



# Vibrationally averaged magnetizabilities and rotational $g$ tensors of the water molecule

Kenneth Ruud <sup>a,\*</sup>, Juha Vaara <sup>b</sup>, Juhani Lounila <sup>b</sup>, Trygve Helgaker <sup>a</sup>

<sup>a</sup> Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo, Norway

<sup>b</sup> NMR Research Group, Department of Physical Sciences, University of Oulu, P.O. Box 333, FIN-90571 Oulu, Finland

Received 13 August 1998; in final form 12 October 1998

---

## Abstract

Using large basis sets, London atomic orbitals and large multiconfigurational self-consistent field wavefunctions, we have calculated the molecular magnetizability and rotational  $g$  tensors of the water molecule, including zero-point vibrational corrections. Whereas the vibrational corrections are found to be negligible for the magnetizability, the inclusion of vibrational effects (being of the order of 2%) makes our calculated rotational  $g$  tensor agree well with experimental observations for D<sub>2</sub>O. For H<sub>2</sub>O we show that earlier agreement between theory and experiment is fortuitous and arises from the neglect of zero-point vibrational contributions in both approaches. We suggest that the rotational  $g$  tensor of H<sub>2</sub>O and HDO be remeasured. © 1998 Elsevier Science B.V. All rights reserved.

---

## 1. Introduction

Modern Zeeman microwave [1] and beam-maser [2] spectroscopic techniques provide data that may serve as a severe test of the quality of ab initio calculated magnetizabilities and rotational  $g$  factors. The error limits of the experimental data are in general much smaller than the errors introduced in an ab initio calculation due to the approximate 1- and  $N$ -electron treatments (basis set and electron correlation). The high experimental accuracy also

makes an account of rovibrational effects necessary to allow for a meaningful comparison with experiment. Assuming that the magnetizability and rotational  $g$  tensors are calculated with the same accuracy as the wavefunction itself, the molecular properties indirectly serve as critical tests of the performance of modern quantum-chemical methods.

Several theoretical studies have been published on zero-point vibrational effects on magnetizabilities and rotational  $g$  tensors at various levels of theory (see, e.g., Refs. [3,4]). These studies have shown that the effects are small but non-negligible. Apart from an early study of the isotropic magnetizability of water [5] and studies of the property surfaces of the ammonia and oxonium ions [6,7], these rovibrational studies have been restricted to diatomic molecules. Little is therefore known about the importance of rovibra-

---

\* Corresponding author. E-mail: kenneth@kjemi.uio.no

tional corrections for these properties in polyatomic molecules.

Until recently, the calculation of magnetic properties in general, and magnetizabilities and rotational  $\mathbf{g}$  tensors in particular, was hampered by a dependence of the calculated properties on the choice of gauge origin and by a slow basis-set convergence [8]. This made it difficult to reach the basis-set limit and thus to estimate the importance of rovibrational corrections from a comparison of theoretical and experimental results. The recent implementation of London atomic orbitals [9] for the calculation of magnetizabilities [10] and rotational  $\mathbf{g}$  tensors [11] has facilitated accurate studies of these properties, since the Hartree–Fock limit is now within reach already at the double-zeta level. The rapid basis-set convergence of magnetizabilities and rotational  $\mathbf{g}$  tensors using London orbitals has been demonstrated in several publications [10,12] and has made it possible to study molecules as large as the fullerenes [13].

The implementation of London orbitals has also enabled the study of the effects of electron correlation on magnetizabilities and rotational  $\mathbf{g}$  tensors in larger molecules [14,15] – although it should be noted that some studies of correlation effects on these properties for polyatomic molecules have been performed using conventional basis sets [3,4,16]. Such studies have shown that correlation effects are in general small, the only exceptions being molecules with near-degenerate electronic ground states [15,17,18]. Still, even for a small and simple molecule – from an electron correlation perspective – such as water, the agreement between theory and experiment for the rotational  $\mathbf{g}$  tensor is not satisfactory [14].

