

Effect of electron correlation and scalar relativistic corrections on the thermochemical and spectroscopic properties of HOF

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ABSTRACT

Bond dissociation energies for the HOF system and an anharmonic force field for HOF are obtained from *ab initio* energies at the CCSD(T)/CBS level of theory, where the complete basis set (CBS) limit energies are obtained by extrapolating CCSD(T)/aug-cc-pVnZ ($n = 2,3,4$) energies. The effects of including core-valence correlation and scalar relativistic effects on the thermochemical and spectroscopic properties are investigated. The results are compared to available experimental results including recent re-evaluations of the properties of OF and OH. Quartic force fields are calculated at each level of theory and basis set used. Excellent agreement between experimental and calculated properties is obtained in most cases, but a few prominent and large differences in rotation-vibration coupling constants and a few force constants are observed. In these cases, our results are consistent with other, high level, *ab initio* evaluations of these properties. Given the ability of large basis set CCSD(T) calculations to yield accurate results for a wide range of molecular parameters, these differences suggest that experimental results may benefit from re-examination in some cases. A new recommendation for the 0 K enthalpy of formation of HOF, $\Delta H_{f,0K}^\circ = -20.02 \pm 0.25$ kcal/mol, is presented based on a careful analysis of recent experimental data and is supported by the high level *ab initio* calculations presented in this work.

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I. Introduction

There have been many determinations of the equilibrium structure of hypofluorous acid (HOF) using SCF^{1,2,3,4} and various correlated methods^{5,6,7,8,9,10,11,12,13} including density functional theory.^{9,10} However, there are remarkably few theoretical investigations of the spectroscopic constants, anharmonic force field, and near-equilibrium potential energy function of the HOF molecule, in spite of the availability of a rather large array of experimental results.^{14,15,16,17,18,19,20,21,22} The earliest attempts in this direction appears to be those of Botschwina² and Murrell *et al.*⁴ The former² reported calculations of a near-equilibrium potential energy surface at the SCF level of theory coupled with empirical corrections to the quadratic force field to improve the predictions of higher-lying overtones and combination bands. The latter⁴ described a global potential energy surface derived partially from a quadratic force field calculated from experimental vibrational frequencies and partially from SCF calculations. The first calculation of spectroscopic properties and an anharmonic force field for HOF that included electron correlation effects appears to be the coupled cluster singles and doubles (CCSD) investigations of Thiel *et al.*²³ Halonen and Ha²⁰ constructed an empirical quartic force field by a constrained least-squares fit to available experimental vibration-rotation data supplemented by several *ab initio* force constants from Thiel *et al.* The most accurate theoretical calculations of the spectroscopic constants and anharmonic force field of HOF to date appears to be that of Breidung *et al.*,²⁴ who used the CCSD method with perturbative triples, CCSD(T),^{25,26} making use of the then-recently implemented analytic second derivatives²⁷ to obtain a quartic force field. To the best of our knowledge, Refs. 23 and 24 represent the only reliable theoretical estimates of the spectroscopic constants of the HOF molecule available at this time.

The present work was undertaken with two goals. One was to examine the accuracy with which “high level” (to be defined below) *ab initio* calculations can predict the thermochemistry of the X^1A' electronic state of the “HOF system,” by which we mean the triatomic molecule and the atom-diatom fragments that correlate with it. This was motivated by a recent re-evaluation of the spectroscopic constants of the OF radical from available high-resolution experimental data,²⁸ the dissociation energy of OH from a combination of experimental data and large-scale *ab initio* calculations,²⁹ and a suspected uncertainty of almost 3.0 kcal/mol in the enthalpy of formation at

0 K, $\Delta H_{f,0K}^\circ$, of HOF.³⁰ The second goal was to examine the spectroscopic constants of HOF, OH, OF and HF molecules from local analytic potential energy surfaces constructed from the above-mentioned “high level” *ab initio* energies.

By “high level,” we mean *ab initio* calculations at the CCSD(T) level of theory coupled with (a) the recovery of correlation energy beyond that afforded by standard correlation consistent basis sets by extrapolation to the complete basis set (CBS) limit, (b) inclusion of core-valence correlation effects, and (c) inclusion of scalar relativistic effects.

The remainder of this paper is organized as follows. In the following Section, we present the details of the calculations. The results of these calculations are presented in Section III and compared to available experimental results. Section IV is a summary of this work.

II. Calculations

The vast majority of calculations were done using the CCSD(T) method with the augmented, correlation consistent, polarized valence n -zeta basis sets of Dunning and coworkers,³¹ (denoted as aug-cc-pVnZ or AVnZ), where $n = 2, 3,$ and 4 (D, T, and Q). Thus, three successively larger calculations were carried out at each geometry of interest. The three AVnZ energies corresponding to each geometry were then extrapolated to the complete basis set (CBS) limit using the expression³²

$$E(n) = E_{\text{CBS}} + Be^{-(n-1)} + Ce^{-(n-1)^2}. \quad (1)$$

With the three CCSD(T)/AVnZ energies corresponding to $n = 2, 3, 4$, this leads to three simultaneous equations which are *solved* for the three unknowns $E_{\text{CBS}}, B,$ and C .

The core-valence correlation energy is obtained from the difference of frozen-core (fc) and all-electron (ae) energies calculated using the cc-pCVTZ (CVTZ) basis set³³

$$\delta E_{\text{CV}} = (E_{\text{CVTZ}}^{\text{CCSD(T)/ae}} - E_{\text{CVTZ}}^{\text{CCSD(T)/fc}}). \quad (2)$$

Note that since the all-electron energy is lower than that from the frozen-core calculation, the left hand side of Eq. (2) is negative. The scalar relativistic corrections δE_{SR} are obtained as the

expectation value of the 1-electron mass velocity and Darwin operators with internally contracted averaged coupled pair functional (ACPF) wave functions,³⁴ where full valence complete active space reference functions were used.

To facilitate discussion of the results in the following Section, we define energies at the following levels of theory in addition to the E_{AVnZ} and E_{CBS} levels. These are

$$E_{CBS+CV} = E_{CBS} + \delta E_{CV}, \quad (3)$$

and

$$E_{CBS+CV+SR} = E_{CBS} + \delta E_{CV} + \delta E_{SR}. \quad (4)$$

All calculations were carried out using the MOLPRO package of programs,³⁵ and in all cases only the pure spherical harmonic components of the angular momentum functions in the basis set were used. For the various open-shell species involved, the R/UCCSD(T) method was used.³⁶

In order to construct near-equilibrium potential energy surfaces for the HOF molecule, a total of 41 points in $(r_{OH}, r_{OF}, \theta_{HOF})$ space spanning the experimental equilibrium geometry were computed at the CCSD(T) level of theory using each of the AVnZ ($n = D, T, Q$ or 2,3,4) basis sets, extrapolated to the CBS limit using Eq. (1), and the core-valence (CV) and scalar relativistic (SR) corrections applied to this energy. These energies were then fitted to a polynomial expansion using displacement coordinates for the two bond lengths and the Carter-Handy coordinate³⁷ for the bend, using the program SURFIT.³⁸ A fourth order expansion in all coordinates was used along with fifth and sixth order “diagonal” terms in each coordinate, to yield a total of 41 linear parameters to be determined by the fitting routines. Since the number of parameters and the number of dependent variables are the same, the fit is, in reality, an interpolation, essentially free of statistical error in every case. The equilibrium geometry reported for the molecule corresponds to the location of the minimum on this potential surface.

