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Two-electron relativistic corrections to the potential energy surface and vibration–rotation levels of water

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Abstract

Two-electron relativistic corrections to the ground-state electronic energy of water are determined as a function of geometry at over 300 points. The corrections include the two-electron Darwin term (D2) of the Coulomb–Pauli Hamiltonian, obtained at the cc-pVQZ CCSD(T) level of theory, as well as the Gaunt and Breit corrections, calculated perturbationally using four-component fully variational Dirac–Hartree–Fock (DHF) wavefunctions and two different basis sets. Based on the calculated energy points, fitted relativistic correction surfaces are constructed. These surfaces are used with a high-accuracy ab initio nonrelativistic Born–Oppenheimer (BO) potential energy hypersurface to calculate vibrational band origins and rotational term values for $H_2{}^{16}O$. The calculations suggest that these two-electron relativistic corrections, which go beyond the usual kinetic relativistic effects and which have so far been neglected in rovibrational calculations on light many-electron molecular systems, have a substantial influence on the rotation–vibration levels of water. The three effects considered have markedly different characteristics for the stretching and bending levels, which often leads to fortuitous cancellation of errors. The effect of the Breit interaction on the rovibrational levels is intermediate between the effect of the kinetic relativistic correction and that of the one-electron Lamb-shift effect. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Many decades of work have been performed measuring, analyzing, and modelling the rovibrational spectrum of water (see, for example, [1–4] and references therein). Despite this considerable effort, much further work remains to be done. For example, Polyansky et al. [3,5] recently assigned 1687 features in the spectrum of sunspots recorded in the 10–20 μm region to transitions in water. These transitions represent only about 15% of the clearly resolved features observed in sunspots in this spectral region, and it is likely that nearly all of the unassigned features are also due to water. Further significant progress in assigning these features requires corresponding theoretical developments. In particular, it is now essential that the

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techniques of ab initio computational methods be extended to consider the many small physical effects which are usually neglected, but which may influence the measured transition frequencies of water.

The major factor determining the accuracy of a variationally calculated vibration–rotation spectrum is the potential energy surface (PES) employed. State-of-the-art ab initio electronic structure calculations are now capable [2,6,7] of predicting vibrational band origins (VBOs) and other spectroscopic properties of water with an accuracy of ~0.1%. To achieve this accuracy several physically significant factors, tacitly neglected in most works in computational molecular spectroscopy, must be considered: core-valence electron correlation, relativistic corrections, and coupling between electronic and nuclear motion, part of which is considered in the so-called Born–Oppenheimer diagonal correction (BODC) [8]. The validity of the Born–Oppenheimer approximation when calculating vibration–rotation spectra of water has been explored [2,9,10]. Relativistic effects [11–13] have also been attracting considerable attention [7,14–21]. The effect of the so-called scalar relativistic correction, comprising the one-electron mass–velocity and Darwin (MVD1) corrections, has been investigated in detail for the VBOs and rotational term values of water [14,15]. It has been assumed in the past that for a molecule such as water, the absolute relativistic energy correction may be significant but its variation with geometry is too small to be important. The most notable result of [14,15], however, was the demonstration of the sensitivity of the results to the inclusion of the dominant relativistic MVD1 correction to the PES of a light closed-shell molecular system. This should be contrasted with inclusion of the BODC, which only has a minor influence [9]. In general, addition of the MVD1 relativistic correction lowers the band origins of the stretching states but raises the band origins of the bending modes, as expected from the increased barrier to linearity of water found upon inclusion of relativistic effects [17,18].

After the dominant MVD1 corrections, the next most significant spin-independent relativistic effect is the two-electron Darwin (D2) term; the sum of these terms, MVD2 = MVD1 + D2, defines the Coulomb–Pauli approximation. Spin–orbit interactions can be neglected for light closed-shell molecules and it is generally assumed that the Coulomb–Pauli Hamiltonian [11] yields good approximations to results obtained from variational four-component solutions of the many-electron relativistic Dirac–Coulomb equation [11,19]. For example, at the grid points of this study (*vide infra*) the maximum relative deviation between the MVD2 and Dirac–Hartree–Fock (DHF) energies is only 0.76 cm^{-1} [19].

