



## Relativistic correction to the potential energy surface and vibration-rotation levels of water

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### Abstract

The relativistic correction to the electronic energy of the water molecule is calculated as a function of geometry using CCSD(T) wavefunctions and first-order perturbation theory applied to the one-electron mass-velocity and Darwin terms. Based on the calculated 324 energy points, a fitted relativistic correction surface is constructed. This surface is used with a high-accuracy ab initio non-relativistic Born–Oppenheimer potential energy surface to calculate the vibrational band origins and rotational term values for H<sub>2</sub><sup>16</sup>O. These calculations suggest that the relativistic correction, has a stronger influence on the vibration-rotation levels of water than the Born–Oppenheimer diagonal correction. The effect is particularly marked for vibrational levels with bending excitation or rotational states with high  $K_a$ . © 1998 Elsevier Science B.V. All rights reserved.

### 1. Introduction

The vibration-rotation spectrum of water is perhaps the most important and intensely studied of all molecular spectra. For instance, water vapour is thought to be responsible for absorbing 70% of the sunlight lost in a cloudless atmosphere [1]. Many decades of work have been performed measuring, analysing and modeling the spectrum of water, yet there remains much to be done.

In a recent theoretical development, Polyansky et al. [2,3] have used a combination of high level ab initio electronic structure calculations and variational

nuclear motion calculations to assign 1687 transitions to water in the spectrum of sunspots recorded in the 10–20 μm region. Yet these transitions represent only about 15% of the clearly resolved features observed in sunspots in this spectral region. It is likely that nearly all the unassigned features are also due to water. Further significant progress in assigning these features will require corresponding theoretical developments. It is therefore important to consider all possible factors which influence the ab initio calculation of transition frequencies.

The major factor determining the accuracy of a computed vibration-rotation spectrum is the potential energy surface (PES) employed. State-of-the-art ab initio electronic structure calculations are now capable of predicting vibrational band origins of water to within a few wavenumbers, and other spectroscopic

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properties with similar ( $\sim 0.2\%$ ) accuracy [4–6]. However, standard treatments of molecular electronic structure theory tacitly neglect several physically significant factors which become important in high-accuracy theoretical work: core-valence electron correlation, coupling between electronic and nuclear motion, part of which is considered in the so-called Born–Oppenheimer diagonal correction (BODC), and relativistic corrections. A number of groups have recently started exploring the validity of the Born–Oppenheimer approximation when calculating vibration-rotation spectra, using water as the test molecule [4,7]. Relativistic effects are also receiving considerable interest [8], but less attention has been paid to the possible spectroscopic consequences of the relativistic correction for light molecules. It has been assumed that for a molecule such as water, the absolute relativistic correction may be significant but its variation with geometry is too small to be important.

In a recent study, Császár et al. [16] looked critically at the various corrections to standard ab initio electronic structure calculations influencing barrier heights in a number of prototypical molecular systems, including water, ammonia, and ethane. Their extrapolated result for the barrier to linearity in water was in good agreement with an empirical value [17]. Császár et al. found that the relativistic correction is particularly important for conformational changes which involve *sp* rehybridisation of lone pairs of electrons and that this correction is significantly larger for water than for all the other systems considered. For water, inclusion of the relativistic correction raised the barrier height by  $50\text{ cm}^{-1}$  or about 0.5%. This is clearly a significant amount and led us to wonder what effect the inclusion of this relativistic correction has on the calculated spectroscopic properties of water. It is this question that we address in this letter.

## 2. Computational methods

### 2.1. Electronic structure calculations

Relativistic effects have been gauged by first-order perturbation theory applied to the one-electron mass-velocity and Darwin terms [8,10], as imple-

mented within the ACES II program system [9,11]. Although no-one has performed a systematic comparison of the geometry dependence of relativistic effects computed with a full Dirac Hamiltonian and the above method, there is considerable evidence [11–13] that first-order perturbation theory gives reliable results for light atoms. The calculations employed correlated coupled cluster wavefunctions at the CCSD(T) level of theory [14] and the extended cc-pVQZ basis set [15]. They have been repeated at 324 structures in the range of bondlengths  $1.47 \leq r \leq 2.79 a_0$  and angles  $41^\circ \leq \theta \leq 180^\circ$ .

