JOURNAL OF CHEMICAL PHYSICS VOLUME 109, NUMBER 19 15 NOVEMBER 1998

Rovibrational effects, temperature dependence, and isotope effects on the nuclear shielding tensors of water: A new ^{17}O absolute shielding scale

Juha Vaara and Juhani Lounila
NMR Research Group, Department of Physical Sciences, University of Oulu, P.O. Box 333, FIN-90571 Oulu, Finland

Kenneth Ruud and Trygve Helgaker
Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway

(Received 12 June 1998; accepted 12 August 1998)

We calculate the rovibrational corrections, temperature dependence and isotope shifts of the isotropic and anisotropic nuclear shieldings of the water molecule. This is the first correlated study of rovibrational effects on the nuclear shieldings in the water molecule and the first study of these effects on the shielding anisotropies. The use of a large restricted active space self-consistent field wave function and a large basis set ensures that the results are of high accuracy. The rovibrational corrections are found to be substantial, 3.7% and 1.8% for the isotropic oxygen and hydrogen shieldings, respectively, in the $^{1}H_2{}^{17}O$ isotopomer at 300 K. For the shielding anisotropies and asymmetry parameters, the corresponding relative corrections are even larger. The changes in the shielding tensors due to molecular rotation and vibration are of the same order of magnitude as—and in some cases even exceed—the changes due to electron correlation. The accuracy of our calculated rovibrationally corrected oxygen shielding leads us to propose a new absolute shielding scale for the ^{17}O nucleus: 324.0 ± 1.5 ppm for the ^{17}O shielding of $^{1}H_2{}^{17}O$ in the gas phase (300 K). This shielding scale is supported by recent high-level CCSD(T) calculations on carbon monoxide. The absolute oxygen shielding constants of some oxygen-containing molecules are calculated using the new shielding scale and experimental data on oxygen chemical shifts, comparing the absolute shieldings to the results of recent high-level theoretical calculations. © *1998 American Institute of Physics.* [S0021-9606(98)30143-9]

I. INTRODUCTION

The determination of nuclear shielding constants in nuclear magnetic resonance (NMR) spectroscopy experiments requires the use of an accurate reference standard to which the measured chemical shifts can be related. In comparison with the results of modern *ab initio* electronic structure theory, the accuracy of the experimental shielding constant depends critically on the accuracy of this reference shielding. Much effort has therefore been invested in assigning absolute shielding scales for various nuclei.[1]

One way of directly obtaining the absolute shielding scale of a given nucleus is from the spin-rotation constants determined in microwave or molecular beam experiments. However, the relevant splittings in the microwave spectra are small and the uncertainty in the spin-rotation constants may therefore be large. To obtain the complete absolute shieldings, the paramagnetic shieldings extracted from the spin-rotation constants are combined with theoretically calculated diamagnetic shieldings, and high-level theoretical calculations are therefore mandatory. Since the dia- and paramagnetic contributions are of opposite sign, the shielding constant is smaller than its two contributions. Small errors in the dia- and paramagnetic terms may therefore give rise to large relative errors in the final shielding constants.

The recent developments in modern *ab initio* methods enable absolute shielding scales to be determined from theoretical calculations alone, with an accuracy that is often higher than that of experiment. In coupled-cluster singles-and-doubles with perturbative corrections for triples (CCSD(T)) investigations by Gauss, Sundholm, and Schäfer, spin–rotation constants and absolute shieldings were determined for a number of diatomic molecules.[2,3] Large basis sets combined with the CCSD(T) method ensured high-quality *ab initio* results, and, by taking rovibrational effects into account, both purely theoretical and revised experimental absolute shieldings could be given. Whereas for most of the nuclei studied, good agreement was observed for the experimental/theoretical and purely theoretical absolute shieldings, an exception was the ^{17}O shielding of carbon monoxide. The theoretical absolute shielding, -59.34 ppm for $^{12}C^{17}O$ at 300 K,[3] was barely within the large error limits of the experimental result, -44.80 ± 17.18 ppm.[4] It is our purpose to confirm and validate this theoretical reevaluation of the ^{17}O absolute shielding scale by performing independent, high-level calculations of the nuclear shieldings in the water molecule, taking proper account of rovibrational contributions to the shielding constants. In addition, we present accurate estimates of the isotope shifts and temperature dependence of the hydrogen and oxygen shieldings in water.

We perform rovibrational averaging of the full second-rank oxygen and hydrogen shielding tensors. While necessitating the use of the Eckart coordinate frame for representing the tensors, this procedure allows us to calculate the rovibrationally averaged principal values, and thus the anisotropy and asymmetry parameter, of the shielding tensors.

In Sec. II, we outline the computational methodology. Section III A describes the basis set and active space used in the calculation of the rovibrational corrections. In Sec. III B, we discuss the results obtained for the isotropic shieldings and, in Sec. III C, the rovibrational corrections to the anisotropic shieldings. Finally, we propose and discuss a new ^{17}O absolute shielding scale in Sec. IV.

II. METHODOLOGY

A. *Ab initio* calculations

The nuclear magnetic shielding tensor of a nucleus K, having a nuclear magnetic moment $\mathbf{m}_K$, may be expressed as the second derivative of the molecular energy with respect to an external magnetic field $\mathbf{B}$ and the nuclear magnetic moment

$$\boldsymbol{\sigma}_K = \mathbf{1} + \left. \frac{\partial^2 E(\mathbf{B},\mathbf{m}_K)}{\partial \mathbf{B} \partial \mathbf{m}_K} \right|_{\mathbf{B},\mathbf{m}_K=\mathbf{0}}. \tag{1}$$

In its most naive implementation, the *ab initio* calculation of nuclear shieldings is hampered by slow basis set convergence and the dependence of the shieldings on the choice of gauge origin. One of the main reasons for the increasing interest in *ab initio* calculations of nuclear shieldings has been the introduction of basis sets that depend explicitly on the external magnetic field—the London atomic orbitals, also known as Gauge-Including Atomic Orbitals (GIAOs).[5] These basis functions respond in a physically correct way to the external magnetic field, thereby giving improved basis-set convergence. Moreover, by multiplying each basis function with a phase factor that transforms the global gauge origin to a local gauge origin for each basis function, the London atomic orbitals remove the dependence of the calculated properties on the global gauge origin. Although London orbitals were used in early *ab initio* calculations,[6,7] it is only after their first implementation using modern analytical derivative techniques by Wolinski, Hinton and Pulay[8] that the London approach has become widely used. The London atomic orbital approach has been extended to the more important correlated wave functions[9–12] and recently to Density Functional Theory (DFT) methods.[13–16] In this work, we use the MCSCF London atomic orbital method described in Ref. 10, as implemented in the Dalton quantum chemistry program.[17]

B. Rovibrational corrections

The calculation of rovibrational corrections, temperature dependence, and isotope shifts follows the strategy of our papers on CSe_2[18] and OCS.[19] The nuclear shielding in water is expanded in a Taylor series to second order in the curvilinear internal displacement coordinates $\{R_i\} = \{\Delta r, \Delta r', \Delta\alpha\}$ around the equilibrium geometry

$$\begin{aligned}\langle\sigma\rangle = {} & \sigma_e + \sigma_r\langle\Delta r\rangle^T + \sigma_{r'}\langle\Delta r'\rangle^T + \sigma_\alpha\langle\Delta\alpha\rangle^T \\ & + \tfrac{1}{2}\sigma_{rr}\langle(\Delta r)^2\rangle^T + \tfrac{1}{2}\sigma_{r'r'}\langle(\Delta r')^2\rangle^T \\ & + \sigma_{rr'}\langle\Delta r\Delta r'\rangle^T + \tfrac{1}{2}\sigma_{\alpha\alpha}\langle(\Delta\alpha)^2\rangle^T \\ & + \sigma_{r\alpha}\langle\Delta r\Delta\alpha\rangle^T + \sigma_{r'\alpha}\langle\Delta r'\Delta\alpha\rangle^T.\end{aligned} \tag{2}$$