The SURFIT program transforms the coefficients of the polynomial expansion of the potential energy function into dimensionless normal coordinate coefficients using the L -tensor algebra of Hoy, Mills, and Strey.³⁹ The resulting normal mode expansion coefficients are used to compute the spectroscopic constants using standard second order perturbation theory expressions⁴⁰ for the ro-vibrational energy levels of the molecule. The force field can also be

obtained in terms of mass-independent internal coordinates in the usual Taylor series expansion about the equilibrium geometry.

The spectroscopic properties of the diatomic molecules were analyzed using a sixth order polynomial interpolation through seven *ab initio* points from which all the required derivatives were evaluated analytically. The reported equilibrium geometries for the diatomics correspond to the minima of these potential energy curves.

III. Results and Discussion

A. Dissociation energies

The Born-Oppenheimer dissociation energies D_e of the HOF system are presented in Table I at the various levels of theory used, and compared to experimental values. Since the *ab initio* calculations do not include spin-orbit coupling, the experimental values used for comparison have been adjusted using experimental atomic⁴¹ and molecular^{28,29} spin-orbit splittings, so that the comparisons are meaningful.

The experimental D_e values reported for the dissociation of the HOF molecule into atom + diatom combinations deserve comment. The $\Delta H_{f,0\text{K}}^\circ$ of HOF from the JANAF Tables⁴² is -22.8 ± 1.00 kcal/mol. However, Pople and Curtiss³⁰ have expressed the opinion that this value is in error and recommended -19.9 kcal/mol as the “best” experimental value, obtained by combining the photoionization process⁴³



for which $\Delta H_{f,0\text{K}}^\circ = 15.07 \pm 0.01$ eV (347.52 ± 0.23 kcal/mol),⁴⁴ with the ionization energy (IE) and the $\Delta H_{f,0\text{K}}^\circ$ of OH and $\text{F}(^2P)$. By combining Eq. (5) with the ionization of OH, we get



If the 0 K enthalpies of formation of OH and $\text{F}(^2P)$ are available, $\Delta H_{f,0\text{K}}^\circ$ for HOF can, therefore, be easily calculated. For IE(OH), Pople and Curtiss used the Katsumata-Lloyd value of 13.01 eV⁴⁵ and for the 0 K enthalpies of formation of OH and $\text{F}(^2P)$, the JANAF Tables values of 9.175 ± 0.29 kcal/mol and 18.47 ± 0.072 kcal/mol, respectively. Two of these values have since

been called into question. We refer the reader to Ref. 29 for a brief history of the measurement of the ionization potential of OH. The Katsumata-Lloyd value is certainly among the more accurate measurements but it seems that the most accurate adiabatic ionization energy of OH to date is from the zero electron kinetic energy (ZEKE) photoionization study of Weidmann *et al.*,⁴⁶ which is reported to be 13.01698 ± 0.00025 eV. Using this result, the 0 K enthalpy of reaction, $\Delta H_{r,0K}^\circ$ for Eq. (6) is 2.05 ± 0.01 eV or 47.34 ± 0.23 kcal/mol. A recommendation for the $\Delta H_{f,0K}^\circ$ for HOF of -19.5 kcal/mol has been made recently,⁴⁷ using this $\Delta H_{r,0K}^\circ$ for Eq. (6) and the JANAF values for the $\Delta H_{f,0K}^\circ$ of OH and F(2P).⁴⁸ However, the recent report of Ruscic *et al.*²⁹ lends strong support for revising the 0 K enthalpy of formation of OH to 8.85 ± 0.07 kcal/mol. With the $\Delta H_{r,0K}^\circ$ of 47.34 ± 0.23 kcal/mol for Eq. (6), the Ruscic *et al.*²⁹ value for the $\Delta H_{f,0K}^\circ$ of OH, and adopting the JANAF value for the $\Delta H_{f,0K}^\circ$ for F(2P), we obtain the “best” experimental value for the $\Delta H_{f,0K}^\circ$ of HOF to be -20.02 ± 0.25 kcal/mol. This is the basis for the experimental D_e values reported for the dissociation of the HOF molecule reported in Table I.

Table I shows that, as expected, the D_e values increase with increasing basis set size and on extrapolation to the CBS limit. The addition of core-valence correlation and scalar relativistic corrections, however, are observed to either increase or decrease the D_e 's compared to the valence-only CBS values. So, for instance, the inclusion of core-valence correlation in HF, F(2P), and O(3P) results in a net increase in the dissociation energy of HF, but the same treatment slightly decreases the D_e value for the OF molecule. In nearly every case, the inclusion of scalar relativistic corrections results in a decrease of the D_e value compared to the CBS+CV level of theory, the only exception being the HOF \rightarrow HF + O(3P) dissociation, in which case the CBS+CV+SR level essentially recovers the D_e calculated at the CBS level. With two notable exceptions, which will be discussed further below, the AVQZ and higher level results are in excellent agreement with the experimental values, the differences being much smaller than the ± 1 kcal/mol error limit generally considered sufficient for “chemical accuracy.”

It should be mentioned here that since CCSD(T) does not accurately reproduce the triplet-singlet gap in atomic oxygen (this requires at least a two-determinant treatment), we have fixed this gap to the experimental value of 45.366 kcal/mol (corrected for SO splitting) when

calculating the D_e values for $\text{HOF} \rightarrow \text{O}(^1D) + \text{HF}$. With this adjustment, the Born-Oppenheimer dissociation energies of HOF are in excellent agreement with the experimental values recalculated from the new recommendation for the $\Delta H_{f,0\text{K}}^\circ$ of HOF given above. Considering the fact that CCSD(T) calculations employing large basis sets have been known to accurately reproduce bond dissociation energies in a large number of cases,^{49,50,51} the agreement between the calculated and experimental D_e values of HOF in Table I lend support to the recommended 0 K enthalpy of formation of HOF we have presented above.