In order to improve significantly on the description provided by the Dirac–Coulomb equation, or by the Coulomb–Pauli approximation to it, the instantaneous charge–charge interaction defining the Coulomb interaction must be supplemented by interactions between electronic currents, and Lorentz covariance must be restored to within some specified approximation by the inclusion of retardation effects. The covariant frequency-dependent transverse Coulomb–gauge interaction is rather complicated in form, but is nevertheless used routinely in high-precision atomic structure studies. The low-frequency form of the Dirac–Coulomb–Breit Hamiltonian contains the leading-order quantum electrodynamic (QED) correction to the Coulomb interaction [13]. It offers a tractable approximation for detailed molecular studies, and incorporates all electronic terms correct to $O(Z\alpha)^2$. From this may be derived the two-component Pauli approximation, introducing spin-dependent interactions in addition to the operators which define the scalar Coulomb–Pauli theory. The Dirac–Coulomb–Gaunt Hamiltonian includes only the magnetic interactions between pairs of electronic currents, neglecting certain $O(Z\alpha)^2$ contributions [13,20,21]. Quiney et al. [21] have already probed the Gaunt and Breit energy corrections for water; their work and simple physical arguments suggest that the inclusion of the geometry dependence of the Breit correction in the ground-state PES of water should have a noticeable effect on the calculated VBOs and rotational term values. It is this possibility which we principally address in this Letter. At this point it should be noted that an even smaller correction due to the leading QED effect requiring renormalization of divergences, the one-electron Lamb-shift effect (self-energy and vacuum polarization [20]), has been investigated for the ground-state PES of water [16]. Estimates of the one-electron Lamb-shift in the PES yield corrections of up to 1 cm^{-1} in magnitude for the rovibrational states of water investigated. Inclusion of the two-electron Lamb-shift effect in the PES has, on the other hand, negligible influence on the rovibrational states [16].

2. Computational techniques

The energy correction due to the D2, has been computed with cc-pVQZ CCSD(T) [22,23] wavefunctions, at the same level as the previous calculations of MVD1 correction energies [14,15].

Relativistic energy corrections due to the Gaunt and Breit interactions were obtained in first order of perturbation theory using the four-component DHF wavefunction [13], the recommended exponent factors for the Gaussian nuclear charge distribution [24], and the following [O, H] basis sets: basis A = [11s6p, 6s] and basis B = [11s6p3d, 6s3p] for the large component. The restricted kinetic balance prescription [13] was used to generate the small-component basis functions from the large component set in a one-to-one mapping. The calculations have been repeated at over 300 structures comprising the data set $1.47 \leqslant \text{distance} \leqslant 2.79\ a_0$ and $41\,\text{deg} \leqslant \text{angle} \leqslant 172\,\text{deg}$. The computer codes DIRCCR12 [25], MOLFDIR [26,27], and BERTHA [13,28] have been employed for the electronic structure calculations involving the D2, Gaunt, and Breit terms, respectively. Values for each energy correction obtained with basis set B have been placed on our web site, see below.

The absolute values of the (Gaunt,Breit) energy correction on the PES of water are about (7.8, 7.6) $\mathrm{m}E_\mathrm{h}$, while the maximum difference within the region covered by our grid is (46,42) cm^{-1}. The D2 effect is smaller, being 3.3 $\mathrm{m}E_\mathrm{h}$ and 6.5 cm^{-1}, respectively. Fig. 1 shows how the two-electron Darwin, Gaunt, and the Breit corrections vary as a function of the bond angle and the symmetric stretching coordinate.

In order to use the calculated relativistic corrections in nuclear motion calculations we have fitted them to an analytic functional form which is the same as the one used in [14,15]. The computer algebra package *Mathematica* [29,30] was used for the fitting and for the automatic generation of the PES subroutines in FORTRAN. The 55 coefficients obtained from a least-squares fit to our data points can be downloaded from the web site ftp://ftp.tampa.phys.ucl.ac.uk/pub/vr/potentials/H2O.rel, and are incorporated within FORTRAN routines representing the PESs. The fit gives an accurate representation of the data and has a standard deviation of only 0.02 cm^{-1} or better.

Nuclear motion calculations were performed using the DVR3D program suite [31] and previously optimized basis sets [32]. Calculations were only performed for the $\mathrm{H_2{}^{16}O}$ isotopomer of water. All calculations presented here used a hydrogen mass midway between the atomic and nuclear value, as recommended by Zobov et al. [9].

Similarly, a recent calculation has shown that spin-orbit interactions make a negligible contribution to the shape of the potential [19].

