Calculations of ^{14}N and ^{2}H Nuclear Quadrupolar Coupling Constants for Liquid Ammonia

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Nitrogen (^{14}N) and deuterium (^{2}H) nuclear quadrupolar coupling constants, $\chi(^{14}N)$ and $\chi(^{2}H)$, have been calculated for liquid ammonia at 197 K, 232 K, and 271 K, using a combination of molecular dynamics simulations and *ab initio* molecular orbital calculations. The basis set and cluster size dependence of the calculated results has been examined. The calculated value of $\chi(^{14}N)$ for liquid ammonia at 197 K, −3.45 MHz, is found to be close to the accepted solid-state value. At 232 K and 271 K, the magnitudes of the calculated values are about 5–10% greater: −3.56 MHz and −3.67 MHz, respectively, but still well below the accepted gas-phase value, −4.09 MHz. The calculated values of $\chi(^{2}H)$ for liquid ammonia are by about 20% smaller than the corresponding values calculated for the gas-phase monomer. On the basis of the calculations presented here and those of previous workers it is clear that the accepted experimental value of $\chi(^{2}H)$ for solid ammonia-d_3 is too small.

1. Introduction

Nitrogen and deuterium nuclear quadrupolar coupling constants (QCCs) are available for isolated ammonia molecules from gas-phase microwave spectroscopy. The generally accepted experimental values are: $\chi(^{14}N) = -4.09$ MHz [1] and $\chi(^{2}H) = 290.6$ kHz [2]. From an ^{14}N nuclear quadrupole resonance (NQR) study [3] of solid ammonia and ammonia-d_3, the corresponding experimental ^{14}N QCCs are: $\chi(^{14}N) = -3.45$ MHz for NH_3 and $\chi(^{14}N) = -3.43$ MHz for ND_3 [4]. These solid-state values have been obtained by extrapolating the experimental values to 0 K [3, 4]. The ^{2}H QCC for solid ammonia is usually taken as 156 ± 7 kHz, based on ^{2}H NMR measurements at 75 K [5]. Unfortunately, there is no technique which directly provides QCC values in the liquid state [6]. In some cases it is possible to obtain estimates from NMR data. For example, in the case of ammonia a crude estimate of $\chi(^{2}H)$, 208 ± 21 kHz, is available from ^{1}H, ^{2}H, and ^{14}N NMR relaxation data [7]. Here we illustrate the combined application of molecular dynamics (MD) simulations and *ab initio* molecular orbital (MO) calculations to determine ^{14}N and ^{2}H QCC values for liquid ammonia. A similar approach has recently been applied to study ^{2}H and ^{17}O QCC values in liquid water [8–11].

In addition to providing more reliable liquid-state QCCs for liquid ammonia, our results permit us to comment on the commonly accepted experimental $\chi(^{2}H)$ values for gaseous and solid ND_3. In particular, reasons for the apparent ≈45% decrease of the ^{2}H QCC of ND_3 on going from the gas phase to the solid state are discussed.

2. Background

2.1 Nuclear Quadrupolar Coupling Constants

The QCC for a quadrupolar nucleus N in a molecule is defined by

$$\chi(N) = eQ(N)\, eq(N)/h, \tag{1}$$

where $eQ(N)$ is the nuclear quadrupole moment of the quadrupolar nucleus (spin $I \geq 1$) and $eq(N)$ is the largest principal component of the electric field gradient (EFG) tensor at the site of the quadrupolar nucleus [12–14]. For any given isotope eQ is a constant [15]; therefore molecular structural information available from the QCC is contained entirely in the EFG term. The EFG is defined as the second spatial derivative of the electric potential V at a specific point in space, the obvious choice being the nucleus of interest. In the so-called principal axis system, the EFG tensor be-

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comes diagonal with the largest principal component being defined as follows

$$q_{zz} = \frac{\partial^2 V}{\partial z^2}\,. \tag{2}$$

The other diagonal components (i.e., q_{xx} and q_{yy}) are defined in an analogous way. The diagonal elements are ordered according to $|q_{zz}| \geq |q_{yy}| \geq |q_{xx}|$. The EFG tensor is traceless, and therefore only two of the diagonal elements are independent. Conventionally, the two independent quantities are expressed as $eq(\equiv eq_{zz})$ and η, the asymmetry parameter:

$$\eta = \frac{q_{xx} - q_{yy}}{q_{zz}}\,. \tag{3}$$

The asymmetry parameter η $(0 \leq \eta \leq 1)$ is a measure of the deviation of the EFG tensor from axial symmetry.

