

Quantum Electrodynamics Effects in Rovibrational Spectra of Molecular Hydrogen

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 Supporting Information

ABSTRACT: The dissociation energies from all rovibrational levels of H₂ and D₂ in the ground electronic state are calculated with high accuracy by including relativistic and quantum electrodynamics (QED) effects in the nonadiabatic treatment of the nuclear motion. For D₂, the obtained energies have theoretical uncertainties of 0.001 cm⁻¹. For H₂, similar uncertainties are for the lowest levels, while for the higher ones the uncertainty increases to 0.005 cm⁻¹. Very good agreement with recent high-resolution measurements of the rotational $\nu = 0$ levels of H₂, including states with large angular momentum J , is achieved. This agreement would not have been possible without accurate evaluation of the relativistic and QED contributions and may be viewed as the first observation of the QED effects, mainly the electron self-energy, in a molecular spectrum. For several electric quadrupole transitions, we still observe certain disagreement with experimental results, which remains to be explained.

1. INTRODUCTION

Due to its simplicity, the hydrogen molecule and its isotopomers D₂ and HD are natural benchmark systems for testing various computational and experimental approaches in molecular spectroscopy. The measurements of their rovibrational levels have reached such a precision level^{1–4} that not only the nonadiabatic and the leading relativistic effects but also quantum electrodynamics (QED) and possibly finite nuclear size corrections become important. In this work, we exploit recent theoretical progress in calculating the spectra of H₂ and D₂ using explicitly correlated basis sets built of Gaussian or exponential functions. For the latter, exact analytic formulas have recently been derived,⁵ making possible the calculation of the Born–Oppenheimer potential with an uncertainty smaller than 10⁻⁹ cm⁻¹. The finite nuclear mass effects are calculated using nonadiabatic perturbation theory (NAPT).^{6,7} In this approach, leading nonadiabatic corrections are obtained by solving a suitable modification of the radial Schrödinger equation for the nuclear motion. The advantage of this procedure is that three universal nonadiabatic potentials entering this equation are sufficient to obtain all rovibrational levels supported by a given electronic state. At the precision level adequate for the present purposes, the relativistic, QED, and finite nuclear size effects can be taken into account at the adiabatic level of theory and included by means of appropriate corrections to the Born–Oppenheimer potential. These corrections are expectation values of the Breit–Pauli Hamiltonian,⁸ or effective QED operators,⁹ computed with the clamped nuclei nonrelativistic electronic wave function. Our approach is based on the expansion of energy levels in powers of fine structure constant α ,^{10,11} which was originally developed for hydrogenic systems and applied in highly accurate calculations for light atoms.^{12–15}

2. HISTORICAL PERSPECTIVE

A meaningful confrontation of theoretically predicted rovibrational levels with high-resolution spectroscopy measurements became possible in 1983 with the appearance of the pioneering work of Wolniewicz,¹⁶ who accurately computed the nonadiabatic corrections to all vibrational levels of H₂, HD, and D₂. For the H₂ molecule, Wolniewicz observed a significant disagreement of up to 0.7 cm⁻¹ with the experimental vibrational excitation energies available at that time.¹⁷ In a subsequent development, Kolos et al.¹⁸ recomputed the Born–Oppenheimer potential for H₂, obtaining the adiabatic levels 0.1–0.2 cm⁻¹ below the Wolniewicz values. Using the nonadiabatic corrections from the Wolniewicz work, the authors of ref 18 obtained improved agreement (with errors up to 0.2–0.3 cm⁻¹) when compared with a more recent measurement of Dabrowski.¹⁹

The works of Wolniewicz¹⁶ and of Kolos et al.¹⁸ were based on the relativistic corrections computed in 1964²⁰ using a rather small basis (of James and Coolidge type²¹) and only for internuclear distances $R \leq 3.7$ bohr. To eliminate this source of uncertainty, Wolniewicz²² recomputed in 1993 the relativistic corrections for a wide range of distances employing a large, asymptotically correct basis set introduced in 1966 by Kolos and Wolniewicz.²³ To obtain the nonadiabatic corrections, Wolniewicz used an *ab initio* based scaling and extrapolation procedure proposed by Schwartz and LeRoy,²⁴ which he believed to be more reliable (except for $\nu = J = 0$) than his *ab initio* data of 1983.¹⁶ This work led to some improvement in agreement with the experimental vibrational spectrum

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of Dabrowski,¹⁹ as compared with the 1986 work of Kolos et al.¹⁸

As the method of Schwartz and LeRoy²⁴ had not been performing very satisfactorily in some applications, especially in the cases of HD and HT,²⁵ in 1995 Wolniewicz²⁶ recomputed the nonadiabatic corrections obtaining significantly more accurate values for higher vibrational levels. This resulted in further improvement of the agreement with the vibrational quanta of ref 19. It is difficult to say how significant this improvement was, since the disagreement with the experimental results of Dabrowski¹⁹ was on the last digit reported by her and the corresponding experimental uncertainty is not clear.

According to Wolniewicz,²⁶ the main source of uncertainty of his results is the QED corrections, which he evaluated only approximately. These corrections are accurately taken into account in the present calculations, with all α^3 and the leading α^4 terms included (α is the fine structure constant). Results for the ground rovibrational state (i.e., for the dissociation energy) of H₂ and D₂ have already been presented by us in ref 27 and for HD in ref 28. Very recently, Salumbides et al.²⁹ reported highly accurate experimental values of the rotational energies of $v = 0$ levels of H₂. The uncertainty of the majority of these levels ranges from 0.0001 cm⁻¹ up to 0.005 cm⁻¹. Such an accuracy, in connection with our calculations, is sufficient to determine the magnitude of QED effects directly from the measurements. It should be noted that QED corrections have also been treated for more complex systems, such as the water molecule,³⁰ but using an approximate one-electron approach; thus not all of the α^3 terms were taken into account. However, for such systems, the nonrelativistic treatment of the spectrum is still not accurate enough to see QED effects in a head-on comparison between theory and experiment.³¹

3. THE NONADIABATIC SCHRÖDINGER EQUATION

The nonrelativistic Schrödinger equation is solved using the NAPT approach.^{6,7} For electronic states of Σ symmetry, the zeroth-order approximation to the total wave function can be assumed to be a product of the electronic ϕ_{el} and nuclear χ functions (atomic units will be used throughout):

$$\phi_a(\vec{r}, \vec{R}) = \phi_{\text{el}}(\vec{r}; \vec{R}) \chi(\vec{R}) \quad (1)$$

The electronic wave function ϕ_{el} satisfies the clamped nuclei Schrödinger equation:

$$[H_{\text{el}} - \mathcal{E}_{\text{el}}(R)]\phi_{\text{el}} = 0 \quad (2)$$

where H_{el} is the electronic Hamiltonian, and thus parametrically depends on the internuclear distance R . The function χ satisfies the nuclear Schrödinger equation

$$\left[-\frac{\nabla_{\vec{R}}^2}{2\mu_{\text{n}}} + \mathcal{E}_{\text{el}}(R) + \mathcal{E}_{\text{a}}(R) \right] \chi(\vec{R}) = E_a \chi(\vec{R}) \quad (3)$$

with μ_{n} being the nuclear reduced mass, and the adiabatic correction $\mathcal{E}_{\text{a}}(R)$ is given by the electronic matrix element

$$\mathcal{E}_{\text{a}}(R) = \langle \phi_{\text{el}} | H_{\text{n}} | \phi_{\text{el}} \rangle_{\text{el}} \quad (4)$$

of the nuclear part $H_{\text{n}} = H - H_{\text{el}}$ of the total Hamiltonian H (the brackets $\langle \dots \rangle_{\text{el}}$ denote integration over the electronic coordinates only). For specified angular momentum J , the nuclear

equation becomes

$$\left[-\frac{1}{R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{J(J+1)}{2\mu_{\text{n}} R^2} + \mathcal{E}_{\text{a}}(R) + \mathcal{E}_{\text{el}}(R) \right] \chi_J(R) = E_a \chi_J(R) \quad (5)$$