Here σ_{R_i} and $\sigma_{R_iR_j}$ are the first and second derivatives of the nuclear shieldings with respect to nuclear distortions along the internal coordinates, evaluated at the equilibrium geometry. We assume that the major part of the rovibrational corrections can be accounted for by the first- and second-order terms.[20] The $\langle R_i\rangle^T$ and $\langle R_iR_j\rangle^T$ are rovibrational averages of the displacement coordinates at a given temperature T, calculated using the approximation of Toyama, Oka, and Morino.[21,22]

In accordance with the Born–Oppenheimer approximation, the derivatives of the nuclear shielding constants are independent of the nuclear masses and temperature, whereas the average displacement coordinates are not. It is therefore the changes in the averaged displacement coordinates that determine the temperature dependence and isotope shift of the nuclear shieldings. The rovibrationally averaged displacement coordinates may be determined from the anharmonic vibrational potential energy function of the molecule, which can be expressed as a third-order Taylor series in the internal displacement coordinates as described previously.[18] The potential energy function used here can be represented as

$$\begin{aligned}V = {} & \tfrac{1}{2}f_{rr}[(\Delta r)^2 + (\Delta r')^2] + f_{rr'}\Delta r\Delta r' + \tfrac{1}{2}f_{\alpha\alpha}(\Delta\alpha)^2 \\ & + f_{r\alpha}(\Delta r + \Delta r')\Delta\alpha + \tfrac{1}{6}f_{rrr}[(\Delta r)^3 + (\Delta r')^3] \\ & + \tfrac{1}{2}f_{rrr'}[(\Delta r)^2\Delta r' + \Delta r(\Delta r')^2] + \tfrac{1}{2}f_{rr\alpha}[(\Delta r)^2 \\ & + (\Delta r')^2]\Delta\alpha + f_{rr'\alpha}\Delta r\Delta r'\Delta\alpha + \tfrac{1}{2}f_{r\alpha\alpha}(\Delta r + \Delta r') \\ & \times(\Delta\alpha)^2 + \tfrac{1}{6}f_{\alpha\alpha\alpha}(\Delta\alpha)^3,\end{aligned} \tag{3}$$

where $f_{R_iR_j}$ denote harmonic and $f_{R_iR_jR_k}$ cubic (anharmonic) force constants.

The derivatives of the nuclear shieldings were obtained by fitting the property surface corresponding to the thermal average expression Eq. (2) to the shieldings obtained from calculations at a total of 33 molecular geometries, suitably chosen in the neighborhood of the equilibrium geometry. The full set of cubic terms was included in the fit as well to improve the quality of the first- and second-order parameters used for averaging the properties. The force constants were similarly obtained by fitting the calculated total energies to Eq. (3), augmented by the three all-diagonal fourth-order terms. All calculations of the thermal average displacements were performed using the AVIBR program of Lounila, Wasser, and Diehl.[22] AVIBR was modified for the present study to take into account the centrifugal distortion contribution to $\langle R_i\rangle^T$ using the classical approximation discussed in Ref. 21.

When performing rovibrational averaging of anisotropic molecular properties such as individual elements of the shielding tensor, the problem of choosing a coordinate frame for representing the tensor emerges. A unique frame that

TABLE I. Basis set dependence at the SCF level of the nuclear shielding constants in the water molecule. Shieldings reported in ppm.

Basis	Basis functions	σ(O)	σ(H)
$cc\text{-}pVDZ$	24	347.5	31.35
$cc\text{-}pVTZ$	58	335.2	30.80
$cc\text{-}pVQZ$	115	331.1	30.58
$cc\text{-}pV5Z$	201	328.2	30.47
$cc\text{-}pV6Z$	322	327.5	30.47
ANO$[4s3p2d1f/3s2p1d]$	58	306.4	30.58
ANO$[5s4p3d2f/4s3p2d]$	92	327.8	30.59
ANO$[6s5p4d3f/5s4p3d]$	126	327.7	30.55
ANO decontracted	152	327.5	30.55

remains fixed at the molecule during its rovibrational motion is the Eckart frame,[23] in which the coupling between vibrational and rotational degrees of freedom is minimized (see for instance Refs. 24 and 25). The conditions introduced by Eckart define a system of molecule-fixed axes in terms of the instantaneous position vectors of the nuclei in the molecule, $\mathbf{r}_K$. The conditions can be derived by requiring that the angular momentum of the nuclei relative to the molecule-fixed axes vanishes when the nuclei are in their equilibrium positions—that is, when $\mathbf{r}_K=\mathbf{r}_K^e$. The resulting conditions are

$$\sum_K m_K \mathbf{r}_K^e \times \mathbf{r}_K = \mathbf{0}, \tag{4}$$

where m_K is the mass of nucleus K. The Eckart frame is placed at the instantaneous center of mass and aligned so that the conditions Eq. (4) are fulfilled (the $\mathbf{r}_K^e$ are constant vectors when referred to the Eckart frame).

The elements of the shielding tensor calculated at a non-equilibrium geometry must thus be transformed to the proper Eckart frame prior to fitting the property surfaces. To obtain the rovibrationally averaged principal values of the shielding tensors of the water molecule, the transformation is applied to the diagonal elements and to the only nonvanishing off-diagonal element of the symmetric component of the shielding tensor—that is, $\sigma_{xy}^{(s)}=\frac{1}{2}(\sigma_{xy}+\sigma_{yx})$, assuming that the molecule is located in the xy-plane. The Eckart frame is uniquely defined by the three sets of parameters $\mathbf{r}_K^e$, $\mathbf{r}_K$, and m_K. Unlike the derivatives of isotropic properties such as the shielding constant, the derivatives of the individual tensor elements therefore depend on the isotopomer in question. The use of the Eckart frame has been discussed by Fowler and Raynes in connection with rovibrational corrections to the dipole moment of water.[26]

III. RESULTS

A. Convergence of shieldings with respect to the basis set and the active space

We tested the convergence of the nuclear shieldings for the correlation-consistent basis sets of Dunning, Wilson, and van Mourik[27,28] and the Atomic Natural Orbitals (ANO) basis set of Widmark, Malmqvist and Roos.[29] The results and the ANO contraction patterns are found in Table I. To compare with the literature, in particular the accurate CCSD(T) calculations of Gauss and Stanton,[12] we have used the experimental geometry.

TABLE II. Correlation dependence of the nuclear shielding constants in the water molecule using the primitive ANO basis set. Shieldings reported in ppm. Comparison are made with literature data.