In order to use the calculated relativistic correction in nuclear motion calculations we have fitted it to an analytic functional form using the following symmetrized displacement coordinates:

$$\begin{aligned} S_1 &= \frac{r_1 + r_2}{2} - r_e \\ S_2 &= \theta - \theta_e \\ S_3 &= \frac{r_1 - r_2}{2} \end{aligned} \quad (1)$$

where  $(r_e, \theta_e)$  are equilibrium values taken to be  $(1.80965 a_0, 1.824045 \text{ rad})$ . The surface was fitted as a simple power series in the displacement coordinates

$$\Delta V_{\text{rel}}(S_1, S_2, S_3) = \sum_{i,j,k} c_{i,j,k} S_1^i S_2^j S_3^k. \quad (2)$$

Terms up to seventh-order,  $i + j + k \leq 7$ , were retained in the expansion, although some terms, which were not well determined, were dropped. The only significant eighth order term  $(ijk) = (080)$  was also retained.

The 55 coefficients resulting from a least-squares fit to our 324 data points are presented in Table 1. The fit gives an accurate representation of the data and has a standard deviation of only  $0.02\text{ cm}^{-1}$ . With the same terms in the expansion and using an angular expansion based on terms of  $S_2 = \cos(\theta) - \cos(\theta_e)$ , as proposed by Jensen [18], the data points are reproduced with a significantly larger standard deviation of  $0.07\text{ cm}^{-1}$ .

The major part of the first-order relativistic energy arises from the oxygen 1s electrons and is geometry independent. Its calculated value is about  $-0.05 E_h$ . Accordingly, the leading, constant term

Table 1  
Coefficients in Eq. (2) for the relativistic correction surface of H<sub>2</sub>O

<i>i</i>	<i>j</i>	<i>k</i>	<i>c</i> <sub><i>i,j,k</i></sub>
0	0	0	-51992.84954
1	0	0	-53.95314
0	1	0	181.69823
2	0	0	-623.11790
0	2	0	52.56205
0	0	2	-480.21449
1	1	0	26.32762
3	0	0	638.79701
0	3	0	21.32618
2	1	0	-281.81284
1	2	0	34.28257
1	0	2	1873.16555
0	1	2	-118.38395
4	0	0	-347.16232
0	4	0	-8.42200
0	0	4	-553.09740
3	1	0	120.23015
1	3	0	141.02871
2	2	0	-72.44424
2	0	2	-2831.20672
0	2	2	-61.31686
1	1	2	-9.86563
5	0	0	450.82710
0	5	0	-5.02180
1	4	0	38.88296
1	0	4	1950.21929
3	2	0	-83.44686
3	0	2	4215.27185
2	3	0	-64.72097
0	3	2	6.90706
1	2	2	75.01079
6	0	0	-480.58626
0	6	0	-14.29775
0	0	6	-106.73778
1	5	0	-32.71663
4	2	0	-150.43974
4	0	2	-6951.40466
2	4	0	94.30314
0	4	2	83.82776
2	0	4	-3495.23102
0	2	4	173.88804
3	3	0	-233.91349
1	1	2	-35.63530
0	7	0	-3.93461
6	1	0	-441.23567
1	6	0	-28.51688
5	0	2	5254.70283
2	5	0	82.57348
4	3	0	357.18441
3	4	0	79.20561
3	0	4	3012.69084
4	1	2	161.31404

Table 1 (continued)

<i>i</i>	<i>j</i>	<i>k</i>	<i>c</i> <sub><i>i,j,k</i></sub>
2	1	4	-596.36895
1	2	4	-1009.70103
0	8	0	1.68231

Units are consistent with bond lengths in *a*<sub>0</sub> and bond angle in rad for energies in μE<sub>h</sub>.

in the fit (see Table 1) is by far the largest. Of course, this term has no influence on the vibration-rotation spectrum. The changes in relativistic energy correction with geometry are two orders of magnitude smaller and have different signs upon bending and stretching of the water molecule.

Fig. 1 shows how the relativistic correction varies as a function of bond angle and the symmetric stretching coordinate. There is a particularly strong angular dependence which is approximately linear for bond lengths close to equilibrium.