It is the purpose of this Letter to investigate the reasons for this discrepancy. In particular, we examine more closely the effects of electron correlation-employing larger active spaces than in Ref. [14] – and zero-point vibrations. Together with recent studies of rovibrational effects on the nuclear shieldings [19] and indirect spin–spin couplings [20] in the water molecule, the present Letter completes a detailed investigation of the effects of molecular rotation and vibration on the magnetic properties of the water molecule.

In Section 2 we give a brief account of the methodology used in this work. In Section 3 we describe the computational details, in Section 4 we

discuss our results and compare them with experiment, and in Section 5 we give some concluding remarks.

## 2. Theoretical background

The molecular magnetizability may be calculated as the second derivative of the molecular energy with respect to an external magnetic field [10]

$$\xi = - \left. \frac{\partial^2 E(\mathbf{B})}{\partial \mathbf{B}^2} \right|_{\mathbf{B}=0}. \quad (1)$$

A straightforward application of perturbation theory using conventional orbitals leads to a very slow basis set convergence of the calculated magnetizability [8,10] and accurate magnetizabilities can then be obtained only for small molecules [16]. In the London atomic orbital approach, each basis function is assigned its own local gauge origin, chosen to coincide with the nucleus to which the basis function is attached. For a one-electron, one-center system, this choice of local gauge origin is correct to first order in the external magnetic field and has been demonstrated to give magnetizabilities that are within 2% of the Hartree–Fock limit at the double-zeta level provided a set of diffuse and polarizing functions is added [8,12].

Because of the smallness of the effect for gases, as well as the need for an accurate calibration standard [12], comparison with experiment is difficult for the isotropic magnetizability of gaseous molecules. In addition, the accuracy of the experimental magnetizability anisotropy may be modest since it appears as a second-order effect in Zeeman experiments [1], and the experimental setup may furthermore be prone to systematic errors [21].

In contrast, highly accurate experimental results are available for the rotational  $\mathbf{g}$  tensor

$$\mathbf{g} = M_p \left. \frac{\partial^2 E(\mathbf{B})}{\partial \mathbf{B} \partial \mathbf{J}} \right|_{\mathbf{B}=\mathbf{J}=0}, \quad (2)$$

where  $M_p$  is the proton mass and  $\mathbf{J}$  is the angular momentum of the molecule. The rotational  $\mathbf{g}$  tensor is related to the magnetizability tensor through [1]

$$g_{\alpha\beta} = - \frac{4M_p}{\mathcal{J}_{\beta\beta}} \xi_{\alpha\beta}^{\text{para}} + g_{\alpha\beta}^{\text{nuc}}, \quad (3)$$

where  $\mathcal{I}$  is the moment of inertia tensor and  $\xi^{\text{para}}$  the paramagnetic part of the magnetizability tensor, related to the total magnetizability tensor by [11]

$$\xi_{\alpha\beta}^{\text{para}} = \xi_{\alpha\beta} - \frac{1}{8} \langle 0 | r_{\text{CM}}^2 \delta_{\alpha\beta} - r_{\text{CM},\alpha} r_{\text{CM},\beta} | 0 \rangle. \quad (4)$$

The last term in Eq. (4) is the diamagnetic magnetizability, which is calculated as an expectation value using the unperturbed wave function  $|0\rangle$  with the center of mass (CM) as gauge origin. We note that Eq. (3) is only valid in the principal axis system of the moment of inertia tensor.

The nuclear contribution to the rotational  $\mathbf{g}$  tensor in Eq. (3) is given by

$$g_{\alpha\beta}^{\text{nuc}} = \frac{M_{\text{p}}}{2\mathcal{I}_{\beta\beta}} \sum_K Z_K (R_K^2 \delta_{\alpha\beta} - R_{K,\alpha} R_{K,\beta}), \quad (5)$$

with  $Z_K$  being the nuclear charge,  $\mathbf{R}_K$  the position of nucleus  $K$  relative to the center of mass, and with the summation running over all nuclei in the molecule. Using the paramagnetic magnetizability as defined in Eq. (4) with the magnetizability calculated using London atomic orbitals, the rotational  $\mathbf{g}$  tensors have been shown to have very fast basis-set convergence [8,12].