3. Discussion

Tables 1 and 2 summarize calculations for selected vibrational and rotational term values of water, respectively. These calculations were all performed with PESs being a sum of nonrelativistic and relativistic correction surfaces, where the nonrelativistic surface is the ab initio Born–Oppenheimer (BO) surface of Partridge and Schwenke [2] [2] corrected with the mass-dependent BODC correction of Zobov et al. [9]. To maintain consistency, the nonrelativistic results are the same as given in [14,15].

Relativistic corrections to the PES can either raise or lower the rovibrational bands. To understand the observed relativistic shifts in the bending band origins it is worth discussing relativistic effects on the barrier to linearity of water and on the one-dimensional bending functions. Recent studies

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[2] Here we used the Partidge and Schwenke's best fit to their ab initio data as defined by the parameter $(c^{5Z}, c^{\mathrm{basis}}, c^{\mathrm{core}}, c^{\mathrm{fit}}) = (1, 0, -1, 0)$ in their potential.

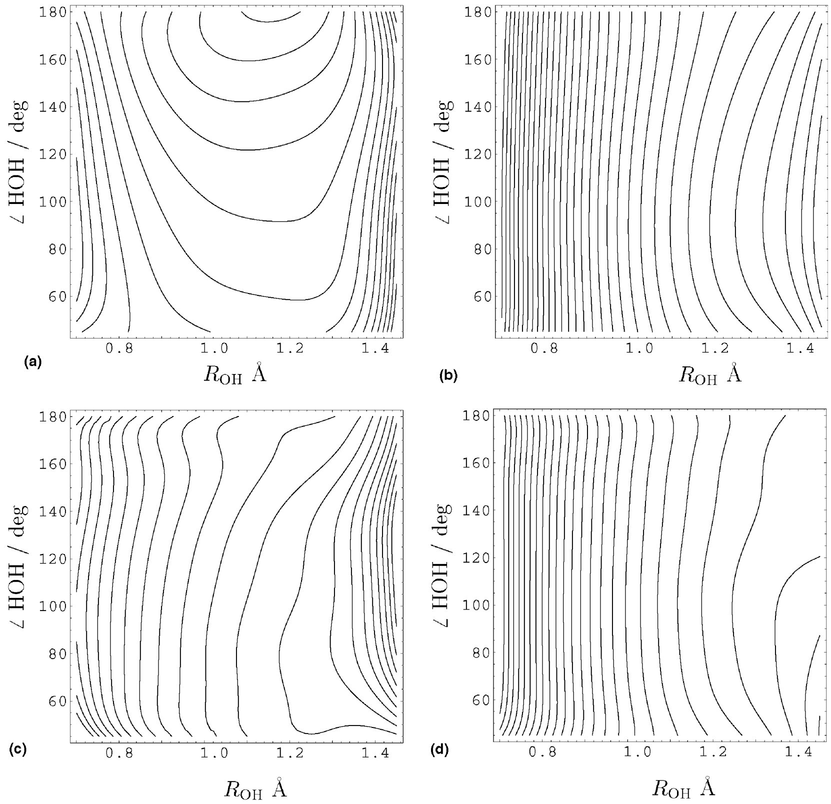

Fig. 1. Contour plot of two-electron relativistic correction surfaces as a function of the bond angle (in degrees) and the symmetric stretching (in Å) coordinates: (a) Two-electron Darwin (D2) surface. The contour lines are separated by 1 cm^{-1} with a maximum at the top of the figure; (b) Gaunt interaction surface. The contour lines are separated by 2.5 cm^{-1} decreasing left to right; (c) Breit–Gaunt interaction surface. The contour lines are separated by 1 cm^{-1} increasing left to right; (d) Breit interaction surface. The contour lines are separated by 2.5 cm^{-1} decreasing left to right.

[7,14–16,19,21], as well as the present one, indicate that the one-electron kinetic relativistic effect (MVD1) raises the barrier by about 55 cm^{-1}, while the D2 term raises the barrier by 2.5 cm^{-1}. Both the MVD1 and the D2 bending curves show monotonic behavior. Beyond these scalar relativistic effects, the Gaunt correction raises the barrier by 6 cm^{-1}, the correction to it in the Breit operator compensates this effect by 2 cm^{-1}, and consequently the Breit correction raises the barrier by 4 cm^{-1}. The approximation to the Lamb-shift correction [16] lowers the barrier by almost 4 cm^{-1}. As seen below, these changes in the PES mostly translate directly into shifts of the computed bending band origins.