Wave function	Determinants	σ(O)	σ(H)
HF	1	327.5	30.55
${}^{1000}\mathrm{CAS}^{6331}$	128 283	341.2	30.59
${}^{1000}\mathrm{RAS}^{4220}_{2111}$	40 636	341.2	30.60
${}^{1000}\mathrm{RAS}^{4220}_{4221}$	117 948	338.4	30.78
${}^{1000}\mathrm{RAS}^{4220}_{6332}$	271 876	337.6	30.82
${}^{1000}\mathrm{RAS}^{4220}_{8553}$	594 428	338.0	30.73
${}^{1000}\mathrm{RAS}^{4220}_{9553}$	650 596	337.9	30.74
${}^{1000}\mathrm{RAS}^{4220}_{10;663}$	834 620	337.5	30.77
${}^{1000}\mathrm{RAS}^{4220}_{12;884}$	1 353 284	337.2	30.80
SCF/GIAO[a]		328.1	31.7
CC2/GIAO[b]		345.6	30.7
CCSD/GIAO[c]		336.9	30.9
CCSD(T)/GIAO[d]		337.9	30.9

[a] Reference 63.
[b] Reference 32.
[c] Reference 31.
[d] Reference 12.

The correlation-consistent basis sets converge systematically, but slowly. In contrast, the ANO sets are almost converged at the second contraction level $[5s4p3d2f/4s3p2d]$, with only minor differences relative to the primitive ANO set and the $cc\text{-}pV6Z$ basis. A similar behavior has been observed for other molecules.[30] Still, since the primitive ANO set contains only 152 basis functions for water, we have chosen to use this basis set in the remaining calculations. For the oxygen shielding we estimate the error due to basis-set incompleteness to be at most 0.3 ppm. Since the ANO and correlation-consistent basis sets converge from opposite sides, with identical results obtained for $cc\text{-}pV6Z$ and the primitive ANO basis, this is probably an overestimate. For the hydrogen shielding, convergence is less obvious, but we estimate the error to be less than 0.05 ppm.

Electron correlation effects were investigated using a number of different restricted active spaces. The results from these studies, as well as a description of the active spaces employed, are collected in Table II. For a description of the notation used for the RASSCF wave functions, we refer to Ref. 30. We note from Table II that the convergence is slow—even our largest active space gives no definite conclusion about the correlation limit of the shieldings. The ${}^{1000}\mathrm{RAS}^{4220}_{6332}$ wave function is seen to be a reasonable approximation to our largest RAS expansion. We estimate the total errors due to approximations in the basis set and the correlation treatment to about 1 ppm for the oxygen shielding and 0.1 ppm for the hydrogen shieldings.

In Table II, we have included some reference values obtained by Gauss, Stanton, and Christiansen using various coupled-cluster models.[12,31,32] The oxygen shielding differs slightly from the CCSD(T) results of Gauss and Stanton. However, comparing their SCF results with that obtained by us using the decontracted ANO basis set, this discrepancy

TABLE III. Calculated cubic anharmonic force field in the water molecule obtained using the decontracted ANO basis together with the $^{1000}\text{RAS}^{4220}_{6332}$ wave function. Experimental and earlier theoretical results are also shown.

Property	This work	Exp.[a]	Exp.[b]	QCISD(T)[c]	Unit
f_{rr}	8.322	8.454	8.452	8.45	aJ Å^{-2}
$f_{rr'}$	−0.108	−0.101	−0.102	−0.10	aJ Å^{-2}
$f_{\alpha\alpha}$	0.717	0.697	0.706	0.71	aJ
$f_{r\alpha}$	0.269	0.219	0.273	0.26	aJ Å^{-1}
f_{rrr}	−59.653	−59.366	−57.389	−59.02	aJ Å^{-3}
$f_{rrr'}$	0.003	0.253	−0.228	−0.06	aJ Å^{-3}
$f_{rr\alpha}$	−0.113	0.404	−0.381	−0.10	aJ Å^{-2}
$f_{rr'\alpha}$	−0.522	−0.402	−0.590	−0.49	aJ Å^{-2}
$f_{r\alpha\alpha}$	−0.298	−0.225	−0.327	−0.30	aJ Å^{-1}
$f_{\alpha\alpha\alpha}$	−0.741	−0.877	−0.728	−0.69	aJ

[a] Reference 34.

[b] Reference 35.

[c] Reference 36.

TABLE V. Calculated results for the isotropic shieldings for a rigid water molecule at the equilibrium geometry, including zero-point vibrational corrections, and at 300 K. All results reported in ppm and obtained using the decontracted ANO basis together with the $^{1000}\text{RAS}^{4220}_{6332}$ wave function.

Molecule	Temperature	σ(O)	$\sigma(\text{H}_1)$	$\sigma(\text{H}_2)$
H_2O	No rovibrational corr.	336.0	30.77	
$H_2{}^{16}O$	0 K	324.32	30.247	
$H_2{}^{17}O$	0 K	324.34	30.248	
$HD^{17}O$	0 K	325.94	30.288	30.349
$D_2{}^{17}O$	0 K	327.52	30.392	
$H_2{}^{16}O$	300 K	323.94	30.221	
$H_2{}^{17}O$	300 K	323.96	30.221	
$HD^{17}O$	300 K	325.55	30.264	30.320
$D_2{}^{17}O$	300 K	327.14	30.365	

appears to arise mainly because of basis set incompleteness in the study of Gauss and Stanton.

The molecular geometry was optimized with the $^{1000}\text{RAS}^{4220}_{6332}$ wave function and the decontracted ANO basis set using the second-order method described in Ref. 33. The optimized geometry, $r=96.08$ pm and $\angle(\text{HOH})=103.82°$, is very similar to the experimental geometry. Due to the geometry optimization, the shieldings change from 337.6 and 30.82 ppm to 336.0 and 30.77 ppm for ^{17}O and ^{1}H, respectively.

B. Rovibrational effects and isotope shifts of the isotropic shieldings

The cubic anharmonic force field obtained from the $^{1000}\text{RAS}^{4220}_{6332}$/primitive ANO calculations is shown in Table III together with experimental results and the results of a previous theoretical investigation. The harmonic part of our force field agrees rather well both with the experimental results[34,35] and the QCISD(T) calculation of Martin, François, and Gijbels.[36] The stretching force constant f_{rr} is slightly underestimated. Most of the cubic parameters from the present calculations fall between the two experimental sets of values and resemble closely the QCISD(T) force constants.

The first and second derivatives of the oxygen and hydrogen shielding constants are collected in Table IV, together with the SCF results of Fowler, Riley and Raynes.[37] Except for the second-derivatives involving the bending angle, the hydrogen shielding derivatives are unaffected by electron correlation. Most of the oxygen derivatives, in contrast, are reduced when electron correlation is introduced.

We have collected our results for the isotropic shieldings, with and without rovibrational corrections, in Table V. Whereas the temperature dependence is modest, the effects of zero-point vibrational corrections are significant for both the oxygen and hydrogen shielding constants. For oxygen in $H_2{}^{17}O$, the zero-point vibrational correction amounts to −11.62 ppm, which is −3.6% of the total, vibrationally corrected shielding constant—an effect that is slightly larger than that of electron correlation. It is noteworthy that the changes due to vibration and electron correlation partially cancel. Our number may be compared with the SCF results of Fowler and Raynes,[26] −13.1 ppm, and Fukui *et al.*,[38] −12.1 ppm. Electron correlation thus reduces the magnitude of the rovibrational correction, although a detailed comparison with the present RASSCF results is complicated by the fact that nonsaturated basis sets were used in these SCF calculations. The temperature dependence is modest from 0 K to 300 K: −0.38 ppm or −0.1% of the total shielding.

