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Accurate Vibrational Frequencies of Borane and Its Isotopologues

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Abstract: Vibrational transitions of borane and its isotopologues ($^{11}BH_3$, $^{11}BD_3$, $^{10}BH_3$, and $^{10}BD_3$) have been obtained from state-specific vibrational configuration interaction calculations. Explicitly correlated coupled-cluster calculations, CCSD(T)-F12a, with additional corrections for high-order terms of the coupled-cluster expansion, i.e., CCSDT(Q), were used to determine multidimensional potential energy surfaces. Additional contributions due to core−valence interactions, scalar relativistic effects, and such arising from the diagonal Born−Oppenheimer correction were accounted for in the one-dimensional terms within the expansion of the potential energy surface. From these, anharmonic vibrational spectra were obtained, which are in excellent agreement with experimental data. Mean absolute deviations from gas phase measurements were found to be in the sub-wavenumber regime.

I. Introduction

The vibrational spectrum of borane has been the subject of many theoretical and experimental studies.[1−9] The empty p orbital accounts for the high reactivity of borane and thus explains its rapid dimerization to the more stable diborane. As a consequence, the measurement of borane by means of spectroscopic techniques is a tedious task, and many attempts failed until Kaldor and Porter[1] and later on Kawaguchi et al.[2−4] successfully reported the detection of the fundamental vibrational transitions. For a discussion of the *borane story*, see the papers of Galbraith et al.[7] and Martin and Lee.[5] From the computational point of view, borane is a challenging system, because its low number of electrons allows for calculations at the highest level, and thus it has been in the focus of theoreticians for a long time. Botschwina,[6] Galbraith et al.,[7] Martin and Lee,[5] and Feller et al.[8] studied the harmonic spectrum of BH_3 and its thermochemistry at different levels of electronic structure theory. From these, Botschwina[6] estimated the anharmonic transitions by scaling and thus provided the first reliable predictions until Martin and Lee used a quartic force field based on CCSD(T) calculations in combination with vibrational perturbation theory for a direct and fully *ab initio* calculation of the fundamentals.[5] A few years later, Schwenke[9] used the quartic force field of Martin and Lee

to perform variational calculations. As a result, many spectroscopic constants are available for the $^{11}BH_3$ and $^{10}BH_3$ isotopologues, while theoretical studies focusing on anharmonic frequencies are still missing for the deuterated species. Moreover, vibrational overtones and combination bands have not yet been calculated, except for a very few. The motivation of this study is two-fold: First, we intend to provide very accurate anharmonic transitions for those isotopologues for which experimental data are not yet available, while verifying our computational scheme on the basis of those fundamentals, which have accurately been determined by experiment. Second, we would like to show that fully automated *ab initio* approaches are capable of predicting vibrational frequencies with very high accuracy.

Our approach for calculating the anharmonic transitions of the borane isotopologues differs substantially from the approach of Schwenke,[9] although it is also based on the variational principle. We use the Watson Hamiltonian and thus expand the potential in terms of normal coordinates, rather than symmetry adapted internal coordinates.

$$V(\mathbf{q}) = \sum_{ri} V_{ri}\left[p_r^{(i)} + \frac{1}{2}\sum_{sj} V_{sj}\left[p_{rs}^{(ij)} + \frac{1}{3}\sum_{tk} V_{tk}[p_{rst}^{(ijk)} + ...]\right]\right] \tag{1}$$

In this expression, V_{ri} denotes single particle potentials, and $p_r^{(i)}$ denotes the corresponding coefficients of the expansion. The

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potential is calculated in a fully automated manner, which allows us to use any electronic structure level as implemented in the Molpro suite of *ab initio* programs.[10] One mode wave functions (modals) are obtained from state-specific vibrational self-consistent field calculations (VSCF)[11−13] and a subsequent accounting of correlation effects by means of vibration configuration interaction calculations (VCI).[14]

II. Computational Details

A. Electronic Structure Calculations. Geometries, normal coordinates, and potential energy surfaces were obtained from explicitly correlated coupled-cluster theory, CCSD(T)-F12a, in combination with a triple-ζ basis set, i.e., vtz-f12.[15] As we have shown recently, results obtained at this level are extremely close to the basis set limit, and thus we consider effects due to the incompleteness of the orbital basis to be essentially negligible.[16] Slater geminals with an exponent of 1.0 a_0^{-1} were used throughout. For the resolution of identity approximation (RI), a complementary auxiliary basis set (CABS) was built from the cc-pVTZ/JKFIT basis and the atomic orbital basis.[17] An aug-cc-pVTZ/MP2FIT basis was used within the density fitting of the integrals.[18] The CABS singles correction to the Hartree−Fock energies was included in all F12 calculations.[19,20]

