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# Ab initio rotation–vibration energy levels of triatomics to spectroscopic accuracy

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## Abstract

The factors that need to be taken into account to achieve spectroscopic accuracy for triatomic molecules are considered focusing on $H_3^+$ and water as examples. The magnitude of the adiabatic and non-adiabatic corrections to the Born–Oppenheimer approximation is illustrated for both molecules, and methods of including them ab initio are discussed. Electronic relativistic effects are not important for $H_3^+$, but are for water for which the magnitude of the various effects is discussed. For $H_3^+$ inclusion of rotational non-adiabatic effects means that levels can be generated to an accuracy approaching 0.01 cm$^{-1}$; for water the error is still dominated by the error in the correlation energy in the electronic structure calculation. Prospects for improving this aspect of the calculation are discussed. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

It has become standard in the quantum chemistry literature to describe calculations with an error of 1 cm$^{-1}$ as being of 'spectroscopic accuracy'. Yet high resolution spectroscopy routinely measures rotation–vibration spectra to accuracies of 0.001 cm$^{-1}$ or even better. Indeed spectra of even light triatomics such as $H_3^+$ [1] or water [2] can have tens or hundreds of transitions per cm$^{-1}$. An accuracy of 1 cm$^{-1}$ has practical convenience because, as discussed below, going beyond these limits requires the consideration of a number of effects which are neglected in standard ab initio formulations.

Spectroscopy not only provides a detailed probe of molecular structure and interactions, it also provides data for numerous applications. Some applications, particularly those which involve the spectra of hot ($T > 1000$ K) species, require datasets which are too large for their laboratory determination to be possible. For example, recent compilations of water rotation–vibration lines considered well in excess of $10^8$

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individual transitions [3–5]. Perforce these datasets have to be constructed computationally but at the same time high accuracy is required. Thus the cited linelists, despite being based on very sophisticated models, are still found to be inadequate for models of cool ($T \sim 3000$ K) oxygen-rich stars [6,7]. The ability to compute reliable linelists thus relies not only on developing computational methods capable of yielding large amounts of data required but also on constructing high accuracy models. This has led us to explore in detail what is actually required to compute spectra of small molecules to real spectroscopic accuracy, i.e. at least better than 0.01 cm$^{-1}$.

We have performed high accuracy ab initio studies for a number of systems including $H_3^+$, $H_2O$, $H_2S$ [8] and HCN [9]. In this article we only consider results for the first two of these molecules, which are important prototypes. In particular $H_3^+$ is the one triatomic system for which the Born–Oppenheimer electronic structure problem has been solved to spectroscopic accuracy [10] and water, besides being particularly important, has been found to be sensitive, perhaps unusually so, to effects often neglected in standard models, see for example, Ref. [11].

## 2. $H_3^+$

$H_3^+$ is probably unique in that essentially all spectral assignments made have relied on first principles calculations based on the use of high accuracy potential energy surfaces and variational nuclear motion calculations [12]. The first assigned spectrum of $H_3^+$, the infrared emissions from its bending fundamental [13], relied heavily on the ab initio calculations of Carney and Porter [14]. Table 1 shows the improvement in electronic structure calculations since these pioneering calculations, concentrating only on those works that gave potential energy surfaces suitable for nuclear motion calculations.

For reliable calculations of vibration–rotation spectra the location of the minimum of the potential and the shape of the potential about the minimum is more important than the absolute error in the potential. Thus, Carney and Porter [15] made excellent predictions despite an absolute error approaching the value of the quantities they were predicting. Similarly Meyer et al. [18] used careful error control techniques to produce a potential which proved highly successful for spectral assignments [12]. Interestingly, the potential of Lie and Frye [19] actually gives results for vibrational band origins closer to the experimental ones than the near-exact potential of Cencek et al. [10]. This is due to fortuitous cancellation of errors: including corrections to the Born–Oppenheimer approximation with Lie and Frye's potential actually moves their results away from the observed ones.