We now comment on the two exceptions to the excellent agreement between calculated and experimental D_e values mentioned above. The first is due to the apparent difficulty of CCSD(T) to accurately recover the bond energy of the OF molecule,⁵² even when CV and SR corrections are included. As discussed below, the second is directly related to the error in the OF bond energy and is reflected in a relatively large discrepancy between the calculated and experimental D_e values for the process $\text{HOF} \rightarrow \text{H}(^2S) + \text{OF}(^2\Pi)$.

The difficulty faced by CCSD(T) and MRCI+Q calculations in reproducing the bond dissociation energy of $\text{ClO}^{53,54}$ and BrO^{55} are well-known. It appears that the OF molecule poses similar difficulties for these methods. Multiple reports have indicated that the O-F bond is among the more challenging chemical bonds for other single determinant *ab initio* methods.^{9,56,57,58} The rather large discrepancy between the calculated and experimental D_e values for the process $\text{HOF} \rightarrow \text{H}(^2S) + \text{OF}(^2\Pi)$ is, therefore, easily explained in terms of the limited accuracy of the D_e value for OF from the calculations. For example, the difference between the CCSD(T)/CBS and experimental D_e values for OF (1.29 kcal/mol) is nearly exactly sufficient to account for the discrepancy between the CCSD(T)/CBS and experimental D_e (1.27 kcal/mol) for $\text{HOF} \rightarrow \text{H}(^2S) + \text{OF}(^2\Pi)$. In spite of these remarks, it should be noted that the experimental D_e value for OF has a significant error bar of ± 2.26 kcal/mol. The *ab initio* results from CCSD(T)/CBS and higher levels of treatment are within this error limit.

We comment on one more item related to the dissociation energies of diatomic molecules from Table I: the tendency for CCSD(T) calculations, when extrapolated to the CBS limit, to over-estimate the D_e of HF. The tendency of large basis set CCSD(T) calculations to over-estimate the D_e for this particular molecule is already known, for example, from the calculations of Feller, Peterson, and coworkers,^{49,50,51} where different functional forms were used for the

extrapolation to the CBS limit. Therefore, our results are in keeping with those from several meticulous analyses of atomization energies of small molecules.

The enthalpies of reaction at 0 K, $\Delta H_{r,0K}^\circ$, can be calculated from these D_e values simply by including the zero-point energies at each level of theory, i.e., by examining the spectroscopic dissociation energies, D_0 . The harmonic frequencies and the anharmonic constants necessary for calculating these quantities are presented next. However, we mention here that the $\Delta H_{r,0K}^\circ = D_0(\text{HO-F})$ for Eq. (6) calculated from the D_e values in Table I and the zero point energies of HOF and OH turn out to be 47.54, 47.64, and 47.57 kcal/mol, respectively, at the CBS, CBS+CV, and CBS+CV+SR levels of theory. These are in better agreement with the experimental value of 47.34 ± 0.23 kcal/mol [see discussion following Eq. (6), above] than the 48.4 kcal/mol³⁰ obtained from the G1 theory,⁵⁹ or a more recent estimate⁶⁰ of 48.11 kcal/mol from the G2 theory.⁶¹

B. Spectroscopic constants

Table II summarizes the spectroscopic constants of the diatomic molecules at the various levels of theory used in this work. The spectroscopic constants for HF and OH are compared to the experimental values tabulated by Huber and Herzberg^{62,63} while those of OF are compared to the recent re-evaluation of the spectroscopic properties of OF by Miller and Brouin²⁸ from high-resolution spectroscopic data. It is seen that the CCSD(T) calculations (all-electrons correlated) over-estimate the frequencies of all three diatomic species by just 5-15 cm^{-1} .

The geometric parameters of HOF are presented in Table III where they are compared with the experimental values of Halonen and Ha.²⁰ It is seen that the higher level calculations are able to reproduce the geometry of the molecule to within the 1σ error estimates from the analysis by Halonen and Ha. This includes the HOF bond angle, which is consistently larger than the Halonen and Ha value by ~ 0.2 - 0.5° for all treatments beyond the CCSD(T)/AVDZ level. This is also consistent with the results obtained by Breidung *et al.*,²⁴ where the optimum geometry was obtained at the CCSD(T) level of theory using analytical derivatives.

The calculated harmonic and fundamental frequencies of HOF are tabulated in Table IV. The “experimental” harmonic frequencies shown for HOF were deduced from the experimental

fundamental frequencies together with calculated anharmonicity constants by Halonen and Ha²⁰ and have fairly large uncertainties. The CBS and higher levels of treatment have a tendency to slightly over-estimate the fundamental frequencies. The CCSD(T)/AVQZ frequencies reported in Table IV are very close to the the CCSD(T)/cc-pVQZ results of Breidung *et al.*,²⁴ who evaluated the frequencies from analytical second derivatives of the CCSD(T) wave function. The calculated fundamental frequencies are also in excellent agreement with the experimental results shown, the average difference for the three CBS+CV+SR frequencies being of the order of 0.5% relative to the experimental values.

The rotational constants of HOF are presented in Table V and the centrifugal distortion constants in Table VI. The rather small differences between the calculated and experimental results can be attributed to the tendency for the calculated OF bond to be slightly too short (~ 0.004 Å), as well as the vibrational effects on the centrifugal distortion constants, which we ignore.

The anharmonicity constants and rotation-vibration couplings are presented in Table VII. The calculations are able to reproduce the two experimentally known anharmonicity constants of HOF within a fraction of a wave number. However, there are significant differences between some of the calculated and experimental rotation-vibration coupling constants α . The largest discrepancies appear to be in the constants $\alpha(s,A)$ and $\alpha(a,B)$. In these cases, the absolute differences between the CBS+CV+SR constants and experimental values are 28% and 80%, respectively. The CCSD(T)/cc-pVTZ values for these constants obtained by Breidung *et al.*²⁴ also have large absolute differences (18.3% and 42.6%, respectively) from the experimental values. Given the ability of high level computational chemistry to accurately predict a wide range of molecular properties, and given the many difficulties of accurately analyzing experimental molecular spectra, it may not be entirely unreasonable to suspect that the experimental constants may be in error in at least these two cases.