Our results clearly indicate that the two-electron relativistic corrections considered in this study have a significant influence on the calculated behavior of both the vibrational and rotational states of water. However, these results are fairly insensitive to the level of sophistication of the calculation. The mean deviation between the changes in the Gaunt VBOs determined with basis A and basis B is only 0.05 cm^{-1}, or approximately 2%, with the larger basis B corrections giving slightly larger values. The results for the Breit correction are similar, indicating that their effects are strongly localized near the nuclei.

The MVD1 relativistic corrections [14,15] for the pure bending levels grow faster than linearly, a good approximate formula for them is $1.221 + 0.024n_2^3$, where n_2 is the bending quantum number. The linear formula $+1.4n_2$ is a good approximation up to $n_2 = 3$. There is a rapid linear

Table 1
Vibrational band origins, in cm^{-1}, for $H_2{}^{16}O$

	Obs[a]	BO + ΔV_{ad}	+ΔV_{rel}	+D2	+Gaunt	+Retard.
(0 1 0)	1594.75	1596.90	1.28	0.09	−0.10	−0.01
(0 2 0)	3151.63	3155.77	2.72	0.18	−0.18	−0.03
(1 0 0)	3657.05	3660.48	−2.80	−0.05	−0.78	0.15
(0 3 0)	4666.80	4672.84	4.38	0.28	−0.21	−0.07
(1 1 0)	5235.00	5240.67	−1.56	0.04	−0.89	0.15
(0 4 0)	6134.03	6141.91	6.38	0.40	−0.20	−0.13
(1 2 0)	6775.10	6782.80	−0.20	0.13	−0.96	0.12
(2 0 0)	7201.54	7207.84	−5.60	−0.09	−1.56	0.29
(0 0 2)	7445.07	7450.15	−5.79	−0.09	−1.65	0.32
(0 5 0)	7542.39	7552.13	8.96	0.54	−0.10	−0.19
(1 3 0)	8273.98	8283.66	1.38	0.23	−1.01	0.09
(2 1 0)	8761.59	8770.17	−4.42	−0.01	−1.66	0.29
(0 6 0)	8870.50	8881.89	12.62	0.73	0.16	−0.27
(0 1 2)	9000.14	9007.43	−4.73	−0.01	−1.77	0.32
(2 2 0)	10284.37	10294.93	−3.16	0.07	−1.75	0.28
(3 0 0)	10599.69	10607.86	−8.38	−0.14	−2.32	0.44
(1 0 2)	10868.88	10877.70	−8.50	−0.14	−2.37	0.45
(3 1 0)	12139.20	12149.75	−7.29	−0.06	−2.44	0.44
(1 1 2)	12407.64	12418.82	−6.81	0.07	−1.97	0.27
(4 0 0)	13828.28	13837.75	−11.06	−0.18	−3.06	0.58
(1 2 2)	13910.90	13924.10	−6.22	0.02	−2.57	0.44
(2 0 2)	14221.16	14233.05	−11.19	−0.18	−3.10	0.58
(0 0 4)	14537.50	14547.06	−11.59	−0.19	−3.25	0.62
(3 3 0)	15108.24	15122.47	−5.03	0.10	−2.62	0.40
(4 1 0)	15344.50	15356.30	−9.92	−0.10	−3.17	0.58
(2 1 2)	15742.80	15757.01	−10.12	−0.11	−3.20	0.59
(3 0 2)	17458.35	17471.62	−13.88	−0.23	−3.84	0.73
(5 1 0)	18392.97	18405.23	−12.11	−0.12	−3.83	0.71
(0 3 4)	18977.30	18993.66	−9.27	0.00	−3.63	0.61
(5 2 0)	19864.10	19877.85	−11.82	−0.07	−4.01	0.72
(6 1 0)	21221.57	21235.42	−14.30	−0.11	−4.48	0.77
(0 0 1)	3755.93	3758.30	−2.90	−0.05	−0.84	0.16
(0 1 1)	5331.27	5335.77	−1.73	0.04	−0.95	0.16
(0 2 1)	6871.52	6878.15	−0.45	0.12	−1.04	0.14
(1 0 1)	7249.80	7255.19	−5.68	−0.09	−1.60	0.30
(0 3 1)	8373.80	8382.57	1.03	0.22	−1.09	0.11
(1 1 1)	8807.00	8814.62	−4.56	−0.02	−1.71	0.30
(0 4 1)	9833.60	9844.25	2.80	0.32	−1.10	0.06
(1 2 1)	10328.70	10338.35	−3.37	0.07	−1.80	0.29
(2 0 1)	10613.40	10621.12	−8.42	−0.14	−2.34	0.44
(0 0 3)	11032.40	11039.71	−8.70	−0.14	−2.46	0.47
(1 3 1)	11813.20	11824.90	−2.01	0.15	−1.87	0.26
(2 1 1)	12151.30	12161.28	−7.36	−0.06	−2.46	0.44
(3 0 1)	13830.94	13840.36	−11.06	−0.18	−3.07	0.58
(0 7 1)	13835.37	13852.00	12.46	0.82	−0.52	−0.16
(0 2 3)	14066.19	14078.00	−6.75	0.00	−2.70	0.46
(1 0 3)	14318.81	14329.06	−11.38	−0.19	−3.17	0.60
(2 3 1)	15119.03	15132.98	−5.10	0.09	−2.64	0.41
(3 1 1)	15347.96	15359.55	−10.06	−0.11	−3.19	0.59
(0 3 3)	15534.71	15548.74	−5.60	0.08	−2.78	0.44
(1 1 3)	15832.76	15845.33	−10.43	−0.11	−3.29	0.61
(3 2 1)	16821.63	16834.24	−9.93	−0.08	−3.39	0.60
(2 0 3)	16898.84	16909.48	−12.98	−0.20	−3.71	0.70