Table 1 shows an improvement by at least a factor of 20 for the potentials computed within the last decade. The common feature of these more recent potentials is the use of explicitly correlated wave functions, i.e. ones which include the $r_{12}$ electron–electron coordinate in the wave function in some form. The potential of Cencek et al. [10] is so accurate that it makes a natural starting point for further investigations. Indeed these workers also calculated the relativistic correction to the electronic motion for $H_3^+$. They found this to be approximately 3 cm$^{-1}$ but to vary little with the geometry of the molecule, see Table III of [10]. This correction therefore makes little significant contribution, less than 0.01 cm$^{-1}$, to the vibration–rotation spectrum of $H_3^+$.

The same cannot be said for corrections to the Born–Oppenheimer approximation. Table 2

Table 1
Minimum electronic energy, $E_{\mathrm{min}}$, as a function of time for $H_3^+$ ab initio potential energy surfaces

| Reference | Year | $E_{\mathrm{min}}/E_{\mathrm{h}}$ | $\Delta E$ (cm$^{-1}$) |
|---|---|---|---|
| Carney and Porter [15] | 1976 | −1.33519 | 1900 |
| Schinke et al. [16] | 1980 | −1.34023 | 790 |
| Burton et al. [17] | 1985 | −1.34188 | 430 |
| Meyer et al. [18] | 1986 | −1.34309 | 160 |
| Lie and Frye [19] | 1992 | −1.343828 | 9 |
| Röhse et al. [20] | 1994 | −1.3438336 | 1 |
| Cencek et al. [10] | 1998 | −1.3438355 | 0.04 |

$\Delta E$ is the approximate error in the absolute electronic energy at the minimum.

Table 2
Vibrational band origins[a], in cm$^{-1}$, for $H_3^+$ and its observed isotopomers [28]

| | $E_{obs}$ | BO | $+\Delta V_{ad}$ | $\mu^V \neq \mu^N$ |
|---|---|---|---|---|
| $H_3^+$ | | | | |
| $01^1$ | 2521.409 | −0.11 | −0.24 | 0.056 |
| $10^0$ | 3178.290 | −1.30 | −0.40 | 0.025 |
| $02^0$ | 4778.350 | 0.00 | −0.50 | 0.020 |
| $02^2$ | 4998.045 | −0.30 | −0.64 | 0.010 |
| $11^1$ | 5554.155 | −1.40 | −0.50 | 0.000 |
| $H_2D^+$ | | | | |
| $v_1$ | 2992.505 | −1.46 | −0.36 | −0.020 |
| $v_2$ | 2205.869 | −0.47 | −0.25 | −0.050 |
| $v_3$ | 2335.449 | 0.47 | −0.14 | 0.090 |
| $D_2H^+$ | | | | |
| $v_1$ | 2736.981 | −1.04 | −0.28 | 0.001 |
| $v_2$ | 1968.169 | 0.58 | −0.11 | 0.023 |
| $v_3$ | 2078.430 | −0.74 | −0.18 | −0.004 |

Results are given as observed—calculated for various models defined as follows: BO, ab initio BO potential+relativistic surface; $+\Delta V_{ad}$, as BO plus adiabatic correction surface, $\Delta V_{ad}$; $\mu^V \neq \mu^N$, as $+\Delta V_{ad}$ with vibrational mass, $\mu^V$, greater than the nuclear mass, $\mu^N$.

[a] Experimentally derived data [24].

shows the sensitivity of the vibrational band origins of $H_3^+$ and its isotopomers to both adiabatic and non-adiabatic corrections to the Born–Oppenheimer calculation. It is relatively easy to calculate the adiabatic correction, which is also known as the Born–Oppenheimer diagonal correction (BODC) as second derivatives of the electronic wave function with respect to displacements of the nuclear positions [21]. The original calculation of BODC surfaces for $H_3^+$ [22] and its mixed isotopomers [23] used self-consistent field (SCF) wave functions and showed that the adiabatic correction was important at the 1 cm$^{-1}$ level. More recently, Cencek et al. [10] recalculated the BODC using their highly correlated wave functions. Their calculations give an effect 13 cm$^{-1}$ larger than the SCF calculations, but found this shift to be nearly uniform with $H_3^+$ geometry, see Table II of [10]. Use of the improved BODC changes the calculated vibrational band origins by less than 0.1 cm$^{-1}$.