In the gas phase, the EFG at a nucleus in a molecule is generally entirely of intramolecular origin, while in solids and liquids intermolecular interactions may have a substantial influence on the observed EFG.

Microwave spectroscopy is the standard method of determining nuclear QCCs in small molecules in the gas phase [12]. Unfortunately the experimental quantities are determined in the inertial frame of the molecule. For solids, nuclear quadrupole resonance (NQR) is generally used for measuring QCCs [14]; however solid-state NMR techniques can also be used [16]. In liquids and orientationally disordered solids, it is sometimes possible to determine QCCs from NMR T_1 relaxation data. The various experimental approaches available for determining QCC values in liquids have recently been reviewed [6, 17]. QCC values determined in liquids are generally associated with large uncertainties because of numerous questionable assumptions [6].

The problem of determining nuclear QCC values for molecules in liquid samples is most difficult in cases where there are strong intermolecular interactions such as hydrogen bonding [6]. It has been suggested that gas-to-solid or gas-to-liquid shifts in QCC values could be used as a measure of the degree of hydrogen bonding in such systems [18].

2.2 *Ammonia*

The normal boiling and freezing points of liquid NH_3 (ND_3) are 239.6 K (242.0 K) and 195.4 K (199.6 K), respectively [19]. The relatively high boiling points of the first-row hydrides, NH_3, H_2O, and HF, compared to their second-row analogues, PH_3, H_2S, and HCl, are usually taken as evidence that hydrogen bonding is important for the first-row hydrides. However, the question of whether or not the structure of liquid ammonia is dominated by hydrogen bonding, as in the case of liquid water, is still disputed in the literature. For example, in the liquid state a water molecule typically has 4–5 nearest neighbors whereas in liquid ammonia each molecule may have as many as 12 neighbors in the first solvation sphere. Also, significantly different radial distribution functions are found for water and ammonia from small-angle X-ray and neutron diffraction [20] and computer simulations [21, 22]. The large coordination number of ammonia, in contrast to that of water, has been interpreted as evidence for a lack of a strong hydrogen-bonding network in liquid ammonia. On the basis of spectroscopic studies of dimeric species in the gas phase, Klemperer and co-workers [23] have questioned the ability of ammonia to act as a proton donor, while its role as a proton acceptor is clear. However, recent studies of the NH_3–Ar dimer suggest that the hydrogen–argon interaction is attractive [24]. Furthermore, in the latter study it was suggested that the interpretation of Klemperer is flawed.

2.3 *Experimental ^{14}N and ^{2}H Nuclear QCCs for Ammonia*

Nitrogen-14: In the gas phase, $\chi(^{14}N)$ has been measured for several isotopomers of ammonia in a variety of rotational states. The experimental values are relatively independent of the isotopomer and the rotational state, $\chi(^{14}N) = -4.09 \pm 0.02$ MHz [1]; however, in the case of NT_3, $\chi(^{14}N) = -4.17 \pm 0.05$ MHz [25]. From NQR studies of solid samples at 77 K, the apparent ^{14}N QCC values for NH_3 and ND_3 are -3.161 MHz and -3.231 MHz, respectively [3]. It should be stressed that the solid-state values are only meaningful if the molecules are rigid. Any molecular motion will tend to reduce the magnitude of a QCC measured by NQR or NMR. In fact, even at 0 K the zero-point motion will decrease the QCC value. Using variable-temperature NQR data and the theory of Bayer [26], Lehrer and O'Konski [3] estimated the QCC values for NH_3 and ND_3 without zero-point vibrations. These static values were found to be -3.48 MHz and -3.46 MHz for NH_3 and ND_3, respectively. Recently, Cummins et al. [4] reanalyzed the temperature dependence of the ^{14}N NQR frequencies reported by Lehrer and O'Konski and obtained static $\chi(^{14}N)$ values of -3.45 MHz and -3.43 MHz for NH_3 and ND_3, respectively. Thus, the gas-to-solid shift in the ^{14}N QCCs is about 15%. This relatively large shift, attributed mainly to hydrogen bonding, can be compared to the corresponding 30% change in $\chi(^{17}O)$ observed for water [6]. An experimental value of $\chi(^{14}N)$ in liquid ammonia is unavailable; however, it has been assumed to be the same as that in the solid state [7].

