely those proportional to $\alpha^2 m_e/M$.

Another α^2 effect, which can be easily incorporated into the relativistic potential, results from the spatial distribution of the nuclear charge. The energy shift caused by this effect is given by the formula

$$\mathscr{E}_{fs}(R) = \frac{2\pi}{3}\frac{\alpha^2}{\lambda_C^2}\sum_A Z_A r_{ch}^2(A)\left\langle\phi_{el}\left|\sum_a\delta(\vec{r}_{aA})\right|\phi_{el}\right\rangle_{el}, \quad (41)$$

where $\lambda_C = 386.159\,264\,59$ fm is the Compton wavelength over 2π and $r_{ch}(A)$ is the root mean square charge radius of the nuclei A, with values of $r_{ch}(p) = 0.8768(69)$ fm and $r_{ch}(d) = 2.1402(28)$ fm.[17,18] For the dissociation energy of the ground rovibrational level this effect is quite small and amounts to $-0.000\,119$ cm^{-1} with tendency to diminish to zero for higher levels.

The leading order QED correction is given by[19]

$$\mathscr{E}^{(3)}(R) = \alpha^3\sum_{a<b}\left\{\left[\frac{164}{15} + \frac{14}{3}\ln\alpha\right]\langle\phi_{el}|\delta(\vec{r}_{ab})|\phi_{el}\rangle_{el}\right.$$
$$\left.-\frac{7}{6\pi}\left\langle\phi_{el}\left|P\left(\frac{1}{r_{ab}^3}\right)\right|\phi_{el}\right\rangle_{el}\right\}$$
$$+ \alpha^3\sum_A\sum_a\left[\frac{19}{30} - 2\ln\alpha - \ln k_0\right]$$
$$\times\frac{4Z_A}{3}\langle\phi_{el}|\delta(\vec{r}_{aA})|\phi_{el}\rangle_{el}. \quad (42)$$

The numerical evaluation of $\mathscr{E}^{(3)}$ has been described in detail in ref. 1. We only mention here that this evaluation includes such terms as the Bethe logarithm $\ln k_0$ and the expectation value of the Araki–Sucher distribution $P(1/r^3)$.[20] As previously,[1] the higher order QED contribution[14] has been estimated by the corresponding one-loop electron self-energy correction

$$\mathscr{E}^{(4)}(R) \approx \pi\alpha^4\left(\frac{427}{96} - \ln 4\right)\sum_A\sum_a\langle\phi_{el}|\delta(\vec{r}_{aA})|\phi_{el}\rangle_{el}. \quad (43)$$

The large-R behaviour of the above relativistic and QED potentials has been determined using asymptotic constants reported in ref. 1 and 21.

The relativistic and QED corrections can be computed directly, as expectation values with the adiabatic wave function. It is more convenient and more accurate, however, to include them into the nonadiabatic Schrödinger eqn (22) by adding

pertinent radial functions into the $\mathscr{Y}(R)$ potential (23). In such an approach, the eigenvalue of the Schrödinger equation represents a total energy including all the mentioned finite nuclear mass, relativistic and QED effects.

VII. Computational details

The radial nonadiabatic eqn (22), apart from the clamped nuclei energy $\mathscr{E}_{el}$ and the adiabatic correction $\mathscr{E}_a$, involves $\mathscr{W}_{\|}$, $\mathscr{W}_\perp$, and the potentials $\delta\mathscr{E}_{na}$ and $\delta\mathscr{E}'_{na}$ in eqn (24). The numerical values for all but the last radial functions were obtained for H_2 and a simple rescaling by the first or second power of the reduced mass ratio converts them to the pertinent HD functions. For this reason, we shall omit a detailed description of how these functions were obtained, referring the reader to our previous work on H_2.[10,11] Below we give only basic information on these functions and then concentrate on the new terms which result from the nuclear mass asymmetry in HD.