## 2.2. Nuclear motion calculations

Nuclear motion calculations were performed using the DVR3D program suite [19] and previously optimized basis sets [20]. Calculations were only performed for the H<sub>2</sub><sup>16</sup>O isotopomer of water. A number of calculations were performed testing different combinations of ab initio Born–Oppenheimer

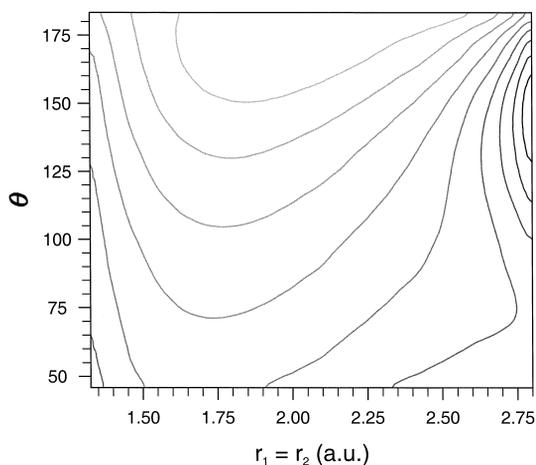


Fig. 1. Variation of the relativistic correction as a function of bond angle,  $\theta$ , and bond lengths,  $r_1$  and  $r_2$ . The plot is for symmetric stretches only. Contours are spaced by 20 cm<sup>-1</sup>.

Table 2  
Band origins (in  $\text{cm}^{-1}$ ) for the  $\text{H}_2^{16}\text{O}$

	Obs <sup>a</sup>	b	c	d
(010)	1594.75	-2.65	-2.15	-3.75
(020)	3151.63	-5.12	-4.13	-7.47
(100)	3657.05	-3.49	-3.42	-0.72
(030)	4666.80	-7.53	-6.05	-11.36
(110)	5235.00	-6.20	-5.70	-4.51
(040)	6134.03	-9.90	-7.88	-15.51
(120)	6775.10	-8.64	-7.70	-8.15
(200)	7201.54	-6.38	-6.30	-0.92
(002)	7445.07	-4.89	-5.08	0.38
(050)	7542.39	-12.39	-9.74	-20.33
(130)	8273.98	-11.06	-9.69	-12.00
(210)	8761.59	-9.07	-8.59	-4.65
(060)	8870.5	-14.9	-11.3	-26.2
(012)	9000.14	-7.50	-7.30	-3.15
(220)	10284.37	-11.39	-10.57	-8.10
(022)	10524.3	-7.5	-7.0	-4.2
(300)	10599.69	-8.20	-8.19	-0.17
(102)	10868.88	-8.81	-8.82	-0.71
(310)	12139.2	-10.9	-10.6	-3.8
(112)	12407.64	-11.53	-11.18	-0.86
(240)	13205.1	-16.0	-14.3	-15.7
(042)	13453.7	-14.8	-13.5	-14.3
(320)	13640.8	-13.0	-12.3	-7.2
(170)	13661.3	-19.7	-16.0	-30.0
(202)	13828.28	-9.43	-9.48	1.09
(122)	13910.90	-13.82	-13.20	-7.77
(400)	14221.16	-12.00	-11.89	-1.15
(004)	14537.5	-9.2	-9.6	1.5
(330)	15108.1	-15.3	-14.4	-10.3
(212)	15344.50	-12.02	-11.80	-2.56
(410)	15742.80	-14.60	-14.23	-4.73
(222)	16825.23	-12.25	-11.78	-4.23
(302)	16898.4	-10.6	-10.7	1.7
(420)	17227.70	-16.36	-15.78	-7.63
(104)	17458.30	-13.38	-13.32	0.03
(500)	17748.07	-13.06	-13.19	0.36
(312)	18392.98	-12.28	-12.25	-0.86
(001)	3755.93	-2.25	-2.34	0.28
(011)	5331.27	-4.83	-4.47	-3.31
(021)	6871.51	-7.39	-6.62	-7.00
(101)	7249.81	-5.32	-5.36	-0.04
(031)	8373.8	-9.9	-8.8	-10.9
(111)	8807.00	-7.95	-7.60	-3.65
(041)	9833.58	-12.24	-10.64	-14.79
(121)	10328.73	-10.29	-9.60	-7.07
(201)	10613.36	-7.72	-7.74	0.22
(003)	11032.41	-7.01	-7.29	0.93
(131)	11813.19	-12.73	-11.69	-10.74
(211)	12151.26	-10.30	-10.00	-3.31
(013)	12565.00	-9.63	-9.56	-2.50

Table 2 (continued)