Core-correlation effects were obtained from conventional all-electron CCSD(T)/cc-pCVTZ energies relative to frozen-core CCSD(T)/cc-pCVTZ results and were added to the CCSD(T)-F12a/vtz-f12 energies. Likewise, high-order correlation effects were determined from CCSDT(Q)/cc-pVTZ calculations in comparison to CCSD(T)/cc-pVTZ results.[21] For performing the CCSDT(Q)/cc-pVTZ calculations, we have used Kallays's string-based many-body Mrcc program[22,23] interfaced to the Molpro suite of *ab initio* programs.[10] In order to account for diagonal Born−Oppenheimer effects, these were computed at the CCSD/cc-pVTZ level, as described in detail by Gauss et al.[24] These calculations were performed with the Cfour program package.[25] Scalar relativistic effects were investigated using the Douglas−Kroll−Hess one-electron Hamiltonian,[26] while spin−orbit effects were not explicitly accounted for as they were estimated as being too small. Note that borane is a closed-shell molecule giving rise to second order spin−orbit effects only and that the spin−orbit splitting of the borane atom, i.e., at the dissociation limit of the borane molecule, is 16 cm^{-1} only. As we consider only a small fraction of the global potential energy surface near the equilibrium structure, we believe that the corrections to the vibrational frequencies are below 0.1 cm^{-1} and thus significantly lower than for example errors in the fitting procedure.

B. Vibrational Structure Calculations. The expansion of the potential in terms of normal coordinates was truncated after the three-mode contributions. Core-correlation effects, high-order corrections to the coupled-cluster expansion, and scalar relativistic and adiabatic effects were added to the one-mode terms only. This essentially corresponds to a multilevel approximation,[27,28] which has successfully been used by several groups.[29,30] The potential has been generated in an automated fashion using an iterative interpolation algorithm.[13] Initially, 20 grid points have been generated along each normal coordinate. From these, single particle potentials were determined in a subsequent step. In the Watson Hamiltonian, vibrational angular momentum terms were accounted for up to the first order in a multimode expansion of the μ tensor.[31] Modals were obtained from a VSCF algorithm on the basis of a discrete variable representation (DVR) and a distributed Gaussian basis.[32,33] Vibration correlation effects were accounted for by state-specific VCI calculations including single to quadruple excitations.[14] No more than 10 431 configurations were considered in the correlation space.

III. Impact of Corrections

The success of frozen-core CCSD(T) calculations is at least partially due to an error compensation of core−valence effects and high-order correlation terms. It is common knowledge that explicitly accounting for just one of these effects usually leads to an unbalanced treatment and thus to worse results. However, this knowledge is primarily based on single point calculations at stationary points or—in the context of calculating accurate vibrational transitions—on two-atomic molecules.[34] With respect to extended parts of potential energy surfaces of polyatomic molecules, knowledge is rather limited.[35] For that reason, we have plotted the core-correlation and high-order corrections along the one-dimensional elongations for all modes in Figure 1. According to Figure 1, core-correlation effects are more important than high-order corrections for all modes. However, for electronically more demanding systems with more valence electrons and multiple bonds between non-hydrogen atoms, this may change. Although core-correlation and high-order corrections partially cancel out for some of the modes, this does not hold true for others. For example, both core-correlation and high-order effects correct the potential related to mode ν_3 in the same direction. As a consequence, error compensation effects are smaller for this molecule than originally anticipated. It is obvious from the shape of correction potentials that core-correlation and high-order terms are more important for an accurate description of high-lying vibrational states than the low-lying fundamental modes. Table 1 shows CCSD(T)-F12a/vtz-f12 anharmonic frequencies and the corresponding corrections due to core-correlation (CC), high-level terms in the coupled-cluster expansion and scalar relativistic (Rel) and adiabatic (DBOC) effects. The latter two corrections provide almost constant shifts of 1390 and 470 cm^{-1} to the potential energy surface but do hardly affect the transitions considered here; i.e., the variation in the region around the equilibrium structure is very small.