Inclusion of non-adiabatic corrections to the Born–Oppenheimer approximation is far from simple. Recently, Schwenke has developed a method which involves estimating the effect by including the coupling due to excited states by summing over a complete set of one-electron excitations [25]. This method has yet to be widely used and has not yet been applied to $H_3^+$. The most common approach for diatomic systems is not to attempt such complete summations but to model the non-adiabatic correction to the vibrational motion by using an effective vibrational reduced mass for the system, $\mu^V$ [27], whose value should lie between that determined using atomic masses, $\mu^A$, and nuclear masses, $\mu^N$. Polyansky and Tennyson [28] adopted this approach and effective masses obtained by Moss [29] for $H_2^+$ and its isotopomers. The success of this approach is shown by the excellent results obtained in the final column of Table 2.

Polyansky and Tennyson [28] also concluded that the non-adiabatic correction to the rotational motion was small for low values of the rotational quantum number, $J$, that they considered. They, therefore, adopted a rotational mass, $\mu^R$, equal to the nuclear mass, $\mu^N$. However, they found that use of $\mu^V \neq \mu^R$ led to an extra term in the Hamiltonian, which, for $H_3^+$, is small but important for obtaining smooth results. It should be noted that the method adopted by Polyansky and Tennyson involves identifying vibrational and rotational motions, and that different ways of making this identification by, for example, using different embedding of the body-fixed rotational axes, will lead to different results. It has long been known that the optimal separation between vibrational and rotational motions is obtained by using the Eckart conditions [30].

Use of the Eckart conditions is not standard in most internal coordinate based variational calculations since they lead to considerably more complicated Hamiltonians, see [31,32]. However, for $H_3^+$ it is possible to get an embedding close to the Eckart one by fixing the $z$-axis perpendicular to the plane of the molecules and noting that, for the equilibrium equilateral triangle structure of $H_3^+$, all orientations of axes within the plane of the molecule are equivalent. Recently, Kostin et al. [33] have implemented a $z$-perpendicular embedding and used it to tackle the $H_3^+$ problem. They obtained rotational energy levels up to $J \leq 15$, the full range for which there is experimental data [34].

These calculations, because of their higher accuracy and larger range of $J$'s considered, show the clear signature of a small contribution due to non-adiabatic effects. This contribution can be estimated approximately as $0.003J(J+1) - 0.002K^2$ cm$^{-1}$, where $K$ is the projection of $J$ on the molecular $z$-axis.

Some time ago Bunker and Moss [35] made a rather complete formulation of the non-adiabatic contributions to the vibration–rotation problem for triatomic molecules. In this formulation they showed that the matrix elements, which determine the non-adiabatic correction to the rotational motion can be directly related to the electronic contribution to the rotational $g$-factor, $g^e$. For $H_3^+$ these factors are rather small but nevertheless have been calculated ab initio [36]. Use of these ab initio $g^e$ in our calculations almost completely account for the observed rotational non-adiabatic effect. Full results of this work will be reported elsewhere.

## 3. Water

Until recently, spectral analysis of the water molecule relied heavily on the use of effective Hamiltonians based on perturbation theory. However, improvements in the theory of variational calculations led to the assignment of spectra which had defied traditional analysis [2] leading to something of a paradigm shift in the analysis of water spectra [37]. The use of variational methods has emphasized the need for accurate, ab initio procedures.

Water spectra has long been used as a test bed for the accuracy of ab initio methods [38]. Table 3 charts the progress in ab initio predictions of the vibrational band origins of water since the original, pioneering variational calculations of Bucknell and Handy [39]. Although the error in the fundamentals has improved by about a factor of about 100 since then, there is some way to go before spectroscopic accuracy can be achieved. We will return to this point in Section 4.