The zero-point vibrational corrections to the magnetizability and rotational  $\mathbf{g}$  tensor are in this work calculated from a vibrationally averaged Taylor series expansion of the molecular property in the displacement coordinates  $\langle \Delta R_i \rangle$  (using the isotropic magnetizability  $\xi$  as an example)

$$\begin{aligned} \langle \xi \rangle = & \xi_{\text{e}} + \sum_i \xi_{R_i} \langle \Delta R_i \rangle + \frac{1}{2} \sum_{ij} \xi_{R_i R_j} \langle \Delta R_i \Delta R_j \rangle \\ & + \dots \end{aligned} \quad (6)$$

at 0 K. In this equation,  $\xi_{\text{e}}$  is the isotropic magnetizability calculated at the equilibrium geometry, while  $\xi_{R_i}$  and  $\xi_{R_i R_j}$  denote the first and second derivatives, respectively, of the isotropic magnetizability with respect to the displacement coordinates  $R_i$ , evaluated at the equilibrium geometry. For a discussion of the method used for the zero-point vibrational corrections, we refer to previous works where this approach has been used [19,22].

For the calculation of the molecular magnetizabilities and rotational  $\mathbf{g}$  tensors the Dalton program has been used [23], whereas the AVIBR program of

Lounila et al. [24] has been used for the calculation of the vibrational corrections.

### 3. Computational details

We have used the experimental and optimized geometries reported previously [19]. In accordance with Refs. [25,26], the molecule has been placed in the  $yz$  plane with the  $z$  axis along the molecular  $C_2$  axis.

We have investigated the basis-set convergence of the magnetizability and rotational  $\mathbf{g}$  tensors using different augmented correlation-consistent [27,28] and atomic natural orbital (ANO) basis sets [29], see Table 1. In accordance with previous observations [10,12,21], the augmented correlation-consistent sets and the ANO sets converge rapidly for the magnetizability. Because of the excellent agreement between the results obtained with the aug-cc-pV5Z set and the primitive ANO set, we have chosen to use the latter in the remaining calculations since it has significantly fewer basis functions than the aug-cc-pV5Z basis set.

We have examined the importance of electron correlation using complete active space (CAS) [30] and restricted active space (RAS) self-consistent field (SCF) wave functions [31], using the same active spaces as in Ref. [19], see Table 2. For both the magnetizability and the rotational  $\mathbf{g}$  tensors, the correlation effects are small, with  $g_{yy}$  having the largest change,  $\sim 2.5\%$ . The relative changes in the magnetizability anisotropies are large, but this is primarily due to the smallness of the anisotropies. In accordance with the predictions of a large study of Hartree–Fock magnetizabilities [12], electron correlation makes the water molecule more diamagnetic. Whereas the correlation correction to the isotropic magnetizability converges smoothly and rapidly, the convergence is less pronounced for the individual components, in particular for the  $\mathbf{g}$  tensor.

To make the single-point calculations manageable, we have used the  $^{1000}\text{RAS}_{6332}^{4220}$  wave function for the calculation of zero-point vibrational corrections, as also employed previously [19]. Although some of the  $\mathbf{g}$  tensor components are not fully converged in this approximation – in particular the  $g_{yy}$  component which is reduced by 0.0017 going to

Table 1

Basis-set dependence at the SCF level of the magnetizability and the rotational  $\mathbf{g}$  tensor of the H<sub>2</sub>O molecule at the experimental geometry

Basis	Basis functions	$\xi$	$\Delta\xi_1^a$	$\Delta\xi_2^a$	$g_{xx}$	$g_{yy}$	$g_{zz}$
aug-cc-pVDZ	41	-232.00	-5.12	6.77	0.6534	0.6870	0.7375
aug-cc-pVTZ	92	-231.44	-4.63	7.86	0.6630	0.6824	0.7346
aug-cc-pVQZ	172	-231.27	-4.79	7.96	0.6635	0.6817	0.7343
aug-cc-pV5Z	287	-231.20	-4.80	7.96	0.6635	0.6815	0.7343
ANO[4s 3p 2d 1f / 3s 2p 1d]	58	-230.12	-2.52	2.04	0.6379	0.6750	0.6805
ANO[5s 4p 3d 2f / 4s 3p 2d]	92	-231.05	-5.09	7.03	0.6604	0.6804	0.7247
ANO[6s 5p 4d 3f / 5s 4p 3d]	126	-231.15	-4.76	7.82	0.6622	0.6815	0.7331
ANO decontracted	152	-231.20	-4.82	7.99	0.6635	0.6814	0.7342

The magnetizabilities are reported in units of  $10^{-30}$  J T<sup>-2</sup>.