Table 1 (Continued)

	Obs[a]	BO + ΔV_{ad}	+ΔV_{rel}	+D2	+Gaunt	+Retard.
(1 2 3)	17312.54	17326.99	−9.48	−0.04	−3.40	0.60
(4 0 1)	17495.53	17507.93	−13.97	−0.23	−3.87	0.74
(3 3 1)	18265.82	18280.83	−8.66	0.01	−3.46	0.58
(4 1 1)	18393.30	18405.78	−12.02	−0.12	−3.82	0.71
(2 1 3)	18989.96	19004.62	−13.03	−0.16	−3.99	0.75
(5 0 1)	19781.10	19791.80	−15.80	−0.25	−4.43	0.84
(5 1 1)	21221.83	21235.74	−14.32	−0.15	−4.48	0.83

Absolute values are given for the observed (Obs) VBOs and for the ab initio PES corresponding to the Born–Oppenheimer (BO) + Born–Oppenheimer Diagonal Correction (ΔV_{ad}) surface, and increments are given for the relativistic one-electron mass–velocity and Darwin (MVD1, +ΔV_{rel}), the two-electron Darwin (+D2), the Gaunt (+Gaunt), and the retardation (+Retard., Breit–Gaunt) surface corrections. Increments are given as individual contributions.

[a] Observed fundamentals are taken from Ref. [33]. All two-electron corrections are referenced to the Born–Oppenheimer (BO) + Born–Oppenheimer Diagonal Correction (ΔV_{ad}) + relativistic MVD1 (ΔV_{rel}) surface result.

increase in the stretching corrections, which is well approximated by $-2.8(n_1 + n_3)$, where n_1 and n_3 are the stretching quantum numbers. Additivity of the stretch and bend corrections seems to hold better than 95%.

The average effect of inclusion of the relativistic two-electron correction terms in the PES on the VBOs of water is not particularly large, considerably smaller than the effect arising from the inclusion of the MVD1 term, but appears to be significant.

The correction from D2 for the pure stretching VBOs is smaller than 0.2 cm^{-1} for the region covered here, and can be approximated well, up to $n_1 + n_3 = 5$, by the relation -0.01–$0.04(n_1 + n_3)$. The D2 correction increases for the bending modes with increasing excitation, it reaches the substantial value of $+0.8$ cm^{-1} for $n_2 = 7$ and can be represented with the simple linear form $-0.07 + 0.12n_2$. For stretch-bend combination levels the stretching and bending corrections seem to be additive to a good approximation; for

Table 2
Rotational term values ($J = 20$), in cm^{-1}, for the vibrational ground state of $H_2{}^{16}O$