The electronic energy, $\mathscr{E}_{el}$, used in this work is exactly the same as the one reported in ref. 1. Its analytic form is based on the energy points calculated by Sims and Hagstrom[22] using Hylleraas wave function and by Cencek[23] using an explicitly correlated Gaussian (ECG) wave function. The relative accuracy of these calculations is of the order of 10^{-12}, which corresponds to about 10^{-10} of the relative accuracy of the Born–Oppenheimer potential. The ground state dissociation energy obtained by numerically solving the adiabatic Schrödinger eqn (21) in the Born–Oppenheimer approximation with this analytic potential is 36401.93319 cm^{-1} (see also Table 1). Also the relativistic and QED corrections to the potential obtained for H_2 in ref. 1 apply directly to HD because they do not depend on the nuclear mass.

The adiabatic correction $\mathscr{E}_a$ has been evaluated analytically by means of a new method described in ref. 10 and 11. The radial function $\mathscr{E}_a$ previously obtained for H_2 has been rescaled to HD by the ratio of the reduced masses of nuclei $\mu_n^{H_2}/\mu_n^{HD}$

$$\mathscr{E}_a^{HD} = \frac{m_p + m_d}{2m_d}\mathscr{E}_a^{H_2} \quad (44)$$

and led to the adiabatic dissociation energy of the ground state equal to 36 406.18407 cm^{-1}.

Similarly, the nonadiabatic potentials $\delta\mathscr{E}_{na}$, $\mathscr{W}_{\|}$, and $\mathscr{W}_\perp$ were obtained for H_2 in ref. 11 and here are rescaled to HD by the square of the reduced mass ratio $\left(\frac{m_p+m_d}{2m_d}\right)^2$. Numerical

Table 1 Components of D_0 (in cm^{-1}) for the $v = 0$, $J = 0$ state of HD. Uncertainties of α^2 and α^3 come from the neglect of nuclear recoil corrections and that of α^4 from the approximate formula

Component	D_0
BO	36 401.9332(1)
Adiabatic correction	4.2509(1)
Nonadiabatic correction	0.3267(2)
α^0 subtotal	36 406.5108(2)
α^2 correction	−0.5299(4)
α^2 finite nuclear size correction	−0.0001(0)
$\alpha^0 + \alpha^2$ subtotal	36 405.9809(5)
α^3 correction	−0.1964(2)
α^4 correction	−0.0016(8)
Total	36 405.7828(10)

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values of the nuclear masses $m_p = 1836.152\,672\,47\ m_e$ and $m_d = 3670.482\,965\,4\ m_e$ used in this study are based on the CODATA 2006 compilation of fundamental physical constants[17] and were taken from the NIST Web Page.[18] The nuclear reduced mass of HD is $\mu_n = 1223.899\,2280\ m_e$ and the nuclear mass asymmetry parameter $\lambda = 1.360\,866\,544\,2 \times 10^{-4}\ m_e$.

The only newly evaluated function of R is the heteronuclear nonadiabatic correction $\delta\mathscr{E}'_{na}$, eqn (24), resulting from those terms of the Hamiltonian $\tilde{H}$, which contain λ [see eqn (14) and (15)]. $\delta\mathscr{E}'_{na}$ comprises three parts. The first part is analogous to the nuclear kinetic energy term in the adiabatic correction (20) and requires evaluation of the derivative of the electronic wave function over the nuclear variable $\vec{R}$. This differentiation can be accomplished with the help of the following formula[24]

$$\vec{\nabla}_R \phi_{el} = \vec{n}\, \frac{1}{(\mathscr{E}_{el} - H_{el})'} \frac{\partial V}{\partial R} \phi_{el} - \frac{i}{R} \vec{n} \times \vec{L}_n \phi_{el}. \quad (45)$$