<sup>a</sup>The anisotropies are defined as, respectively,  $\Delta\xi_1 = 2\xi_{xx} - \xi_{yy} - \xi_{zz}$  and  $\Delta\xi_2 = -\xi_{xx} + 2\xi_{yy} - \xi_{zz}$ .

the largest RAS wave function – we shall take this lack of convergence into account when estimating error limits. Clearly, further improvements in the description of the electronic wavefunction are desirable.

Since the rotational  $\mathbf{g}$  tensor is defined with respect to the center of mass of the molecule (see Eqs. (3) and (4)), separate calculations have to be performed for each isotopic species. We have therefore restricted our investigations to consider only the hydrogen-substituted species –that is, H<sub>2</sub>O, HDO and D<sub>2</sub>O. For each isotopomer, we have calculated the magnetizability and rotational  $\mathbf{g}$  tensors at a total of 33 points. Although this small number of points

restricts the number of significant digits in our vibrationally corrected results to three, this accuracy is comparable to that imposed by the approximate treatment of the electron correlation effects. Whereas the calculated force field can be found in Ref. [19], the property surfaces can be obtained from the authors.

#### 4. Results and discussion

We have collected our results for the isotropic and anisotropic magnetizabilities and the rotational  $\mathbf{g}$  tensor components for H<sub>2</sub>O in Table 3, together with

Table 2

Correlation dependence of the magnetizability and the rotational  $\mathbf{g}$  tensor of the H<sub>2</sub>O molecule using the primitive ANO basis set at the experimental geometry

Wave function <sup>a</sup>	Determinants	$\xi$	$\Delta\xi_1^b$	$\Delta\xi_2^b$	$g_{xx}$	$g_{yy}$	$g_{zz}$
HF	1	-231.20	-4.81	7.99	0.6635	0.6814	0.7342
<sup>1000</sup> CAS <sup>6331</sup>	128283	-235.31	-4.08	6.75	0.6579	0.6747	0.7336
<sup>1000</sup> RAS <sup>4220</sup> <sub>2111</sub>	40636	-235.29	-4.08	6.68	0.6574	0.6744	0.7332
<sup>1000</sup> RAS <sup>4220</sup> <sub>4221</sub>	117948	-235.19	-3.60	6.84	0.6544	0.6634	0.7288
<sup>1000</sup> RAS <sup>4220</sup> <sub>6332</sub>	271876	-235.41	-4.22	6.75	0.6513	0.6668	0.7283
<sup>1000</sup> RAS <sup>4220</sup> <sub>8553</sub>	594428	-235.31	-4.18	6.88	0.6537	0.6696	0.7303
<sup>1000</sup> RAS <sup>4220</sup> <sub>9553</sub>	650596	-235.27	-4.11	6.93	0.6536	0.6688	0.7297
<sup>1000</sup> RAS <sup>4220</sup> <sub>10:663</sub>	834620	-235.30	-4.08	6.82	0.6520	0.6661	0.7285
<sup>1000</sup> RAS <sup>4220</sup> <sub>12:884</sub>	1353284	-235.28	-4.22	6.84	0.6508	0.6651	0.7280

The magnetizabilities are reported in units of  $10^{-30}$  J T<sup>-2</sup>.

<sup>a</sup>The notation <sup>inactive</sup>RAS<sup>RAS2</sup><sub>RAS3</sub> gives the number of orbitals in the four symmetries A<sub>1</sub>, B<sub>1</sub>, B<sub>2</sub>, A<sub>2</sub>, respectively. All orbitals are doubly occupied in the inactive space, a full CI calculation is carried out in the RAS2 space, and a maximum of two electrons are allowed to be excited into the RAS3 space.

<sup>b</sup>The anisotropies are defined as, respectively,  $\Delta\xi_1 = 2\xi_{xx} - \xi_{yy} - \xi_{zz}$  and  $\Delta\xi_2 = -\xi_{xx} + 2\xi_{yy} - \xi_{zz}$ .