The quartic force fields at each level of theory examined are calculated from SURFIT in terms of displacement coordinates $q_1 = r_{\text{OH}} - r_{\text{OH}}^e$, $q_2 = r_{\text{OF}} - r_{\text{OF}}^e$, and $q_3 = \theta_{\text{HOF}} - \theta_{\text{HOF}}^e$, where the superscript ‘e’ indicates the equilibrium value, and are presented in Table VIII. Since the CCSD(T)/AVDZ results are of limited interest, we have omitted them in favor of the CCSD(T) results of Breidung *et al.*,²⁴ in which the quadratic force constants were obtained at the

CCSD(T)/cc-pVQZ level and the cubic and quartic force constants at the CCSD(T)/cc-pVTZ level of theory using analytical second derivatives. The present results are comparable to those of Breidung *et al.* in most cases but a few significant differences do exist, e.g., the force constants (2,0,1), (0,0,4), (3,1,0), (1,3,0), (3,0,1), (0,3,1), and (1,2,1). However, the present results shown in Table VIII indicate that most of these are very sensitive to the basis set used, as well as core-valence correlation and scalar relativistic effects. For these reasons we believe that the present CBS+CV+SR results for (2,0,1), (0,0,4), (3,1,0), (3,0,1), and (1,2,1) are probably the more reliable. Our (1,3,0) and (0,3,1) force constants are larger than those of Breidung *et al.* and can not be easily explained by the larger basis sets and other corrections used in this work and hence these differences are perhaps due to artifacts in the fits to *ab initio* data.

It is also essential to comment on the differences between the present results and the empirical force field of Halonen and Ha,²⁰ which is also shown in Table VIII. This empirical force field is based on a constrained least-squares fit to available experimental vibration-rotation data combined with several force constants that were fixed at the *ab initio* values then available.²³ These *ab initio* force constants are easily recognized in Table VIII by the absence of uncertainties in the last digits, which are shown in parentheses in the case of the experimentally obtained values. Comparing these experimental force constants to those calculated in this work, we note that the calculated force constants differ from the experimental values by less than 5%, with the notable exception of (0,0,4), in which case the CBS+CV+SR value differs from the experimental value by about 64%. The case of (0,0,4) was discussed above, as being one among the seven instances in which our results differ significantly from those of Breidung *et al.*²⁴ The value reported from SCF/TZP//CCSD/TZP calculations²³ is -0.78 , which is also in considerable disagreement with the experimental value. The extreme sensitivity of this force constant to the basis set and corrections used is evident from the fact that, between the CCSD(T)/AVTZ and the CBS+CV+SR levels of treatment, the calculated value changes by more than 62% relative to the latter value. Note that the (0,0,4) force constant depends on a fourth order derivative with respect to the HOF angle. The presence of diffuse functions in the basis set has been found to improve the accuracy with which *ab initio* calculations reproduce the angular dependence of potential energy functions in the case of HOCl⁵³ and HOBr.⁵⁵ Therefore, we believe that the CCSD(T)/AVQZ and higher results of the present work may be more reliable, in spite of the fact that the CCSD(T)/VTZ value of Breidung *et al.* is in better agreement with the experimental

value in this case. In this context, it is important to remember that the values obtained for the experimental force constants depend on the values provided for the remaining force constants in the analysis. Since constrained minimization affects all force constants that are not frozen, it is possible that using the CBS+CV+SR results in the development of a new force field could improve the agreement between the calculated and the experimental value in this particular case, and further improve the agreement in the remaining cases.

IV. Summary

We have presented calculations at the CCSD(T) level of theory for the X^1A' electronic state of the HOF molecule and the atom-diatom fragments that correlate with it. The *ab initio* calculations using the aug-cc-pVnZ ($n = D, T, Q$) basis sets of Dunning and co-workers were followed by explicit pointwise extrapolation to the complete basis set (CBS) limit and the inclusion of core-valence (CV) and scalar relativistic (SR) corrections. These calculations have been shown to be capable of accurately reproducing the Born-Oppenheimer dissociation energies of most of the species examined with the possible exception of the OF molecule, in which case the highest level of treatment (CBS+CV+SR) is still smaller by 1.35 kcal/mol than the experimental value, but within the rather large error bar of ± 2.26 kcal/mol associated with the experimental result. The 1.42 kcal/mol discrepancy between the experimental and calculated (CBS+CV+SR) D_e value for $\text{HOF} \rightarrow \text{H} + \text{OF}$ can be directly attributed to this error.

Note that the JANAF value of -22.8 kcal/mol for the $\Delta H_{f,0\text{K}}^\circ$ of HOF would have led to serious discrepancies between the calculated and experimental D_e values in the last four rows of Table I. The approach taken in this work—large basis set CCSD(T) calculations supplemented by the various corrections—has been well-tested and has been shown to yield extremely accurate results in a large number of cases.^{49,50,51} Therefore, the *ab initio* results lend support to the recommendation of -20.02 ± 0.25 kcal/mol for the $\Delta H_{f,0\text{K}}^\circ$ of HOF made above.

This work also reports calculations of the spectroscopic constants for the HOF molecule and the diatomic fragments, as well as a quartic force field for the HOF molecule, at each level of theory and basis set employed, from analytic fits to a moderate number of *ab initio* energies spanning near-equilibrium geometries. The larger basis set CCSD(T) calculations and further

corrections to them are shown to accurately reproduce the spectroscopic properties of the diatomic molecules. The calculated spectroscopic constants for the HOF molecule, especially those at the CCSD(T)/AVQZ and higher levels of treatment, are also found to be in good agreement with experimental results with the exception of two rotation-vibration coupling constants. In these cases, there are large absolute differences between the experimental values and the present results as well as those of Breidung *et al.*²⁴ In each case, the present results are in fair agreement with those of Ref. 24. This observation, coupled with the well-documented ability of large basis set CCSD(T) calculations to accurately reproduce a wide range of molecular properties, suggests that the experimental results may need to be re-evaluated in at least these two cases.

To the best of our knowledge, the empirical force-field of Halonen and Ha²⁰ is the only one for HOF that combines available experimental vibration-rotation data with the only correlated *ab initio* calculations of force constants available at the time.²³ The *ab initio* force constants incorporated into this force field were obtained at the CCSD/TZP//CCSD/TZP (quadratic and cubic) and SCF/TZP//CCSD/TZP (quartic) levels of theory.²³ There is no doubt that the CCSD(T) results of Breidung *et al.*²⁴ and the present results are more reliable, because the perturbative inclusion of triple excitations in the CCSD(T) method represents a significant improvement over CCSD. Use of some of these force constants in the place of those of Thiel *et al.*²³ along with available experimental data may lead to a more accurate empirical force field for HOF and, perhaps, even better agreement between the calculated force constants presented in this work and those that are determined by constrained minimization.