The simple comparison of the fundamentals computed with a non-relativistic electronic structure methods with experiment is actually misleading. Calculations by Császár et al. [11,44] have shown that the electronic relativistic corrections are surprisingly large for water and therefore cannot be ignored. The result of including this effect is to significantly improve the predictions for the stretching fundamentals (and indeed overtones [11]), to within 1 cm$^{-1}$, but at the expense of worsening the agreement with the bending overtones. This finding is very much in line with error analysis of Partridge and Schwenke [3] who found their ab initio model to be significantly poorer for bending than stretching modes; however, it suggests that the excellent agreement with experiment obtained in the non-relativistic, force field calculations of Martin et al. [42] is actually fortuitous.

Table 3
Ab initio predictions of the vibrational fundamentals of water, in cm$^{-1}$, as a function of year

| Reference | Method[a] | Year | $\nu_2$ | $\nu_1$ | $\nu_3$ |
|---|---|---|---|---|---|
| Bucknell and Handy [39] | SCF | 1974 | 1728 | 4045 | 4139 |
| Bartlett et al. [40] | MBBT | 1979 | 1610 | 3702 | 3789 |
| Knowles et al. [41] | CASSCF | 1982 | 1645 | 3691 | 3794 |
| Martin et al. [42] | QCISD (T) | 1992 | 1595 | 3657 | 3756 |
| Kedziora and Shavitt [43] | MRCISD | 1997 | 1604.6 | 3650.5 | 3758.2 |
| Partridge and Schwenke (PS) [3] | CCSD (T) | 1997 | 1597.4 | 3660.5 | 3757.2 |
| PS + relativistic correction [11] |  | 1998 | 1598.2 | 3657.7 | 3755.3 |
| Experiment [45] |  |  | 1594.75 | 3657.05 | 3755.93 |

[a] For basis sets and explanations of methods see original publication. Note that all band origins are based on the use of variational nuclear motion calculations except those of Martin et al., who used vibrational perturbation theory.

Table 4
Coefficients for the $H_2O$ Born–Oppenheimer diagonal correction (BODC) surface, see Eq. (1)

| $i$ | $j$ | $k$ | $C_{ijk}$ | $i$ | $J$ | $K$ | $C_{ijk}$ |
|---|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 2745.1055606459 | 3 | 1 | 0 | −26.4139825271 |
| 1 | 0 | 0 | −59.4634051943 | 1 | 3 | 0 | 6.0253244059 |
| 0 | 1 | 0 | 52.4468059982 | 2 | 2 | 0 | 96.0354596696 |
| 2 | 0 | 0 | 209.0157347415 | 2 | 0 | 2 | 400.8671847238 |
| 0 | 2 | 0 | −30.9569390720 | 0 | 2 | 2 | 64.3311129088 |
| 0 | 0 | 2 | 222.8220666155 | 1 | 1 | 2 | −159.3984157719 |
| 1 | 1 | 0 | −32.0954739957 | 5 | 0 | 0 | 26.5108357242 |
| 3 | 0 | 0 | −84.5603232875 | 0 | 5 | 0 | 27.9528744878 |
| 0 | 3 | 0 | 28.3636764469 | 4 | 1 | 0 | 3.3262475087 |
| 2 | 1 | 0 | −82.9317097732 | 1 | 4 | 0 | 23.3582782463 |
| 1 | 2 | 0 | 74.5702444206 | 1 | 0 | 4 | −62.8395365075 |
| 1 | 0 | 2 | −301.3739913256 | 0 | 1 | 4 | 33.1944328259 |
| 0 | 1 | 2 | 0.4721526758 | 3 | 2 | 0 | 31.8104538207 |
| 4 | 0 | 0 | 17.0778691448 | 3 | 0 | 2 | −11.0876529850 |
| 0 | 4 | 0 | 9.6100487312 | 2 | 3 | 0 | −151.9675922959 |
| 0 | 0 | 4 | 118.9501245531 | 0 | 3 | 2 | −33.6314521634 |

The coefficients are in $\mathrm{cm}^{-1}$ for bond lengths in $a_0$ and angles in radians.

