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# Ab initio calculation of the deuterium quadrupole coupling in liquid water

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The quadrupole coupling constant and asymmetry parameter for the deuteron in liquid heavy water was determined using purely theoretical methods. Molecular-dynamics simulations with the *ab initio* potential-energy surface of Lie and Clementi were used to generate snapshots of the liquid. The electric-field gradient at the deuteron was then calculated for these configurations and averaged to obtain the liquid quadrupole coupling constant. At 300 K a quadrupole coupling constant of  $256 \pm 5$  kHz and an asymmetry parameter of  $0.164 \pm 0.003$  were obtained. The temperature dependence of the quadrupole coupling constant was investigated.

## I. INTRODUCTION

Since 1959 several groups have experimentally determined the quadrupole coupling constant (QCC) for the deuteron of water in the gas phase (see Refs. 1–3 and references therein). In addition, the electric-field gradient, which is equivalent to the quadrupole coupling if the quadrupole moment of the deuteron is accurately known, has been calculated by many theoreticians (Refs. 2 and 4–6 and references therein). Therefore this property is known very accurately, i.e., with an error of about 0.1 kHz in the principal axes of the moment of inertia.<sup>1</sup> Even in the principal axes of the coupling tensor the coupling has an error of only about 1 kHz.

The situation is different for the liquid phase. Although many measurements have been published,<sup>7–15</sup> the values at room temperature scatter over quite a large range (208–259 kHz) and only the more recent measurements seem to converge to about 254 kHz with an error limit between 5 and 10 kHz at 300 K. To our knowledge no calculated values are available for the coupling in the liquid phase. Cummins *et al.* estimated values of 280 kHz (Ref. 16) and 256 kHz.<sup>17</sup> They assumed that the structure of the liquid-water molecule is equivalent to that of the vapor and that a given H atom in the liquid is hydrogen bonded 75% of the time. Hence, the difference in the QCC with a change from vapor to liquid is taken as 75% of the difference due to a change from the vapor to the pentamer ice fragment of *Ih* (Ref. 16) or to ice *VIII*.<sup>17</sup> The current situation is such that there are many experimental values available which are scattered over a large range as a result of the assumptions in the evaluation of the coupling from NMR relaxation times, and no theoretical values due to the difficult calculation of such properties in the liquid phase. Thus, it is desirable to calculate the couplings, independently of the NMR relaxation rates.

Some groups have studied the dependence of the quadrupole coupling on pressure and temperature making different assumptions. Powles, Rhodes, and Strange<sup>8</sup> found the QCC to be  $230 \pm 10$  kHz and independent of temperature in measurements up to 573 K at unspecified pressures.

Hindman *et al.*<sup>9</sup> report that between 278 and 333 K there is no significant deviation from the average of 258.6 kHz. Jonas, DeFries, and Wilbur<sup>11</sup> measured the QCC at 283, 303 and 363 K at pressures up to 900 MPa. However, their results show no clearcut temperature or pressure dependence and many assumptions had to be made. Lang and co-workers<sup>12,13</sup> measured the coupling at various temperatures below 286 K. They determined a value of  $214 \pm 12$  kHz in supercooled heavy water at 192 K and 225 MPa and found that the temperature dependence was within the limits of error. Struis, De Bleijser, and Leyte<sup>15</sup> found a slight increase of the coupling from 237 to 254 kHz at temperatures from 263 to 326 K, the estimated error being about 7 kHz. All these results show that the coupling hardly changes with temperature or pressure, but the situation is still unclear.

Several measurements of the quadrupole coupling in ice in various forms have been reported.<sup>18–22</sup> The values are all between 213 and 226 kHz depending on the crystal lattice and site within the lattice and independent of the conditions. Cummins *et al.*<sup>16,17</sup> report values which were calculated using various basis sets and are in agreement with experiment.