In the above equation, the first term gives the parallel component and requires an additional basis set of $^1\Sigma_g^+$ symmetry to evaluate the reduced resolvent. The perpendicular component is obtained by evaluation of the expectation value of an operator resulting from the last term, which involves the nuclear angular momentum operator $\vec{L}_n = -i\vec{R} \times \vec{\nabla}_R$. Here we made use of the following identity valid for the Σ states: $\vec{L}_n \phi_{el} = -\vec{L}_{el} \phi_{el}$, where $\vec{L}_{el}$ is the electronic angular momentum operator $\vec{L}_{el} = -i\sum_a \vec{r}_a \times \vec{\nabla}_a$. In this new formulation, it is possible to avoid the involvement of Π symmetry functions—the perpendicular component is obtained directly from the electronic ground state wave function as

$$-\frac{1}{R^2} \langle \phi_{el} | L_{el}^2 | \phi_{el} \rangle_{el}. \quad (46)$$

The second part of $\delta\mathscr{E}'_{na}$ contains operators which are difficult in numerical evaluation, so we transform it to a more convenient form using the following identity

$$\nabla_R^i \nabla_R^j (V) = (\nabla_R^i \nabla_R^j - \nabla_{el}^i \nabla_{el}^j)(V) + \nabla_{el}^i \nabla_{el}^j (V). \quad (47)$$

The first term on the right hand side of eqn (47) is

$$(\nabla_R^i \nabla_R^j - \nabla_{el}^i \nabla_{el}^j)(V) = \frac{3R^i R^j - \delta^{ij} R^2}{R^5} - \frac{4\pi}{3} \delta^{ij} \delta^3(R), \quad (48)$$

(the $\delta^3(R)$ part can be neglected), while the second term is evaluated using integration by parts

$$\langle \phi_{el} | r^i r^{j'} \nabla_{el}^i \nabla_{el}^j (V) | \phi_{el} \rangle_{el} = \int d\vec{r}\, V \nabla_{el}^i \nabla_{el}^j (r^i r^{j'} \phi_{el}^2). \quad (49)$$

The third part of the heteronuclear nonadiabatic correction

$$\delta\mathscr{E}'_{na},$$

eqn (24), is again a second order quantity, which requires evaluation of the resolvent in the basis set of $^1\Sigma_u^+$ symmetry.

All these expectation values as well as the second order quantities were evaluated in the basis of exponentially correlated Gaussians (ECG) functions[25]

$$\psi_k(\vec{r}_1, \vec{r}_2) = (1 + \hat{P}_{12})(1 \pm \hat{i})\Xi$$
$$\times \exp\left[-\sum_{i,j=1}^2 A_{k,ij}(\vec{r}_i - \vec{s}_{k,i})(\vec{r}_j - \vec{s}_{k,j})\right], \quad (50)$$

where the matrices $\mathbf{A}_k$ and vectors $\vec{s}_k$ contain nonlinear parameters, 5 per basis function, to be variationally optimized with respect to either the electronic energy or pertinent Hylleraas functional. The antisymmetry projector $(1 + \hat{P}_{12})$ ensures singlet symmetry, the spatial projector $(1 \pm \hat{i})$ ensures the gerade $(+)$ or ungerade $(-)$ symmetry, and the Ξ_k prefactor enforces Σ states when equal to 1, or Π states when equal to y_i (the perpendicular Cartesian component of the electron coordinate). For the second order matrix elements we generated a 600-term ECG basis set of $^1\Sigma_g^+$ or $^1\Sigma_u^+$ symmetries. The nonlinear parameters of this basis were optimized by minimizing the functional corresponding to this matrix element.

Finally, the total potential $\mathscr{Y}$ in the Schrödinger eqn (22) reads

$$\mathscr{Y}(R) = \mathscr{E}_{el}(R) + \mathscr{E}_a(R) + \delta\mathscr{E}_{na}(R) + \delta\mathscr{E}'_{na}(R) + \mathscr{E}^{(2)}(R)$$
$$+ \mathscr{E}_{fs}(R) + \mathscr{E}^{(3)}(R) + \mathscr{E}^{(4)}(R). \quad (51)$$

All its components were shifted by subtracting corresponding atomic values (see section V and ref. 1) so that they asymptotically tend to zero.