Using NAPT,^{6,7} all of the finite nuclear mass corrections are obtained perturbatively in progressive powers of the electron–nuclear mass ratio. Up to the order $\mathcal{O}(\mu_{\text{n}}^{-2})$, they can all be included in the following radial equation as an R -dependent modification of the effective nuclear reduced mass and of the interaction potential:

$$\left[-\frac{1}{R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{J(J+1)}{2\mu_{\perp}(R) R^2} + \mathcal{Y}(R) \right] \tilde{\chi}_J(R) = E \tilde{\chi}_J(R) \quad (6)$$

where

$$\mathcal{Y}(R) = \mathcal{E}_{\text{el}}(R) + \mathcal{E}_{\text{a}}(R) + \delta \mathcal{E}_{\text{na}}(R) \quad (7)$$

The modifications of the effective nuclear reduced mass are of the form

$$\frac{1}{2\mu_{\parallel}(R)} \equiv \frac{1}{2\mu_{\text{n}}} + \frac{1}{\mu_{\text{n}}^2} \left\langle \vec{n} \cdot \vec{\nabla}_R \phi_{\text{el}} \left| \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})^{\prime}} \right| \vec{n} \cdot \vec{\nabla}_R \phi_{\text{el}} \right\rangle_{\text{el}} \quad (8)$$

and

$$\frac{1}{2\mu_{\perp}(R)} \equiv \frac{1}{2\mu_{\text{n}}} + \frac{1}{\mu_{\text{n}}^2} \sum_{ij} \frac{(\delta^{ij} - n^i n^j)}{2} \left\langle \nabla_R^i \phi_{\text{el}} \left| \frac{1}{\mathcal{E}_{\text{el}} - H_{\text{el}}} \right| \nabla_R^j \phi_{\text{el}} \right\rangle_{\text{el}} \quad (9)$$

with $\vec{n} = \vec{R}/R$ and the *prime* in the resolvent indicating the orthogonalization to ϕ_{el} . The concept of the variable nuclear reduced mass has been present in the literature for a long time now,^{32–35} and NAPT supplies explicit formulas for their numerical evaluation. The nonadiabatic correction $\delta \mathcal{E}_{\text{na}}(R)$ to the interaction potential can also be expressed in terms of the second-order electronic matrix elements. Since the corresponding formula is rather complicated, we refer the reader to refs 6 and 7 for its detailed form. The main advantage of the presented approach is that a single radial equation (eq 6) gives quite accurately all (nonrelativistic) rovibrational states of a diatomic molecule. In the present implementation of NAPT, the computational precision is limited by neglected $\mathcal{O}(\mu_{\text{n}}^{-5/2})$ corrections, which for the dissociation energy of the lowest rovibrational state are estimated to amount about 0.0001 cm⁻¹. Other important corrections are considered in the following section.

4. RELATIVISTIC AND QED CORRECTIONS

When computed using the adiabatic wave function of eq 1, the leading-order relativistic, QED, and finite nuclear size corrections enter only through an effective potential $\mathcal{V}(R)$, namely

$$\mathcal{V}(R) = \mathcal{E}_{\text{el}}(R) + \mathcal{E}_{\text{a}}(R) + \delta\mathcal{E}_{\text{na}}(R) + \mathcal{E}^{(2)}(R) + \mathcal{E}^{(3)}(R) + \mathcal{E}^{(4)}(R) + \mathcal{E}_{\text{fs}}(R) \quad (10)$$

The relativistic correction $\mathcal{E}^{(2)}(R)$ is the electronic expectation value of the Breit–Pauli Hamiltonian,⁸ which for a Σ state of a many-electron molecule is

$$\mathcal{E}^{(2)}(R) = \alpha^2 \left\langle \phi_{\text{el}} \left| -\frac{1}{8} \sum_a p_a^4 + \frac{\pi}{2} \sum_{a,A} Z_A \delta(\vec{r}_{aA}) + \pi \sum_{a < b} \delta(\vec{r}_{ab}) - \frac{1}{2} \sum_{a < b} \left(\vec{p}_a \frac{1}{r_{ab}} \vec{p}_b + \vec{p}_a \cdot \vec{r}_{ab} \frac{1}{r_{ab}^3} \vec{r}_{ab} \cdot \vec{p}_b \right) \right| \phi_{\text{el}} \right\rangle \quad (11)$$

where the indices a and A correspond to electrons and nuclei, respectively.

The leading QED correction for a Σ state is

$$\mathcal{E}^{(3)}(R) = \alpha^3 \sum_{a < b} \left\{ \left[\frac{164}{15} + \frac{14}{3} \ln \alpha \right] \langle \phi_{\text{el}} | \delta(\vec{r}_{ab}) | \phi_{\text{el}} \rangle_{\text{el}} - \frac{7}{6\pi} \left\langle \phi_{\text{el}} \left| \frac{1}{r_{ab}^3} \right| \phi_{\text{el}} \right\rangle_{\text{el}} \right\} + \alpha^3 \sum_{a,A} \left[\frac{19}{30} - 2 \ln \alpha - \ln k_0(R) \right] \frac{4Z_A}{3} \langle \phi_{\text{el}} | \delta(\vec{r}_{aA}) | \phi_{\text{el}} \rangle_{\text{el}} \quad (12)$$

The matrix element of $1/r_{ab}^3$ requires subtraction of a divergence at $r_{ab} = 0$; for details, see ref 9. In the adiabatic approximation, the R -dependent Bethe logarithm $\ln k_0(R)$ is defined by²⁷

$$\ln k_0(R) = \frac{\langle \phi_{\text{el}} | \sum_a \vec{p}_a (H_{\text{el}} - \mathcal{E}_{\text{el}}) \ln[2(H_{\text{el}} - \mathcal{E}_{\text{el}})] \sum_b \vec{p}_b | \phi_{\text{el}} \rangle}{\langle \phi_{\text{el}} | \sum_a \vec{p}_a (H_{\text{el}} - E_{\text{cl}}) \sum_b \vec{p}_b | \phi_{\text{el}} \rangle} \quad (13)$$

The α^4 and higher-order QED corrections^{36,37} are in general not known for molecules. One can however approximate them by the numerically dominating one-loop self-energy and vacuum polarization corrections known from the hydrogenic Lamb shift:³⁶

$$\mathcal{E}_{\text{one-loop}}^{(4)}(R) = \pi\alpha^4 \left(\frac{427}{96} - \ln 4 \right) \sum_{a,A} Z_A \langle \phi_{\text{el}} | \delta(\vec{r}_{aA}) | \phi_{\text{el}} \rangle_{\text{el}} \quad (14)$$

On the basis of the atomic calculations,^{36,37} we conservatively estimate that this formula approximates the accurate value of $\mathcal{E}^{(4)}$ with an error of at most 50%.

The finite nuclear size correction $\mathcal{E}_{\text{fs}}(R)$ is given, to a very good approximation, by the root-mean-square nuclear charge radius r_{ch} :

$$\mathcal{E}_{\text{fs}}(R) = \frac{2\pi}{3} \alpha^2 \sum_{a,A} Z_A \frac{r_{\text{ch}}^2(A)}{\lambda_C^2} \langle \phi_{\text{el}} | \delta(\vec{r}_{aA}) | \phi_{\text{el}} \rangle_{\text{el}} \quad (15)$$

where $\lambda_C = 386.15926459$ fm is the Compton wavelength over 2π ($r_{\text{ch}}(\text{H}) = 0.84184(67)$ fm and $r_{\text{ch}}(\text{D}) = 2.1402(28)$ fm). For H_2 , the energy level shift resulting from this correction is always less than 0.0001 cm^{-1} , whereas for D_2 it amounts to only 0.0002 cm^{-1} or less. Nevertheless, in both cases, this correction has been included in our final results. According to our knowledge, there are no further corrections to the rovibrational energies which contribute above 0.001 cm^{-1} . The atomic hyperfine splittings are larger than that but are subtracted from the experimental dissociation energies. Recently reported³⁸ *gerade*–*ungerade* mixing and splitting effects in H_2 turned out to be smaller than 10^{-6} cm^{-1} and thus are entirely negligible for the present purposes.