For the hydrogen shielding, the zero-point vibrational

TABLE IV. Calculated quadratic property surfaces for hydrogen and oxygen nuclear shielding constants in the water molecule obtained using the decontracted ANO basis together with the $^{1000}\text{RAS}^{4220}_{6332}$ wave function. For H, r denotes the length of the bond attached to the nucleus, while r' is used for the other bond length. Included are also the SCF results of Fowler, Riley and Raynes (Ref. 37).

	O		H		
Parameter	This work	Fowler *et al.*	This work	Fowler *et al.*	Unit
σ_r	−236.36	−270.94	−34.71	−35.33	ppm Å^{-1}
$\sigma_{r'}$			−4.87	−4.63	ppm Å^{-1}
σ_α	−9.40	−27.33	−3.93	−4.04	ppm rad^{-1}
σ_{rr}	−934.30	−1045.57	114.41	109.97	ppm Å^{-2}
$\sigma_{r'r'}$			−25.55	−24.52	ppm Å^{-2}
$\sigma_{rr'}$	41.15	22.60	20.40	20.39	ppm Å^{-2}
$\sigma_{\alpha\alpha}$	109.19	138.78	−1.43	−2.99	ppm rad^{-2}
$\sigma_{r\alpha}$	−8.14	−10.90	−2.63	−2.59	ppm Å^{-1} rad^{-1}
$\sigma_{r'\alpha}$			1.36	2.24	ppm Å^{-1} rad^{-1}

TABLE VI. Isotope shifts on the ^{17}O shielding constant upon hydrogen/deuterium substitution at 300 K. All results reported in ppm relative to $H_2{}^{17}O$.

Method	Ref.	$HD^{17}O$	$D_2{}^{17}O$
MCSCF	This work	1.60	3.18
SCF	26		3.68
Exp. (cyclohexane solution)	48	1.550(0.005)	3.090(0.005)
Exp. (gas phase)	47		4.04(0.35)
Exp. (liquid)	64		3.08(0.20)

TABLE VII. Isotope shifts on the ^1H shielding constant upon isotopic substitution at 300 K. All results reported in ppb relative to $H_2{}^{16}O$.

Method	Ref.	$HD^{16}O$	$H_2{}^{18}O$
MCSCF	This work	43	2
SCF	26	43	2
Exp. (liquid phase)	65		12(4)
Exp. (acetone solution)	66	30(3)	

correction of -0.525 ppm ($H_2{}^{16}O$) amounts to -1.7% of the total shielding constant. This change is twice as large as the correlation correction. As for the oxygen atom, the electron-correlation and rovibrational corrections work in opposite directions, and the temperature dependence is a modest -0.026 ppm (-0.1% from 0 K to 300 K). Introducing correlation thus makes the agreement with experiment worse than for the SCF shieldings. We emphasize that the partial or complete cancellation of the electron-correlation and rovibrational corrections is not a universal feature of corrections to SCF shieldings. In HF, for instance, they work in the same direction.[39]

Raynes proposed that the absolute hydrogen shielding in gaseous water should be 30.052(15) ppm.[40] Although in quite good agreement with this number, our result is not within the very narrow error limits stated. This value is derived from highly accurate measurements of the ratio between the proton magnetic moment and the Bohr magneton in liquid water. However, in the conversion from liquid water to water in the gas phase—given by Raynes as $\sigma(H_2O, \text{liq., } 35\,°C) - \sigma(H_2O, \text{gas}) = -4.262(5)$ ppm—several assumptions were made regarding susceptibility corrections and intermolecular interactions. The experimental error limit may therefore be too small.

A way of estimating the accuracy of our calculated hydrogen shielding constant would be to compare the hydrogen chemical shift with hydrogen or hydrogen fluoride, for which there exist accurate theoretical numbers.[3,30,39,41] Unfortunately, the measurements of Hindermann and Cornwell on gaseous hydrogen and hydrogen fluoride relative to gaseous methane contain rather large error limits.[42] Presently, the best way of checking the accuracy of the calculated rovibrationally corrected hydrogen shielding appears to be to perform similar shielding calculations on methane, using wave functions of similar quality to that employed in this work, and using for instance the potential surfaces developed by Oddershede, Raynes, and coworkers.[43–45] By comparing the theoretical hydrogen shift obtained in this way with the accurate value determined experimentally by Hindman,[46] an estimate of the accuracy of the calculated rovibrationally corrected hydrogen shieldings in water should be obtainable.

In Table VI, we have collected various experimental determinations of the isotope shifts on the ^{17}O shielding due to hydrogen/deuterium substitutions. The agreement with the measurements of Wasylishen and Friedrich obtained in cyclohexane is very good. In contrast, our results do not reflect the gas-phase isotope shift measured by Raynes. The difference between the gas- and solution-phase isotope shifts was previously ascribed to strong medium effects due to hydrogen bonding.[47] However, it is noteworthy that the two experimental measurements in solution—using cyclohexane and water as solvents, respectively—give almost identical results, even though, in the experiment by Wasylishen and Friedrich, great care was exercised to avoid water association.[48] Combining this observation with our calculated isotope shifts, we are inclined to state that the importance of molecular association on the ^{17}O isotope shifts in liquid water has been exaggerated, and that there is a need for a new determination of the isotope shift in the gas phase. We also note that the experimental value of Raynes in the gas phase[47] was determined from *separate* measurements on the $H_2{}^{17}O$ and $D_2{}^{17}O$ samples.

Turning our attention to the isotope shifts of the hydrogen shieldings, some of these are presented in Table VII together with available experimental data. Our calculations on the effects of the $^{16}O/^{18}O$ and H/D substitutions agree completely with the previous SCF results of Fowler and Raynes[26] as could be anticipated since the proton shielding surface is not significantly affected by electron correlation; see Table IV. The agreement with the old liquid-state experiments is poor. It appears probable that hydrogen bonding has a relatively larger effect on the ^1H isotope effects than on those of ^{17}O. We suggest that the experiment be repeated using modern equipment both in the liquid and low-pressure gas phases. Indeed, a recent study of the $^{18}O/^{16}O$ induced proton shifts in H_2O, gave a shift of about 1.1 ± 0.1 ppb,[49] in good agreement with our estimate.

Generally, the magnitude of the isotope effects on any molecular property depends on the relative mass change of the substituted nucleus.[50] Thus, the dynamical factors in Eq. (2) are changed much less by $^{16/18}O$ substitution than by H/D substitution. Successive H/D substitutions from $H_2{}^{17}O$ to $HD^{17}O$ to $D_2{}^{17}O$ produce very slightly decreasing steps in the one-bond secondary isotope shift of the oxygen shielding, reflecting the decreasing fractional change in the total mass of the molecule.