References

- ¹ Buenker, R. J.; Peyerimhoff, S. D. *J. Chem. Phys.* **1966**, *45*, 3682.
- ² Kim, H.; Sabin, J. R. *Chem. Phys. Lett.* **1973**, *20*, 215.
- ³ Botschwina, P. *Chem. Phys.* **1979**, *40*, 33.
- ⁴ Murell, J. N.; Carter, S.; Mills, I. M.; Guest, M. F.; *Mol. Phys.* **1979**, *37*, 1199.
- ⁵ Frenking, G.; Koch, W. *Chem. Phys. Lett.* **1984**, *105*, 659.
- ⁶ Francisco, J. S.; Zhao, Y.; Lester, Jr., W. A.; Williams, I. H. *J. Chem. Phys.* **1992**, *96*, 2861.
- ⁷ Burke, P.; Koppel, I. A.; Rummel, A.; Trummal, A. *J. Phys. Chem.* **1995**, *99*, 1432.
- ⁸ Lee, T. J.; Rice, J. E.; Dateo, C. E. *Mol. Phys.* **1996**, *89*, 1359.
- ⁹ Ventura, O. N.; Kieninger, M. *Chem. Phys. Lett.* **1996**, *245*, 488.
- ¹⁰ Dressler, S.; Thiel, W. *Chem. Phys. Lett.* **1997**, *273*, 71.
- ¹¹ Helgaker, T.; Gauss, J.; Jørgensen, P.; Olsen, J. *J. Chem. Phys.* **1997**, *106*, 6430.
- ¹² Berski, S.; Lundell, J.; Latajka, Z.; Leszczynski, J. *J. Phys. Chem. A* **1998**, *102*, 10768.
- ¹³ Berski, S.; Silvi, B.; Latajka, Z.; Leszczynski, J. *J. Chem. Phys.* **1999**, *111*, 2542.
- ¹⁴ Kim, H.; Pearson, E. F.; Appleman, E. H. *J. Chem. Phys.* **1972**, *56*, 1.
- ¹⁵ Pearson, E. F.; Kim, H. *J. Chem. Phys.* **1972**, *57*, 4230.
- ¹⁶ Lovas, F. J. *J. Phys. Chem. Ref. Data* **1978**, *7*, 1445.
- ¹⁷ Appleman, E. H.; Kim, H. *J. Chem. Phys.* **1972**, *57*, 3272.
- ¹⁸ Rock, S. L.; Pearson, E. F.; Appleman, E. H.; Norris, C. L.; Flygare, W. H. *J. Chem. Phys.* **1973**, *59*, 3940.
- ¹⁹ Bürger, H.; Pawelke, G.; Rahner, A.; Appleman, E. H.; Mills, I. M. *J. Mol. Spectrosc.* **1988**, *128*, 278.
- ²⁰ Halonen, L.; Ha, T. -K. *J. Chem. Phys.* **1988**, *89*, 4885.
- ²¹ Bürger, H.; Pawelke, G.; Sommer, S.; Rahner, A.; Appleman, E. H.; Mills, I. M. *J. Mol. Spectrosc.* **1989**, *136*, 197.
- ²² Bürger, H.; Pawelke, G.; Rahner, A.; Appleman, E. H.; Halonen, L. *J. Mol. Spectrosc.* **1989**, *138*, 346.
- ²³ Thiel, W.; Scuseria, G.; Schaffer III, H. F.; Allen, W. D. *J. Chem. Phys.* **1988**, *89*, 4965.
- ²⁴ Breidung, J.; Thiel, W.; Gauss, J.; Stanton, J. F. *J. Chem. Phys.* **1999**, *110*, 3687.
- ²⁵ Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.
- ²⁶ Purvis III, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.
- ²⁷ Gauss, J.; Stanton, J. F. *Chem. Phys. Lett.* **1997**, *276*, 70.

-
- ²⁸ Miller, C. E.; Drouin, B. J. *J. Mol. Spectrosc.* **2001**, *205*, 312.
- ²⁹ Ruscic, B.; Wagner, A. F.; Harding, L. B.; Asher, R. L.; Feller, D.; Dixon, D. A.; Peterson, K. A.; Song, Y.; Qian, X.; Ng, C. -Y.; Liu, J.; Chen, W.; Schwenke, D. W. *J. Phys. Chem. A* **2002**, *106*, 2727.
- ³⁰ Pople, J. A.; Curtiss, L. A. *J. Chem. Phys.* **1989**, *90*, 2833.
- ³¹ Kendall, R. A.; Dunning, Jr., T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796; Woon D. E.; Dunning, Jr., T. H. *J. Chem. Phys.* **1993**, *98*, 1358.
- ³² Peterson, K. A.; Woon, D. E.; Dunning, Jr., T. H. *J. Chem. Phys.* **1994**, *100*, 7410.
- ³³ Woon, D. E.; Dunning, Jr., T. H. *J. Chem. Phys.* **1995**, *103*, 4572.
- ³⁴ Gdanitz, R. J.; and Ahlrichs, R. *Chem. Phys. Lett.* **1988**, *143*, 413. Werner, H. -J.; Knowles, P. J. *Theor. Chim. Acta* **1990**, *78*, 175.
- ³⁵ MOLPRO is a package of *ab initio* programs written by H.-J. Werner and P.J. Knowles with contributions from Almlöf, J.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Celani, P.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Elbert, S. T.; Hampel, C.; Hetzer, G.; Korona T.; Lindh, R.; Lloyd, A. W.; McNicholas, S. J.; Manby, F. R.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Peterson, K. A.; Pitzer, R. M.; Pulay, P.; Rauhut, G.; Schütz, M.; Stoll, H.; Stone, A. J.; Tarroni, R.; Taylor, P. R.; Thorsteinsson. T. Molpro2000 (2000).
- ³⁶ Rittby, M.; Bartlett, R. J. *J. Phys. Chem.* **1988**, *92*, 3033; Scuseria, G. E. *Chem. Phys. Lett.* **1991**, *176*, 27; Knowles, P. J.; Hampel, C.; Werner, H. -J. *J. Chem. Phys.* **1994**, *99*, 5219.
- ³⁷ Carter, S.; Handy, N. C. *J. Chem. Phys.* **1987**, *87*, 4294.
- ³⁸ SURFIT is described in “Spektroskopische Eigenschaften aus elektronischen Wellenfunktionen,” Senekowitsch, J., Ph.D. thesis, Johann Wolfgang Goethe Universitaet, Frankfurt am Main, Germany, 1988.
- ³⁹ Hoy, A. R.; Mills, I. M.; Strey, G. *Mol. Phys.* **1972**, *24*, 1265.
- ⁴⁰ Papousek, D.; Aliev, M. R. *Molecular Vibrational Spectra: Theory and Applications of High Resolution Infrared, Microwave, and Raman Spectroscopy of Polyatomic Molecules*, Elsevier, Amsterdam, 1982.
- ⁴¹ Moore, C.E. *Atomic Energy Levels*, NSRD-NBS 35, Office of Standard Reference Data, National Bureau of Standards, Washington, D.C., 1971.
- ⁴² Chase, Jr., M. W.; Davies, C. A.; Downey, Jr., J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. No. 1.
- ⁴³ Berkowitz, J.; Appleman, E. H.; Chupka, W. A. *J. Chem. Phys.* **1973**, *58*, 1950.
- ⁴⁴ Ref. 43 does not specify the experimental error in this measurement but we have assumed that it is equal to that in $\text{HOF} \rightarrow \text{HOF}^+ + e^-$; 12.71 ± 0.01 eV, measured in the same experiment.
- ⁴⁵ Katsumata, S.; Lloyd, D. R. *Chem. Phys. Lett.* **1977**, *45*, 519.