Table 3  
Magnetizabilities rotational  $\mathbf{g}$  tensors of H<sub>2</sub>O, both with without corrections for zero-point vibrations

Ref.	Method	$\xi$	$\Delta\xi_1^a$	$\Delta\xi_2^a$	$g_{xx}$	$g_{yy}$	$g_{zz}$
	Hartree–Fock <sup>b</sup>	–231.20	–4.81	7.99	0.6635	0.6814	0.7342
This Letter	<sup>1000</sup> RAS <sub>6332</sub> <sup>4220</sup> <sup>c</sup>	–235.41	–4.22	6.75	0.651(1)	0.667(3)	0.728(3)
	<sup>1000</sup> RAS <sub>6332</sub> <sup>4220</sup> /ZPV <sup>d</sup>	–236.4	–4.02	7.34	0.637(1)	0.640(3)	0.709(3)
[3,16]	MP2(NoLon)	–238.4		7.26	0.6640	0.6830	0.7453
[16]	L-CCD(NoLon)	–234.6		6.91	0.6507	0.6682	0.7288
[14]	CASSCF(London)	–236.6	–4.4	7.3	0.6514	0.6634	0.7273
[26]	Exp.(BM) <sup>e</sup>		–4.4(2)	7.7(4)	0.645(6)	0.657(1)	0.718(7)
[25]	Exp.(MW) <sup>f</sup>				0.6465(20)	0.6650(20)	0.7145(20)
	Exp. (MW) <sup>g</sup>	–218(30)					

The magnetizabilities are reported in units of  $10^{-30}$  J T<sup>-2</sup>.

<sup>a</sup>The anisotropies are defined as, respectively,  $\Delta\xi_1 = 2\xi_{xx} - \xi_{yy} - \xi_{zz}$  and  $\Delta\xi_2 = -\xi_{xx} + 2\xi_{yy} - \xi_{zz}$ .

<sup>b</sup>Experimental geometry, see Ref. [19].

<sup>c</sup>Results at the optimized geometry for this wave function, see Ref. [19].

<sup>d</sup>RASSCF wave function including the effects of zero-point vibrational corrections.

<sup>e</sup>Beam-maser experiment.

<sup>f</sup>Microwave spectroscopy.

<sup>g</sup>Result quoted in Ref. [32].

experimental data and results of other theoretical calculations presented in the literature. Included in Table 3 are also our Hartree–Fock results, to better illustrate the relative importance of the effects of electron correlation and zero-point vibrations.

For the  $\mathbf{g}$  tensor, correlation and vibrational corrections appear to be of almost similar importance, with the vibrational correction being slightly dominating for  $g_{xx}$  and  $g_{zz}$ . In all cases, electron correlation and vibrations reduce the magnitude of the  $\mathbf{g}$  tensor components, leading to overall corrections of 4.2%, 6.5% and 3.6% for  $g_{xx}$ ,  $g_{yy}$  and  $g_{zz}$ , respectively. Clearly, neither electron correlation nor zero-point vibrational corrections can be neglected for this molecule if a meaningful comparison with experiment is to be made.

In contrast to the  $\mathbf{g}$  tensor, the change in the isotropic magnetizability is very modest, even though electron correlation and zero-point vibrational corrections act in the same direction also for this quantity. Moreover, although the relative changes in the magnetizability anisotropies due to correlation and zero-point vibrations are large, the absolute changes are very small. Electron correlation and zero-point vibrational corrections work in opposite directions for  $\Delta\xi_2$ , reflecting the different magnitudes of the corrections for the individual tensor components, as seen also in the rotational  $\mathbf{g}$  tensor components.

Ignoring the vibrational corrections, our correlated results are in good agreement with the MP2 and L-CCD results of Cybulski and Bishop [16]. Our vibrationally corrected results are in only moderate agreement with the Zeeman microwave and beam-maser experiments from the late 1960s. In particular we note the poor agreement of the calculated difference between the  $g_{xx}$  and  $g_{yy}$  components with experiment. However, the experimental results are based mostly on measurements recorded for D<sub>2</sub>O. We shall later argue that the experimental results for H<sub>2</sub>O are incorrect.