The finding that the first-order relativistic correction to the electron kinetic energy, strictly the one-electron mass–velocity plus Darwin (MVD1) corrections, is significant has led to the investigation of other high-order relativistic effects. In particular Quiney et al. [46] found that the two-electron kinetic contribution via the two-electron Darwin term (D2) was fairly small, but the relativistic correction to the Coulomb potential, represented by the Breit interaction or the simpler, approximate Gaunt term, often contributed more than 1 $\mathrm{cm}^{-1}$ to the higher vibrational band origins and therefore should not be neglected. Perhaps even more intriguingly an estimate of the quantum electrodynamic Lamb shift suggests that this too can contribute changes of the order 1 $\mathrm{cm}^{-1}$ to the vibrational band origins and a similar amount to the $J = 20$ rotational levels [47]. Conversely, recent calculations have shown that spin–orbit interactions, which might have been thought to be significant in the region of linear geometries, can safely be neglected [48].

Inclusion of non-Born–Oppenheimer effects can play an important contribution to the spectrum of water. Zobov et al. [49] computed an SCF adiabatic or BODC surface. In contrast to $H_3^+$, where use of such a surface resolved most of the problems of treating the vibrations of the isotopomers, Zobov et al. found that the BODC did not explain differences between the various isotopomers of water although its use did lead to significant shifts in the $J = 20$ energy levels. More recently, Schwenke [26] has recalculated the BODC using a correlated wave function calculated at the complete active space self-consistent field (CASSCF) level. He found that this correction is on an average 8 $\mathrm{cm}^{-1}$ larger than the SCF level calculation, and that the new surface showed significant differences to surface calculated at the SCF level.

Unfortunately, Schwenke's fit to his CASSCF BODC data extrapolates very poorly outside the relatively small region defined by his ab initio calculations. Use of this surface with our codes gave unstable results. We have therefore refitted his CASSCF data to the functional form

$$\Delta V_{\mathrm{ad}}(r_1,r_2,\theta) = \sum_{i,j,k} C_{i,j,k}\left[\frac{1}{2}(r_1+r_2)-r_{\mathrm{e}}\right]^i[\cos(\theta)-\cos(\theta_{\mathrm{e}})]^j \left[\frac{1}{2}(r_1-r_2)\right]^k \tag{1}$$

where $r_1$ and $r_2$ are the two O–H bond lengths and $\theta$ is the bond angle. Equilibrium is given by

$r_e = 1.80965034a_0$ and $\theta_e = 1.82404493$ radians. The coefficients of this fit, which reproduces the original data with a standard deviation of 0.01 cm$^{-1}$, are given in Table 4. This surface is no longer unstable but its behaviour for large values of the stretching coordinates are not well constrained by the ab initio data.

Table 5 shows the effect of the various BODC surfaces on the lower vibrational band origins. The BO results in this table used the ab initio surface of Partridge and Schwenke [3], which includes, separately, both valence correlation and core correlation effects. The calculations all used nuclear masses except for the column marked $\mu^V$, which is defined, as previously [11,49], by the O atomic mass and an H mass midway between the atomic and nuclear mass. Use of our refitted BODC surface, while not giving the same results as Schwenke's surface, does support his finding that there are significant differences between the BODC surface calculated at the SCF level and that calculated using a CASSCF model. The two surfaces give similar behaviour for the bending modes but significant difference with respect to stretching excitations.

The main purpose of Schwenke's work [26] was to develop a model for including non-adiabatic corrections in the nuclear motion problem. His method involved explicitly calculating full, three-dimensional coupling surfaces and is therefore a much more complete method than the use of mass scaling discussed for $H_3^+$ above. Interestingly, Schwenke found that use of the relatively simple, vibrationally averaged, diagonal components of his coupling surfaces gave results very similar to those of his full calculation. The final column of Table 4 presents results obtained by Schwenke using his full non-adiabatic correction. We have implemented a simplified, diagonal version of this correction within our vibration–rotation program DVR3D [50]. In this we have only considered two non-adiabatic parameters, the ones which scale the second derivative (or kinetic energy terms) in $\theta$ and $r_i$. These results are compared to ones computed using the simple mass scaling procedure used for $H_3^+$.