C. Rovibrational effects and isotope shifts of the anisotropic shieldings

The quadratic property surfaces for the individual elements of the oxygen and hydrogen shielding tensors are given in Tables VIII and IX, respectively. The small differences between the listed parameters for different isotopomers are significant, reflecting the different dependencies of the

TABLE VIII. Calculated quadratic property surfaces for the individual elements of the oxygen nuclear shielding tensor in the water molecule obtained using the decontracted ANO basis together with the $^{1000}\mathrm{RAS}^{4220}_{6332}$ wave function. The units for shielding, length, and angle are ppm, Å, and rad, respectively.[a]

Molecule	a	a_r	$a_{r'}$	a_α	a_{rr}	$a_{r'r'}$	$a_{rr'}$	$a_{\alpha\alpha}$	$a_{r\alpha}$	$a_{r'\alpha}$
$H_2{}^{16}O$	$\sigma_{xx}{}^{b}$	−237.10		0.73	−866.29		−396.39	−38.22	80.54	
$H_2{}^{17}O$		−237.10		0.73	−867.82		−394.87	−38.22	80.54	
$HD^{17}O$		−237.04	−236.89	0.68	−856.93	−852.90	−408.45	−40.99	151.78	10.09
$D_2{}^{17}O$		−237.10		0.73	−845.13		−417.53	−38.19	80.49	
$H_2{}^{16}O$	$\sigma_{yy}{}^{b}$	−237.39		37.73	−1052.97		274.34	100.65	18.97	
$H_2{}^{17}O$		−237.39		37.73	−1051.45		272.82	100.65	18.96	
$HD^{17}O$		−237.42	−237.36	37.74	−1059.72	−1055.84	279.70	103.22	−52.51	93.75
$D_2{}^{17}O$		−237.39		37.73	−1074.13		295.49	100.62	19.02	
all $C_{2v}{}^{c}$	$\sigma_{zz}{}^{b}$	−234.60		−66.66	−883.61		245.50	265.15	−123.92	
$HD^{17}O$		−234.72	−234.66	−66.68	−895.89	−858.32	241.43	266.56	−124.23	−117.91
$HD^{17}O$	$\sigma^{(s)}_{xy}$	−230.15	230.05	6.53	−972.44	968.86	1.71	−10.60	72.55	−73.47

[a] The molecule is placed in the xy-plane with the symmetry axis of the C_{2v} isotopomers in the y-direction (the molecular electric dipole moment is in the $-y$ direction).

[b] For the diagonal elements in the C_{2v} symmetric isotopomers, $a_{r'}=a_r$, $a_{r'r'}=a_{rr}$, and $a_{r'\alpha}=a_{r\alpha}$.

[c] The derivatives of the σ_{zz} components of the tensors are common to all the C_{2v} isotopomers.

tensor elements on the internal coordinates. The variation is particularly clear in the nonsymmetric $HD^{17}O$ isotopomer.

The rovibrationally averaged tensor elements are listed in Table X. Our data for the anisotropies and asymmetry parameters, calculated by diagonalizing the rovibrationally averaged tensors, are collected in Table XI. The changes in the point group symmetry of the water molecule from $H_2{}^{17}O$, to $HD^{17}O$ and then to $D_2{}^{17}O$ cause changes in the principal values of the tensors. In particular, the site symmetry of the oxygen nucleus in $HD^{17}O$ is C_s and consequently the $\sigma^{(s)}_{xy}$ component does not vanish for this isotopomer, unlike in the C_{2v} site-symmetric isotopomers, where the average oxygen shielding tensor is diagonal in the principal axis frame of the moment of inertia tensor.[51]

For oxygen, the zero-point vibrational correction to the shielding anisotropy is about −5% (for the $H_2{}^{17}O$ isotopomer), and thus slightly larger than the change in the isotropic shielding. In absolute terms, however, the change is rather modest, −2.4 ppm. The temperature dependence is very small, with the change in the shielding anisotropy being only −0.04 ppm (−0.09%) from 0 K to 300 K. Whereas the oxygen shielding anisotropy is unaffected by oxygen substitution, it increases substantially when the hydrogens are replaced by deuterium. It is interesting to note that, whereas

TABLE IX. Calculated quadratic property surfaces for the individual elements of the hydrogen nuclear shielding tensor in the water molecule obtained using the decontracted ANO basis together with the $^{1000}\mathrm{RAS}^{4220}_{6332}$ wave function. The units are as in Table VIII.[a]

Molecule	a	a_r	$a_{r'}$	a_α	a_{rr}	$a_{r'r'}$	$a_{rr'}$	$a_{\alpha\alpha}$	$a_{r\alpha}$	$a_{r'\alpha}$
$H_2{}^{16}O$	$\sigma_{xx}(H)$	−48.74	−3.09	4.42	136.53	−44.87	18.07	0.72	−22.66	−7.36
$H_2{}^{17}O$		−48.77	−3.06	4.42	136.70	−44.95	18.03	0.72	−22.64	−7.37
$HD^{17}O$	$\sigma_{xx}(H_1)$	−48.61	−3.21	7.09	136.41	−43.79	17.47	−2.23	−28.92	−10.17
$HD^{17}O$	$\sigma_{xx}(H_2)$	−48.62	−3.21	1.76	136.22	−44.11	17.73	2.71	−15.54	−5.58
$D_2{}^{17}O$	$\sigma_{xx}(H)$	−48.34	−3.49	4.42	134.09	−43.76	18.73	0.71	−22.87	−7.15
$H_2{}^{16}O$	$\sigma_{yy}(H)$	−31.13	−10.15	−13.73	106.58	−34.63	34.44	1.42	18.40	8.34
$H_2{}^{17}O$		−31.10	−10.18	−13.73	106.40	−34.55	34.48	1.42	18.39	8.35
$HD^{17}O$	$\sigma_{yy}(H_1)$	−31.25	−10.06	−16.40	107.69	−35.50	34.17	4.30	24.67	11.60
$HD^{17}O$	$\sigma_{yy}(H_2)$	−31.26	−10.04	−11.07	107.78	−33.68	33.24	−0.81	11.80	6.51
$D_2{}^{17}O$	$\sigma_{yy}(H)$	−31.53	−9.76	−13.73	109.01	−35.74	33.78	1.43	18.62	8.14
all[b]	$\sigma_{zz}(H)$	−24.28	−1.38	−2.47	100.12	2.87	8.70	−6.42	−3.65	3.11
$H_2{}^{16}O$	$\sigma^{(s)}_{xy}(H_1)^{c}$	22.63	7.09	3.77	−24.02	37.11	−19.99	5.25	−9.95	3.73
$H_2{}^{17}O$		22.62	7.10	3.77	−23.95	37.11	−20.03	5.25	−9.98	3.76
$HD^{17}O$		22.69	7.03	5.04	−25.57	35.21	−18.09	11.68	−12.13	3.86
$HD^{17}O$	$\sigma^{(s)}_{xy}(H_2)$	−22.70	−7.04	−2.50	27.34	−36.72	17.95	−0.75	7.48	−2.34
$D_2{}^{17}O$	$\sigma^{(s)}_{xy}(H_1)^{c}$	22.82	6.90	3.77	−25.00	36.98	−19.44	5.24	−9.53	3.34

[a] The placement of the molecule is as in Table VIII. The hydrogen atom H_1 (H_2) is placed toward positive (negative) x-axis.

[b] The derivatives of the σ_{zz} components of the tensors are common to all the isotopomers.

[c] For the H_2 shielding tensors in the symmetric isotopomers, all the derivatives of the $\sigma^{(s)}_{xy}$ elements can be obtained by multiplying the corresponding H_1 derivatives by the factor of −1.

TABLE X. Rovibrationally averaged nonvanishing elements of the oxygen and hydrogen nuclear shielding tensors in the water molecule obtained using the decontracted ANO basis together with the $^{1000}\mathrm{RAS}^{4220}_{6332}$ wave function. All values in ppm.