VIII. Results and discussion

Table 1 shows the dissociation energy of the ground rovibrational level decomposed into all the known significant contributions. Particular corrections have been computed as a difference between the eigenvalues obtained adding successively corresponding contributions to the potential $\mathscr{Y}$, eqn (51). For instance, the α^2 relativistic correction has been evaluated from two eigenvalues: one obtained with $\mathscr{Y} = \mathscr{E}_{el} + \mathscr{E}_a + \delta\mathscr{E}_{na} + \delta\mathscr{E}'_{na} + \mathscr{E}^{(2)}$ and the other with $\mathscr{Y} = \mathscr{E}_{el} + \mathscr{E}_a + \delta\mathscr{E}_{na} + \delta\mathscr{E}'_{na}$. Relativistic and QED corrections can also be obtained without the nonadiabatic potential $\delta\mathscr{E}_{na} + \delta\mathscr{E}'_{na}$. The difference for the ground state is quite small 10^{-6} cm^{-1}, however for excited states the difference can be larger.

There are several possible sources of the uncertainty in the final dissociation energy. The three dominating are (i) the missing relativistic and QED recoil terms of $\mathcal{O}(m_e/M)$, (ii) the neglect of the nonadiabatic terms of $\mathcal{O}[(m_e/\mu_n)^3]$, and (iii) the approximate treatment of the α^4 contribution. Although the formulas for the omitted relativistic recoil terms are explicitly known,[24] no numerical calculations have been performed so far. The error caused by the neglect of this term can be estimated as m_e/μ_n times the α^2 correction (see ref. 1) and, analogously, times the α^3 correction to account for the missing QED recoil term. For D_0 of the ground rovibronic level these two contributions are 0.00043 cm^{-1} and 0.00016 cm^{-1}, respectively. In a similar fashion, the contribution to the error budget from the missing higher order nonadiabatic terms can be approximated as proportional to m_e/μ_n times the second order nonadiabatic correction, which amounts to 0.00026 cm^{-1} at the ground level. The last meaningful part of the uncertainty results from the incomplete treatment of the higher order QED effects. As previously, (ref. 1) we conservatively estimate that the terms omitted in $\mathscr{E}^{(4)}$, eqn (43), contribute ca. 50% of the one-loop term, which yields 0.0008 cm^{-1} of the uncertainty.

The quadratic sum of these four error components leads to the overall uncertainty on the ground state D_0 of less then 0.0010 cm^{-1}. For the rotationally and vibrationally excited levels, the uncertainty changes in accord with the size of the corrections. Its estimation for individual levels is listed in the ESI.† In total, there are 400 bound levels with the vibrational quantum number v ranging from 0 to 17. The number of the rotational levels decreases with growing v from 37 for $v = 0$ to only 2 in the highest $v = 17$ state. The full set of the total dissociation energies is presented in Table 5. Moreover, a detailed specification, similar to that in Table 1, has been prepared for each bound rovibrational level and is available in the ESI.† For each combination of the vibrational and rotational quantum numbers there are 8 entries corresponding to: six components of the dissociation energy, the total D_0, and the estimated uncertainty of the total D_0. The six components of the total D_0 are, respectively: the Born–Oppenheimer, adiabatic, nonadiabatic, α^2 relativistic (including finite nuclear size), α^3 QED, and α^4 QED.

Table 2 assembles several experimental and theoretical nonadiabatic values of D_0 obtained over the years for the ground rovibrational level. More details on the progress in determining the dissociation energy of HD can be found in a brief review by Stoicheff.[26] The first variational nonadiabatic calculation for HD has been performed by Bishop and Cheung.[8] They used 858 basis functions, each being a product of an electronic James–Coolidge function and some radial Gaussian-type function, and obtained the nonrelativistic $D_0 = 36\,405.97$ cm^{-1} with an estimated convergence error of 0.28 cm^{-1}. Approximate relativistic (-0.54 cm^{-1}) and radiative (-0.22 cm^{-1}) corrections completed the dissociation energy to the value displayed in Table 2.