Table 5
Band origins, in cm$^{-1}$, for water showing the effects of introducing non-Born–Oppenheimer effects

| $(v_1,v_2,v_3)$ | BO[a] | Adiabatic correction[b] | | | Non-adiabatic correction[c] | | |
|---|---|---|---|---|---|---|---|
| | | SCF [49] | CASSCF | | $\mu^V \neq \mu^N$ | Diag[d] | Accurate |
| | | | [26] | Refit | | | [26] |
| (010) | 1597.60 | −0.50 | −0.46 | −0.46 | −0.19 | −0.06 | −0.07 |
| (020) | 3157.14 | −0.99 | −0.94 | −0.93 | −0.38 | −0.12 | −0.15 |
| (100) | 3661.00 | −0.06 | 0.39 | 0.55 | −0.46 | −0.72 | −0.70 |
| (030) | 4674.88 | −1.48 | −1.46 | −1.43 | −0.55 | −0.18 | −0.23 |
| (110) | 5241.83 | −0.51 | −0.01 | 0.16 | −0.65 | −0.77 | −0.76 |
| (040) | 6144.64 | −2.02 | −2.03 | −2.00 | −0.71 | −0.23 | −0.30 |
| (120) | 6784.56 | −0.94 | −0.42 | −0.23 | −0.83 | −0.83 | −0.84 |
| (200) | 7208.80 | −0.08 | 0.96 | 1.25 | −0.88 | −1.39 | −1.37 |
| (002) | 7450.86 | 0.19 | 1.22 | 1.47 | −0.90 | −1.47 | −1.57 |
| (050) | 7555.62 | −2.65 | −2.71 | −2.71 | −0.84 | −0.28 | −0.37 |
| (130) | 8286.03 | −1.37 | −0.87 | −0.67 | −1.00 | −0.89 | −0.91 |
| (210) | 8771.71 | −0.47 | 0.66 | 0.95 | −1.07 | −1.44 | −1.43 |
| (012) | 9008.72 | −0.20 | 0.90 | 1.17 | −1.08 | −1.52 | −1.65 |

Comparison with the results of Schwenke [26].

[a] BO: ab initio Born–Oppenheimer potential of Partridge and Schwenke [3].

[b] Adiabatic correction given relative to BO.

[c] Non-adiabatic correction given relative to the refitted CASSCF BODC.

[d] Simplified diagonal correction, see text, multiplied by 1.1 as recommended by Schwenke [26].

Table 6
Band origins for higher vibrational states, in cm$^{-1}$, for water showing the effects of introducing non-Born–Oppenheimer effects

| $(v_1, v_2, v_3)$ | BO[a] | Adiabatic correction[b] | | Non-adiabatic correction[c] | |
|---|---|---|---|---|---|
| | | SCF [49] | CASSCF | $\mu^V \neq \mu^N$ | Diag[d] |
| (220) | 10297.00 | −0.83 | 0.64 | −1.24 | −1.49 |
| (300) | 10609.14 | −0.02 | 2.23 | −1.30 | −1.99 |
| (102) | 10879.00 | 0.01 | 2.01 | −1.32 | −2.10 |
| (230) | 11782.64 | −1.19 | 0.30 | −1.41 | −1.55 |
| (032) | 12021.78 | −0.88 | 0.57 | −1.42 | −1.64 |
| (310) | 12151.51 | −0.34 | 2.03 | −1.47 | −2.03 |
| (112) | 12400.72 | −3.59 | −3.36 | −1.42 | −0.78 |
| (240) | 13222.66 | −1.63 | −0.15 | −1.56 | −1.61 |
| (042) | 13470.04 | −1.25 | 0.19 | −1.58 | −1.69 |
| (320) | 13655.39 | −0.72 | 1.65 | −1.64 | −2.05 |
| (170) | 13682.51 | −3.65 | −3.15 | −1.54 | −1.05 |
| (400) | 13839.28 | 0.05 | 3.44 | −1.73 | −2.52 |
| (122) | 13926.37 | −0.61 | 1.56 | −1.67 | −2.19 |
| (202) | 14234.86 | −0.11 | 2.73 | −1.74 | −2.70 |
| (004) | 14548.39 | 0.37 | 3.22 | −1.72 | −2.79 |
| (330) | 15125.11 | −0.88 | 1.63 | −1.81 | −2.15 |
| (410) | 15358.27 | −0.22 | 3.27 | −1.93 | −2.54 |
| (132) | 15395.63 | −0.85 | 1.40 | −1.83 | −2.26 |
| (212) | 15759.25 | −0.36 | 2.60 | −1.91 | −2.73 |
| (500) | 16910.87 | 0.08 | 4.71 | −1.79 | −2.92 |
| (302) | 17473.72 | −0.06 | 3.86 | −2.17 | −3.23 |
| (430) | 18284.98 | −0.56 | 3.28 | −2.20 | −2.71 |
| (510) | 18407.30 | −0.03 | 4.77 | −2.11 | −2.94 |
| (600) | 19793.59 | 0.05 | 6.27 | −0.77 | −3.31 |
| (402) | 20549.65 | 0.06 | 5.31 | −2.22 | −3.65 |
| (610) | 21237.93 | −0.17 | 6.12 | −1.15 | −3.34 |
| (700) | 22540.31 | 0.18 | 8.87 | −3.35 | −3.75 |
| (620) | 22646.30 | −0.44 | 5.63 | −1.91 | −3.32 |
| (800) | 25119.49 | 0.24 | 1.40 | −9.20 | −2.17 |