The goal of this work is the *ab initio* calculation of the D nuclear quadrupole coupling tensor in liquid water at different temperatures. As the approximations in the calculations are completely different from those in the experimental evaluations, we hope to make a significant contribution to the accurate determination of the D QCC in liquid water and to clarify the extent of its temperature dependence. In addition, a theoretical evaluation will assist in understanding the quadrupole coupling in liquid water at a molecular level.

The approach used here is to take snapshots of molecular configurations from a classical molecular-dynamics simulation, which are used then for a quantum chemical calculation of the electrical-field gradient. Methodological questions such as the number of snapshots to be used for averaging and the size of the shell around the water molecule which contributes to the QCC are studied. Previous

work for molecules in the gas phase<sup>2,5,6</sup> showed that the concept of a basis set of “local high quality” yields deuterium coupling constants with an error of less than 5% on the self-consistent-field (SCF) level<sup>5</sup> and less than 3% including electron correlation.<sup>6</sup> For water in the gas phase the SCF value with the basis set used in this work is 316 kHz compared to the experimental value of 308 kHz, i.e., the error is less than 3%. Quantum chemical calculations on the SCF level provide a firm base for comparison of the quadrupole coupling of liquid water at different temperatures as the relative errors for similar systems can be assumed to be even smaller than the above absolute errors. We know less about the error introduced by unrealistic molecular configurations due to an inaccurate force field. Further studies with different force fields are underway in our group in order to assess the sensitivity of the quadrupole coupling to those errors.

We are aware of only two theoretical studies of the quadrupole coupling of solutions which are related to this work. Aqueous solutions of  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{Cl}^-$  have been studied by Engström, Jönsson, and Impey (Ref. 23 and references therein) and of xenon by Schnitker and Geiger.<sup>24</sup> In both cases the investigated species have no coupling due to their spherical symmetry, i.e., the coupling is fully due to the solvent. Engström, Jönsson, and Impey were interested in the relaxation, and therefore fluctuation, of the coupling which they had to extract from time correlation functions. To make this task feasible, they constructed a two-particle hypersurface using *ab initio* calculations for the coupling. The coupling could then be evaluated analytically during the simulation. Schnitker and Geiger calculated the field gradient from a classical point-charge distribution on the surrounding water molecules.

A similar approach to the one used in this paper has recently been reported by Hermansson, Knuts, and Lindgren<sup>25</sup> for the calculation of infrared shifts in the liquid phase.

## II. METHOD

Liquid water was simulated within a microcanonical (constant  $NVE$ ) ensemble, using molecular-dynamics methods as described by Allen and Tildesley.<sup>26</sup> A cubic box with periodic boundary conditions was filled with flexible water molecules interacting classically. The equations of motion were integrated using the leap-frog version of the velocity-Verlet algorithm. Inter- and intramolecular interactions were included in the potential model with a spherical truncation of the short-range intermolecular interactions and long-range interactions treated using the Ewald method.<sup>26</sup> Initially the molecules were either placed on a cubic lattice with random orientation, or were obtained from a snapshot of a previous simulation. The initial vibrational and rotational velocities of the molecules were set to zero and they were given a random initial translational velocity with a Gaussian distribution. The translational velocities were scaled so that the desired temperature was obtained.

The system was allowed to equilibrate until the lattice structure was lost and the temperature stabilized. The loss

of lattice structure was indicated by the translational order parameter.<sup>26</sup> During the equilibration periods of approximately 10 000 time steps, the velocities were rescaled every 100 steps to ensure that the required equilibrium temperature was attained. Subsequently, the simulation was allowed to run for 10 000 time steps (2500 fs) with a snapshot of the liquid configuration taken after 1000 time steps and every 100 steps (25 fs) after the 2000th step.

From each snapshot the electric-field gradient at a randomly selected deuterium atom was calculated at the SCF level using GAUSSIAN 90 (Ref. 27) or OBELIX 2.0.<sup>28</sup> By inclusion of surrounding water molecules in the SCF calculation, the effects of the liquid environment are incorporated into the electric-field gradient.