	$H_2{}^{16}O$		$H_2{}^{17}O$		$HD^{17}O$		$D_2{}^{17}O$	
Parameter	0 K	300 K	0 K	300 K	0 K	300 K	0 K	300 K
$\langle\sigma_{xx}(O)\rangle$	355.64	355.23	355.66	355.25	357.47	357.06	359.32	358.92
$\langle\sigma_{yy}(O)\rangle$	313.32	312.85	313.35	312.88	315.04	314.57	316.64	316.18
$\langle\sigma_{zz}(O)\rangle$	304.01	303.74	304.02	303.75	305.34	305.07	306.59	306.32
$\langle\sigma^{(s)}_{xy}(O)\rangle$	0	0	0	0	-1.89	-1.87	0	0
$\langle\sigma_{xx}(H_1)\rangle$	37.959	37.906	37.960	37.908	37.974	37.920	38.153	38.101
$\langle\sigma_{yy}(H_1)\rangle$	29.774	29.764	29.774	29.765	29.870	29.867	29.932	29.921
$\langle\sigma_{zz}(H_1)\rangle$	23.008	22.991	23.009	22.992	23.022	23.006	23.091	23.073
$\langle\sigma^{(s)}_{xy}(H_1)\rangle$	-8.161	-8.143	-8.162	-8.144	-8.169	-8.154	-8.336	-8.317
$\langle\sigma_{xx}(H_2)\rangle$[a]					38.135	38.084		
$\langle\sigma_{yy}(H_2)\rangle$[a]					29.840	29.824		
$\langle\sigma_{zz}(H_2)\rangle$[a]					23.075	23.056		
$\langle\sigma^{(s)}_{xy}(H_2)\rangle$	8.161	8.143	8.162	8.144	8.318	8.296	8.336	8.317

[a] The diagonal elements of $\boldsymbol{\sigma}(H_2)$ in the C_{2v} symmetric isotopomers equal those of H_1.

the deuterium substitutions give almost perfectly additive contributions to the isotropic shielding, in agreement with what has been found for a number of molecules,[52,53,48] no such additivity is observed for the oxygen shielding anisotropy, the shifts at 0 K being 0.43 and 0.31 ppm for the first and second deuterium substitutions, respectively. This is a manifestation of the change in the ^{17}O site symmetry discussed above.

The zero-point vibrational corrections to the hydrogen shielding anisotropy are about as large as the change in the oxygen shielding anisotropy, about -5% ($H_2{}^{16}O$ and $H_2{}^{17}O$), which corresponds to an absolute change of slightly more than -1 ppm. The temperature dependence is weak also for the hydrogen shielding anisotropy. We note that only isotopic substitutions on the nucleus being studied induce substantial changes in the hydrogen shielding anisotropy (a primary isotope effect). On the other hand, the hydrogen anisotropy is almost unaffected by secondary isotope effects arising from isotopic substitutions at both the other hydrogen and the oxygen atom.

We are unaware of any experimental data for the hydrogen shielding anisotropy in the gas phase. However, there has been a number of studies of the hydrogen shielding anisotropy in crystalline ice, with different experiments predicting a value of about 28.5 ± 1 ppm (H_2O) at 195 K,[54] 34.2 ± 1 ppm (H_2O) at 173 K,[55] and 34 ± 4 ppm (D_2O) at 183 K,[56] respectively. Our theoretical gas-phase anisotropy is approximately one half of these results. The almost twofold increase of $\Delta\sigma(H)$ for a nucleus that is involved in a hydrogen bond appears to be a general feature.[57,58] As shown in theoretical studies, it is important to include the closest neighboring molecules in the water crystal to get reasonable hydrogen shielding anisotropies for ice.[59,60] Such supermolecule calculations give support to the larger of the two experimental anisotropies. The small vibrational dependence and isotope shift observed in the hydrogen shielding anisotropy indicate that isotope effects are not likely to change the conclusions of the calculations of Pulay, Hinton, and Wolinski.[59]

TABLE XI. Calculated results for the shielding anisotropies[a] (in ppm) and asymmetry parameters[b] for a rigid water molecule at the equilibrium geometry, including zero-point vibrational correction, and at 300 K. All results obtained using the decontracted ANO basis together with the $^{1000}\mathrm{RAS}^{4220}_{6332}$ wave function.

Molecule	Temperature	$\Delta\sigma(O)$	$\eta(O)$	$\Delta\sigma(H_1)$	$\eta(H_1)$	$\Delta\sigma(H_2)$	$\eta(H_2)$
H_2O	No rovibrational corr.	49.33	0.0323	20.159	0.03369		
$H_2{}^{16}O$	0 K	46.98	0.0262	19.124	0.04019		
$H_2{}^{17}O$	0 K	46.97	0.0262	19.126	0.04018		
$HD^{17}O$	0 K	47.40	0.0269	19.127	0.04140	19.398	0.037 39
$D_2{}^{17}O$	0 K	47.71	0.0280	19.418	0.03823		
$H_2{}^{16}O$	300 K	46.94	0.0256	19.078	0.04053		
$H_2{}^{17}O$	300 K	46.94	0.0257	19.080	0.04052		
$HD^{17}O$	300 K	47.36	0.0264	19.084	0.04173	19.350	0.037 74
$D_2{}^{17}O$	300 K	47.67	0.0275	19.372	0.03857		

[a] The shielding anisotropies in the principal axis frame of the shielding tensors, defined as $\Delta\sigma=\sigma_{33}-\frac{1}{2}(\sigma_{11}+\sigma_{22})$, with the principal values ordered according to $\sigma_{11}\leqslant\sigma_{22}\leqslant\sigma_{33}$.

[b] The asymmetry parameters in the principal axis frame defined as $\eta=(\sigma_{22}-\sigma_{11})/\sigma_{33}$.

TABLE XII. Oxygen-17 chemical shifts and nuclear magnetic shielding constants (in ppm).

Molecule	Chemical shift	Nuclear shielding constant		Wasylishen *et al.* (Ref. 61)
	δ	σ_{absolute}[a]	$\sigma_{\text{theoretical}}$	σ_{absolute}
H_2O (gas)	-36.1	324 ± 1.5	337.9[b]	344.0
H_2O (liquid)	0	287.9	300.3[c]	307.9
CO_2 (gas)	64.5	223.4	234.6[d]/237.1[e]	243.4
N_2O (gas)	107.4	180.5	199.7[f]	200.5
OCS (gas)	200.0	87.9	105.4/98.8[g]	107.9
CO (gas)	350.2	-62.3	-59.2[h]	-42.3
OF_2	781	-493.1	-479.8[e]	-473.1

[a] Absolute shielding determined from the experimental shifts relative to liquid water, assuming the absolute shielding of gaseous water to be 324 ± 1.5 ppm.

[b] CCSD(T) result from Ref. 12.

[c] Based on the gas-to-liquid shift determined in a combined molecular dynamics/DFT approach (Ref. 67). However, this shift includes rovibrational corrections for the liquid state (implicit), but not for the gas−phase molecule.

[d] Full-valence CAS/IGLO calculations from Ref. 68.

[e] CCSD calculations from Ref. 69.

[f] CCSD(T) result from Ref. 12.

[g] RASSCF calculations without/with rovibrational corrections from Ref. 19.

[h] CCSD(T) calculations including rovibrational corrections from Ref. 3.