5. NUMERICAL APPROACH

A very accurate clamped nuclei potential for the $X^1\Sigma_g^+$ state was reported recently in ref 5. For the whole energy curve, an accuracy on the order of 10^{-9} cm^{-1} has been reached. This is the most accurate potential to date for H_2 itself but also for any molecular system with two or more electrons. Increasing the accuracy to this level has been possible thanks to the discovery of analytic formulas for two-center two-electron integrals with exponential functions.³⁹ To achieve this high numerical accuracy, different basis sets were used, depending on the internuclear distance R . For $R < 12$ bohr, the James–Coolidge basis functions²¹ of the form

$$\psi_k(\vec{r}_1, \vec{r}_2) = (1 + \hat{P}_{12})(1 + \hat{i}) \exp(-\alpha(r_{1A} + r_{1B}) - \alpha(r_{2A} + r_{2B})) \times r_{12}^{n_{1k}} (r_{1A} - r_{1B})^{n_{2k}} (r_{2A} - r_{2B})^{n_{3k}} (r_{1A} + r_{1B})^{n_{4k}} (r_{2A} + r_{2B})^{n_{5k}} \quad (16)$$

have been employed. The symmetry projector $(1 + \hat{P}_{12})$ ensures a singlet state, while the spatial projector $(1 + \hat{i})$ ensures the *gerade* symmetry. Since in the actual numerical calculations one can use only a finite number of basis functions, one has to somehow select the most appropriate finite subset of functions of eq 16. We assumed, therefore, that the finite basis consists of all functions ψ_k with nonnegative integers n_{ik} such that

$$\sum_{i=1}^5 n_{ik} \leq \Omega \quad (17)$$

with $\Omega = 3-20$, and the final result is obtained by a numerical extrapolation with $\Omega \rightarrow \infty$. The nonlinear parameters were optimized separately for each internuclear distance R , and then the exponential convergence to a complete basis set as $\Omega \rightarrow \infty$ was observed.

To represent the electronic wave function at $12 \leq R \leq 20$ bohr, a special case of the Kolos and Wolniewicz basis⁴⁰ was used

$$\psi_k(\vec{r}_1, \vec{r}_2) = (1 + \hat{P}_{12})(1 + \hat{i}) \exp(-(r_{1A} + r_{2B})) r_{12}^{n_{1k}} r_{1A}^{n_{2k}} r_{1B}^{n_{3k}} r_{2A}^{n_{4k}} r_{2B}^{n_{5k}} \quad (18)$$

Table 1. Theoretically Predicted Dissociation Energies (in cm^{-1}) of All 302 Bound States of H_2^a

$\nu \setminus J$	0	1	2	3	4	5	6	7
0	36118.0696	35999.5827	35763.6964	35412.5507	34949.2721	34377.8800	33703.1726	32930.5991
1	31956.9034	31844.3290	31620.2311	31286.6781	30846.6902	30304.1479	29663.6809	28930.5440
2	28031.0670	27924.2753	27711.7087	27395.3676	26978.1720	26463.8724	25856.9411	25162.4519
3	24335.6787	24234.5818	24033.3726	23733.9878	23339.2543	22852.8015	22278.9563	21622.6265
4	20867.7039	20772.2598	20582.3263	20299.7818	19927.3669	19468.6008	18927.6785	18309.3586
5	17626.1400	17536.3593	17357.7260	17092.0653	16742.0411	16311.0741	15803.2433	15223.1787
6	14612.2901	14528.2461	14361.0627	14112.5194	13785.2138	13382.4836	12908.3120	12367.2247
7	11830.1543	11751.9964	11596.5661	11365.6062	11061.6626	10688.0095	10248.5600	9747.7694
8	9286.9790	9214.9526	9071.7726	8859.1575	8579.6206	8236.3999	7833.3746	7374.9763
9	6994.0292	6928.5057	6798.3271	6605.2057	6351.6504	6040.9022	5676.8602	5264.0027
10	4967.6786	4909.1996	4793.1191	4621.1702	4395.9005	4120.6166	3799.3225	3436.6592
11	3230.9712	3180.3202	3079.9265	2931.5894	2737.9677	2502.5403	2229.5680	1924.0695
12	1815.8955	1774.2213	1691.8517	1570.7364	1413.7847	1224.8610	1008.8062	771.5140
13	766.7551	735.8177	675.0810	586.8399	474.5979	343.1936	199.1012	51.2532
14	144.7964	127.6357	94.9453	50.2393	0.0265 ^b			
$\nu \setminus J$	8	9	10	11	12	13	14	15
0	32066.1266	31116.1067	30087.1493	28986.0061	27819.4682	26594.2780	25317.0575	23994.2505
1	28110.4874	27209.6288	26234.3321	25191.0967	24086.4605	22926.9171	21718.8492	20468.4759
2	24385.9548	23533.3534	22610.7880	21624.5312	20580.8960	19486.1590	18346.4985	17167.9474
3	20889.1803	20084.3279	19214.0114	18284.3049	17301.3289	16271.1794	15199.8715	14093.2980
4	17618.8479	16861.6882	16043.6518	15170.6479	14248.6434	13283.5982	12281.4160	11247.9099
5	14575.9499	13866.9601	13101.8471	12286.3973	11426.4734	10527.9578	9596.7126	8638.5554
6	11764.1860	11104.4981	10393.7108	9637.5433	8841.8215	8012.4332	7155.3007	6276.3735
7	9190.5379	8582.1192	7928.0390	7234.0292	6505.9792	5749.9080	4971.9605	4178.4321
8	6866.1012	6312.0299	5718.3612	5090.9637	4435.9509	3759.6871	3068.8309	2370.4348
9	4807.3140	4312.2229	3784.5601	3230.5444	2656.8077	2070.4770	1479.3467	892.2132
10	3037.8559	2608.7032	2155.5628	1685.4344	1206.1180	726.5520	257.5346	
11	1591.8264	1239.4455	874.5218	506.0045	145.0445			
12	520.1248	263.4848	13.3741					
$\nu \setminus J$	16	17	18	19	20	21	22	23
0	22632.0799	21236.5171	19813.2627	18367.7376	16905.0813	15430.1579	13947.5677	12461.6638
1	19181.8142	17864.6524	16522.5351	15160.7573	13784.3676	12398.1776	11006.7791	9614.5672
2	15956.3587	14717.3851	13456.4677	12178.8362	10889.5174	9593.3530	8295.0256	6999.0945
3	12957.2014	11797.1591	10618.5796	9426.7112	8226.6608	7023.4255	5821.9382	4627.1316
4	10188.7828	9109.6212	8015.9040	6913.0252	5806.3338	4701.1940	3603.0755	2517.6864
5	7659.2518	6664.5260	5660.0900	4651.6971	3645.2264	2646.8145	1663.0640	701.3929
6	5381.6434	4477.1860	3569.2356	2664.3109	1769.4191	892.4054	42.5995	
7	3375.8309	2570.9911	1771.2705	984.8942	221.6033			
8	1672.1303	982.4662	311.5626					
9	319.5464							
$\nu \setminus J$	24	25	26	27	28	29	30	31
0	10976.5735	9496.2237	8024.3709	6564.6364	5120.5483	3695.5928	2293.2796	917.2285
1	8225.7696	6844.4839	5474.7238	4120.4784	2785.7900	1474.8629	192.2238	
2	5710.0438	4432.3453	3170.5449	1929.3851	713.9904			
3	3444.0280	2277.8701	1134.3209	19.7931 ^b				
4	1451.1807	410.5020						

^a ν and J are the vibrational and rotational quantum numbers, respectively. Error estimation for individual states is given in the Supporting Information.