For the deuterated species, these effects are even smaller and, in addition, cancel each other out in most cases. As we consider the error in the fitting of our potential energy surfaces to be larger than these effects, we do not discuss them any further. In contrast to that, core-correlation and high-order effects are significantly larger and thus need to be accounted for in order to obtain accurate results.

Martin and Lee computed the harmonic frequencies at the CCSD(T)/cc-pVQZ level for $^{11}BH_3$ and $^{10}BH_3$ (see Table 2), which are in very nice agreement with our results at the
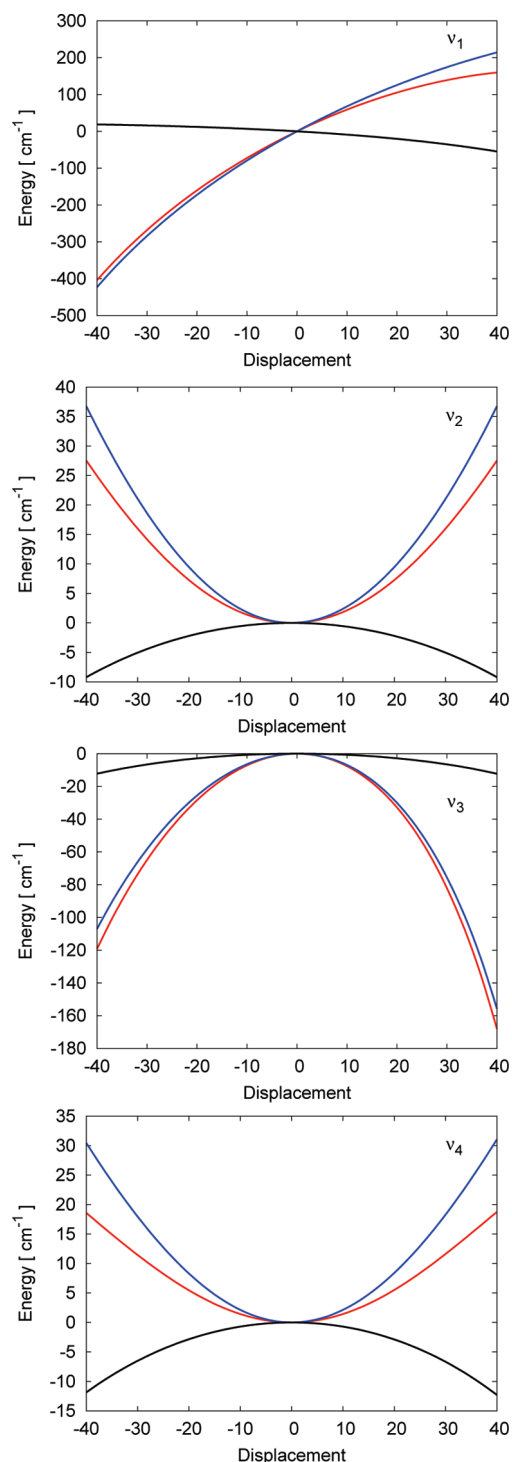
Figure 1. Impact of core-correlation (black) and high-order corrections (black) on the 1D potentials of BH₃. The resulting correction is shown in red; the order of the potentials is ν_1 (uppermost), ν_2, ν_3, and ν_4 (bottom).

CCSD(T)-F12a/vtz-f12 level, i.e., $\omega_1 = 2568.0$ cm^{-1}, $\omega_2 = 1156.6$ cm^{-1}, $\omega_3 = 2701.1$ cm^{-1}, and $\omega_4 = 1218.3$ cm^{-1} for ^{11}BH₃.

The largest deviation is thus 1.7 cm^{-1}, which may either arise from the incompleteness of the cc-pVQZ basis used by Martin and Lee or the numerical noise caused by the auxiliary basis sets in the explicitly correlated coupled-cluster calculations. However, corrections due to core-correlation and high-order terms are significantly larger (up to 5.7 cm^{-1})

Table 1. Impact of Core-Correlation Effects, High-Order Coupled-Cluster Terms, Relativistic Contributions, and Diagonal Born−Oppenheimer Corrections on the Fundamental Modes of ^{11}BH₃ (All Quantities Are Given in cm^{-1})

	$\nu_i^{F12,a}$	$\Delta\nu_i^{CC,b}$	$\Delta\nu_i^{HLT,c}$	$\Delta\nu_i^{Rel,d}$	$\Delta\nu_i^{DBOC,e}$
ν_1	2494.4	5.9	−2.4	0.1	−0.7
ν_2	1146.2	1.5	−0.7	0.3	−0.2
ν_3	2597.0	5.9	−2.1	−0.1	−0.6
ν_4	1194.9	1.9	−0.7	0.2	−0.1

[a] CCSD(T)-F12a/vtz-f12 anharmonic frequencies. [b] Correction due to core correlation. [c] Correction due to high-level terms in the coupled-cluster expansion. [d] Scalar relativistic corrections. [e] Diagonal Born−Oppenheimer correction.