	Obs <sup>a</sup>	b	c	d
(141)	13256.2	-15.0	-13.6	-14.6
(221)	13652.66	-12.33	-11.75	-6.27
(301)	13830.94	-9.36	-9.40	1.10
(071)	13835.37	-20.23	-16.61	-31.66
(023)	14066.19	-12.12	-11.79	-5.91
(103)	14318.81	-10.09	-10.23	0.58
(231)	15119.03	-14.77	-13.93	-9.87
(311)	15347.96	-11.77	-11.58	-2.24
(033)	15534.71	-14.60	-14.02	-9.47
(113)	15832.77	-12.66	-12.55	-2.86
(321)	16821.64	-12.94	-12.59	-3.50
(203)	16898.84	-10.53	-10.60	1.72
(123)	17312.54	-14.76	-14.44	-5.84
(401)	17495.53	-12.30	-12.38	0.94
(331)	18265.82	-15.60	-14.99	-7.34
(213)	18393.31	-12.49	-12.44	-1.19
(411)	18989.96	-14.72	-14.65	-2.38
(303)	19781.11	-10.60	-10.66	4.36
(501)	20543.14	-13.65	-13.73	-1.61
(511)	21221.8	-14.0	-13.9	-0.5
(403)	22529.4	-9.4	-9.6	8.2

Results calculated using Born–Oppenheimer (BO), Born–Oppenheimer Diagonal Correction ( $\Delta V^{\text{ad}}$ ) and with the relativistic correction ( $\Delta V_{\text{rel}}$ ) are given as observed – calculated.<sup>a</sup> Observed fundamentals from refs [21,22,25,26].<sup>b</sup> Born–Oppenheimer (BO) potential only.<sup>c</sup> BO +  $\Delta V^{\text{ad}}$ .<sup>d</sup> BO +  $\Delta V^{\text{ad}}$  +  $\Delta V_{\text{rel}}$ .

and adiabatically corrected potentials with our relativistic correction. Different possible hydrogenic masses were also tested. All calculations presented here used a hydrogenic mass midway between the atomic and nuclear value, as recommended by Zobov et al. [7]. In practice plausible choices of this mass have much less influence on the spectrum than inclusion of the relativistic correction.

Tables 2 and 3 summarize calculations for the vibrational and rotational levels of water. These calculations were all performed with the non-relativistic ab initio Born–Oppenheimer (BO) surface of Partridge and Schwenke [4].<sup>2</sup> Calculations were per-

<sup>2</sup> Here we used the Partridge and Schwenke's best fit to their ab initio data as defined by the parameter  $(c^{5Z}, c^{\text{basis}}, c^{\text{core}}, c^{\text{fit}}) = (1.0, -1.0)$  in their potential. Previous studies by us [2,3,7] used a preliminary fit. The two surfaces give results typically differing by  $0.1\text{--}0.2 \text{ cm}^{-1}$ .

formed with and without the mass dependent Born–Oppenheimer diagonal correction (BODC or adiabatic correction) of Zobov et al. [7].

The most notable result of Table 2 is how sensitive the results are to the inclusion of the relativistic

correction. This should be compared with inclusion of the BODC, which only has a minor influence. In general, addition of the relativistic correction lowers the band origins of the stretching states, *i.e.*, those for which  $\nu_2 = 0$ , but raises the band origins of the

Table 3

Rotational term values (in  $\text{cm}^{-1}$ ) for the vibrational ground state and (010) state of  $\text{H}_2^{16}\text{O}$