A more accurate relativistic dissociation energy of the HD molecule was first obtained by Wolniewicz[27] in 1983, and later by Kołos and coworkers.[28,29] In 1995 Wolniewicz has markedly improved his electronic wave functions and refined the final dissociation energy to get 36 405.787 cm^{-1} shown in Table 2. This value differs from ours by a few thousands of a wave number in accord with the uncertainty estimated by Wolniewicz. Concerning the QED correction to the ground

state D_0 we mention the old but very good estimation -0.197 cm^{-1} by Ladik.[30] It agrees surprisingly well with the current rigorous result, see Table 1.

Last year, Stanke et al.[9] performed new variational nonadiabatic calculation employing 10 000 explicitly correlated Gaussian basis functions. Their nonrelativistic total energy of $-1.165\,471\,922\,0(20)$ E_{h}, when subtracted from the sum of the atomic nonadiabatic energies, eqn (34), yields $D_0 = 36\,406.5105$ cm^{-1} in good agreement with our nonrelativistic subtotal value in Table 1 (the difference is 0.0003(2) cm^{-1}). Their relativistic correction computed with the nonadiabatic wave function is $-1.089\,307 \times 10^{-5}$ E_{h}. Because the corresponding atomic limit ($-\alpha^2/4$ E_{h}) is known to a high accuracy (the leading order recoil term vanishes), the relativistic D_0 can be inferred from this data as equal to 36 405.9794 cm^{-1}. We note here that now the discrepancy increases to 0.0012(5) cm^{-1} in comparison with our relativistic result. If this difference were attributed to the relativistic recoil contribution, it would be almost 3 times larger than the conservative estimate of this effect discussed above.

Table 2 also collects dissociation energies determined experimentally. The first measurement of D_0 for HD was performed by Herzberg and Monfils in 1960[31] yielding 36 400.5 cm^{-1}. Motivated by a discrepancy with the famous theoretical results by Kołos and Wolniewicz,[32] Herzberg repeated his experiment[33,34] using an improved apparatus and established $D_0 = 36\,406.2(4)$ cm^{-1} shown in Table 2.

Table 3 Comparison of theoretical and experimental results for the energy difference ΔE (in cm^{-1}) between $v = 0$ and $v = 1$ rotationless states of HD. δ is a difference from our result

Source	ΔE	δ
This work	3632.1604(5)	
Theory		
Stanke et al. (2009)[9]	3632.1614^a	0.0010
Wolniewicz (1995)[43]	3632.161	0.001
Kołos and Rychlewski (1993)[29]	3632.161	0.001
Experiment		
Stanke et al. (2009)[9]	3632.1595(17)^b	-0.0009
Rich et al. (1982)[44]	3632.159(6)^c	-0.001
McKellar et al. (1976)[45]	3632.152(9)^c	-0.008

^{a} The original $\Delta E = 3632.1802$ cm^{-1} from ref. 9 has been augmented by a sum of our α^3 and α^4 QED corrections equal to -0.0187 cm^{-1}. ^{b} 1σ uncertainty. ^{c} 3σ uncertainty.

Table 2 Comparison of theoretical and experimental results for D_0 (in cm^{-1}) of the $v = 0$, $J = 0$ state of HD. δ is a difference from our result

Component	D_0	δ
This work	36 405.7828(10)	
Theory		
Stanke et al. (2009)[9]	36 405.7814^a	-0.0014
Wolniewicz (1995)[43]	36 405.787	0.004
Kołos and Rychlewski (1993)[29]	36 405.763	-0.020
Kołos, Szalewicz, Monkhorst (1986)[28]	36 405.784	0.001
Wolniewicz (1983)[27]	36 405.73	0.05
Bishop and Cheung (1978)[8]	36 405.49	-0.29
Experiment		
Zhang et al. (2004)[38]	36 405.828(16)	0.045
Balakrishnan et al. (1993)[37]	36 405.83(10)	0.05
Eyler and Melikechi (1993)[35]	36 405.88(10)	0.10
Herzberg (1970)[33,34]	36 406.2(4)	0.4

^{a} The original $D_0 = 36\,405.9794$ cm^{-1} from ref. 9 has been augmented by a sum of our α^3 and α^4 QED corrections equal to -0.1980 cm^{-1}.