^b This state is entirely due to nonadiabatic effects. Since it does not appear at the adiabatic approximation, its energy may be substantially less accurate than the energies of the remaining rovibrational states.

with Ω up to 16. This basis, which may be viewed as a generalized Heitler–London basis (it contains the Heitler–London function),

is needed to correctly describe molecular dissociation. At $R = 12$ bohr, the accuracy achieved with the basis set of eq 18 is close to

Table 2. Theoretically Predicted Dissociation Energies (in cm^{-1}) of All 598 Bound States of D_2^a

$\nu \setminus J$	0	1	2	3	4	5	6	7	8	9	10
0	36748.3634	36688.5828	36569.2963	36391.0490	36154.6478	35861.1488	35511.8412	35108.2289	34652.0088	34145.0488	33589.3635
1	33754.7463	33697.0758	33582.0029	33410.0597	33182.0337	32898.9554	32562.0824	32172.8812	31733.0063	31244.2778	30708.6583
2	30880.2430	30824.6456	30713.7129	30547.9643	30328.1686	30055.3317	29730.6810	29355.6472	28931.8440	28461.0461	27945.1666
3	28122.7615	28069.2076	27962.3556	27802.7132	27591.0311	27328.2917	27015.6934	26654.6328	26246.6848	25793.5810	25297.1880
4	25480.6486	25429.1157	25326.3000	25172.6976	24969.0422	24716.2938	24415.6231	24068.3944	23676.1459	23240.5687	22763.4852
5	22952.7114	22903.1852	22804.3772	22656.7728	22461.0894	22218.2657	21929.4464	21595.9654	21219.3265	20801.1827	20343.3156
6	20538.2479	20490.7226	20395.9113	20254.2889	20066.5579	19833.6368	19556.6462	19236.8915	18875.8444	18475.1232	18036.4718
7	18237.0868	18191.5664	18100.7600	17965.1331	17785.3739	17562.3826	17297.2573	16991.2773	16645.8854	16262.6681	15843.3359
8	16049.6405	16006.1398	15919.3685	15789.7833	15618.0596	15405.0808	15151.9249	14859.8479	14530.2666	14164.7400	13764.9495
9	13976.9722	13935.5186	13852.8377	13729.3782	13565.8044	13362.9849	13121.9801	12844.0261	12530.5179	12182.9911	11803.1038
10	12020.8819	11981.5173	11903.0111	11785.8056	11630.5553	11438.1169	11209.5363	10946.0334	10648.9863	10319.9134	9960.4560
11	10184.0153	10146.7989	10072.5866	9961.8154	9815.1328	9633.3864	9417.6115	9169.0172	8888.9705	8578.9799	8240.6789
12	8470.0026	8435.0143	8365.2566	8261.1634	8123.3777	7952.7421	7750.2867	7517.2160	7254.8939	6964.8287	6648.6575
13	6883.6348	6850.9801	6785.8889	6688.7948	6560.3401	6401.3676	6212.9089	5996.1728	5752.5308	5483.5039	5190.7489
14	5431.0906	5400.9066	5340.7582	5251.0815	5132.5237	4985.9347	4812.3575	4613.0166	4389.3065	4142.7793	3875.1345
15	4120.2289	4092.6936	4037.8462	3956.1303	3848.2050	3714.9379	3557.3966	3376.8392	3174.7048	2952.6049	2712.3169
16	2960.9710	2936.3160	2887.2361	2814.1894	2717.8581	2599.1427	2459.1559	2299.2164	2120.8431	1925.7521	1715.8578
17	1965.8035	1944.3335	1901.6362	1838.1950	1754.7324	1652.2069	1531.8105	1394.9679	1243.3394	1078.8290	903.6027
18	1150.4486	1132.5743	1097.0897	1044.5231	975.6684	891.5869	793.6143	683.3726	562.7936	434.1618	300.1927
19	534.7343	521.0330	493.9347	454.0526	402.3180	339.9993	268.7360	190.6028	108.2387	25.1501	
20	143.4642	134.8278	117.9548	93.6691	63.2806	28.7401					
21	1.6642	0.0491 ^b									
$\nu \setminus J$	11	12	13	14	15	16	17	18	19	20	21
0	32987.0905	32340.4669	31651.8060	30923.4758	30157.8783	29357.4315	28524.5520	27661.6407	26771.0694	25855.1707	24916.2279
1	30128.2296	29505.1695	28841.7298	28140.2145	27402.9610	26632.3216	25830.6476	25000.2755	24143.5140	23262.6347	22359.8626
2	27386.2346	26786.3718	26147.7718	25472.6790	24763.3702	24022.1367	23251.2697	22453.0464	21629.7184	20783.5020	19916.5706
3	24759.4845	24182.5401	23568.4939	22919.5347	22237.8832	21525.7751	20785.4464	20019.1210	19228.9994	18417.2497	17586.0005
4	22246.8277	21692.6167	21102.9411	20479.9386	19825.7789	19142.6472	18432.7304	17698.2055	16941.2288	16163.9280	15368.3950
5	19847.6143	19316.0545	18750.6790	18153.5798	17526.8807	16872.7226	16193.2502	15490.6008	14766.8946	14024.2276	13264.6654
6	17561.7401	17052.8634	16511.8438	15940.7327	15341.6146	14716.5931	14067.7784	13397.2768	12707.1824	11999.5701	11276.4914
7	15389.7037	14903.6716	14387.2068	13842.3268	13271.0842	12675.5536	12057.8202	11419.9700	10764.0828	10092.2265	9406.4537
8	13332.6805	12869.8040	12378.2591	11860.0373	11317.1686	10751.7089	10165.7299	9561.3111	8940.5334	8305.4757	7658.2131
9	11392.6185	10953.3842	10487.3206	9996.4033	9482.6509	8948.1137	8394.8655	7824.9967	7240.6106	6643.8215	6036.7566
10	9572.3616	9157.4667	8717.6828	8254.9820	7771.3865	7268.9587	6749.7950	6216.0214	5669.7926	5113.2944	4548.7496
11	7875.8101	7486.2101	7073.7960	6640.5542	6188.5304	5719.8236	5236.5818	4741.0024	4235.3355	3721.8929	3203.0627
12	6308.1321	5945.1055	5561.5208	5159.4021	4740.8480	4308.0294	3863.1902	3408.6539	2946.8363	2480.2668	2011.6212
13	4876.0459	4541.2881	4188.4733	3819.6987	3437.1601	3043.1557	2640.0964	2230.5252	1817.1485	1402.8863	990.9510
14	3588.2093	3283.9721	2964.5198	2632.0792	2289.0159	1937.8510	1581.2918	1222.2810	864.0776	510.3933	165.6395
15	2455.7797	2185.0946	1902.5323	1610.5491	1311.8159	1009.2686	706.1933	406.3736	114.3694		
16	1493.2790	1260.3555	1019.6781	774.1419	527.0394	282.2304	44.4834				
17	720.1223	531.2062	340.1405	150.8950							
18	164.1866	30.3695									
$\nu \setminus J$	22	23	24	25	26	27	28	29	30	31	32
0	23956.4683	22978.0571	21983.0935	20973.6071	19951.5567	18918.8293	17877.2405	16828.5352	15774.3900	14716.4151	13656.1575
1	21437.3699	20497.2704	19541.6158	18572.3932	17591.5237	16600.8620	15602.1976	14597.2554	13587.6991	12575.1334	11561.1078
2	19031.0480	18129.0038	17212.4502	16283.3399	15343.5655	14394.9594	13439.2953	12478.2906	11513.6089	10546.8645	9579.6270
3	16737.3351	15873.2873	14995.8389	14106.9182	13208.4000	12302.1065	11389.8096	10473.2340	9554.0614	8633.9359	7714.4708
4	14556.6818	13730.7962	12892.7006	12044.3114	11187.4992	10324.0917	9455.8769	8584.6075	7712.0074	6839.7795	5969.6154
5	12490.2391	11702.9433	10904.7348	10097.5334	9283.2241	8463.6608	7640.6720	6816.0677	5991.6492	5169.2212	4350.6073
6	10539.9706	9792.0047	9034.5628	8269.5895	7499.0087	6724.7301	5948.6581	5172.7034	4398.7986	3628.9187	2865.1080
7	8708.8007	8001.2872	7285.9202	6564.6983	5839.6198	5112.6937	4385.9547	3661.4828	2941.4313	2228.0638	1523.8081
8	7000.8179	6335.3630	5663.9281	4988.6099	4311.5357	3634.8825	2960.9045	2291.9703	1630.6160	979.6255	342.1539