	Ground state				(010) state			
	Obs <sup>a</sup>	b	c	d	Obs <sup>a</sup>	b	c	d
20 <sub>020</sub>	4048.252	0.542	0.972	0.045	4016.581	0.845	1.216	0.386
20 <sub>120</sub>	4048.252	0.542	0.972	0.045	4016.581	0.844	1.216	0.386
20 <sub>119</sub>	4412.317	0.604	1.077	0.050	4428.049	1.016	1.414	0.554
20 <sub>219</sub>	4412.317	0.603	1.077	0.049	4428.051	1.014	1.406	0.556
20 <sub>218</sub>	4738.624	0.590	1.114	−0.082	4784.599	1.010	1.464	0.404
20 <sub>318</sub>	4738.636	0.590	1.116	−0.081	4784.645	1.010	1.460	0.450
20 <sub>317</sub>	5031.796	0.529	1.116	−0.316	5100.008	0.959	1.493	0.113
20 <sub>417</sub>	5031.977	0.530	1.117	−0.308	5100.554	0.959	1.489	0.159
20 <sub>416</sub>	5292.096	0.402	1.086	−0.719	5374.660	0.802	1.465	−0.435
20 <sub>516</sub>	5294.035	0.441	1.105	−0.610	5379.620	0.880	1.495	−0.175
20 <sub>515</sub>	5513.266	0.192	1.036	−1.479	5598.487	0.488	1.382	−1.608
20 <sub>615</sub>	5527.046	0.364	1.096	−0.886	5627.511	0.832	1.496	−0.384
20 <sub>614</sub>	5680.787	−0.200	0.877	−2.683	5762.306	0.201	1.311	−2.589
20 <sub>714</sub>	5739.232	0.374	1.122	−0.881	5857.784	0.908	1.549	−0.111
20 <sub>713</sub>	5812.074	−0.190	0.894	−2.703	5909.823	0.429	1.398	−1.886
20 <sub>813</sub>	5947.327	0.549	1.227	−0.369	6090.365	1.126	1.630	0.570
20 <sub>812</sub>	5966.827	0.285	1.107	−1.202	6101.535	0.915	1.530	0.040
20 <sub>912</sub>	6167.909	0.985	1.519	0.672	6339.423	1.413	1.728	1.628
20 <sub>911</sub>	6170.964	0.871	1.434	0.438	6341.018	1.385	1.723	1.523
20 <sub>1011</sub>	6407.084	1.071	1.434	1.453	6608.002	1.682	1.797	2.707
20 <sub>1010</sub>	6407.446	1.063	1.426	1.429	6608.180	1.681	1.805	2.685
20 <sub>1110</sub>	6664.138	1.315	1.518	2.395	6893.156	1.925	1.851	3.761
20 <sub>119</sub>	6664.172	1.317	1.512	2.395	6893.153	1.903	1.828	3.758
20 <sub>129</sub>	6935.425	1.536	1.575	3.304	7191.043	2.126	1.858	4.648
20 <sub>128</sub>	6935.428	1.537	1.578	3.305	7191.041	2.121	1.856	4.646
20 <sub>138</sub>	7217.560	1.711	1.590	4.160	7498.245	2.290	1.840	5.550
20 <sub>137</sub>	7217.560	1.710	1.590	4.159	7498.245	2.286	1.840	5.550
20 <sub>147</sub>	7507.575	1.863	1.585	4.989	7811.766	2.805	2.371	6.471
20 <sub>146</sub>	7507.575	1.863	1.585	4.989	7811.736	2.410	1.771	6.441
20 <sub>156</sub>	7802.700	1.974	1.540	5.778	8128.763	2.495	1.668	7.268
20 <sub>155</sub>	7802.700	1.974	1.540	5.778	8128.763	2.495	1.668	7.268
20 <sub>165</sub>	8100.292	2.054	1.472	6.541	8446.615	2.532	1.520	8.020
20 <sub>164</sub>	8100.292	2.054	1.472	6.541	8446.615	2.532	1.520	8.020
20 <sub>174</sub>	8397.625	2.056	1.305	7.231	8762.590	2.526	1.315	8.695
20 <sub>173</sub>	8397.625	2.056	1.305	7.231	8762.590	2.526	1.315	8.695
20 <sub>183</sub>	8691.916	2.043	1.126	7.919	9073.744	2.441	1.029	9.349
20 <sub>182</sub>	8691.916	2.043	1.126	7.919	9073.744	2.441	1.029	9.349
20 <sub>192</sub>	8979.854	1.939	0.844	8.536	9376.758	2.307	0.673	10.063
20 <sub>191</sub>	8979.854	1.939	0.844	8.536	9376.758	2.307	0.673	10.063
20 <sub>201</sub>	9257.408	1.745	0.458	9.099	9667.337	2.080	0.192	10.542
20 <sub>200</sub>	9257.408	1.745	0.458	9.099	9667.337	2.080	0.192	10.542

Results calculated using Born–Oppenheimer (BO), Born–Oppenheimer Diagonal Correction ( $\Delta V^{\text{ad}}$ ) and with the relativistic correction ( $\Delta V_{\text{rel}}$ ), are given as observed – calculated. <sup>a</sup> Observed rotational term values from Refs. [21,23,24]. <sup>b</sup> Born–Oppenheimer (BO) potential only. <sup>c</sup> BO +  $\Delta V^{\text{ad}}$ . <sup>d</sup> BO +  $\Delta V^{\text{ad}}$  +  $\Delta V_{\text{rel}}$ .

bending modes. The effect on the bending modes is generally larger. As both the BO and the BODC calculations systematically overestimate the band origins, the effect of including the relativistic correction is to move the predicted stretching band origins significantly closer to the experimental values but, at the same time, to make predictions for the bending states considerably worse.