Two potential models were used in this work. An empirical potential was used in order to investigate methodological questions for the calculation of the liquid QCC; however, a purely *ab initio* potential was selected in order to achieve our goal of determining the QCC theoretically. The empirical potential of Dang and Pettitt<sup>29</sup> was employed (DP potential). This model assumes a three-site water molecule with intermolecular interactions treated with the TIPS (Lennard-Jones plus Coulomb) potential of Jorgensen<sup>30</sup> and intramolecular interactions with an anharmonic potential. For the final calculation of the QCC at various temperatures, the *ab initio* potential of Lie and Clementi<sup>31</sup> was used (LC potential). This model assumes a four-site water molecule with the intermolecular forces determined by the potential of Matsuoka, Clementi, and Yoshimine<sup>32</sup> and the intramolecular forces by the potential of Bartlett, Shavitt, and Purvis.<sup>33</sup> One site was located on each of the nuclei and the fourth at M, on the bisector of the D–O–D angle with the distance from the O nuclei defined as  $r_{\text{OM}}/r_{\text{OM}'}=0.456\ 826$  where M' is the intersection of the D–O–D bisector and the line connecting the two deuterium atoms. The equilibrium bond length and angle for the monomer (95.76 pm and 104.59°) are close to the experimental values (95.72 pm and 104.52°). Long-range forces were treated using an Ewald summation<sup>26</sup> with a convergence parameter of 5.0/ $L$  (where  $L$  is the length of the simulation box) and 122 vectors in the reciprocal space sum. The cut-off radius for the short-range interactions and the real-space summation was 738 pm, and the periodic box contained 125 molecules. A time step of 0.25 fs was used in both the equilibration period and the equilibrium simulation in order to simulate the intramolecular vibrations (which have a period of the order of 10 fs).<sup>26</sup>

The basis sets used in the quantum chemical calculations on the water clusters were those developed for determination of the deuterium QCC in single molecules.<sup>5,6</sup> The quality of these basis sets has been tested on a wide variety of molecules. The high-quality uncontracted ( $6s4p4d$ ) basis of Huzinaga<sup>34</sup> was used for the deuterium of interest. For the oxygen atom which is bonded to that deuterium the ( $9s5p$ ) basis of Dunning<sup>35</sup> was enhanced with two polarization functions and contracted to give a [ $4s2p2d$ ] basis and a smaller basis was located on all other nuclei (the Dunning<sup>35</sup> ( $4s$ )/[ $2s$ ] basis for D and the Roos and Siegbahn<sup>36</sup> ( $7s3p$ )/[ $4s2p$ ] basis for O). The basis-set superposi-

TABLE I. Temperature dependence of the deuterium quadrupole coupling constant (QCC) and asymmetry parameter,  $\eta$ .<sup>a</sup>

Potential	Temperature (K)	QCC (kHz)	$\eta$	QCC <sup>b</sup> (kHz)	QCC <sup>c</sup> (kHz)
LC	260	254 ± 5	0.169 ± 0.003	254 ± 5	259.5 ± 0.3
LC	274	252 ± 5	0.168 ± 0.003	252 ± 5	260.5 ± 0.3
LC	300	256 ± 5	0.164 ± 0.003	256 ± 5	260.9 ± 0.3
LC	359	262 ± 5	0.165 ± 0.003	260 ± 5	263.4 ± 0.3
DP	303	263 ± 3	0.172 ± 0.003	259 ± 3	260.8 ± 0.2

<sup>a</sup>In each case the error is the standard error of the mean.

<sup>b</sup>Values determined using the model of Eq. (4) and the 82 selected deuterium atoms.

<sup>c</sup>Values determined using the model of Eq. (4) and all deuterium atoms in the 82 snapshots.

tion error for the QCC of the selected deuterium atom in a water pentamer was found to be negligible using the full counterpoise correction of Boys and Bernardi.<sup>37</sup>

Although parameters for the molecular-dynamics simulations could be determined by reference to published water simulations, various trial calculations were required in order to answer methodological questions for the determination of the liquid QCC from the snapshots. The number of surrounding molecules which should be considered, the way in which the molecules were selected, and the number of snapshots required were investigated.