In Table 4 we have collected our results for the three isotopic species H<sub>2</sub>O, HDO and D<sub>2</sub>O, together with the microwave Zeeman data of Kukolich [25] and the molecular beam data of Verhoeven and Dymanus [26]. The error limits reported for our rotational  $\mathbf{g}$  tensor components are based on the convergence of the RAS spaces for H<sub>2</sub>O (Table 2) and crude estimates of the errors in the zero-point vibrational averaging procedure, and scaled by the change in the moment of inertia for the different isotopic species.

Focusing on the isotopomer for which most experimental data are available (i.e., D<sub>2</sub>O) we note that our vibrationally corrected  $\mathbf{g}$  tensor components are in excellent agreement with the results of Kukolich, with all components within the experimental error

Table 4

Isotope dependence of the magnetizabilities and rotational  $\mathbf{g}$  tensors corrected for zero-point vibrations in the water molecule

	H <sub>2</sub> O		HDO		D <sub>2</sub> O	
	theory	exp. <sup>a</sup>	theory	exp. <sup>a</sup>	theory	exp. <sup>a</sup>
$\xi$	-236.4		-236.1		-236.1	
$\Delta\xi_1$ <sup>b</sup>	-4.0		-3.9		-3.4	-3.3(8)/n.a. <sup>c</sup>
$\Delta\xi_2$ <sup>b</sup>	7.3		7.3		6.9	7.7(4)/n.a. <sup>c</sup>
$g_{xx}$	0.637(1)	0.645(6)/ 0.6465(20)	0.405(1)	0.413(4)/n.a.	0.322(1)	0.32513(15)/ 0.3226(10)
$g_{yy}$	0.640(3)	0.657(1)/ 0.6650(20)	0.433(2)	0.437(4)/n.a.	0.323(2)	0.32530(10)/ 0.3233(10)
$g_{zz}$	0.709(3)	0.718(7)/ 0.7145(20)	0.608(2)	0.618(6)/n.a.	0.357(1)	0.36009(22)/ 0.3580(10)

All calculations have been done using the RASSCF wave functions described in the text. The magnetizabilities are reported in units of  $10^{-30} \text{ J T}^{-2}$ .

<sup>a</sup>The first number is from a beam-maser experiment by Verhoeven and Dymanus [26], the second is from a microwave Zeeman study by Kukolich [25].

<sup>b</sup>The anisotropies are defined as, respectively,  $\Delta\xi_1 = 2\xi_{xx} - \xi_{yy} - \xi_{zz}$  and  $\Delta\xi_2 = -\xi_{xx} + 2\xi_{yy} - \xi_{zz}$ .

<sup>c</sup>Not available.

limits. The agreement with the data of Verhoeven and Dymanus is less satisfactory, in particular considering the smaller error limits reported for their data. Verhoeven and Dymanus argue that their results are of higher accuracy than those of Kukolich. Although we may not be fully converged with respect to electron correlation, the remaining errors should not exceed 0.0015 (as indicated by the number of digits reported), with our results probably being too large (see Table 2). We believe our results are sufficiently accurate to support the results of Kukolich.

If we assume that the molecular charge distribution is unaffected by isotopic substitution, the  $\mathbf{g}$  tensors of different isotopomers are related as [1,33]

$$\begin{aligned}
 (\mathbf{g}'\mathbf{I}')_{\alpha\beta} - (\mathbf{g}\mathbf{I})_{\alpha\beta} \\
 = M_p \left[ -2(\mathbf{q} \cdot \mathbf{d}) \delta_{\alpha\beta} + q_\alpha d_\beta + q_\beta d_\alpha \right]. \quad (7)
 \end{aligned}$$

Here  $\mathbf{q}$  represents the change in the center-of-mass coordinates occurring upon isotopic substitution (see Eq. (4)) and  $\mathbf{d}$  is the dipole moment of the molecule. This equation may also serve as a means of experimentally determining the direction of the molecular dipole moment [1]. Eq. (7) is fulfilled for variational wave functions (e.g., SCF and MCSCF wave functions) in the limit of a complete basis set, provided the geometry is the same for all isotopomers. In our calculations, Eq. (7) is satisfied to better than

0.0015% (i.e., it is fulfilled to within numerical accuracy).