	Obs[a]	BO + ΔV_{ad}	+ΔV_{rel}	+D2	+Gaunt	+Retard.
20_{020}	4048.252	4048.396	−1.264	0.884	−1.060	0.175
20_{119}	4412.316	4412.458	−1.363	0.963	−1.154	0.190
20_{218}	4738.620	4738.806	−1.356	1.021	−1.226	0.201
20_{317}	5031.798	5032.044	−1.260	1.065	−1.280	0.207
20_{416}	5292.107	5292.440	−1.014	1.089	−1.313	0.208
20_{515}	5513.235	5513.708	−0.399	1.073	−1.301	0.196
20_{614}	5680.793	5681.431	0.575	1.015	−1.243	0.171
20_{713}	5812.071	5812.728	0.551	1.040	−1.272	0.175
20_{812}	5966.826	5967.311	−0.838	1.189	−1.440	0.223
20_{911}	6170.841	6171.179	−2.281	1.353	−1.622	0.273
20_{1010}	6407.447	6407.716	−3.398	1.490	−1.778	0.314
20_{119}	6664.173	6664.418	−4.417	1.623	−1.927	0.352
20_{128}	6935.419	6935.671	−5.397	1.749	−2.074	0.390
20_{137}	7217.573	7217.850	−6.377	1.880	−2.221	0.427
20_{146}	7507.580	7507.923	−7.336	2.003	−2.367	0.464
20_{155}	7802.714	7803.154	−8.311	2.133	−2.511	0.501
20_{164}	8100.284	8100.871	−9.262	2.250	−2.654	0.538
20_{173}	8397.645	8398.419	−10.241	2.376	−2.795	0.574
20_{182}	8691.921	8692.929	−11.204	2.488	−2.933	0.610
20_{191}	8979.884	8981.191	−12.204	2.607	−3.069	0.646
20_{200}	9257.451	9259.161	−13.223	2.717	−3.202	0.681

[a] Observed rotational term values are taken from Ref. [33]. For explanation of column headings see Table 1.

example, the corrections for (1 0 0), (0 2 0), and (1 2 0) are +0.05, −0.17, and −0.12 cm^{-1}, respectively.

The Gaunt correction for the bending VBOs does not seem to follow a simple pattern. First it increases, peaks at about $n_2 = 3$ at $+0.21\ cm^{-1}$, and decreases to $-0.15\ cm^{-1}$ at $n_2 = 6$. The Gaunt correction is much larger for the stretching levels, grows linearly with excitation, and is well approximated as $-0.8(n_1 + n_3)\ cm^{-1}$. Similarly to the behavior of the D2 correction, there seems to be an additivity of stretching and bending Gaunt correction for the stretch-bend combination levels.

The Breit corrections are always smaller, except for the pure bending VBOs, than the Gaunt corrections, in most cases by some 20–30%. The retardation correction, defined as Breit–Gaunt, is linear for the stretching modes, $0.15(n_1 + n_3)$. The retardation correction for the bending modes varies, up to $n_2 = 3$, as $-0.02n_2$, and it seems to decrease faster than linear after this.

Table 2 shows the $J = 20$ rotational term values for the vibrational ground-state calculated using the same models analyzed above for the VBOs. The effect of the inclusion of two-electron relativistic corrections on the rotational term values is interestingly rather small as it would appear that the three contributions we consider here: D2, Gaunt, and Breit–Gaunt, approximately cancel each other out.

4. Conclusions

In this Letter, we have calculated ab initio the contribution of various two-electron relativistic correction terms to the PES of water and their consequence on the vibration–rotation energy levels. Using this information it is possible to quantify the contributions of various terms which are neglected in a standard nonrelativistic Born–Oppenheimer Schrödinger treatment of the electronic structure problem. For water the largest contribution to the vibrational band origins that have been assigned arises from the scalar one-electron relativistic correction, given by the MVD1 terms, and it is $-19\ cm^{-1}$, while the D2 contributes only $+0.8\ cm^{-1}$, the Gaunt term contributes $-5\ cm^{-1}$, and the Breit (= Gaunt + retardation) term contributes $-4\ cm^{-1}$. These can be compared with Lamb-shift effects which contribute a maximum of $+1.3\ cm^{-1}$ [16], the adiabatic correction (or BODC) which contributes $+5\ cm^{-1}$ and the nonadiabatic correction contributes $-4\ cm^{-1}$. In considering these numbers it should be remembered that lack of convergence of the best nonrelativistic Born–Oppenheimer electronic structure calculations gives an error of up to 30 cm^{-1} in the vibrational band origins.

Some important points should be noted about the above contributions. First, the maximum contribution does not distinguish between the behavior of the bending and stretching modes, although for nearly all cases the magnitude and the sign of the contribution is mode dependent. For example, the error in the electronic structure calculation is predominantly in the bending mode [2]. Second, the corresponding contributions to the pure rotational energies are rather small so that the net effect is that two-electron relativistic effects contribute little. Finally, the differing signs of the various contributions may lead to a fortuitous cancellation of errors, and results whose agreement with the observations is superficial, and possibly misleading with respect to the accuracy of the individual contributions.

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