-
- ⁴⁶ Weidmann, R. T.; Tonkyn, R. G.; White, M. G.; Wang, K.; McKoy, V. *J. Chem. Phys.* **1992**, *97*, 768.
- ⁴⁷ Ruscic, B.; Berkowitz, J. *J. Chem. Phys.* **1994**, *101*, 7995.
- ⁴⁸ It is possible that this calculation has a small error, because using the same numbers, we get -19.7 kcal/mol.
- ⁴⁹ Feller, D.; Peterson, K. A. *J. Chem. Phys.* **1999**, *110*, 8384.
- ⁵⁰ Feller, D. *J. Chem. Phys.* **1999**, *111*, 4373.
- ⁵¹ Feller, D.; Peterson, K. A.; de Jong, W. A.; Dixon, D. A. *J. Chem. Phys.* **2003**, *118*, 3510.
- ⁵² Chase, M. W. *J. Phys. Chem. Ref. Data* **1996**, *25*, 551. A D_0 value of $18,030 \pm 800$ cm^{-1} is recommended. This, combined with the spectroscopic constants and the $\text{OF}(^2\Pi)$ spin-orbit coupling constant of 196.6284 cm^{-1} obtained in Ref. 28 yields the experimental D_e value shown.
- ⁵³ Skokov, S.; Peterson, K. A.; Bowman, J. M. *J. Chem. Phys.* **1998**, *109*, 2662; Peterson, K. A.; Skokov, S.; Bowman, J. M. *J. Chem. Phys.* **1999**, *111*, 7446.
- ⁵⁴ Ramachandran, B.; Peterson, K. A. *J. Chem. Phys.* (submitted).
- ⁵⁵ Peterson, K. A. *J. Chem. Phys.* **2000**, *113*, 4598.
- ⁵⁶ Jensen, F. *Chem. Phys. Lett.* **1990**, *169*, 519.
- ⁵⁷ Tozer, D. J.; Handy, N. C.; Amos, R. D.; Pople, J. A.; Nobes, R. H.; Xie, Y.; Schaefer, H. F. *Mol. Phys.* **1993**, *79*, 777.
- ⁵⁸ Li, X. Z.; Paldus, J., *J. Chem. Phys.* **1996**, *104*, 9555.
- ⁵⁹ Curtiss, L.A.; Pople, J. A. *J. Chem. Phys.* **1988**, *88*, 7405; **1988**, *89*, 614.
- ⁶⁰ Glukhovtsev, M. N.; Pross, A.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 3498.
- ⁶¹ Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; J. A. Pople, *J. Chem. Phys.* **1991**, *94*, 7221.
- ⁶² Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*, Van Nostrand Reinhold, New York, 1979.
- ⁶³ Also available at <http://webbook.nist.gov/chemistry>.

Table I. Born-Oppenheimer dissociation energies D_e of the HOF system. All energies are in kcal/mol. Spin orbit splittings have been removed from experimental energies shown.

| | AVDZ | AVTZ | AVQZ | CBS | CBS+CV | CBS+CV +SR | Expt. ^(a) |
|---|--------|--------|--------|--------|--------|---------------|-------------------------|
| $\text{HF}(^1\Sigma^+) \rightarrow \text{H}(^2S) + \text{F}(^2P)$ | 134.45 | 139.29 | 140.93 | 141.88 | 142.05 | 141.85 | $141.46 \pm 0.2^{(b)}$ |
| $\text{OH}(^2\Pi) \rightarrow \text{H}(^2S) + \text{O}(^3P)$ | 99.86 | 104.28 | 106.28 | 107.15 | 107.20 | 107.08 | $107.15 \pm 0.07^{(c)}$ |
| $\text{OF}(^2\Pi) \rightarrow \text{O}(^3P) + \text{F}(^2P)$ | 42.05 | 49.22 | 51.08 | 52.08 | 52.07 | 52.02 | $53.37 \pm 2.26^{(d)}$ |
| $\text{HOF} \rightarrow \text{O}(^3P) + \text{HF}$ | 9.03 | 14.38 | 15.60 | 16.23 | 16.21 | 16.23 | $16.41 \pm 0.25^{(e)}$ |
| $\text{HOF} \rightarrow \text{O}(^1D) + \text{HF}^\ddagger$ | 54.40 | 59.75 | 60.97 | 61.60 | 61.58 | 61.60 | $61.78 \pm 0.25^{(e)}$ |
| $\text{HOF} \rightarrow \text{F} + \text{OH}$ | 43.62 | 48.94 | 50.25 | 50.95 | 51.06 | 51.00 | $50.94 \pm 0.25^{(e)}$ |
| $\text{HOF} \rightarrow \text{H} + \text{OF}$ | 101.43 | 104.45 | 105.46 | 106.04 | 106.31 | 106.19 | $104.77 \pm 0.25^{(e)}$ |

[†] The singlet-triplet splitting is fixed at the experimental value of 45.366 kcal/mol in all cases.

^(a) The experimental values are corrected for spin-orbit splittings since the *ab initio* calculations do not include them. The corrections used are: $\text{O}(^3P)$: 0.216 kcal/mol [Ref. 41], $\text{F}(^2P)$: 0.385 kcal/mol [Ref. 41], $\text{OH}(^2\Pi)$: 0.109 kcal/mol [Ref. 29], and $\text{OF}(^2\Pi)$: 0.281 kcal/mol [Ref. 28].

^(b) Calculated from D_0 value given in Ref. 42.

^(c) Ref. 29.

^(d) Ref. 52.

^(e) Based on the “best experimental value” for the $\Delta H_{f,0\text{K}}^\circ$ of HOF, -20.02 ± 0.25 kcal/mol (see text).