Experimental studies on the structure of liquid water have shown that the first shell of each liquid-water molecule contains approximately 4.5 molecules.<sup>38</sup> However, it is unclear whether only the hydrogen-bonded molecule, the first shell, or even further molecules will influence the QCC of a deuterium. Therefore, from each snapshot three to nine molecules were selected and considered in the *ab initio* calculation. Using 12 snapshots, it was found that the mean was not significantly effected with a change from five to nine molecules, with a maximum change of  $\pm 2\%$  in the QCC for individual configurations. Therefore, in subsequent calculations five molecules were considered.

Three schemes for the selection of the “nearest-neighbor” molecules were investigated. First, the molecules were ordered in terms of the smallest distances between any nuclei and any nuclei on the molecule of interest. Second, they were ordered in terms of the distances between their center of mass and that of the molecule of interest. Third, the distance between any nuclei and the deuterium of interest was considered. The maximum variation in the QCC due to the selection scheme was  $\pm 4\%$  for an individual configuration, and the change in the mean QCC of 12 configurations was negligible. The influence of the selection scheme is very small since in each case the molecule which is hydrogen bonded to the deuterium of interest is included in the calculation. Therefore, if four “nearest-neighbor” molecules are considered, any of these schemes is satisfactory. In subsequent work, the third scheme was used.

The trial calculations showed that the standard error of the QCC was 5 kHz when 22 individual configurations generated with the DP potential were used. Since this potential model considerably underestimates the root-mean-square change,  $\langle \Delta R_{OD} \rangle_{\text{rms}}$  of the intramolecular O–D

bond length [simulated:  $\sim 0.9$  pm; experimental:  $\sim 9.5 \pm 0.5$  pm (Ref. 39)] the standard error in the QCC is expected to increase for a potential which models  $\langle \Delta R_{OD} \rangle_{\text{rms}}$  more accurately. Lie and Clementi<sup>31</sup> obtained a value for  $\langle \Delta R_{OD} \rangle_{\text{rms}}$  of 2.3 pm in their molecular-dynamics simulations using the LC potential. Hence, the standard error was recalculated and found to be 9 kHz using 22 configurations generated from the LC potential. In order to attain a standard error of similar magnitude to the experimental error, in this work the QCC was therefore determined by taking the average over 82 configurations.

Each *ab initio* calculation of the electric-field gradient requires approximately 21 min on a Cray-2. Therefore, the 82 *ab initio* calculations together with the molecular-dynamics simulation requires approximately 30 h for each temperature.

### III. RESULTS AND DISCUSSION

The liquid-water deuterium QCC was determined at four temperatures: 260, 274, 300, and 359 K. For each temperature, the density was chosen as the experimental density for heavy water at standard pressure. The electric-field gradient in its principal axis system was calculated for a randomly selected deuterium atom using 82 snapshots from molecular-dynamics simulations. The quadrupole coupling tensor is determined by multiplying the components of the electric-field gradient by the quadrupole moment of the deuteron (672.0 kHz/a.u.). The components of the quadrupole coupling tensor are defined such that  $|\chi_{\alpha\alpha}| > |\chi_{\beta\beta}| > |\chi_{\gamma\gamma}|$ . Hence,  $\chi_{\alpha\alpha}$  is the QCC and the asymmetry parameter  $\eta$  is given by

$$\eta = (\chi_{\gamma\gamma} - \chi_{\beta\beta}) / \chi_{\alpha\alpha} \quad (1)$$

Table I gives the QCC and  $\eta$  for each temperature. The QCC and  $\eta$  for the liquid were evaluated as the square root of the mean square of the values for the 82 individual configurations.