Deuterium: The nuclear quadrupolar coupling constant for ^{2}H in gaseous ammonia is reported as 282 ± 12 kHz [27] and 290.6 ± 0.7 kHz [2]. These values are based on the assumption that the ^{2}H EFG tensor is axially symmetric. On the basis of more recent experiments [28] and *ab initio* MO calculations [29] the EFG is not axially symmetric. As well, the calculations indicate that the accepted experimental values of the QCC are upper limits (*vide infra*). It must be emphasized that experimentally the diagonal components of the quadrupolar tensor are only known in the inertial reference frame. From ^{2}H NMR measurements on solid ammonia-d$_3$ at 75 K, Rabideau and Waldstein reported $\chi(^2H) = 156 \pm 7$ kHz [5]. Although it has been assumed that the reported value at 75 K represents the rigid-lattice value, this is not supported by the present study (*vide infra*). Cummins et al. [4] find that the gas-to-solid shift for $\chi(^2H)$ can in part be explained as a result of the increased N–H bond length in the solid compared to the gas. The N–H bond length in the gas phase is 1.012 Å [30], while it is found to be 1.06 Å in the solid based on neutron diffraction data [31]. The 5% increase in the bond length was attributed to hydrogen bonding in the solid state. The HNH bond angle of ammonia is virtually identical in the gas and solid states.

Several attempts have been made to obtain an estimate of $\chi(^2H)$ for liquid ammonia [32, 33]. The most recent value, $\chi(^2H) = 208 \pm 21$ kHz [7], was obtained from ^{2}H and ^{14}N NMR relaxation data on liquid ammonia. In this latter study it was assumed that the ^{14}N QCC is the same in solid and liquid ammonia.

2.4 Calculation of Electric Field Gradients

Obviously, when a value for the nuclear quadrupole moment is available, theoretical values for nuclear QCCs can be determined from quantum mechanical calculations of EFGs at the position of the quadrupolar nucleus. The results of calculations on single molecules are generally compared to experimental gas-phase values. Solid-state values can be obtained by quantum mechanical cluster calculations [34] based on crystallographical arrangements of molecules or using computational schemes [34] specifically designed to make use of the periodicity in crystals to produce results corresponding to bulk material [35, 36].

Palmer and coworkers have systematically studied ^{14}N QCCs for individual molecules [37] and for small clusters of molecules taken from the known crystal structure [38]. Cummings and coworkers have also studied the effects of intermolecular interactions on EFGs [4, 39, 40].

Ab initio MO calculations of nuclear QCCs using carefully optimized basis sets have been reported by Huber and coworkers during the last 10 years [41–46]. The basis sets used in these studies are specially tailored to be flexible around the nuclei at which the EFGs are calculated. For example, much larger basis sets are used for the hydrogens than are normally used in energy calculations.

Quite recently a promising approach to calculate QCCs in liquids was presented by Huber et al. [8–11]. The approach is analogous to earlier cluster calculations in which a test molecule is taken with its nearest neighbors from the crystal lattice configuration; a number of randomly chosen computer simulated configurations of molecules are given as input to a series of quantum mechanical calculations to give a statistical mean value corresponding to a liquid state value [39]. Calculated QCCs for ^{2}H and ^{17}O in water based on MD simulations of liquid water appear to be in agreement with previously reported experimental values [8–11].

In the present work we report the calculations of ^{14}N and ^{2}H nuclear QCCs for liquid ND_3 by combining MD simulations and *ab initio* MO calculations. Our objective is to study: i) the basis set dependence, ii) the effect of cluster size in terms of the number of nearest neighbors and iii) the effect of temperature on the calculated nuclear quadrupolar coupling constants.

3. Computational Methods

3.1 Molecular Dynamics Simulations

A series of MD simulations was carried out for liquid deuterated ammonia at 197 K ($V_m = 23.28 \times 10^{-6}$ m^3/mol), 232 K ($V_m = 24.80 \times 10^{-6}$ m^3/mol) and 271 K ($V_m = 26.50 \times 10^{-6}$ m^3/mol). The ammonia was modeled flexible by placing a harmonic force field on an experimental gas phase geometry to mimic the stretching and bending motion of the bonds and covalent angles, respectively. The bond stretching force constant was taken as 1578.6 kJ mol^{-1} Å^{-2}, the equilibrium N–H bond length as 1.0124 Å, while the angle bending force constant was taken as 195.3 kJ mol^{-1} degree^{-2} and the equilibrium H–N–H bond angle as 106.67° [30].