Table II. Spectroscopic constants for the diatomic molecules. Bond lengths are in Angstroms, all other quantities are in cm^{-1} .

| | AVDZ | AVTZ | AVQZ | CBS | CBS + CV | CBS+CV +SR | Expt. ^(a) |
|----------------|---------|---------|---------|---------|----------|---------------|----------------------|
| HF | | | | | | | |
| r_e | 0.9241 | 0.9210 | 0.9177 | 0.9156 | 0.9151 | 0.9151 | 0.9168 |
| ω_e | 4080.76 | 4124.69 | 4141.59 | 4152.46 | 4156.63 | 4153.68 | 4138.33 |
| $\omega_e x_e$ | 97.01 | 85.57 | 87.72 | 89.74 | 89.83 | 89.81 | 89.881 |
| B_e | 20.6259 | 20.7670 | 20.9152 | 21.0121 | 21.0356 | 21.0330 | 20.9558 |
| α_e | 0.8297 | 0.7617 | 0.7840 | 0.8017 | 0.8027 | 0.8030 | 0.7981 |
| OF | | | | | | | |
| r_e | 1.3783 | 1.3601 | 1.3536 | 1.3498 | 1.3482 | 1.3487 | 1.3542 |
| ω_e | 989.67 | 1054.42 | 1063.87 | 1068.41 | 1070.30 | 1068.55 | 1053.01 |
| $\omega_e x_e$ | 10.13 | 10.38 | 10.21 | 10.14 | 10.14 | 10.13 | 9.919 |
| B_e | 1.02177 | 1.04945 | 1.05948 | 1.06548 | 1.06802 | 1.06716 | 1.0587 |
| α_e | 0.0136 | 0.0129 | 0.0132 | 0.0134 | 0.0134 | 0.0134 | 0.0133 |
| OH | | | | | | | |
| r_e | 0.9796 | 0.9733 | 0.9707 | 0.9691 | 0.9683 | 0.9684 | 0.9697 |
| ω_e | 3683.65 | 3717.94 | 3738.88 | 3752.19 | 3757.32 | 3754.84 | 3737.76 |
| $\omega_e x_e$ | 87.12 | 80.87 | 83.09 | 84.81 | 84.89 | 84.88 | 84.881 |
| B_e | 18.5299 | 18.7699 | 18.8724 | 18.9335 | 18.9618 | 18.9597 | 18.9102 |
| α_e | 0.7288 | 0.7058 | 0.7164 | 0.7242 | 0.7251 | 0.7256 | 0.7242 |

(a) Reference [62] for HF and OH, Reference [28] for OF.

Table III. The geometric parameters of HOF. Bond lengths are in Angstroms, and angles are in degrees. Experimental uncertainties shown in parentheses are $\pm 1\sigma$ in the least significant digits.

| | AVDZ | AVTZ | AVQZ | CBS | CBS+CV | CBS+CV +SR | Expt. ²⁰ |
|------------------------------------|-------------|-------------|-------------|-------------|-------------|---------------|---------------------|
| E (a.u.) | -175.203601 | -175.351315 | -175.397370 | -175.423402 | -175.531273 | -175.670112 | - |
| $r_{\text{OH}}(\text{\AA})$ | 0.9759 | 0.9703 | 0.9676 | 0.9660 | 0.9653 | 0.9654 | 0.9657(16) |
| $r_{\text{OF}}(\text{\AA})$ | 1.4640 | 1.4418 | 1.4357 | 1.4322 | 1.4304 | 1.4311 | 1.4350(31) |
| $\theta_{\text{HOF}}(\text{deg.})$ | 97.18 | 97.74 | 97.89 | 97.98 | 98.04 | 98.00 | 97.54(50) |

Table IV. Harmonic and fundamental vibrational frequencies of HOF in cm^{-1} . Experimental uncertainties are $\pm 1\sigma$.

| | AVDZ | AVTZ | AVQZ | CBS | CBS+CV | CBS+CV +SR | Expt. |
|------------|--------|--------|--------|---------|--------|---------------|-------------------------|
| ω_s | 855.8 | 914.6 | 919.7 | 921.2 | 923.0 | 921.4 | $916.84 \pm 19^{(a)}$ |
| ω_b | 1366.0 | 1390.2 | 1399.0 | 1404.2 | 1406.5 | 1405.1 | $1396.22 \pm 7.0^{(a)}$ |
| ω_t | 3718.8 | 3745.5 | 3765.2 | 3778.03 | 3783.7 | 3780.9 | $3763.95 \pm 4.6^{(a)}$ |
| ν_s | 826.8 | 886.3 | 892.0 | 893.8 | 895.6 | 893.8 | $889.1^{(b)}$ |
| ν_b | 1321.2 | 1346.3 | 1355.1 | 1360.4 | 1362.6 | 1361.1 | $1353.4^{(b)}$ |
| ν_a | 3524.4 | 3564.6 | 3579.3 | 3588.3 | 3593.8 | 3591.0 | $3577.9^{(b)}$ |

(a) Ref. 20.

(b) Ref. 22.

Table V. Rotational constants of HOF in cm^{-1} .

| | AVDZ | AVTZ | AVQZ | CBS | CBS+CV | CBS+CV +SR | Expt.^{21,22} |
|-------|-------------|-------------|-------------|------------|---------------|-----------------------|------------------------------|
| A_e | 19.20810 | 19.50288 | 19.62923 | 19.70560 | 19.74460 | 19.73580 | 19.66380 |
| B_e | 0.86560 | 0.89146 | 0.89889 | 0.90320 | 0.90530 | 0.90440 | 0.90026 |
| C_e | 0.82830 | 0.85246 | 0.85950 | 0.86360 | 0.86560 | 0.86480 | 0.86084 |

Table VI. Centrifugal distortion constants of HOF in MHz.

| | AVDZ | AVTZ | AVQZ | CBS | CBS+CV | CBS+CV +SR | Expt.²² |
|----------|-------------|-------------|-------------|------------|---------------|-----------------------|---------------------------|
| D_J | 0.0955 | 0.0911 | 0.0923 | 0.0933 | 0.0935 | 0.0936 | 0.09337 |
| D_{JK} | 2.2828 | 2.3254 | 2.3671 | 2.3945 | 2.4068 | 2.4034 | 2.387 |
| D_K | 70.8423 | 74.2277 | 75.3437 | 75.9935 | 76.4119 | 76.2804 | 75.125 |

Table VII. Anharmonicity (in cm^{-1}) and vibration-rotation constants of HOF (in 10^{-3} cm^{-1}). Experimental uncertainties shown in parentheses are $\pm 1\sigma$ in the least significant digits.