IV. A NEW ABSOLUTE SHIELDING SCALE FOR ^{17}O

Our calculated oxygen shielding constant in $H_2{}^{17}O$ of 324 ± 1.5 ppm, differs substantially from the experimental absolute shielding constant 344.0 ± 17.2 ppm determined on the basis of the proposal of Wasylishen *et al.*[61] However, the oxygen chemical shift of water in the gas phase relative to $C^{17}O$ is experimentally 386.3 ppm, in fairly good agreement with the theoretical oxygen shift obtained in this work relative to the carbon monoxide shielding of Sundholm and Gauss,[3] 383.3 ppm. We take this as an indication that, by taking proper account of rovibrational corrections and using saturated basis sets and highly correlated wave functions, agreement with experiment can be obtained for the chemical shift, and that the experimental absolute shielding constant can now be determined on the basis of the results presented here and in Ref. 3.

The results of this investigation and that of Sundholm and Gauss overlap if both estimated error limits are taken into account. In proposing a new shielding scale we are faced with making a choice between the results of the present investigation—obtained using large RASSCF wave functions—and the CCSD(T) results of Ref. 12. In both cases, the oxygen shielding is quite sensitive to the geometry. We note that the introduction of a perturbative triples correction leads to quite large changes in the shielding of carbon monoxide relative to the CCSD result (-3 ppm).[3] Furthermore, the basis set used in Ref. 3 derives back to a paper by Gauss, where the basis set is compared only to smaller basis sets, displaying a rather large basis-set dependence, the difference between this set and the second largest being about 4 ppm.[62] This lack of basis saturation was noted also in Sec. III A, in our discussion of the SCF calculations. Since the description of electron correlation in water is much simpler than that in carbon monoxide and since all our larger RASSCF wave functions give a narrow range for the oxygen shielding of water—smaller than the triples corrections observed in the coupled-cluster calculations on CO—we choose to use our oxygen shielding constant to establish the new absolute shielding scale, noting that the basis set used by us is much larger than the basis set used by Sundholm and Gauss. We therefore propose 324.0 ± 1.5 ppm in gaseous $H_2{}^{17}O$ water at 300 K as a new reference for the absolute shielding constant of the ^{17}O nucleus. Alternatively, using the experimental chemical shift of water relative to carbon monoxide, the shielding scale could be based on an absolute shielding of -62.3 ± 1.5 ppm in $C^{17}O$.

It is of some interest to investigate how this new shielding scale affects the agreement between theory and experiment for some molecules where both experimental and theoretical results are available. Such a comparison is presented in Table XII. More specifically, we have taken as a starting point Table 2 of the paper by Wasylishen *et al.*[61] and estimated, based on experimental chemical shifts, new absolute shieldings for various oxygen-containing molecules. In Table XII, we have included also recent high-level *ab initio* results. However, it should be noted that only for a few molecules do these calculated numbers include rovibrational corrections. In these cases, our new shielding scale improves the agreement of the theoretical results with experiment as compared to the old scale. Furthermore, the sign and magnitude of the deviations of the other theoretical numbers—not corrected for rovibrational effects—from the experimental values is consistent with the observation that, apart from OF_2, rovibrational corrections lead to a deshielding of roughly 10 ppm rather than shielding of the oxygen nucleus, as found here for water and elsewhere for CO[3] and OCS.[19] Subtracting this estimate from the rovibrationally uncorrected theoretical results leads to a clear preference of the present shielding scale over the old one. This general conclusion was already anticipated by Wasylishen *et al.*,[61] and our work together with Ref. 3 validate their prediction.

V. CONCLUSION

We have presented rovibrational corrections and the related temperature and isotope dependencies of the nuclear magnetic shielding tensors (shielding constants and anisotropies) of the water molecule. The corrections have been based on RASSCF calculations where a large active space and a large basis set have been employed. For the water molecule, the rovibrational effects are as important as those of electron correlation. On the basis of these calculations, we propose a new absolute scale for the ^{17}O shielding in the $H_2{}^{17}O$ isotopomer in the gas phase at 300 K, 324.0 ± 1.5 ppm. This is in close agreement with the value obtained by combining the experimental gas-phase chemical shift between water and the CO molecule with earlier CCSD(T) calculations for the absolute shielding of CO. Thus, we are able to verify the latter calculation and suggest that the earlier experimentally based absolute ^{17}O shielding scale be abandoned.

The new scale leads to a significantly better agreement of modern theoretical calculations with experiment, in particular when considering that the—in most cases—omitted rovibrational corrections to the calculated results appear to typically lead to a deshielding of roughly 10 ppm. The case of OF_2 forms an interesting exception and should be examined further.

The accuracy of the presently calculated secondary isotope effects on ^1H and ^{17}O shielding constants will allow a meaningful comparison with modern gas-phase experiments, once the latter become available. The gas-phase isotope effects on the corresponding shielding anisotropies and asymmetry parameters found are likely to be too small for experimental detection.

Note added in proof. We have been informed by Prof. J. Gauss that he has reinvestigated the oxygen shielding in $C^{17}O$ using larger basis sets, obtaining an absolute nuclear shielding of -60.6 ppm. This result is in much better agreement with our result. Indeed, using the nuclear shielding in water calculated at the experimental rather than optimized geometry (being 1.7 ppm larger), we derive from our data an oxygen shielding in $C^{17}O$ of -60.7 ppm, which gives a perfect agreement between the CCSD(T) study on $C^{17}O$ and the RASSCF study on water presented here.

ACKNOWLEDGMENT

This work has received support from The Research Council of Norway (Program for Supercomputing) through a grant of computer time.

[1] C. J. Jameson, in *Encyclopedia of NMR Spectroscopy*, edited by D. M. Grant and R. K. Harris, (Wiley, New York, 1996), p. 1273.

[2] J. Gauss and D. Sundholm, Mol. Phys. **91**, 449 (1997).

[3] D. Sundholm, J. Gauss, and A. Schäfer, J. Chem. Phys. **105**, 11 051 (1996).

[4] M. A. Frerking and W. D. Langer, J. Chem. Phys. **74**, 6990 (1981).

[5] F. London, J. Phys. Radium **8**, 397 (1937).

[6] H. F. Hameka, Mol. Phys. **1**, 203 (1958).

[7] R. Ditchfield, J. Chem. Phys. **56**, 5688 (1972).

[8] K. Wolinski, J. F. Hinton, and P. Pulay, J. Am. Chem. Soc. **112**, 8251 (1990).

[9] J. Gauss, Chem. Phys. Lett. **191**, 614 (1992).

[10] K. Ruud, T. Helgaker, R. Kobayashi, P. Jørgensen, K. L. Bak, and H. J. Aa. Jensen, J. Chem. Phys. **100**, 8178 (1994).

[11] J. Gauss and J. F. Stanton, J. Chem. Phys. **102**, 251 (1995).

[12] J. Gauss and J. F. Stanton, J. Chem. Phys. **104**, 2574 (1996).

[13] A. M. Lee, N. C. Handy, and S. M. Colwell, J. Chem. Phys. **103**, 10095 (1995).

[14] G. Schreckenbach and T. Ziegler, J. Phys. Chem. **99**, 606 (1995).

[15] G. Rauhut, S. Puyear, K. Wolinski, and P. Pulay, J. Phys. Chem. **100**, 6310 (1996).

[16] J. R. Cheeseman, G. W. Trucks, T. A. Keith, and M. J. Frisch, J. Chem. Phys. **104**, 5497 (1996).