The intermolecular interactions were described through Lennard-Jones type potentials on the nitrogen atom with the depth of the potential well: $\varepsilon(\mathrm{N}) = 1.849$ kJ/mol and the collision radius $\sigma(\mathrm{N}) = 3.40$ Å [47]. The electrostatic interactions were described by placing a fractional charge $q = +0.3092\,|e|$ at the deuterons and $-3q$ at the nitrogen. The charges were taken from work by K. P. Sagarik et al. [48]. This charge distribution gives an electric dipole moment of 1.70 D, about 15% larger than the experimental gas phase value, 1.47 D [49].

The number of flexible ammonia molecules in a cubic cell was 256 and periodic boundaries and the minimum image convention were used to maintain the constant density in an NVT ensemble. The Nose-Hoover thermostat was used to keep the temperature constant [50, 51] and the Ewald summation method was applied to treat the long-range electrostatic interactions [52]. As the integration scheme, the two-time-step algorithm of Tuckerman et al. [53] was used. The short time step, 0.05 fs, was used for the bond stretching and angle bending. The long time step is 1.0 fs and was used for the rest of the dynamics.

Before the production run at each of the three temperatures, the liquid ammonia was equilibrated for 100 ps. During the production runs one ammonia molecule was chosen randomly after every tenth time step. A specified number (a parameter whose optimum value was searched during the simulation by increasing it successively) of nearest neighbors was selected, and the coordinates of the cluster were used as an input to a quantum mechanical program to calculate the EFGs. While the EFGs were calculated, the MD program stopped and waited for the results. The EFG tensor elements were accumulated as running averages before diagonalization. The calculations were terminated when the largest component of the diagonal elements converged. Typically, about 200–300 EFG calculations for randomly chosen configurations were required to obtain mean values fluctuating by less than 1%.

A series of calculations was carried out by varying basis sets, cluster size and temperature, as will be discussed below. The cluster size was assumed to be adequate (converged) when the EFGs did not change with a further increase in cluster size (*vide infra*). All the calculations were carried out on an IBM RISC 6000/580 workstation at the Chemistry Department of Dalhousie University. The MD simulation program package is a modified version of McMoldyn [54].

3.2 Quantum Mechanical Calculations

All of the *ab initio* calculations were carried out using a workstation version of the Gaussian 92 package [55]. The EFG tensors were calculated and diagonalized to give the principal components. The basis set size was successively increased from 3-21G* to 6-31G** and the calculations were taken beyond the HF level by means of MP2 calculations.

4. Results and Discussion

A large number of computer simulations have been reported for liquid ammonia in the literature [21, 22, 47, 48, 56, 57]. Therefore, we do not present an analysis of various liquid properties of ammonia based on our simulation results since they are essentially the same as reported in previous studies.

The simulated internal energies in our simulations were -19.5 ± 0.5, -26.1 ± 0.8, and -27.2 ± 0.8 kJ/mol at 271 K, 232 K, and 197 K, respectively. Since the geometry of ammonia was rendered flexible by means of the harmonic intramolecular force field, the dipole moment was monitored during the simulation. The average values were 1.78 ± 0.30, 1.81 ± 0.33, and 1.82 ± 0.36 D at 271 K, 232 K, and 197 K, respectively. A small nuclear polarization which resulted from using the flexible model caused a small effective decrease in the HNH angles.

The procedure for calculating liquid-state QCCs as described in the previous Section has the advantage of allowing the molecules to become deformed as a result of both the intermolecular interactions and the thermal motion at the specified physical conditions. In the present work, experimental densities [58] are applied although the effect of pressure on QCC values could also be investigated using MD simulations.

4.1 Nitrogen-14 Quadrupolar Coupling Constants

A series of single molecule calculations was carried out first to investigate the basis set effects. The results of these calculations are found in the first column of Table 1. Also included in Table 1 are the "Hartree-Fock limit" value and the value from a large scale CI calculation [59]. The gas-phase value, $\chi(^{14}N) = -4.0924$ MHz [1], and the CI value are used to give a value for the nitrogen nuclear quadrupole moment in the same manner as was done by Ha [59]. The value obtained, $eQ = 20.8$ mbarn, was used to convert the calculated EFG values at nitrogen to ^{14}N quadrupolar coupling constants.