Table 3 shows the  $J = 20$  rotational term values calculated using the same models analyzed above for the vibrational fundamentals. Results are only presented for the vibrational ground state and the bending fundamental. These are the only states for which a complete set of experimentally determined  $J = 20$  rotational term values are available [21].

The effect of the inclusion of the relativistic correction on the rotational term values is strongly dependent on  $K_a$ . For low values of  $K_a$ , the relativistic correction has almost no effect. For mid  $K_a$  values, about  $K_a = 3$  to 9 for  $J = 20$ , it raises rotational energies by  $0.5$ – $1.0$   $\text{cm}^{-1}$  bringing the calculated and observed values into reasonably good agreement. This is probably due to a cancellation of errors. For high values of  $K_a$ , the relativistic correction lowers the rotational term values leading to significant disagreement with the observed levels. As discussed below, this is consistent with the large increase observed in the vibrational band origins.

### 3. Discussion and conclusions

Our results clearly show that the relativistic correction has a significant influence on the calculated behaviour of both the rotational and vibrational states of water. As expected from the increased barrier to linearity found upon inclusion of relativistic effects [16], the relativistic correction raises band origins of the bending states. Conversely, we find that these corrections lower the energy of rotationally excited states with high  $K_a$ . This is apparently counterintuitive as the high  $K_a$  states are also sensitive to the bending potential. However, the relativistic correction has a strong linear dependence on the angular coordinate. Test calculations which augmented the BO potential with a simple term proportional to  $S_2$  also found an increase in bending band origins and a lowering of the high  $K_a$  rotational states.

This observation is particularly interesting because of notable difficulties encountered in representing bending excitations both in water [17] and in  $\text{H}_2\text{S}$  [27] by fitting to spectroscopic data. We note that for both of these molecules the potentials were represented using  $S_2 = \cos(\theta) - \cos(\theta_e)$ , as recommended by Jensen [18]. This form of the potential was selected as it ensures the correct behaviour of the derivatives of the potential at linear geometries. However, our experience with fitting the relativistic correction suggests that this functional form may actually artificially constrain the potential making it difficult to get highly accurate representations of the potential in the bending coordinate.

The average discrepancy between ab initio theory and observation for the vibrational states of water is not significantly changed by inclusion of the relativistic correction in the calculation. However, there is a marked shift in the error. The error in all band origins using the non-relativistic BO potential surface of Partridge and Schwenke's [4] is approximately constant at  $0.1$ – $0.2\%$ . Inclusion of the relativistic correction in the potential greatly improves predictions for the stretching states at the expense of worsening (doubling) the error for the pure bending modes. Therefore, one wonders how to improve the representation of the bending potential.

In their study Császár et al. [16] considered the effect of a number of factors, including basis set effects, both for uncorrelated and correlated wavefunctions, the effect of different correlation models, and the effect of core-valence correlation. They found that whereas most of these effects are reliably modelled with state-of-the-art electronic structure calculations, such as those of Partridge and Schwenke [4], inclusion of higher angular momentum functions in the basis set has a significant effect on the correlation energy. These and new [28] results also indicate that the correlation energy is not yet converged with respect to increasing basis set size in the calculations of Partridge and Schwenke. This effect, which would generally act to lower the barrier to linearity and hence the bending band origins, could well be enough to compensate for the errors we find in the bending states. Furthermore, off-diagonal or non-adiabatic corrections to the Born–Oppenheimer approximation may well also be stronger for linear geometries leading to a lowering of the effective barrier height.

Test calculations, in which we added a term linear in the angle to our calculations based on the potential plus relativistic correction, substantially improved the representation of the bending overtones. This gives an important pointer as how a future, improved, spectroscopically determined effective potential energy surface might be determined.

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