Table 4 Components of theoretically predicted transition energy ΔE between $J = 0$ and $J = 1$, and between $J = 0$ and $J = 2$ rotational levels of the ground vibrational state ($v = 0$) of HD. All entries in cm^{-1}

Component	$\Delta E(0 \to 1)$	$\Delta E(0 \to 2)$
BO	89.270 629	267.196 840
Adiabatic correction	$-0.036\,086$	$-0.107\,842$
Nonadiabatic correction	$-0.007\,782(6)$	$-0.023\,287(19)$
α^0 subtotal	89.226 761(6)	267.065 711(19)
α^2 correction	0.001 948(2)	0.005 813(5)
$\alpha^0 + \alpha^2$ subtotal	89.228 709(6)	267.071 524(20)
α^3 correction	$-0.000\,771(1)$	$-0.002\,303(2)$
α^4 correction	$-0.000\,007(4)$	$-0.000\,018(9)$
Total	89.227 933(8)	267.069 205(22)
Experiment[46,47]	89.227 950(5)	267.086(10)

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Table 5 Dissociation energy (in cm⁻¹) of all 400 bound states of HD. v and J are the vibrational and rotational quantum numbers, respectively

v/J	0	1	2	3	4	5	6	7	8	9	10	11	12
0	36405.7828	36316.5549	36138.7136	35873.4735	35522.6205	35088.4710	34573.8214	33981.8890	33316.2492	32580.7701	31779.5467	30916.8389	29997.0121
1	32773.6224	32688.2505	32518.1034	32264.3604	31928.7546	31513.5337	31021.4092	30455.4998	29819.2695	29116.4637	28351.0463	27527.1389	26648.9644
2	29318.9058	29237.3125	29074.7056	28832.2304	28511.5704	28114.9074	27644.8730	27104.1260	26497.1260	25826.4033	25096.1664	24310.4092	23473.2237
3	26038.1525	25960.2800	25805.0987	25573.7219	25267.7856	24889.4100	24441.1515	23925.9482	23347.0616	22708.0166	22012.5422	21264.5155	20467.9102
4	22928.8940	22854.7061	22706.8788	22486.4954	22195.1476	21834.8977	21408.2320	20918.0081	20367.3975	19759.8282	19098.9275	18388.4681	17632.3192
5	19989.7501	19919.2343	19778.7372	19569.3140	19292.5156	18950.3510	18545.2424	18079.9739	17557.6361	16981.5705	16355.3151	15682.5527	14967.0643
6	17220.5367	17153.7075	17020.5709	16822.1567	16559.9785	16235.9975	15852.5788	15412.4415	14918.6057	14374.3390	13783.1048	13148.5131	12474.2769
7	14622.4158	14559.3194	14433.6367	14246.3756	13999.0170	13693.4808	13332.0831	12917.4886	12452.6597	11940.8057	11385.3335	10789.8022	10157.8828
8	12198.0988	12138.8186	12020.7590	11844.9092	11612.7237	11326.0890	10987.2827	10598.9285	10163.9474	9685.5103	9166.9919	8611.9292	8023.9861
9	9952.1180	9896.7836	9786.6084	9622.5684	9406.0989	9139.0636	8823.7159	8462.6556	8058.7844	7615.2618	7135.4634	6622.9449	6081.4127
10	7891.1923	7839.9908	7738.0776	7586.4219	7386.4504	7140.0186	6849.3743	6517.1183	6146.1638	5739.6971	5301.1434	4834.1375	4342.5051
11	6024.7189	5977.9115	5884.5187	5746.3189	5563.9384	5339.5138	5075.3150	4773.9795	4438.4781	4072.0831	3678.3444	3261.0743	2824.3466
12	4365.4408	4323.3876	4239.7798	4115.6059	3952.3271	3751.8548	3516.5234	3249.0634	2952.5769	2630.5204	2286.6991	1925.2806	1550.8364
13	2930.3661	2893.5633	2820.4750	2712.1287	2570.0495	2396.2435	2193.1810	1963.7825	1711.4152	1439.9049	1153.5779	857.3517	556.9166
14	1742.0495	1711.1919	1650.0313	1559.6737	1441.7714	1298.5202	1132.6624	947.5072	746.9799	535.7292	319.3516	104.8977	
15	830.4030	806.5001	759.3242	690.1412	600.8685	494.1095	373.2271	242.4988	107.4717				
16	235.0929	219.7427	189.8566	147.1120	94.1833	35.1032							
17	3.6424		0.4156										