The extended CI calculations of Ha and our single-molecule calculations up to the MP2 level were carried out using the experimental gas-phase geometry for ammonia with the N–H bond length of 1.012 Å and the H–N–H angle of 106.7°. No vibrational corrections were applied to the results. Grigolini and Moccia [60] have performed ^{14}N EFG calculations on ammonia with vibrational averaging at the Hartree-Fock limit using good quality wave functions. Vibrational averaging was found to reduce the ^{14}N EFG by approximately 1.8%.

Four columns of Table 1 contain calculated ^{14}N QCCs for the test molecule in the center of a cluster of 5, 7, 9 or 11 molecules at 271 K, taken from the MD simulations as described in the previous Section. The results show a clear convergence close to a cluster size of around 10 for all the basis sets used. The calculations beyond the Hartree-Fock level were carried out using the second order Møller-Plesset perturbation scheme. The gap between the MP2 results and the results from a full CI is extrapolated based on single-particle results. The extrapolated estimate is −3.67 MHz for the liquid-state ^{14}N QCC at 271 K. Similarly, the extrapolated value at 232 K for the largest cluster size is −3.56 MHz. The calculations were also repeated at the lowest temperature, 197 K, using the largest cluster size ($N = 11$). An estimated value of −3.43 MHz was obtained after a similar extrapolation, which is in excellent agreement with the solid-state value.

4.2 Deuterium Quadrupolar Coupling Constants

Calculated values of the deuterium nuclear quadrupolar coupling constants for ND_3 are given in Table 2. In addition to being positive and smaller in magnitude, the theoretical ^{2}H QCC values are relatively insensitive to the size of the basis set. Also, the effect from the electron correlation seems to be small, at least at the MP2 level. As well, the calculated ^{2}H QCCs are essentially independent of temperature.

Finally, included in Table 2 are values from two single-molecule calculations, performed at a higher level of approximation. The result, $\chi(^{2}H) = 283.3$ kHz, of Cummins et al. [4, 61], was obtained at the CI level with all of the singlet and doublet excitations included. The other result reported by Gerber and Huber [29], $\chi(^{2}H) = 252.5$ kHz, was obtained using the

Table 1. Nitrogen-14 quadrupolar coupling constants (MHz) for ammonia.

	Gas	271 K	271 K	271 K	271 K	232 K	197 K	Solid
Cluster Size:	1	5	7	9	11	11	11	
Basis Sets:								
3-21 G**	−5.18	−4.80	−4.73	−4.69	−4.69			
6-31 G	−4.98	−4.72	−4.67	−4.60	−4.62		−4.47	
6-31 G*	−4.72	−4.49	−4.38	−4.35	−4.36		−4.27	
6-31 G**	−4.67	−4.43	−4.34	−4.32	−4.32		−4.27	
"HF-LIMIT"	−4.31 [a]							
6-31 G/MP2	−4.52				−4.20	−3.96	−3.90	
6-31 G*/MP2	−4.28				−3.83	−3.72	−3.55	
6-31 G**/MP2	−4.25				−3.78	−3.67	−3.54	
CI	−4.092 [a, b]				−3.67 [c]	−3.56 [c]	−3.43 [c]	
Exp.	−4.092							−3.45

[a] T.-K. Ha, Z. Naturforsch. **41a,** 163 (1985); [b] $eQ(^{14}N) = 20.8$ mbarn; [c] Extrapolated value.

Table 2. Deuterium quadrupolar coupling constants (kHz) for ammonia.[1]

	Gas	271 K	271 K	271 K	271 K	232 K	197 K	Solid
Cluster Size:	1	5	7	9	11	11	11	
Basis Sets:								
3-21 G**	370	305	290	290	290			
6-31 G	352	290	290	292	288		288	
6-31 G*	324	266	264	265	266		264	
6-31 G**	321	267	263	264	263		260	
6-31 G/MP2	346				288	286	285	
6-31 G*/MP2	322				264	262	259	
6-31 G**/MP2	317				264	260	255	
MP4(SDQ)[a]	252.5							
CI[b]	283.3							
Exp.	282[c]				245[e]			156[g]
	290.6[d]				208[f]			

[1] $eQ(^2H) = 0.286$ mbarn.

[a] Gerber and Huber, J. Mol. Spectrosc. **134,** 168 (1989); extended basis set on hydrogens.

[b] Cummins et al., Chem. Phys. **115,** 325 (1987); [4, 3, 1/2, 1], CI (SD).