Table 2. Harmonic and Anharmonic Vibrational Frequencies of ^{11}BH₃ in cm^{-1}

	ML[a]/Schwenke[b]			this work		
	ω_i^a	ν_i^a	ν_i^b	ω_i	ν_i	exp.
ν_1	2568.3	2494.9	2491.9	2562.4	2497.4	
ν_2	1158.0	1134.2	1148.1	1160.0	1147.1	1147.50
ν_3	2700.3	2587.5	2591.5	2695.5	2600.3	2601.57
ν_4	1220.0	1196.4	1199.1	1220.9	1196.3	1196.66
$2\nu_2$			2277.8		2277.1	
$2\nu_4^0$		2361.5	2381.2		2383.6	
$\nu_1 + \nu_2$					3650.3	
$\nu_1 + \nu_4$					3685.2	
$\nu_2 + \nu_3$					3736.3	
$\nu_2 + \nu_4$			2354.9		2351.4	

[a] Data taken from ref 5. [b] Data taken from ref 9.

and thus are mainly responsible for the differences between the data sets of Martin and Lee and ours. Note that two modes (ω_1, ω_3) are red-shifted by the corrections, while the other two (ω_2, ω_4) are blue-shifted; i.e., there appears not to be a general tendency.

IV. Results and Discussion

The BH bond length was determined to be $r_e = 1.1895$ Å at the CCSD(T)-F12a/vtz-f12 level, which is in excellent agreement with the CCSD(T)/cc-pVQZ value of $r_e = 1.1899$ Å obtained by Martin and Lee.[5] Both values are slightly larger than that determined from the experimental data of Kawaguchi,[3] i.e., $r_e = 1.185$ Å. However, the latter value was estimated from an r_0 bond length, which has subsequently been corrected to r_e by an increment taken from the CH₃⁺ cation.

Our computed harmonic and anharmonic frequencies are summarized for all isotopologues in Tables 2−4. The agreement of our computed fundamentals with the experimental data of Kawaguchi et al.[2−4] is excellent, with a mean absolute deviation of just 0.9 cm^{-1}. We believe that the remaining errors arise mainly from the fitting procedure and the truncation of the potential after the three-mode terms in the vibrational structure calculations.

Although a direct comparison of our computed values for vibrational overtones and combination bands with experimental data is not possible, we expect slightly larger errors for these modes. A comparison with the data of Kaldor and Porter[1] or Tague and Andrews[36] has not been provided, as these data are affected by matrix isolation effects, which can be quite substantial for these light molecules.

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Table 3. Harmonic and Anharmonic Vibrational Frequencies of $^{10}BH_3$ in cm^{-1}

	ML[a]		this work		
	ω_i	ν_i	ω_i	ν_i	exp.
ν_1	2568.3	2498.4	2562.4	2500.3	
ν_2	1170.3	1145.9	1172.4	1159.0	
ν_3	2716.0	2601.6	2711.2	2614.5	2615.79
ν_4	1225.9	1202.0	1226.8	1201.3	
$2\nu_2$				2297.6	
$2\nu_4^0$		2367.6		2394.7	
$\nu_1 + \nu_2$				3667.3	
$\nu_1 + \nu_4$				3695.5	
$\nu_2 + \nu_3$				3762.1	
$\nu_2 + \nu_4$				2369.1	

a Data taken from ref 5.