v/J	13	14	15	16	17	18	19	20	21	22	23	24	25
0	29024.4839	28003.6768	26938.9769	25834.6998	24695.0621	23524.1599	22325.9517	21104.2469	19862.6992	18604.8024	17333.8914	16053.1441	14765.5876
1	25720.7960	24746.9115	23731.5555	22678.9061	21593.0497	20477.9601	19337.4841	18175.3317	16995.0699	15800.1215	14593.7664	13379.1463	12159.2718
2	22588.7509	21661.1387	20694.5047	19692.9066	18660.3180	17600.6100	16517.5390	15414.7380	14295.7132	13163.8441	12022.3880	10874.4865	9723.1764
3	19626.7494	18745.0660	17826.8681	16876.1114	15896.6776	14892.3583	13866.8443	12823.7206	11766.4648	10698.4508	9622.9561	8543.1737	7462.2285
4	16834.4021	15998.6523	15128.9885	14229.2866	13303.3617	12354.9540	11387.7220	10405.2397	9411.0003	8408.4239	7400.8713	6391.6642	5384.1125
5	14212.6878	13423.2833	12602.7041	11754.7747	10883.2755	9991.9332	9084.4176	8164.3445	7235.2859	6300.7862	5364.3875	4429.6661	3500.2837
6	11764.1743	11022.0166	10251.6236	9456.8054	8641.3516	7809.0275	6963.5779	6108.7389	5248.2595	4385.9352	3525.6567	2671.4828	1827.7489
7	9493.3238	8799.9242	8081.5132	7341.9385	6585.0622	5814.7666	5034.9701	4249.6560	3462.9182	2679.0314	1902.5582	1138.5187	392.6763
8	7406.9236	6764.5794	6100.8550	5419.7136	4725.1884	4021.4061	3312.6267	2603.3098	1898.2188	1202.5889	522.4130		
9	5514.7025	4926.7680	4321.6815	3703.6489	3077.0439	2446.4679	1816.8504	1193.6140	582.9620				
10	3830.2546	3301.5839	2760.9064	2212.9053	1662.6275	1115.6479	578.3592	58.5350					
11	2372.5158	1910.2635	1442.6887	975.4703	515.1674	69.8220							
12	1168.4295	783.7811	403.5930	36.2340									
13	259.1098												

v/J	26	27	28	29	30	31	32	33	34	35	36
0	13474.1053	12181.4463	10890.2366	9602.9923	8322.1343	7050.0050	5788.8882	4541.0321	3308.6771	2094.0906	899.6125
1	10937.0326	9715.2096	8496.4896	7283.4834	6078.7473	4884.8089	3704.1998	2539.4972	1393.3807	268.7111	
2	8571.4037	7422.0415	6277.9114	5141.8124	4016.5555	2905.0113	1810.1737	735.2519			
3	6383.1991	5309.1459	4243.1485	3188.3557	2148.0549	1125.7723	125.4269				
4	4381.5521	3387.3960	2405.2063	1438.8004	492.4142						
5	2580.0600	1673.0818	783.8704								
6	999.2369	191.4601									