Table 2. Continued

$\nu \setminus J$	22	23	24	25	26	27	28	29	30	31	32
9	5421.5600	4800.4013	4175.4879	3549.0832	2923.5329	2301.3016	1685.0260	1077.5947	482.2723		
10	3978.4290	3404.6679	2829.8912	2256.6490	1687.6692	1125.9370	574.8194	38.2756			
11	2681.3328	2159.3251	1639.8473	1125.9722	621.1627	129.4853					
12	1543.7728	1079.8706	623.4674	178.7378							
13	584.9779	189.2547									
$\nu \setminus J$	33	34	35	36	37	38	39	40	41	42	43
0	12595.1047	11534.6886	10476.2901	9421.2440	8370.8452	7326.3541	6289.0044	5260.0106	4240.5776	3231.9113	2235.2318
1	10547.1215	9534.6279	8525.0406	7519.7400	6520.0811	5527.4021	4543.0351	3568.3189	2604.6139	1653.3230	715.9165
2	8613.4269	7649.7624	6690.1076	5735.9218	4788.6608	3849.7912	2920.8076	2003.2555	1098.7610		
3	6797.2565	5883.8701	4975.8879	4074.9000	3182.5291	2300.4554	1430.4494	574.4182			
4	5103.2079	4242.2662	3388.5358	2543.8247	1710.0382	889.2289					
5	3537.6706	2732.3404	1936.6489	1152.7828	383.1585						
6	2109.5182	1364.4607	632.4843								
7	831.3351	153.6817									

^a ν and J are the vibrational and rotational quantum numbers, respectively. Error estimation for individual states is given in the Supporting Information. ^b This state does not exist in the Born–Oppenheimer approximation and its energy may be substantially less accurate than the energies of the remaining rovibrational states.

that obtained with the James–Coolidge basis. The Born–Oppenheimer energies obtained as described above were fitted with an analytic function of the form given in ref 27. We estimate that it represents the Born–Oppenheimer potential with accuracy better than 10^{-5} cm^{-1} . Fortran code to compute this analytic function can be supplied upon request.

For the evaluation of adiabatic, nonadiabatic, relativistic, and QED corrections, we have not used exponential functions, like Kolos and Wolniewicz in refs 40 and 22, because we have not yet developed integrals with inverse quadratic powers of electronic variables. Instead, we used explicitly correlated Gaussian (ECG) functions of the form

$$\begin{aligned} \psi_k(\vec{r}_1, \vec{r}_2) \\ = (1 + \hat{P}_{12})(1 \pm \hat{i}) \exp\left[-\sum_{i,j=1}^2 A_{k,ij}(\vec{r}_i - \vec{s}_{k,i})(\vec{r}_j - \vec{s}_{k,j})\right] \end{aligned} \quad (19)$$

where the symmetric 2×2 matrices \mathbf{A}_k and vectors \vec{s}_k (lying on the internuclear axis) contain nonlinear parameters, five per basis function, to be variationally optimized. The 1200-term ECG bases were optimized with respect to \mathcal{E}_{el} for R spread over the range 0–12 bohr and employed to evaluate all of the corrections. At larger values of R , the relativistic and QED corrections to the potential were represented using the asymptotic constants reported in refs 41 and 27. Details of numerical evaluations of adiabatic and nonadiabatic corrections were presented in refs 6 and 7, while the evaluation of relativistic and QED corrections to the potential was presented in ref 27.

It should be stressed that the method of computing the rovibrational levels employed in this work differs slightly from that of ref 27. In this reference, the relativistic and QED corrections were obtained directly by averaging the corrections to the potential with nuclear wave functions obtained in the adiabatic approximation. In the present work, the relativistic and QED corrections to the potential are used in the nonadiabatic equation for the nuclear motion, so we can deal with exceptional states which do not exist on the adiabatic level. The

corresponding corrections to the rovibrational levels were obtained as appropriate differences in calculated energies. Thus, the present “ α^2 ” energies contain very small contributions of the fourth and higher order in α as well as the first and higher order in α^2/μ_n . Similarly, the “ α^3 ” energies contain some very small contributions from the fifth and higher powers of α . For low values of the vibrational quantum number ν , both approaches give results differing by 0.0001 cm^{-1} or less. At the highest values of ν , apart from exceptional states described later on, the differences reach 0.0005 cm^{-1} , i.e., are of the order of the neglected recoil corrections. These differences appear only at the relativistic level. The QED corrections differ always less than 0.0001 cm^{-1} .

6. RESULTS FOR HYDROGEN AND DEUTERIUM MOLECULES

In Tables 1 and 2, we present the complete rovibrational spectrum of molecular hydrogen and deuterium in the electronic ground state ($X^1\Sigma_g^+$) in terms of dissociation energies with a precision of about 0.001 cm^{-1} for D_2 and from 0.001 to 0.005 cm^{-1} for H_2 . The individual adiabatic, nonadiabatic, relativistic, and QED contributions for each level of H_2 and D_2 are listed in the Supporting Information files associated with this article (the very small finite-size contribution is included in the relativistic correction). The estimated theoretical uncertainties corresponding to each level are also listed in these files. The largest uncertainty comes from the α^4 and higher-order QED corrections, which have been included only approximately, see eq 14, and from the higher-order $\mathcal{O}(\mu_n^{-5/2})$ NAPT corrections. Other significant sources of uncertainty are the neglected nonadiabatic relativistic effects. To estimate the uncertainty of each rovibrational level, we used the following procedure. We assumed that the error caused by the neglect of the relativistic recoil term can be estimated as m_e/μ_n times the α^2 correction and, analogously, times the α^3 correction to account for the missing QED recoil term. Similarly, we calculate the contribution to the error budget from the missing higher-order nonadiabatic terms as proportional to m_e/μ_n times the second-order

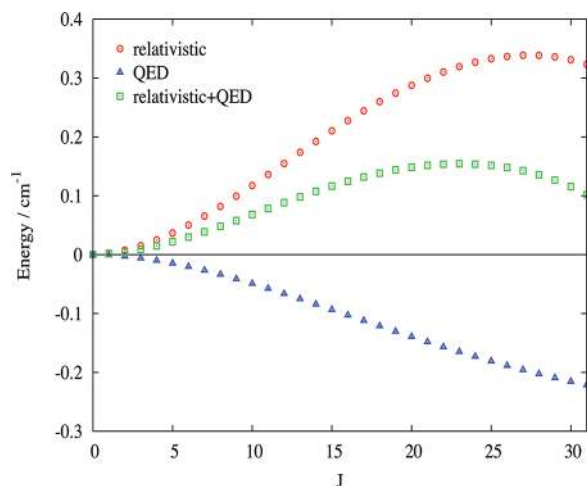


Figure 1. J dependence of the relativistic and QED contributions to the rotational excitation energies at $\nu = 0$. The relativistic and QED corrections to the ground, $J = 0$ level are $0.5318(5) \text{ cm}^{-1}$ and $0.1964(8) \text{ cm}^{-1}$, respectively.