[17] T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, J. Olsen, K. Ruud, H. Ågren, T. Andersen, K. L. Bak, V. Bakken, O. Christiansen, P. Dahle, E. K. Dalskov, T. Enevoldsen, H. Heiberg, H. Hettema, D. Jonsson, S. Kirpekar, R. Kobayashi, H. Koch, K. V. Mikkelsen, P. Norman, M. J. Packer, T. Saue, P. R. Taylor, and O. Vahtras, *Dalton, an ab initio electronic structure program, Release 1.0 (1997). See http://www.kjemi.uio.no/software/dalton/dalton.html*.

[18] J. Lounila, J. Vaara, Y. Hiltunen, A. Pulkkinen, J. Jokisaari, M. Ala-Korpela, and K. Ruud, J. Chem. Phys. **107**, 1350 (1997).

[19] K. Jackowski, M. Jaszuński, W. Makulski, and J. Vaara, J. Magn. Reson. (in press).

[20] C. J. Jameson, in *Theoretical Models of Chemical Bonding. Part 3. Molecular Spectroscopy, Electronic Structure, and Intramolecular Interactions*, edited by Z. B. Maksic (Springer, Berlin, 1991), p. 457.

[21] M. Toyama, T. Oka, and Y. Morino, J. Mol. Spectrosc. **13**, 193 (1964).

[22] J. Lounila, R. Wasser, and P. Diehl, Mol. Phys. **62**, 19 (1987).

[23] C. Eckart, Phys. Rev. **47**, 552 (1935).

[24] P. R. Bunker, *Molecular Symmetry and Spectroscopy* (Academic, New York, 1979).

[25] J. D. Louck and H. W. Galbraith, Rev. Mod. Phys. **48**, 69 (1976).

[26] P. W. Fowler and W. T. Raynes, Mol. Phys. **43**, 65 (1981).

[27] T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).

[28] A. K. Wilson, T. van Mourik, and T. H. Dunning Jr., J. Mol. Struct.: THEOCHEM **388**, 339 (1996).

[29] P.-O. Widmark, P.-Å. Malmqvist, and B. O. Roos, Theor. Chim. Acta **77**, 291 (1990).

[30] P.-O. Åstrand, K. Ruud, K. V. Mikkelsen, and T. Helgaker, J. Chem. Phys. (submitted).

[31] J. Gauss and J. F. Stanton, J. Chem. Phys. **103**, 3561 (1995).

[32] O. Christiansen, J. Gauss, and J. F. Stanton, Chem. Phys. Lett. **266**, 53 (1997).

[33] T. U. Helgaker, J. Almlöf, H. J. Aa. Jensen, and P. Jørgensen, J. Chem. Phys. **84**, 6266 (1986).

[34] A. R. Hoy, I. M. Mills, and G. Strey, Mol. Phys. **24**, 1265 (1972).

[35] P. Jensen, S. A. Tashkun, and Vl. G. Tyuterev, J. Mol. Spectrosc. **168**, 271 (1994).

[36] J. M. L. Martin, J. P. François, and R. Gijbels, J. Chem. Phys. **96**, 7633 (1992).

[37] P. W. Fowler, G. Riley, and W. T. Raynes, Mol. Phys. **42**, 1463 (1981).

[38] H. Fukui, T. Baba, J. Narumi, H. Inomata, K. Miura, and H. Matsuda, J. Chem. Phys. **105**, 4692 (1996).

[39] P.-O. Åstrand and K. V. Mikkelsen, J. Chem. Phys. **104**, 648 (1996).

[40] W. T. Raynes, Spec. Per. Reps. Nucl. Magn. Reson. **7**, 1 (1978).

[41] D. Sundholm, J. Gauss, and R. Ahlrichs, Chem. Phys. Lett. **243**, 264 (1995).

[42] D. K. Hindermann and C. D. Cornwell, J. Chem. Phys. **48**, 4148 (1968).

[43] J. Geertsen, J. Oddershede, W. T. Raynes, and T. L. Marvin, Mol. Phys. **82**, 29 (1994).

[44] W. T. Raynes, J. Geertsen, and J. Oddershede, Int. J. Quantum Chem. **52**, 153 (1994).

[45] R. D. Wigglesworth, W. T. Raynes, S. P. A. Sauer, and J. Oddershede, Mol. Phys. **92**, 77 (1997).

[46] J. C. Hindman, J. Chem. Phys. **44**, 4582 (1966).

[47] W. T. Raynes, Mol. Phys. **49**, 443 (1983).

[48] R. E. Wasylishen and J. O. Friedrich, Can. J. Chem. **65**, 2238 (1987).

[49] N. D. Sergeyeva, J. P. Jacobsen, and N. M. Sergeyev, J. Chem. Soc. Chem. Commun. **1998**, 1355.

[50] C. J. Jameson and H.-J. Osten, J. Chem. Phys. **81**, 4293 (1984).

[51] A. D. Buckingham and S. M. Malm, Mol. Phys. **22**, 1127 (1971).

[52] W. T. Raynes and M. Nightingale, Int. J. Quantum Chem. **60**, 529 (1996).

[53] N. M. Sergeyev, N. D. Sergeyeva, and W. T. Raynes, J. Chem. Soc. Chem. Commun. , 485 (1994).

[54] W. K. Rhim, D. P. Burum, and D. D. Elleman, J. Chem. Phys. **71**, 3139 (1979).

[55] L. M. Ryan, R. C. Wilson, and B. C. Gerstein, Chem. Phys. Lett. **52**, 341 (1977).

[56] A. Pines, D. J. Ruben, S. Vega, and M. Mehring, Phys. Rev. Lett. **36**, 110 (1976).

[57] J. Vaara, J. Kaski, J. Jokisaari, and P. Diehl, J. Phys. Chem. A **101**, 5069 (1997), *ibid.* **101**, 9185 (1997).

[58] J. Vaara, J. Lounila, and J. Jokisaari, Chem. Phys. Lett. (submitted).

[59] P. Pulay, J. F. Hinton, and K. Wolinski, in *Nuclear Magnetic Shieldings and Molecular Structure*, edited by J. A. Tossell, NATO ASI series, (Plenum, New York, 1993).

[60] K. V. Mikkelsen, K. Ruud, and T. Helgaker, Chem. Phys. Lett. **253**, 443 (1996).

[61] R. E. Wasylishen, S. Mooibroek, and J. B. Macdonald, J. Chem. Phys. **81**, 1057 (1984).

[62] J. Gauss, J. Chem. Phys. **99**, 3629 (1993).

[63] J. Gauss, Chem. Phys. Lett. **229**, 198 (1994).

[64] O. Lutz and H. Oehler, Z. Naturforsch. A **32**, 131 (1977).

[65] B. Sredni and S. Pinchas, J. Magn. Reson. **7**, 289 (1972).

[66] J. R. Holmes, D. Kivelson, and W. C. Drinkard, J. Chem. Phys. **37**, 150 (1962).

[67] V. G. Malkin, O. L. Malkina, G. Steinebrunner, and H. Huber, Chem.-Eur. J. **2**, 452 (1996).

[68] Ch. van Wüllen, Ph.D. thesis, Ruhr-Universität Bochum (1992).

[69] K. Jackowski, M. Jaszuński, and W. Makulski, J. Magn. Reson. **127**, 139 (1997).