| | AVDZ | AVTZ | AVQZ | CBS | CBS+CV | CBS+CV +SR | Expt. ^(a) |
|---------------|---------|---------|---------|---------|---------|---------------|---------------------------|
| $x(a,a)$ | -88.37 | -82.25 | -84.60 | -86.39 | -86.47 | -86.47 | - |
| $x(b,b)$ | -9.21 | -9.66 | -9.52 | -9.42 | -9.44 | -9.46 | -9.942(2) ^(b) |
| $x(s,s)$ | -8.96 | -9.01 | -8.68 | -8.49 | -8.47 | -8.51 | - |
| $x(a,b)$ | -32.84 | -30.73 | -31.20 | -31.59 | -31.60 | -31.65 | - |
| $x(a,s)$ | -2.41 | -2.07 | -2.25 | -2.38 | -2.38 | -2.44 | - |
| $x(b,s)$ | -19.88 | -18.48 | -18.48 | -18.56 | -18.54 | -18.64 | -18.502(2) ^(b) |
| $\alpha(a,A)$ | 739.20 | 716.49 | 729.70 | 739.16 | 740.53 | 741.01 | 738.733(9) |
| $\alpha(b,A)$ | -451.94 | -467.31 | -471.45 | -473.81 | -476.19 | -475.40 | -499.595(9) |
| $\alpha(s,A)$ | 22.56 | 22.92 | 23.77 | 24.47 | 24.65 | 24.73 | 19.301(11) |
| $\alpha(a,B)$ | 0.80 | 0.63 | 0.66 | 0.68 | 0.69 | 0.69 | 0.3834(8) |
| $\alpha(b,B)$ | 4.74 | 3.86 | 3.86 | 3.89 | 3.88 | 3.91 | 3.7816(6) |
| $\alpha(s,B)$ | 11.12 | 10.80 | 10.88 | 10.96 | 10.99 | 11.00 | 11.1685(22) |
| $\alpha(a,C)$ | 1.89 | 1.71 | 1.76 | 1.80 | 1.81 | 1.82 | 1.6223(8) |
| $\alpha(b,C)$ | 7.71 | 7.00 | 7.03 | 7.07 | 7.07 | 7.10 | 7.2037(6) |
| $\alpha(s,C)$ | 10.84 | 10.60 | 10.69 | 10.78 | 10.80 | 10.81 | 10.9837(22) |

^(a) Ref. 22 unless otherwise indicated.

^(b) Ref. 21.

Table VIII. The quartic force field for HOF in internal coordinates in aJ $a_0^{-(n_1+n_2)} \text{ rad}^{-n_3}$ (1 aJ = 1 mdyn Å). The indices n_1 , n_2 , and n_3 indicate the order of the derivative with respect to the internal coordinates $q_1 = r_{\text{OH}} - r_{\text{OH}}^e$, $q_2 = r_{\text{OF}} - r_{\text{OF}}^e$, and $q_3 = \theta_{\text{HOF}} - \theta_{\text{HOF}}^e$.

| $n_1 n_2 n_3$ | Ref. 24 | AVTZ | AVQZ | CBS | CBS+CV | CBS+CV +SR | Empirical ²⁰ |
|---------------|---------|----------|----------|----------|----------|---------------|-------------------------|
| 2 0 0 | 8.000 | 7.827359 | 7.910119 | 7.964132 | 7.988109 | 7.976437 | 7.898(44) |
| 0 2 0 | 4.723 | 4.590851 | 4.64969 | 4.670939 | 4.690732 | 4.672575 | 4.634(50) |
| 0 0 2 | 0.998 | 0.990743 | 0.99745 | 1.001499 | 1.002958 | 1.001268 | 0.9906(54) |
| 1 1 0 | -0.139 | -0.13468 | -0.13773 | -0.14046 | -0.14094 | -0.14075 | -0.135 |
| 1 0 1 | -0.027 | -0.03293 | -0.03151 | -0.03059 | -0.02973 | -0.03036 | -0.037 |
| 0 1 1 | 0.572 | 0.550296 | 0.561888 | 0.568789 | 0.571587 | 0.569158 | 0.572(38) |
| 3 0 0 | -56.276 | -54.3741 | -55.4265 | -56.1584 | -56.3612 | -56.2978 | -54.366 |
| 0 3 0 | -31.212 | -29.8537 | -30.2942 | -30.512 | -30.6675 | -30.5575 | -30.87(30) |
| 0 0 3 | -0.598 | -0.59544 | -0.60326 | -0.60792 | -0.61401 | -0.61025 | -0.619(51) |
| 2 1 0 | 0.801 | 0.747268 | 0.771159 | 0.7896 | 0.78951 | 0.784401 | 0.844 |
| 1 2 0 | -0.417 | -0.36393 | -0.39149 | -0.40483 | -0.41234 | -0.41796 | -0.396 |
| 2 0 1 | -0.060 | -0.0484 | -0.03794 | -0.03008 | -0.03144 | -0.03382 | -0.080 |
| 0 2 1 | -2.628 | -2.58022 | -2.61402 | -2.63527 | -2.64557 | -2.64037 | -2.736(48) |
| 1 1 1 | -0.211 | -0.20894 | -0.21198 | -0.21289 | -0.2171 | -0.21319 | -0.245 |
| 1 0 2 | -0.271 | -0.3028 | -0.30916 | -0.31394 | -0.31337 | -0.31416 | -0.236 |
| 0 1 2 | -1.910 | -1.9019 | -1.91086 | -1.91805 | -1.91854 | -1.91952 | -1.859(12) |
| 4 0 0 | 348.09 | 339.7102 | 346.0883 | 350.3262 | 351.8754 | 351.8014 | 320.96 |
| 0 4 0 | 148.18 | 140.0799 | 148.9171 | 154.6646 | 156.0977 | 155.2735 | 147(53) |
| 0 0 4 | -0.42 | -0.27575 | -0.21586 | -0.16466 | -0.17237 | -0.16961 | -0.473(1100) |
| 3 1 0 | -0.01 | 0.00000 | -0.1668 | -0.27799 | -0.33359 | -0.47259 | -0.98 |
| 1 3 0 | 6.77 | 8.22861 | 8.395407 | 8.528843 | 8.528844 | 8.278649 | 6.00 |
| 2 2 0 | -3.22 | -3.11353 | -3.22473 | -3.30256 | -3.30256 | -3.34148 | -1.99 |
| 3 0 1 | -0.62 | -1.05953 | -0.9248 | -0.83053 | -0.84727 | -0.9751 | 0.25 |
| 0 3 1 | 5.91 | 6.744007 | 6.809863 | 6.866182 | 6.815165 | 6.946736 | 5.60 |
| 2 1 1 | -0.12 | -0.13454 | -0.10089 | -0.07734 | -0.09414 | -0.11264 | -0.08 |
| 1 2 1 | 1.62 | 1.799523 | 1.866407 | 1.919975 | 1.919812 | 1.941791 | 1.96 |
| 2 0 2 | -0.61 | -0.70506 | -0.68429 | -0.67595 | -0.68094 | -0.66923 | -0.50 |
| 0 2 2 | 3.06 | 3.117164 | 3.191791 | 3.25139 | 3.243819 | 3.215378 | 3.61 |
| 1 1 2 | 0.55 | 0.68593 | 0.743201 | 0.787793 | 0.793249 | 0.784869 | 0.59 |
| 1 0 3 | 0.84 | 1.647493 | 1.707556 | 1.747063 | 1.747366 | 1.736356 | 0.72 |
| 0 1 3 | 1.87 | 2.407367 | 2.456053 | 2.50224 | 2.499096 | 2.490849 | 2.56 |