The QCC of  $256 \pm 5$  kHz is in agreement with recent experimental results. Using NMR measurements of the spin-lattice relaxation time, Struis, DeBleijser, and Leyte<sup>15</sup> determined a QCC of  $254 \pm 8$  and  $253 \pm 8$  kHz at 298 and 309 K, respectively. Van der Maarel *et al.*<sup>14</sup> also determined the QCC from NMR measurements,<sup>40</sup> obtaining a value of  $253 \pm 6$  kHz at 298 K. In the calculation of the

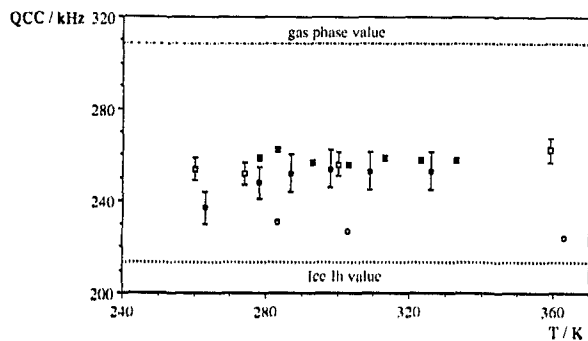


FIG. 1. Variation of the QCC with temperature and comparison of the values calculated in this work ( $\square$ ) with experimental results ( $\bullet$ , Ref. 15;  $\circ$ , Ref. 11;  $\blacksquare$ , Ref. 9). The standard errors are shown as error bars, where available.

QCC from the spin-lattice relaxation time a number of assumptions are made. For the deuterium atom in the case of extreme narrowing (i.e., as is the case for liquid water at standard pressure), the QCC is related to relaxation time  $T_1$  by

$$1/T_1 = 12\pi^2/8(\text{QCC})^2(1 + \eta^2/3)\tau, \quad (2)$$

where  $\tau$  is the correlation time for the relaxation process. In each of the above papers, the error in the relaxation time is estimated to be approximately 1%. For the deuterium atom,  $\eta$  is often assumed to be zero, equal to the gas-phase value or is taken to be a value intermediate of the ice and gas-phase value. No significant effect on the QCC is caused by these assumptions. Since the correlation time cannot be measured directly, further assumptions are invoked in the estimation of this value. Both Struis, DeBleijser, and Leyte and Van der Maarel, Lankhorst, and DeBleijser assumed that the water molecule undergoes isotropic rotation. Struis, DeBleijser, and Leyte<sup>15</sup> and Lankhorst, Schriever, and Leyte<sup>40</sup> showed that the correlation time for the spin-lattice relaxation of the deuteron in HDO, scaled for isotope effects, was approximately equal to the <sup>17</sup>O-enhanced proton correlation time and used these assumptions in the determination of the QCC.

In Fig. 1, the calculated QCCs are compared with experimental data. The values agree within the limits of error, with the error bars for the experimental and theoretical results being of similar magnitude.

In addition to the statistical error in the calculated QCCs, there is an error due to inadequacies in the basis set. For the gas phase, the *ab initio* calculations were found to overestimate the QCC by 8 kHz or 2.6%. It can be assumed that the effect will be of a similar percentage over the range of values investigated. As can be seen from Fig. 1, this shift does not deteriorate the agreement between the experimental and current results.

The asymmetry parameter  $\eta$  of D in liquid water has not been evaluated experimentally. However, it is generally assumed to lie between the gas phase of 0.135 (Ref. 41) and the ice values which range between approximately 0.100 and 0.134, depending on the structure of the ice. The current results do not support this assumption. The effects