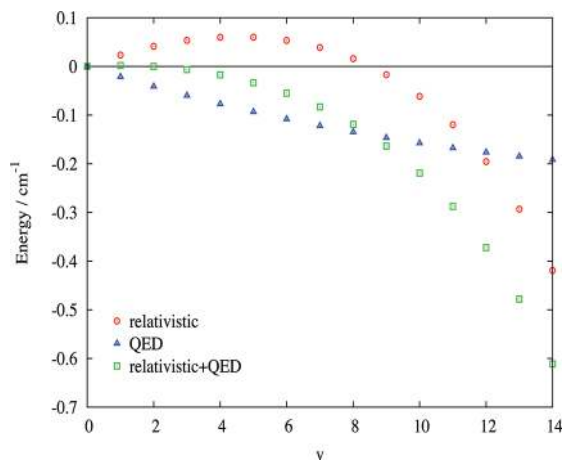


Figure 2. Vibrational quantum number dependence of the relativistic and QED contributions to the excitation energies at $J = 0$. The relativistic and QED corrections to the ground, $\nu = 0$ level are $0.5318(5) \text{ cm}^{-1}$ and $0.1964(8) \text{ cm}^{-1}$, respectively.

nonadiabatic correction. Another part of the uncertainty comes from the incomplete treatment of the higher-order QED effects. As previously,²⁷ we conservatively estimate that the $\mathcal{O}^{(4)}$ terms other than the one-loop term of eq 14 as well as all higher-order $\mathcal{O}^{(n)}$ terms, $n > 4$, contribute at most 50% of the value of $\mathcal{O}^{(4)}$. The quadratic sum of the four error components described above leads to the overall uncertainty on D_0 or any other computed energy difference.

Among the levels listed in Tables 1 and 2, we note a couple of curiosities—the bound levels, which are absent in the Born–Oppenheimer approximation. Such levels do not reveal themselves until the finite mass corrections are taken into account. In H_2 , there are two such “nonadiabatic” levels: $(\nu, J) = (3, 27)$ and $(14, 4)$, with dissociation energies of about 19.79 cm^{-1} and 0.03 cm^{-1} , respectively. The former state was observed by Dabrowski¹⁹ as lying 36098.04 cm^{-1} above the $(0, 0)$ level, which corresponds to $D_0 = 20.03 \text{ cm}^{-1}$. The latter one, located $36\,118.12 \text{ cm}^{-1}$ above the reference state, she describes as “the

Table 3. Dissociation Energies (in cm^{-1}) of H_2 and D_2 in Their Ground State—A Comparison with the Experiment

	D_0/cm^{-1}	
	H_2	D_2
experiment (1993)	$36118.06(4)^a$	$36748.32(7)^a$
experiment (2004)	$36118.062(10)^b$	$36748.343(10)^b$
experiment (2009/10)	$36118.06962(37)^c$	$36748.36286(68)^d$
theory	$36118.0696(11)$	$36748.3634(9)$
difference	$0.0000(12)$	$0.0005(11)$

^a Ref 66. ^b Ref 67. ^c Ref 1. ^d Ref 2.

Table 4. The Lowest Rotational and Vibrational Excitation Energies (in cm^{-1})

	H_2	
	$J = 0 \rightarrow 1$	$\nu = 0 \rightarrow 1$
theory	$118.486812(9)$	$4161.1661(9)$
experiment	$118.48684(10)^a$	$4161.1660(3)^b$
difference	$-0.00003(10)$	$0.0001(9)$
	D_2	
	$J = 0 \rightarrow 1$	$\nu = 0 \rightarrow 1$
theory	$59.780615(3)$	$2\,993.6171(2)$
experiment	$59.78130(95)^c$	$2\,993.6130(19)^d$
difference	$-0.00068(95)$	$0.0041(19)$

^a Ref 68. ^b Ref 46. ^c Ref 2. ^d Ref 45.

last observed” and “presumably bound”. However, if we assign the up-to-date value of D_0 to the $(0, 0)$ level, the state observed by Dabrowski becomes a resonance located 0.05 cm^{-1} above the dissociation threshold. This value is an order of magnitude smaller than the accuracy declared by Dabrowski; therefore, from the experimental point of view, the question whether this state is bound or not remains open. In the D_2 spectrum, we predict the existence of only one such level $(21, 1)$ with $D_0 = 0.05 \text{ cm}^{-1}$. In this case, it is the adiabatic correction which makes this state bound. We note also the presence of another level located just below the dissociation threshold—the $(21, 0)$ state with $D_0 = 1.66 \text{ cm}^{-1}$. This state, in contrast, is a regular one, accommodated already by the Born–Oppenheimer potential.

The ν and J dependence of the relativistic and QED corrections to the rotational and vibrational excitation energies (relative the ground $\nu = 0, J = 0$ level) is shown in Figures 1 and 2. It may be pointed out that individual terms in eqs 11 and 12, like, e.g., mass velocity, Darwin, Breit or Araki-Sucher ones, lead to a monotonic dependence on ν or J . The nonmonotonic behavior observed in Figures 1 and 2 is due to cancellation effects and can be rationalized on the basis of the different R dependence of the corresponding corrections to the potential. One may observe that the QED correction is not much smaller than the relativistic one and that the neglect of the former would lead to a qualitatively incorrect ν or J dependence of the relativistic + QED contribution.

Theoretical predictions for the ground rovibrational state of H_2 and D_2 have already been presented by us in ref 27. Here, in Table 3, we compare these results with the most recent

Table 5. Energy of Rotational Excitations $\Delta E(J)$ in H_2 ($\nu = 0$) with Respect to the Ground Level ($\nu = 0, J = 0$)—A Comparison with the Experimental Results of Salumbides et al.^{27a}

J	$\Delta E_{\text{theo}}(J)$	$\Delta E_{\text{exptl}}(J)$	$\delta(\text{theo} - \text{exptl})$	$\Delta E_{\text{theo}}^{\text{QED}}(J)$	$\Delta E_{\text{exptl}}^{\text{QED}}(J)$
1	118.486812(9)	118.48684(10)	-0.00003(10)	-0.001030(4)	-0.00100(10)
2	354.37313(3)	354.3733(2)	-0.0002(2)	-0.00307(1)	-0.0029(2)
3	705.51883(5)	705.5189(3)	-0.0001(3)	-0.00610(2)	-0.0060(3)
4	1168.79743(9)	1168.7982(2)	-0.0008(2)	-0.01005(4)	-0.0093(2)
5	1740.1895(1)	1740.1895(3)	-0.0000(3)	-0.01487(6)	-0.0148(3)
6	2414.8970(2)	2414.898(5)	-0.001(5)	-0.02050(8)	-0.019(5)
7	3187.4705(2)	3187.472(5)	-0.002(5)	-0.0268(1)	-0.025(5)
8	4051.9430(3)	4051.943(5)	-0.000(5)	-0.0338(1)	-0.034(5)
9	5001.9628(4)	5001.963(5)	-0.000(5)	-0.0414(2)	-0.041(5)
10	6030.9202(5)	6030.921(5)	-0.001(5)	-0.0494(2)	-0.049(5)
11	7132.0634(6)	7132.066(5)	-0.003(5)	-0.0578(2)	-0.055(5)
12	8298.6014(6)	8298.600(5)	0.001(5)	-0.0665(3)	-0.068(5)
13	9523.7916(7)	9523.794(7)	-0.002(7)	-0.0754(3)	-0.073(7)
14	10801.0121(9)	10801.008(9)	0.004(9)	-0.0846(3)	-0.089(9)
15	12123.819(1)	12123.83(1)	-0.01(1)	-0.0938(4)	-0.08(1)
16	13485.990(1)	13485.99(1)	-0.00(1)	-0.1030(4)	-0.10(1)

^aThe two last columns show contributions to this energy from the QED effects: $\Delta E_{\text{theo}}^{\text{QED}}(J)$, predicted in our calculations, and $\Delta E_{\text{exptl}}^{\text{QED}}(J)$, extracted from the experimental data by subtracting our relativistic energies from the measured values given in column $\Delta E_{\text{exptl}}(J)$. All entries in cm^{-1} .