This value, however, is in fact an arithmetic mean of two independent measurements: 36 405.8 cm^{-1} and 36 406.6 cm^{-1}, the former being very close to our value. In 1993, Eyler and Melikechi[35] determined the dissociation threshold from the EF $^1\Sigma_g^+$ state and, in combination with the spectra measured by Diecke,[36] obtained $D_0 = 36\ 405.88(10)$ cm^{-1}. At the same time, Balakrishnan et al.[37] performed a delayed detection of the fluorescence spectrum of photodissociated hydrogen and arrived at $D_0 = 36\ 405.83(10)$ cm^{-1}. These results, although systematically larger, are in agreement within their uncertainties with current theoretical predictions. An order of magnitude more accurate measurements were reported by the Eyler group in 2004.[38] In a three-step experiment aiming at determination of the second dissociation threshold they obtained $D_0 = 36\ 405.828(16)$ cm^{-1}. This result is 3σ away from our theoretical value. In view of an increased precision on both the experimental and theoretical side it must be stated that currently there is a discrepancy of ca. 0.05 cm^{-1} in the determination of D_0 for HD.

Accuracy of the present results can also be assessed by comparison of the energy difference corresponding to the lowest rotationless vibrational transition with the available literature data (see Table 3). The most accurate theoretical predictions by Wolniewicz and by Kołos and Rychlewski as well as the experimental data are in very good agreement with the present result 3632.1604(5) cm^{-1}. Here, we estimated the uncertainty in the same way as for the dissociation energy (see above) i.e. assuming that the error components are proportional to corresponding corrections.

In contrast to the homonuclear isotopomers, the electric dipole transitions between the lowest rotational states of HD are allowed and the transition energy can, in principle, be measured directly. In Table 4 we present values of all significant contributions to the lowest $J = 0 \rightarrow 1, 2$ transition energies and compare with the available experimental data – we note a 2σ difference between the theory and measurements.

The ionization potential (IP) of HD can be related to its dissociation energy by

$$\text{IP} = D_0(\text{HD}) - E(\text{H}) - D_0(\text{HD}^+). \quad (52)$$

Since the dissociation energy of HD$^+$, as well as the total energy of the hydrogen atom, is known very accurately, we can evaluate IP with an accuracy adequate to that of $D_0(\text{HD})$. Up-to-date values of $E(\text{H}) = -109\ 678.7717$ cm^{-1} and $D_0(\text{HD}^+) = 21\ 516.069\ 60$ cm^{-1} have been compiled by Liu et al.[3] on the basis of current fundamental constants[17] and calculations by Korobov.[39,40] IP computed for HD from the above formula amounts to 124 568.4849(10) cm^{-1} with the uncertainty transferred directly from D_0.

IX. Conclusion

The high accuracy of 0.001 cm^{-1} for the theoretically predicted dissociation energy of H$_2$ and isotopomers has been achieved due to the recent progress made in two directions. The first one, enabled a complete treatment of the leading QED effects. In particular, the approach to effectively calculate the many electron Bethe logarithm and mean values of singular operators, like the Araki–Sucher term, has been developed.[1,41,42] The second direction, indispensable for reaching this accuracy, is the nonadiabatic perturbation theory,[10,11,24] which enables a rigorous approach to the finite nuclear mass effects beyond the adiabatic approximation. However, an accurate nonadiabatic correction to relativistic contribution still remains to be evaluated.

In comparison of theoretical predictions with recent experimental results we observe a very good agreement for dissociation energies of H$_2$ and D$_2$, and a small discrepancy of 0.045(16) cm^{-1} for HD. Therefore, a new measurement with an increased precision of dissociation and transition energies of HD molecule would be very desirable.

Note added in proof

After submitting this paper we became aware of a new measurements of HD dissociation energy [D. Sprecher, J. Liu, C. Jungen, W. Ubachs, F. Merkt, 2010, to be published]. The new value of $D_0 = 36405.78366(36)$ cm^{-1} is in a very good agreement with our theoretical prediction.

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