[a] BO: ab initio Born–Oppenheimer potential of Partridge and Schwenke [3].

[b] Adiabatic correction given relative to BO.

[c] Non-adiabatic correction given relative to the refitted CASSCF BODC.

[d] Simplified diagonal correction, see text, multiplied by 1.1 as recommended by Schwenke [26].

Non-adiabatic effects, as calculated either by mass scaling or more explicitly are significantly larger for water than for $H_3^+$. This finding is in line with previous predictions [49,51]. The simplified two-term diagonal treatment of the non-adiabatic problem gives results in excellent agreement with Schwenke's full calculation; however, the use of mass scaling to include non-adiabatic effects predicts shifts of similar magnitude to the accurate treatment but differs considerably in detail. The mass scaling method systematically over-estimates non-adiabatic effects for the bending motion and under-estimates them for the stretches. Since the mass scaling results are insensitive to the choice of O mass used [49], this method essentially involves the change of a single parameter, the H mass. Schwenke's diagonal approximation, while very greatly simplified compared to his full treatment, involves four parameters for the vibrational motion, plus a constant which does not affect band origins. We have used only two of these constants, with no noticeable further loss of accuracy. These are the parameters that scale the bending and stretching kinetic energy operators and are the same parameters that are scaled in the mass scaling method, where they are constrained to the same value. Table 6 presents results for the higher band origins of water. Schwenke does not present results for these states, so no comparison is made with his work.

## 4. Discussion and conclusions

From the high accuracy study of only two molecules, which show markedly contrasting sensitivity to the inclusion of effects normally neglected in the ab initio treatment of vibration–rotation spectra, it would be unwise to draw too many conclusions. However, a number of the observations made below are supported by other studies, in particular our high accuracy work on $H_2S$ [8] and HCN [9]. Table 7 presents a summary of the influence of each effect. In each case the largest shift, or an estimate of the largest shift, is given. It should be noted that in compiling this table only band origins for which experimental data are available have been considered. Since many more vibrational bands are known for water than $H_3^+$, this leads to some bias in the magnitude of the corrections towards the water case. In particular the adiabatic corrections for $H_3^+$ are actually larger for the low-lying states, the only ones for which a direct comparison can be made.

As a purely hydrogenic system, it is probably not surprising that relativistic effects are found to be largely unimportant for $H_3^+$. Conversely, Császár et al. [44] found that the potential energy surface of water showed a particularly strong sensitivity to relativistic effects. This they ascribed to the re-hybridisation of the O electrons as the molecule changes from bent to linear geometries. Although other systems containing first row elements do not seem to show the same sensitivity to electronic relativistic effects as water [9,44], these effects are certainly not negligible. Methods for calculating these effects are becoming readily available. Unsurprisingly, relativistic effects in the heavier $H_2S$ system are larger than those in water [8]. Studies on whether higher order relativistic corrections are important in other systems, particularly $H_2S$, are presently underway.