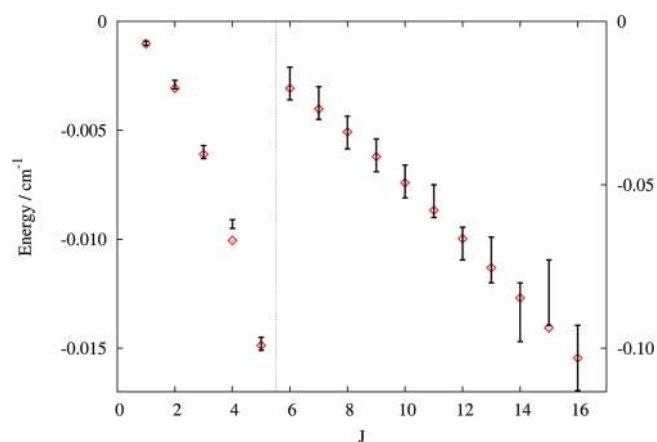


Figure 3. QED contributions to the rotational excitation energies at $\nu = 0$. Comparison of the present theoretical calculations (open diamonds) with the experimental data of ref 29. The left/right energy scale is for the levels to the left/right from the vertical line. The extent of the vertical bars shows the experimental uncertainties (listed in Table 5). The theoretical uncertainties (not shown) are at least an order of magnitude smaller than the experimental ones, except for $J = 4$ and $J = 5$, when they are 5 times smaller.

experimental data. Our present theoretical value of the dissociation energy of H_2 , $D_0 = 36\,118.0696(11) \text{ cm}^{-1}$, differing very slightly from that of ref 27, agrees very well with the value $36\,118.06962(37) \text{ cm}^{-1}$ derived experimentally by Liu et al.¹ The dissociation energies for D_2 are $36\,748.3634(9) \text{ cm}^{-1}$ from theory and $36\,748.36286(68) \text{ cm}^{-1}$ from the most recent experiment.² The perfect agreement with the sophisticated high-resolution measurements (see also ref 42 for a confirmation of the result from ref 2) indicates that we control numerical accuracy of the included energy contributions as well as all physical effects down to 0.001 cm^{-1} . It is worth emphasizing that this excellent agreement would have been impossible

Table 6. Vibrational Excitation Energies $E(\nu, J = 0) - E(\nu = 0, J = 0)$ for H_2 and Their Differences with the Experimental Values of Dabrowski¹⁹ (δ_{exptl}) and with the Best Previous Theoretical Values by Wolniewicz²⁶ (δ_{Wol})^a

ν	theory	δ_{exptl}^b	δ_{Wol}^c
1	4161.1661(9)	0.03	-0.001(1)
2	8087.0026(17)	0.07	0.000(2)
3	11782.3908(25)	0.03	-0.001(3)
4	15250.3656(32)	0.06	-0.002(3)
5	18491.9296(37)	0.01	-0.002(4)
6	21505.7795(43)	0.00	-0.004(4)
7	24287.9152(47)	0.01	-0.004(5)
8	26831.0906(50)	-0.07	-0.003(5)
9	29124.0404(52)	-0.05	-0.004(5)
10	31150.3909(51)	-0.08	-0.004(5)
11	32887.0983(49)	-0.03	-0.004(5)
12	34302.1740(42)	-0.03	-0.004(4)
13	35351.3145(31)	-0.05	-0.003(3)
14	35973.2731(16)	-0.11	0.000(2)

^aAll energies in cm^{-1} . ^bDabrowski¹⁹ estimates the uncertainty of the measurements as 0.1 cm^{-1} . ^cWolniewicz²⁶ does not give uncertainties for individual levels. He estimates overall accuracy as 0.001 cm^{-1} . The error estimation in this column comes only from the uncertainty of our calculations.

without including the Araki-Sucher term^{43,44} and the interatomic distance dependence of the two-electron Bethe logarithm.

In Table 4, we compare our predictions for the lowest rotational and vibrational excitation energies. Agreement with the experimental values for H_2 is excellent, but for the vibrational excitation in D_2 , a small discrepancy (of 2 experimental σ) is observed. Note that the experimental vibrational energies shown in this table are not measured directly but are extracted from a set of experimental literature lines fitted to the Dunham expansion.

Table 7. Comparison of the Theoretical and Experimental Quadrupole Transition Energies in H₂. δ is their difference and carries the combined experimental/theoretical uncertainty. All energies in cm⁻¹.

<i>J</i>	S ₀ (<i>J</i>)			S ₁ (<i>J</i>)		
	theory	experiment ⁵³	δ	theory	experiment ²⁹	δ
0	354.373 13(3)	354.373 50(40)	-0.000 37(40)		354.373 3(2)	-0.000 2(2)
1	587.032 02(4)	587.032 11(17)	-0.000 09(17)		587.032 1(3)	0.000 0(3)
2	814.424 30(6)	814.424 73(8)	-0.000 43(10)		814.424 9(2)	-0.000 6(2)
3	1 034.670 68(8)	1 034.670 24(3)	0.000 44(9)		1 034.670 6(3)	0.000 1(3)
4	1 246.099 54(9)	1 246.098 11(17)	0.001 43(19)		1 246.100(5)	0.000(5)
5	1 447.280 93(11)	1 447.278 82(41)	0.002 11(42)		1 447.282(5)	-0.002(5)

<i>J</i>	Q ₁ (<i>J</i>)			S ₁ (<i>J</i>)		
	theory	experiment ⁵⁴	δ	theory	experiment ⁵⁴	δ
0				4497.8384(9)	4497.8391(2)	-0.0007(9)
1	4155.2538(9)	4155.25469(8)	-0.0009(9)	4712.9046(9)	4712.9054(2)	-0.0008(9)
2	4143.4653(9)	4143.4660(3)	-0.0007(9)	4917.0063(10)	4917.0069(3)	-0.0006(10)
3	4125.8726(9)	4125.8739(4)	-0.0013(10)	5108.4029(10)	5108.4040(6)	-0.0011(12)
4	4102.5820(9)	4102.582(4)	0.000(4)			

<i>J</i>	Q ₂ (<i>J</i>)			S ₂ (<i>J</i>)		
	theory	experiment ⁵⁴	δ	theory	experiment ⁵⁴	δ
0				8406.3608(18)	8406.365(2)	-0.004(3)
1	8075.3074(17)	8075.3114(6)	-0.0040(18)	8604.2152(18)	8604.2189(8)	-0.0037(20)
2	8051.9877(17)	8051.991(7)	-0.003(7)	8785.5244(18)	8785.529(6)	-0.005(6)
3	8017.1831(17)	8017.19(1)	-0.01(1)			

Table 8. Comparison of the Theoretical and Experimental Quadrupole Transition Energies in D₂. δ is their difference and carries the combined experimental/theoretical uncertainty. All energies in cm⁻¹.

<i>J</i>	S ₀ (<i>J</i>)			S ₁ (<i>J</i>)		
	theory	experiment ⁵⁵	δ	theory	experiment ⁵⁶	δ
0	179.06710(1)	179.068(2)	-0.001(2)	3166.3605(2)	3166.3596(40)	0.0009(40)
1	297.53374(1)	297.533(3)	0.001(3)	3278.5231(2)	3278.5222(40)	0.0009(40)
2	414.64845(2)	414.648(2)	0.000(2)	3387.2626(2)	3387.2606(50)	0.0020(50)
3	529.90025(2)	529.900(4)	0.000(4)	3492.0937(2)	3492.0913(40)	0.0024(40)
4	642.80664(2)	642.806(4)	0.001(4)			
5	752.91993(3)	752.923(20)	-0.003(20)			
6	859.83237(3)	859.845(20)	-0.013(20)			

<i>J</i>	O ₁ (<i>J</i>)			Q ₁ (<i>J</i>)		
	theory	experiment ⁵⁶	δ	theory	experiment ⁵⁶	δ
1				2991.5070(2)	2991.5043(40)	0.0027(40)
2	2814.5500(2)	2814.5459(40)	0.0041(40)	2987.2934(2)	2987.2955(40)	-0.0021(40)
3	2693.9733(2)	2693.9723(40)	0.0010(40)	2980.9894(2)	2980.9882(40)	0.0012(40)
4	2572.645 0(2)	2572.6428(50)	0.0022(50)	2972.6141(2)	2972.6128(50)	0.0013(50)

The error estimation of the obtained value is one standard deviation of this fit.^{45,46} We can also compare our result for D₂ with recent fully nonadiabatic relativistic calculations through order α^2 (including all recoil terms of the order of α^2/μ_n) performed by Bubin et al.⁴⁵ For the energy difference of rotationless $\nu = 1$ and $\nu = 0$ states of D₂, these authors obtained

2993.6326(10) cm⁻¹, in perfect agreement with our value 2993.6326(2) cm⁻¹ obtained neglecting recoil terms. The authors of ref 45 attributed a discrepancy of their value with experimental results to the missing QED correction, unknown when their work was published. In fact, when our QED correction, amounting to -0.0155 cm⁻¹, is added, a small

disagreement of $0.004(2) \text{ cm}^{-1}$, the same as shown in Table 4, remains.