In the original derivation of this equation [33], the importance of molecular vibrations in restricting the applicability of Eq. (7) was pointed out. Hübner et al. later showed that the dipole moment obtained from Eq. (7) for formaldehyde is meaningless unless the effects of zero-point vibrations are accounted for [34].

Kukolich applied Eq. (7) to one of the  $\mathbf{g}$  tensor components to help resolve his data for H<sub>2</sub>O. Verhoeven and Dymanus, on the other hand, were able to analyze the complete  $\mathbf{g}$  tensor for H<sub>2</sub>O as well as D<sub>2</sub>O. However, the dipole moment obtained through the use of Eq. (7) from these data were in poor agreement with the dipole moment obtained in Stark-effect measurements. For this reason, they chose to report for HDO and H<sub>2</sub>O only the  $\mathbf{g}$  tensor components derived using Eq. (7) from the D<sub>2</sub>O data (since these data had the highest experimental accuracy). The experimentally derived data for HDO and H<sub>2</sub>O thus depend on the validity of Eq. (7).

The excellent agreement of our theoretical zero-point vibrationally corrected  $\mathbf{g}$  tensor components with experiment for D<sub>2</sub>O as well as the large disagreement for H<sub>2</sub>O, cast some doubts on the validity of Eq. (7) for determining the dipole moment of water by deuterium substitution – as was the case also for formaldehyde [34].

A comparison of the  $g$  tensor components obtained for  $D_2O$  at the equilibrium geometry without vibrational corrections ( $g_{xx} = 0.324$ ,  $g_{yy} = 0.333$ , and  $g_{zz} = 0.362$ ) with the vibrationally corrected results in Table 4, demonstrates that the numerical similarity of  $g_{xx}$  and  $g_{yy}$  arises from vibrational corrections. A similar behavior of these  $g$  tensor components is expected and theoretically observed also for  $H_2O$ , once again due to zero-point vibrational corrections. However, the experimental data fail to meet this expectation. Our data thus suggest that there is a need for an experimental reinvestigation of the rotational  $g$  tensor of the  $H_2O$  and HDO isotopomers of water in order to obtain new, accurate data for these properties.

## 5. Conclusions

We have presented correlated calculations of the zero-point vibrational corrections to the magnetizability and rotational  $g$  tensor of the water molecule. We have demonstrated that, by taking both electron correlation and vibrational corrections into account, good agreement with accurate Zeeman microwave and molecular beam experiments can be obtained for the rotational  $g$  tensor. Our study has provided another example of a molecule for which the relationship between the molecular dipole moment and the  $g$  tensors of isotopomers breaks down due to vibrational effects, and our study calls for a reinvestigation of the rotational  $g$  tensor of the  $H_2O$  and HDO isotopomers of the water molecule.

The zero-point vibrational corrections have been shown to be of about the same magnitude as the electron correlation effects for the water molecule. Both corrections reduce the rotational  $g$  tensor components, producing a rather large overall correction to the Hartree–Fock rotational  $g$  tensors. In contrast, electron correlation and vibration give small contributions to the isotropic magnetizability. Likewise, for the magnetizability anisotropies the absolute changes due to electron correlation and vibrations are small. However, since even small changes in the magnetizability anisotropies may significantly change the temperature dependence of for instance the Cotton–Mouton constant, these effects must both be considered if an accurate estimate of the temperature

dependence of the Cotton–Mouton constant is needed [35].