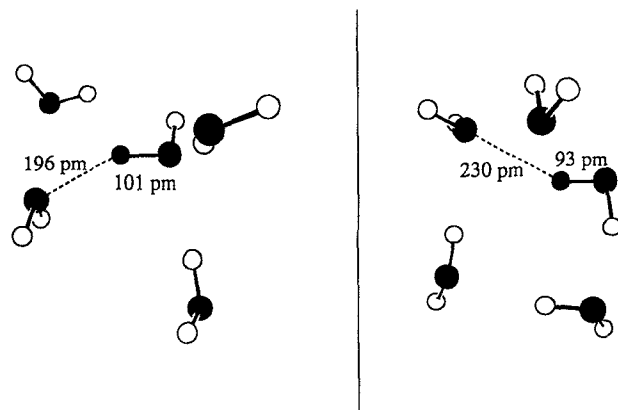


FIG. 2. Snapshots from a molecular-dynamics simulation of liquid water at 300 K which give extreme values of the quadrupole coupling constant. The deuterium for which the constant was calculated is painted black. The configuration on the left gives a quadrupole coupling constant of 180 kHz, and that on the right 373 kHz.

are not due to the basis set as SCF calculations on H<sub>2</sub>O in the gas phase yielded a value of 0.145,<sup>6</sup> which is lower than the liquid-phase value of  $0.164 \pm 0.003$ . Therefore, this has to be taken as a new finding. It would be very interesting if it could be confirmed experimentally.

The QCC at the D varies greatly for different snapshots. At 300 K the values range from 373 kHz, which is greater than the gas-phase value of approximately  $307.9 \pm 0.1$  kHz,<sup>41</sup> to 180 kHz, which is below the value for normal ice, *Ih* [ $213.4 \pm 0.3$  kHz (Ref. 19)]. This very large range is due to the wide variation of configurations in the liquid.

Figure 2 shows two configurations which were generated in the molecular-dynamics simulation.

The configuration on the left-hand side gave the lowest QCC from the set of 82 snapshots, while that on the right-hand side gave the highest value. It is clear that the deuterium of interest is strongly hydrogen bonded to the neighboring molecule in the configuration on the left, whereas in that on the right, the closest oxygen is 231 pm away. Moreover, the intramolecular O–D bonds of the deuterium of interest in both of the configurations are substantially distorted from their equilibrium values. The  $r_{OD}$  for the configuration on the left is similar to that observed in *Ih*, while 93 pm is lower than the equilibrium gas-phase value.

The influence of the monomer geometry and hydrogen bonding on the deuterium QCC has been considered in previous theoretical (Refs. 5, 16, 22, and 42–48, and references therein), and experimental (Refs. 15, 49, 50, 20, 21, 51, and 52, and references therein) studies. It has been found that the length of the bond between the deuterium of interest and the oxygen atom of the same molecule ( $r_{OD}$ ) has a strong effect on the QCC, while the intramolecular D–O–D' bond angle has only a small effect. An influence of the distance of the closest oxygen to the deuterium of interest ( $r_{O...D}$ ) has been observed in the experimental studies and in theoretical studies on clusters.

These effects are evident in our data. That is, there is a strong dependence of the quadrupole coupling on  $r_{OD}$  and  $r_{O...D}$  and a weak dependence on the intramolecular D–O–D angle. In some of the studies mentioned above, the QCC was expressed as a function of geometric parameters using fits to experimental and/or theoretical data.<sup>6,15,43,49,45,46,51,52</sup> In most cases, the QCC is expressed as a function of a single intermolecular distance.<sup>43,45,49,51,52</sup> That is,

$$\text{QCC} = f(r_{X...Y}), \quad (3)$$

where  $r_{X...Y}$  is  $r_{O...D}$  or  $r_{O...O}$ . Relationships of this type fail in representing our data for individual configurations as the relationships are determined using data from equilibrium structures, which show strong correlation between  $r_{OD}$  and  $r_{X...Y}$ . Our data for individual snapshots show no correlation between  $r_{OD}$  and  $r_{X...Y}$ , and therefore an additional term which accounts for the strong correlation between the QCC and  $r_{OD}$  must be included in the relationship. Struis, DeBleijser, and Leyte<sup>15</sup> used *ab initio* and experimental data of hydrogen-bonded molecules to express the QCC as a function of  $r_{OD}$ . This relationship was more successful in representing our data, giving a RMS deviation of predicted from observed data of 14.0 kHz. However, this model does not treat intermolecular effects explicitly.