Table 4. Harmonic and Anharmonic Vibrational Frequencies of $^{10}BD_3$ and $^{11}BD_3$ in cm^{-1}

	$^{10}BD_3$			$^{11}BD_3$		
	GVS[a]	this work		GVS[a]	this work	
	ω_i	ω_i	ν_i	ω_i	ω_i	ν_i
ν_1	1813	1812.3	1731.6	1813	1812.3	1724.8
ν_2	936	920.5	910.5	920	904.7	895.1
ν_3	2040	2038.7	1984.2	2018	2016.9	1963.9
ν_4	916	905.7	890.8	910	899.8	885.1
$2\nu_2$			1841.7			1820.7
$2\nu_4^0$			1778.2			1766.7
$\nu_1 + \nu_2$			2619.9			2596.9
$\nu_1 + \nu_4$			2606.6			2595.0
$\nu_2 + \nu_3$			2887.3			2852.0
$\nu_2 + \nu_4$			1804.7			1783.8

a CISDTQ/TZ2P data taken from ref 7.

The largest difference between the data sets of Martin and Lee,[5] Schwenke,[9] and ourselves is observed for ν_3 of $^{10}BH_3$ *and* $^{11}BH_3$. In both cases, the values relying on the quartic force field appear to be too low. Therefore, we assume that this is mainly an effect arising from the approximation of the PES. Moreover, our value for the $2\nu_4^0$ overtone of $^{11}BH_3$ is in nice agreement with the value of Schwenke but differs considerably from Martin and Lee's value. Therefore, we believe that Martin and Lee's value for the corresponding overtone in $^{10}BH_3$ is too low. Anharmonic frequencies for the perdeuterated species are provided for the first time and can thus not be compared. However, we consider the anharmonic frequencies predicted for these system to be accurate enough in order to guide experiments to come. Zero point vibrational energies (ZPVE) have been determined for all four isotopologues: 5715.5 cm^{-1} ($^{11}BH_3$), 5742.6 cm^{-1} ($^{10}BH_3$), 4242.9 cm^{-1} ($^{11}BD_3$), and 4277.9 cm^{-1} ($^{10}BD_3$). Our *ab initio* value for the ZPVE of $^{11}BH_3$ essentially is identical with the value of Feller et al.[8] (5715.6 cm^{-1}) obtained from a combined experimental/theoretical scaling procedure.

We like to state once more that the calculations including core-correlation effects and high-order terms have been performed in a fully automated fashion, controlled by some very few keywords in the input section only. Consequently, this study shows that modern *ab initio* programs are able to predict highly accurate vibrational spectra without extensive fitting etc. by hand.

V. Summary and Conclusions

Vibrational frequencies of borane and its isotopologues have been determined from multidimensional potential energy surfaces obtained from high-level *ab initio* calculations. Mean absolute deviations were found to be below one wavenumber with respect to the most accurate gas phase measurements. Likewise, zero point vibrational energies, which are important for an accurate calculation of heats of formation, were found to be in excellent agreement with previous data. Several vibrational transitions were provided for the first time. Moreover, core-correlation effects and high-order contributions in the coupled-cluster treatment do not cancel out for all types of vibrations and were thus found to be important to be included in the calculations. Scalar relativistic effects and diagonal Born−Oppenheimer corrections were found to be negligible.

References

(1) Kaldor, A.; Porter, R. *J. Am. Chem. Soc.* **1971**, *93*, 2140.

(2) Kawaguchi, K.; Butler, J. E.; Yamada, C.; Bauer, S. H.; Minowa, T.; Kanamori, H.; Hirota, E. *J. Chem. Phys.* **1987**, *87*, 2438.

(3) Kawaguchi, K. *J. Chem. Phys.* **1992**, *96*, 3411.

(4) Kawaguchi, K. *Can. J. Phys.* **1994**, *72*, 925.

(5) Martin, J. M. L.; Lee, T. J. *Chem. Phys. Lett.* **1992**, *200*, 502.

(6) Botschwina, P. In *Ion and cluster spectroscopy and structure*; Maier, J. P., Ed.; Elsevier: Amsterdam, 1989; p 59.

(7) Galbraith, J. M.; Vacek, G.; Schaefer, H. F., III. *J. Mol. Struct.* **1993**, *300*, 281.

(8) Feller, D.; Dixon, D. A.; Peterson, K. A. *J. Phys. Chem. A* **1998**, *102*, 7053.

(9) Schwenke, D. W. *J. Phys. Chem.* **1996**, *100*, 2867.

(10) Werner, H.-J.; Knowles, P. J.; Lindh, R.; Manby, F. R.; Schütz, M. Molpro, development version 2009 3, a package of ab initio programs (2008). http://www.molpro.net (accessed Nov 2010).