Table 7
Sensitivity of vibrational band origins to the various effects, see text for details

| Effect | Contribution ($cm^{-1}$) | |
|---|---|---|
| | $H_2O$ | $H_3^+$ |
| BO convergence | +30 | ±0.003 |
| Relativistic correction (1e) | −19 | ±0.003 |
| Darwin term (2e) | −0.8 | 0[a] |
| Gaunt correction | +5 | 0[a] |
| Breit correction | +6 | 0[a] |
| QED Lamb shift | +1.3 | 0[a] |
| Adiabatic correction (BODC) | +5 | ±1.5 |
| Non-adiabatic correction | −4 | −0.5 |

[a] Not known, assumed to be negligible.

Corrections to the Born–Oppenheimer approximation are probably only important for high accuracy work on molecules containing H atoms. The adiabatic or BODC is relatively easy to calculate ab initio [21]. For $H_3^+$ the adiabatic correction to the Born–Oppenheimer approximation is more important than the non-adiabatic correction. For water the two effects have similar magnitude. As yet there is no other triatomic system for which similar comparisons can be made but when these results are combined with studies of diatomics [29,52,53], it would appear to be a general property of only pure hydrogen systems that the adiabatic correction is the most important correction to the Born–Oppenheimer approximation.

We have compared a number of models for including non-adiabatic corrections. The full treatment by Schwenke [26] represents a significant advance, but it is to be hoped that it will not generally prove necessary to calculate the large number of coupling surfaces involved to model what is a fairly small effect. It is therefore encouraging that the two parameter diagonal reduction of Schwenke's full treatment gives such good results. This method gives significantly better results than the single parameter mass scaling which works well for $H_3^+$. It is unclear at this stage whether the single parameter method works well for $H_3^+$ but not water because (a) the non-adiabatic effects are smaller in $H_3^+$ so a lower accuracy is acceptable, (b) the higher symmetry of $H_3^+$

means that only one parameter is required, (c) the lack of available experimental data on the band origins $H_3^+$ or (d) because of some other reason.

While there is a Born–Oppenheimer electronic potential for $H_3^+$ [10] of unprecedented accuracy, the Born–Oppenheimer potential remains the major source of error for water and is likely to be the main error in a similar study for any other triatomic molecule. Partridge and Schwenke [3] expended considerable efforts in both trying to produce well-converged results and to analyse the errors in their results. Their conclusion, which is supported by the study of Császár et al. [44], is that the major source of error is due to the lack of convergence of the basis set used to represent valence correlation in the bending coordinate. That the main error with the BO potential is in the bending coordinate is consistent with our error analysis of the vibrational energy levels.

It would seem unlikely that this problem will be resolved by simply using larger correlation consistent (CC) basis sets since such calculations are likely to suffer from problems with linear dependence. However, there are two new approaches, which offer hope that further improvements in the Born–Oppenheimer potential may well be achievable in the near future. One is the careful use of extrapolation techniques to accelerate the convergence of such studies with respect to basis set size [44] and level of electron correlation [54,55]; such methods has already been shown to yield satisfactory results for $H_2S$ [8,55]. The other method is the use of wave functions which explicitly include the electron–electron coordinate [56,57]. Such methods are known to lead to accelerated convergence of the basis set required to represent correlation effects and have already been demonstrated to give high accuracy for HF [58] which is a ten electron system like water. It is therefore to be hoped that an ab initio solution to the vibration–rotation energy levels of water to spectroscopic accuracy, along the lines of the one that has already been achieved for $H_3^+$, will be achievable in the fairly near future. This will represent a major triumph for ab initio quantum chemistry.

Finally, it should be noted that besides the obvious goal of achieving spectroscopic accuracy by ab initio procedures, there is another important use of improved ab initio procedures. Potential energy surfaces derived from fitting to spectroscopic data are now becoming a standard tool for the analysis of spectra of small molecules. Our experience shows that the quality of such potentials improves significantly with the quality of the ab initio starting point.

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