[c] Thaddeus et al., J. Chem. Phys. **41,** 1542 (1964). This value is an upper limit; see text and Ref. [28, 29, and 43].

[d] Kukolich, J. Chem. Phys. **49,** 5523 (1968). Again, this value is an upper limit; see text and Ref. [28, 29, and 43].

[e] Powles and Rhodes, Mol. Phys. **12,** 399 (1967); (liquid $T < 300$ K).

[f] Hauer et al., Ber. Bunsenges. Phys. Chem. **83,** 1262 (1979); (liquid $T < 300$ K).

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Møller-Plesset scheme up to fourth order and using a very large basis set on the hydrogen (up to *f*-functions). The result of Cummins et al. [4, 61] is very close to the early experimental gas phase values, 282 kHz and 290.3 kHz, while the result by Gerber and Huber is somewhat below these values. However, it should be noted that the ^2H EFG tensor components (in the inertial reference frame) calculated by Huber [43] and by Gerber and Huber [29] are in excellent agreement with the more recent experimental data of Cederberg [28].

Our observation was that inclusion of electron correlation (by means of the MP2 method) did not have a particularly large effect on the EFG values at the hydrogens. This also seems to be the conclusion by Cummins et al. [61], whose results did not change very much after going beyond the Hartree-Fock level.

For the isolated ammonia molecule, the value of $\chi(^2H)$ calculated using 6-31 G**/MP2, 317 kHz, is about 10% greater than the value calculated with larger basis sets and CI. The excellent agreement between observed [28] and calculated [29, 43] ^2H EFG tensor components in the inertial frame of reference suggests that the accepted experimental value of $\chi(^2H)$, 290.6 kHz, is too large. It should be noted that the experimental value was obtained by assuming the EFG tensor is axially symmetric. Both theory and more recent experiments indicate that this is not the case. In fact, the most recent calculations yield $\eta = 0.15$. Clearly, high-level MO calculations which attempt to include the effects of vibrational averaging would help clarify the situation.

In the case of the present study, it is sufficient to discuss the calculated changes in $\chi(^2H)$. On going from the gas phase to the liquid state, the reduction in the ^2H QCC is 17% at 271 K and 20% at 197 K. Calculations on an ammonia cluster, $(NH_3)_4$, by Cummins et al. [4], indicate a decrease of 28% in the value of $\chi(^2H)$ on going from the gas phase to the solid state. It is interesting to note that if the N–H bond length in the solid cluster was assumed to be the same as that in the gas phase, 1.012 Å, the calculated gas-to-solid shift was only 3.7%.

If one takes $\chi(^2H)$ of an isolated ammonia molecule as ≈ 265 kHz, the calculated liquid and solid-state values are ≈ 215 kHz and ≈ 190 kHz based on the calculations in Table 2 and [4], respectively. The results strongly suggest that the accepted solid-state value for $\chi(^2H)$, 156 ± 7 kHz, is much too small. The experimental value was obtained from ^2H NMR measurements at 75 K. At this temperature, the ammonia molecule is not static; hence, the reported value is a partially motionally averaged value. In fact, the "unexplained" central feature observed in the ^2H NMR spectrum at 75 K is almost certainly the result of molecular motion. Clearly, a low-temperature ^{2}H NMR study of solid ammonia is warranted.

Asymmetry parameters can be calculated from our results using (3). This value appears to be relatively insensitive to any variation of basis sets, methods, cluster sizes or temperature. The value of $\eta = 0.13 \pm 0.01$ throughout the calculations is close to the value 0.14, reported by Gerber and Huber [29].

5. Conclusions

Liquid-state values for ^{14}N and ^{2}H quadrupolar coupling constants in liquid ammonia-d$_3$ have been calculated using a combined scheme of MD simulations and *ab initio* MO calculations. The method is straightforward and the computational effort does not exceed the capacity of the now available fast workstations. Our calculations and the similar calculations by Eggenberger et al. [8–10] clearly show that MD simulations in combination with *ab initio* MO calculations provide a reliable method of calculating liquid-state nuclear quadrupolar coupling constants. This is particularly valuable in cases where there is a large difference between the experimental gas-phase and solid-state values. Also, variations in QCC values with temperature, as predicted here for $\chi(^{14}\text{N})$ in liquid ammonia, can be examined using MD simulations and *ab initio* MO calculations. In principle, the MD simulations could also be used in combination with *ab initio* MO calculations to predict gas-to-liquid shifts in nuclear magnetic shielding constants [62, 63].

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