## Acknowledgements

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

## References

- [1] W.H. Flygare, Chem. Rev. 74 (1974) 653.
- [2] N.F. Ramsey, Molecular Beams, Clarendon, Oxford, 1956.
- [3] S.M. Cybulski, D.M. Bishop, J. Chem. Phys. 100 (1994) 2019.
- [4] S.P.A. Sauer, I. Paidarová, Chem. Phys. 201 (1995) 405.
- [5] P.W. Fowler, W.T. Raynes, Mol. Phys. 43 (1981) 65.
- [6] S.P.A. Sauer, V. Špirko, I. Paidarová, J. Oddershede, Chem. Phys. 184 (1994) 1.
- [7] S.P.A. Sauer, V. Špirko, J. Oddershede, Chem. Phys. 153 (1991) 189.
- [8] K. Ruud, T. Helgaker, Chem. Phys. Lett. 264 (1997) 17.
- [9] F. London, J. Phys. Radium 8 (1937) 397.
- [10] K. Ruud, T. Helgaker, K.L. Bak, P. Jørgensen, H.J.A. Jensen, J. Chem. Phys. 99 (1993) 3847.
- [11] J. Gauss, K. Ruud, T. Helgaker, J. Chem. Phys. 105 (1996) 2804.
- [12] K. Ruud, H. Skaane, T. Helgaker, K.L. Bak, P. Jørgensen, J. Am. Chem. Soc. 116 (1994) 10135.
- [13] D. Jonsson, P. Norman, K. Ruud, H. Ågren, T. Helgaker, J. Chem. Phys. 109 (1998) 572.
- [14] K. Ruud, T. Helgaker, P. Jørgensen, J. Chem. Phys. 107 (1997) 10599.
- [15] P.-O. Åstrand, K. Ruud, K.V. Mikkelsen, T. Helgaker, Mol. Phys. 92 (1997) 89.
- [16] S.M. Cybulski, D.M. Bishop, J. Chem. Phys. 106 (1997) 4082.
- [17] S.P.A. Sauer, T. Enevoldsen, J. Oddershede, J. Chem. Phys. 98 (1993) 9748.
- [18] K. Ruud, T. Helgaker, K.L. Bak, P. Jørgensen, J. Olsen, Chem. Phys. 195 (1995) 157.
- [19] J. Vaara, J. Lounila, K. Ruud, T. Helgaker, J. Chem. Phys. 109 (1998) 8388.
- [20] R.D. Wigglesworth, W.T. Raynes, S.P.A. Sauer, J. Oddershede, Mol. Phys. 94 (1998) 851.
- [21] P.-O. Åstrand, K. Ruud, K.V. Mikkelsen, T. Helgaker, J. Chem. Phys. (submitted).
- [22] J. Lounila, J. Vaara, Y. Hiltunen, A. Pulkkinen, J. Jokisaari, M. Ala-Korpela, K. Ruud, J. Chem. Phys. 107 (1997) 1350.
- [23] T. Helgaker, H.J.A. 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, B. Fernandez, 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, O. Vahtras, Dalton, an ab initio electronic structure program, Release 1.0, 1997. See <http://www.kjemi.uio.no/software/dalton/dalton.html>.
- [24] J. Lounila, R. Wasser, P. Diehl, *Mol. Phys.* 62 (1987) 19.
- [25] S.G. Kukolich, *J. Chem. Phys.* 50 (1969) 3751.
- [26] J. Verhoeven, A. Dymanus, *J. Chem. Phys.* 52 (1970) 3222.
- [27] T.H. Dunning Jr., *J. Chem. Phys.* 90 (1989) 1007.
- [28] D.E. Woon, T.H. Dunning Jr., *J. Chem. Phys.* 100 (1994) 2975.
- [29] P.-O. Widmark, P.-Å. Malmqvist, B.O. Roos, *Theor. Chim. Acta* 77 (1990) 291.
- [30] P.E.M. Siegbahn, J. Almlöf, A. Heiberg, B.O. Roos, *J. Chem. Phys.* 74 (1981) 2384.
- [31] J. Olsen, B.O. Roos, P. Jørgensen, H.J.A. Jensen, *J. Chem. Phys.* 89 (1988) 2185.
- [32] P. Lazzeretti, R. Zanasi, B. Cadioli, *J. Chem. Phys.* 67 (1977) 382.
- [33] C.H. Townes, G.C. Dousmanis, R.L. White, R.F. Schwarz, *Discuss. Faraday Soc.* 19 (1955) 56.
- [34] D. Hübner, M. Stolze, D.H. Sutter, *J. Mol. Struct.* 97 (1983) 173.
- [35] S. Coriani, A. Rizzo, K. Ruud, T. Helgaker, *Chem. Phys.* 216 (1997) 53.