A detailed comparison of the theoretical rotational excitation energies with a very recent experimental determination²⁹ is presented in Table 5. The error estimation assigned to the theoretical energy differences has been computed in the same fashion as the uncertainty for the individual levels, described earlier. In general, the assumed theoretical uncertainties are much smaller than the experimental ones. Very good agreement between the theoretical and experimental values is observed for all measured levels up to $J = 16$, except for $J = 4$, where a 4 σ unexplained discrepancy is present.

In the two last columns of Table 5, we also present the pure QED contribution to each measured rotational level obtained by subtracting the nonrelativistic and our relativistic energies from either the total theoretical or the experimental values. The comparison of the theoretical and experimental QED contributions is shown in Figure 3. The observed agreement is remarkably good (except for $J = 4$), confirming the accuracy of both the measurement and the calculations. To our knowledge, this agreement represents the first observation of QED effects in a molecular spectrum. Specifically, these effects include the electron self-energy (interaction of the electron with the vacuum fluctuations of the electromagnetic field), the vacuum polarization (electron–positron virtual pair creation), and the retardation of the electron–electron interaction.⁹ The conventional relativistic quantum mechanics based on the Dirac–Coulomb (DC) or Dirac–Coulomb–Breit (DCB) equations³¹ neglects this complicated physics. Had we assumed the presence of exactly two electrons in the molecule and solved the DC or DCB equations using the direct perturbation theory (DPT) expansion in even powers of α ,^{47,48} then all theoretical points in Figure 3 would have lain very close to the straight line $E = 0$. The deviation from this line is a quantitative demonstration of QED contribution to the rotational excitation energies of H_2 . It may be pointed out in this context that due to the Brown–Ravenhall disease,⁴⁹ the eigenenergies of the DC or DCB equations are not precisely defined⁵⁰ and have an intrinsic uncertainty on the order of α^3 ,⁵¹ the same as the leading QED effects. Thus, when adding the α^3 QED contribution to relativistic energies obtained using methods other than DPT, one should take special care to avoid double counting.

Whereas the effects of QED are well seen in the rotational spectrum, their influence on the bond length in H_2 is very small. The rotational constant B , defined as half of the smallest rotational spacing, decreases only by about 8×10^{-6} in relative terms, which leads to an increase of the H–H bond distance (assumed to be proportional to $B^{-1/2}$) by merely $3 \times 10^{-6} \text{ \AA}$. One should note, however, that for very weakly bound dimers, like e.g. He_2 , the QED effects may significantly affect the bond length.⁵²

It appears that the experimental pure vibrational excitation energies ($J = 0$) have not been measured with accuracy comparable to that of pure rotational ones ($\nu = 0$) of ref 29. In Table 6, we show a comparison of our values with the experimental data of Dabrowski¹⁹ and with the theoretical values of Wolniewicz.²⁶ The agreement in both cases is very good, although it should be kept in mind that the accuracy of Dabrowski's results is limited. She estimates it as 0.1 cm^{-1} without referring to any specific part of the spectrum. We observed, however, that for some high-lying levels (i.e., the highest bound levels shown in Table 4 of ref 19), her energies differ from ours by $0.2\text{--}0.4 \text{ cm}^{-1}$, i.e., much more

than our estimated uncertainties. The excellent agreement between ours and Wolniewicz's results, seen in Table 6, is likely due to the fact that the contribution of the two-electron QED effects, neglected by Wolniewicz, is small for the presented vibrational energy differences.

Some highly accurate values of the Q and S branch quadrupole transition frequencies of H_2 and D_2 are available in the literature^{53–56} and are compared with our results in Tables 7 and 8. Both for H_2 and for D_2 we observe now some disagreements between theory and experimental results. The most significant discrepancies occur for the $S_0(2) - S_0(5)$ transitions in H_2 measured by Jennings and Brault.⁵³ Their transition energies differ from 5 up to 15 experimental σ from our values. The reason for this discrepancy is not obvious to us. We speculate that an explanation may come from a possible underestimation of higher-order nonadiabatic effects, which are larger for H_2 than D_2 . An alternative explanation, put forward for consideration by Campargue,⁵⁷ is a small pressure shift affecting the experimental result. On the other hand, we observe good agreement of our predictions with somewhat less accurate $S_0(J)$ transition energies that can be obtained from very recent measurement by Salumbides et al.²⁹ [except for the $S_0(2)$ line related to a similar exception noted in Table 5 for $J = 4$]. For the Q_1 and S_1 transitions, the discrepancies exceed the experimental error but fit within the sum of the theoretical and experimental uncertainties. Among the Q_2 and S_2 transitions, two lines ($J = 1$) do not conform to the above description and show discrepancies almost twice the size of the sum of these two uncertainties. Campargue,⁵⁷ on the basis of his own measurements and a comparison with Rahn and Rosasco's results,⁵⁸ suggests that the discrepancy in the Q_1 branch may be due to the calibration of the spectra of ref 54. What is more, we observe very good agreement of theoretical line positions with the measurements by Ferguson et al.⁵⁹ for higher transitions (not shown in Tables): $S_4(0)$, $S_4(1)$, and $S_5(1)$. The differences (and the experimental uncertainties) are $0.0008(36)$, $0.0001(10)$, and $0.0014(200) \text{ cm}^{-1}$, respectively.

For D_2 (see Table 8), we find general agreement with the measurements of Jennings et al.⁵⁵ and of McKellar and Oka.⁵⁶ The differences δ between the experimental and theoretical frequencies fit well within the experimental uncertainties of several thousandths of cm^{-1} . We observe, however, a discrepancy with recently reported measurements⁶⁰ of $S_1(0)$ and $S_1(1)$ lines. The experimental values $3166.3620(2) \text{ cm}^{-1}$ and $3278.5220(2) \text{ cm}^{-1}$ differ from our predictions by several combined experimental/theoretical uncertainties.

7. CONCLUSION

The accuracy of about 0.001 cm^{-1} for most of the dissociation energies of rovibrational levels 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 α^3 QED effects. In particular, an effective approach to calculating the many-electron Bethe logarithm and mean values of singular operators, like the Araki–Sucher term,^{43,44} has been developed and is given in refs 27, 61 and 62. The second direction, indispensable to reaching this accuracy, is the nonadiabatic perturbation theory, NAPPT,^{6,7,63} which enables a rigorous approach to the finite nuclear mass effects beyond the adiabatic approximation. However, nonadiabatic contributions to the relativistic and QED energies (the so-called recoil corrections)

still remain to be evaluated. These corrections as well as the higher-order nonadiabatic $\mathcal{O}(\mu_n^{-5/2})$, the complete α^4 QED, and the leading term in α^5 correction have to be evaluated in order to reach a 10^{-6} cm^{-1} level of accuracy, where the H_2 spectrum becomes sensitive to uncertainties in the electron–proton mass ratio and in the proton charge radius.⁶⁴ One may speculate that at this level of precision exotic forces between hadrons carried by very weakly interacting sub-electronvolt particles (WISPs) might also become spectroscopically observable.⁶⁵

■ ASSOCIATED CONTENT

S Supporting Information. Components of the dissociation energy as well as its uncertainty for all the rovibrational levels of H_2 and D_2 . This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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