With use of the data from the 82 snapshots at 300 K, it was found that the QCCs of individual configurations could be represented by

$$\text{QCC}(\text{kHz}) = c_1[r_{OD}(\text{pm}) - c_2]^{-3} + c_3[r_{O...D}(\text{pm})]^{-3}, \quad (4)$$

where  $c_1 = (2.20 \pm 0.13) \times 10^7$ ,  $c_2 = 54.5 \pm 0.8$ , and  $c_3 = (-2.06 \pm 0.16) \times 10^8$ . This relationship gave an rms deviation of 5.7 kHz, was able to reproduce the mean QCC within the limits of error, and gave a value for the gas phase of 315 kHz which agrees with the value determined using SCF calculations of 316.1 kHz.<sup>6</sup> In contrast to previous models, this model gives the correct physical behavior as  $r_{OD}$  and  $r_{O...D}$  become large. However, it gives a value for the QCC in ice *Ih* which is 30 kHz lower than the experimental result. With use of the experimental geometry for an ice pentamer, an SCF calculation of the QCC gave a result which is in agreement with that determined using our model, showing that this underestimation is not an error in the model. The underestimation of the calculated QCC for ice *Ih* is discussed by Davidson and Morokuma.<sup>22</sup>

The derivatives of the electric-field gradient are of interest for vibration and rovibration coupling corrections in liquid-crystal NMR. With use of Eq. (4), the first derivative of the QCC with respect to  $r_{OD}$  is  $-22.9 \text{ kHz pm}^{-1}$  and the second derivative is  $2.2 \text{ kHz pm}^{-2}$ , which is in good agreement with the values of  $-21.79 \text{ kHz pm}^{-1}$  and  $1.37 \text{ kHz pm}^{-2}$  determined from SCF calculations on the monomer.<sup>53</sup> Hence, Eq. (4) gives an accurate model for the QCC in the liquid and gas phase.

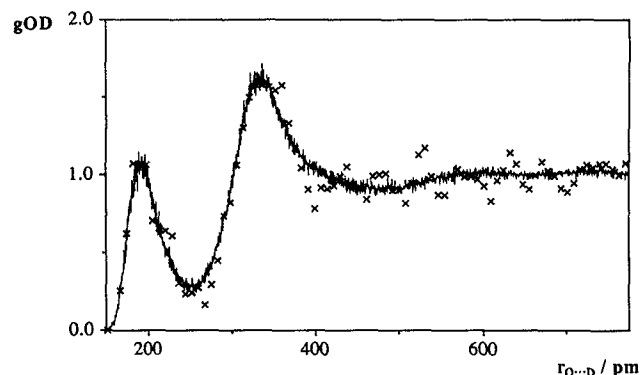


FIG. 3. Oxygen–deuterium intermolecular distribution function,  $g_{OD}(r)$ . The function represented by a line was determined using a 10 000 step molecular-dynamics simulation at 300 K. The points (x) show a histogram using only the 82 deuterium atoms selected for calculation of the QCC.

By zeroing  $c_3$  in Eq. (4), and recalculating the QCC using  $r_{OD}$  for the 82 deuterium atoms considered at 300 K, an indication of the relative contributions of the distortions of the monomer geometry and the hydrogen bonding to the change in QCC from the gas to the liquid phase can be determined. A QCC of  $280 \pm 4 \text{ kHz}$  is obtained. That is, approximately 60% of the reduction in the QCC is due to changes in the monomer geometry.

In order to assure that the 82 randomly chosen configurations were representative of those generated in the entire simulation, the O–D radial distribution function,  $g_{OD}(r)$ , for the 82 snapshots was compared with that for the complete equilibrium simulation. Figure 3 compares the intermolecular  $g_{OD}(r)$  at 300 K.

It is evident from the figure that the sample is representative of the configurations.