(11) Bowman, J. *Acc. Chem. Res.* **1986**, *19*, 202.

(12) Gerber, R.; Ratner, M. *Adv. Chem. Phys.* **1988**, *70*, 97.

(13) Rauhut, G. *J. Chem. Phys.* **2004**, *121*, 9313.

(14) Neff, M.; Rauhut, G. *J. Chem. Phys.* **2009**, *131*, 124129.

(15) Peterson, K.; Adler, T.; Werner, H.-J. *J. Chem. Phys.* **2008**, *128*, 084102.

(16) Rauhut, G.; Knizia, G.; Werner, H.-J. *J. Chem. Phys.* **2009**, *130*, 054105.

(17) Weigend, F. *Phys. Chem. Chem. Phys.* **2002**, *4*, 4285.

(18) Weigend, F.; Köhn, A.; Hättig, C. *J. Chem. Phys.* **2002**, *116*, 3175.

(19) Adler, T.; Knizia, G.; Werner, H.-J. *J. Chem. Phys.* **2007**, *127*, 034106.

(20) Knizia, G.; Werner, H.-J. *J. Chem. Phys.* **2008**, *128*, 154103.

(21) Kallay, M.; Gauss, J. *J. Chem. Phys.* **2005**, *123*, 214105.

(22) Kallay M. Ph. D. Thesis, Budapest University of Technology and Economics, Budapest, Hungary, 2001.

(23) Kallay, M.; Surjan, P. *J. Chem. Phys.* **2001**, *115*, 2945.

(24) Gauss, J.; Tajti, A.; Kallay, M.; Stanton, J. F.; Szalay, P. G. *J. Chem. Phys.* **2006**, *125*, 144111.

(25) *CFOUR*, Coupled-Cluster techniques for Computational Chemistry, a quantum-chemical program package by Stanton, J. F.; Gauss, J.; Harding, M. E.; Szalay, P. G. with contributions from Auer, A.A.; Bartlett, R. J.; Benedikt, U.; Berger, C.; Bernholdt, D. E.; Bomble, Y. J.; Cheng, L.; Christiansen, O.; Heckert, M.; Heun, O.; Huber, C.; Jagau, T.-C.; Jonsson, D.; Juselius, J.; Klein, K.; Lauderdale, W. J.; Matthews, D. A.; Metzroth, T.; O'Neill, D. P.; Price, D. R.; Prochnow, E.; Ruud, K.; Schiffmann, F.; Schwalbach, W.; Stopkowicz, S.; Tajti, A.; Vazquez, J.; Wang, F.; Watts, J. D. And the integral packages *MOLECULE* (Almlof, J.; Taylor, P. R.), *PROPS* (Taylor, P. R.), *ABACUS* (Helgaker, T.; Jensen, H. J. Aa.; Jørgensen, P.; Olsen, J.), and ECP routines by Mitin, A. V.; van Wullen, C. For the current version, see http://www.cfour.de (accessed Nov 2010).

(26) Douglas, M.; Kroll, N. M. *Ann. Phys.* **1974**, *82*, 89.

(27) Pflüger, K.; Paulus, M.; Jagiella, S.; Burkert, T.; Rauhut, G. *Theor. Chim. Acta* **2005**, *114*, 327.

(28) Rauhut, G.; Barone, V.; Schwerdtfeger, P. *J. Chem. Phys.* **2006**, *125*, 054308.

(29) Yagi, K.; Hirata, S.; Hirao, K. *Theor. Chim. Acta* **2007**, *118*, 681.

(30) Sparta, M.; Høyvik, I.-M.; Toffoli, D.; Christiansen, O. *J. Phys. Chem. A* **2009**, *113*, 8712.

(31) Watson, J. K. G. *Mol. Phys.* **1968**, *15*, 479.

(32) Light, J.; Hamilton, I.; Lill, J. *J. Chem. Phys.* **1985**, *82*, 1400.

(33) Hamilton, I.; Light, J. *J. Chem. Phys.* **1986**, *84*, 306.

(34) Ruden, T. A.; Helgaker, T.; Jørgensen, P.; Olsen, J. *J. Chem. Phys.* **2004**, *121*, 5874.

(35) Koput, J.; Peterson, K. A. *J. Chem. Phys.* **2006**, *125*, 044306.

(36) Tague, T.; Andrews, J. *J. Am. Chem. Soc.* **1994**, *116*, 4970.

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