A further confirmation of this is given in Table I. The QCCs predicted using Eq. (4) are shown in column 5 calculated with the configurations of the 82 selected deuterium atoms and in column 6 with all the deuterium atoms in each of the snapshots. At each temperature, the agreement with the *ab initio* calculated value is excellent and it is easily seen that the sample of the 82 deuteriums (column 5) gives within the error limits the same QCC's as using all deuteriums (column 6).

From the results of the *ab initio* calculations given in Table I, no clear temperature dependence of the QCC can be observed. However, the error in the QCC's using all deuteriums (column 6) is sufficiently small to see a slight increase with temperature. A linear regression indicates a positive slope of  $0.037 \text{ kHz/K}$ , which is significantly different from zero using 95% confidence limits.

The differences between the gas-, liquid-, and solid-phase QCC can be explained in terms of changes in structure, particularly the changes in  $r_{OD}$ . The  $r_{OD}$  increases by up to 5 pm with a change from gas to solid (depending on the structure of the ice), and is accompanied by the formation of hydrogen bonds. These trends cause a decrease in the QCC. However,  $r_{OD}$  and  $r_{O...D}$  do not vary greatly

with a change in temperature of the liquid. The molecular-dynamics simulations of Reimers and Watts<sup>54</sup> show that  $r_{OD}$  changes by only 0.2 pm with a temperature change of 77 K, and a neutron-diffraction study by Ichikawa *et al.*<sup>55</sup> show no temperature dependence of  $r_{OD}$ , within experimental error, between 298 and 473 K. Experimental studies have determined the intermolecular radial distribution functions at various temperatures.<sup>56,57</sup> The hydrogen-bond distribution is found to broaden with an increase in temperature and the position of the maxima in the O–O distribution function increases by approximately 4 pm with a 77 K increase in temperature.<sup>57</sup> Examination of the radial distribution functions obtained in this work also shows significant broadening over the temperature range examined, but little change in the position of the maxima due to hydrogen bonding. The small temperature dependence of QCC in liquid water is consistent with these structural changes.

Comparison of the radial distribution functions generated using molecular dynamics with various model potentials and with experimental curves show some discrepancies.<sup>58</sup> Calculation of the QCC using various potential models is in progress and will show the sensitivity of the QCC to these differences. Preliminary results using the DP potential are given in Table I and indicate that the QCC is not highly sensitive to the potential.

#### IV. CONCLUSIONS

Using theoretical methods, it is possible to calculate the deuterium QCC in liquid heavy water with a similar precision as can be obtained from experiment. The calculated value of  $256 \pm 5$  kHz is in agreement with experimental measurements. In addition, the asymmetry parameter (which is yet to be determined experimentally) was calculated to be  $0.164 \pm 0.003$ . Although it is often assumed that the asymmetry parameter in the liquid phase would be between that in the gas and solid phase, this value is larger than both of these.

A function which expresses the QCC in terms of  $r_{OD}$  and  $r_{O...D}$  was developed. The function was obtained by fitting data from the SCF calculations of the QCC for liquid configurations at 300 K. It was able to accurately determine the QCC for temperatures from 260 to 359 K.

With use of the 82 *ab initio* calculations no temperature dependence of the QCC was observed. That is, the variation in the QCC with change in temperature from 260 to 360 K was less than the statistical errors of the QCC. However, using the model function to predict the QCC at a large number of configurations, a small temperature dependence was found. In order to assess whether a real temperature dependence exists it is necessary to reduce the statistical error in the results by considering more liquid configurations in the *ab initio* calculations.

Although the LC *ab initio* water potential is a suitable model for many properties, it has a number of deficiencies. For example, the simulated pressure is much greater than the empirical value, the dimer binding energy is too high, and the radial distribution functions show some differences to those obtained experimentally. In order to obtain more

accurate values for the QCC, more accurate *ab initio* or empirical potentials should be used. Further studies on liquid water are underway in order to determine the influence of the potential-energy surface and molecular-dynamics parameters on the QCC.

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