Polarizability of the nitrate anion and its solvation at the air/water interface

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1. Introduction

The nitrate anion belongs together with sulfate, bisulfate, and chloride to the most abundant ions in the atmosphere. It can be found in atmospheric aerosols both in the polluted and remote troposphere, and it plays an important role in many atmospheric chemical processes. It has been shown recently that the chemistry of these ions in aqueous aerosols can strongly depend on their location, either in the bulk or at the surface of the aerosol. Molecular dynamics (MD) simulations of halide ions in large aqueous clusters and in water slabs clearly showed that it is the value of the anionic polarizability which determines bulk vs. surface solvation. While hard, non-polarizable ions such as fluoride solvate in the aqueous bulk, all the heavier halides, which have a large value of polarizability, are predicted to have a significant propensity for the extended air/water interface. As a matter of fact, bromide and iodide even behave as surfactants with a larger concentration at the surface than in the bulk.

Since polarizability plays a crucial role in aqueous solvations, we attempted to determine accurately its value for two prominent atmospheric anions—chloride and sulfate. We used a combination of quantum chemistry and the Atoms in Molecules theory. Aqueous solvation of NO$_3^-$ in interfacial environments is investigated by a Car–Parrinello molecular dynamics simulation of a cluster, and classical molecular dynamics of an extended slab system with bulk interfaces using a polarizable force field based on the Atoms in Molecules analysis. Both in aqueous clusters and in systems with extended interfaces the nitrate anion clearly prefers interfacial over bulk solvation. This is primarily due to its large value of molecular polarizability, the gas phase value of which is reduced by only 5–10% in the aqueous environment. For polarizable force field simulations of ionic solvation, we recommend to cast the NO$_3^-$ polarizability into three equal contributions of roughly 1.3 Å$^3$ placed on the oxygen atoms of the anion.

2. Computational approaches

In both cases that we have investigated previously, i.e., polarizability and aqueous solvation of the Cl$^-$ and SO$_4^{2-}$ species,
the polarizability tensor of the ion was isotropic or almost isotropic.\textsuperscript{10,11} Therefore, it was well justified to employ either a single number (for chloride) or evenly distributed values among the oxygen atoms (for sulfate) to define the polarizability force field for MD simulations. For nitrate anion and, more generally, in the case of non-spherically symmetric ions, we encounter two difficulties. First, the ionic polarizability is not isotropic and, second, the partitioning into atomic contributions may not be straightforward. Empirical polarizable force fields, such as that implemented in the MD program Amber,\textsuperscript{26} work with scalar, isotropic atomic polarizabilities. However, molecular polarizabilities obtained, e.g., via \textit{ab initio} quantum chemical calculations are generally tensors, which reflect the anisotropic response of the whole molecule to an external electric field.

We now address the question of how to best approximate the anisotropic molecular polarizability by a superposition of isotropic atomic contributions. Obviously, the response of a collection of isotropically polarizable atoms to a constant electric field is isotropic, no matter how asymmetric the geometry of the atoms in the molecule might be. However, the electric field created by the water molecules surrounding a molecular ion is far from homogeneous and isotropic. It is shown below, by comparison to accurate \textit{ab initio} calculations, that by properly choosing the values of isotropic atomic polarizabilities in a molecular ion, it is actually possible to faithfully model the ion–water interactions. Note, that in the present case of the nitrate anion, parametrization can be simplified by the fact that the contribution of the nitrogen atom, which bears a partial charge of about +1.1 $e$, to the total polarizability is very small and can, therefore, be neglected. The molecular polarizability of the $\text{NO}_3^-$ ion can thus be evenly distributed among the three equivalent oxygen atoms.

There are several approaches in the literature to derive atomic polarizabilities from the molecular values.\textsuperscript{15,17} In this study we use the AIM theory\textsuperscript{15} to first partition the electron density into atomic domains. For each atom, the atomic polarizability tensor is determined from the change of the atomic dipole moment after the application of an external electric field. Within this approach, the molecular polarizability is then obtained as the sum of the atomic polarizability tensors.

For studies of solvated ions one has to take into account the fact that the polarizability of the ionic species can be significantly reduced in aqueous solutions compared to the gas-phase value. This reduction is connected with the shrinking of the electronic cloud of the anion upon aqueous solvation (note, that polarizability is closely connected with the “volume” of the valence electrons). In order to account for the solvent effect, one can proceed in several different ways. We have recently proposed to determine the ionic polarizability in solution by including in the \textit{ab initio} calculation fractional point charges at the positions of water oxygen and hydrogen atoms.\textsuperscript{10,11} Within this approach, the solvent induced change in ionic polarizability can be determined for clusters, as well as for the aqueous bulk, where we performed averaging over a large number of snapshots from \textit{ab initio} or classical MD simulations.

Previously, a dielectric continuum model to account for the solvation effects on the solute polarizability has been proposed.\textsuperscript{18} Interestingly, results from that study almost coincide with those obtained by computing the solute polarizability in the cluster as the difference between the polarizability of the whole system and that of the solvent.\textsuperscript{18} We can, therefore, validate our point charges approach by evaluating the ratio between the polarizability of the ion in the gas phase and in solution, assuming the additivity of the polarizability and properly taking into account the Basis Set Superposition Error (BSSE).\textsuperscript{19} Finally, the AIM decomposition,\textsuperscript{15} described above for the case of isolated molecular ions, can also be applied to solution in clusters. One can then extract the atomic contributions to the polarizability of the whole the solute ion and the solvent molecules from the total polarizability of the whole system.

3. Computational details

\textit{Ab initio} calculations for the gas phase nitrate anion and for $\text{NO}_3^-$ in small water clusters were performed at the MP2 and B3LYP levels of theory using standard aug-cc-pvzd and aug-cc-pvtz basis sets. For these calculations we employed the Gaussian98 program package.\textsuperscript{20} The AIM polarizability decomposition was carried out using the program PROAIM.\textsuperscript{21}

An \textit{ab initio} MD simulation of a cluster consisting of $\text{NO}_3^-$ and ten water molecules was generated according to the method of Car and Parrinello\textsuperscript{22} with a time step of 0.121 $\text{fs}$ and a fictitious electron mass of 800 au. The electronic structure was computed within the Kohn–Sham formulation of density functional theory\textsuperscript{23} with the BLYP exchange-correlation functional.\textsuperscript{24,25} Only the valence electrons were treated explicitly, with norm-conserving pseudopotentials representing the valence–core interactions.\textsuperscript{26} The Kohn–Sham orbitals were expanded in a plane wave basis set to an energy cutoff of 70 $\text{Ry}$ in a cubic box of edge length 32 $\text{au}$, with cluster boundary conditions.\textsuperscript{27} A 5.1 $\text{ps}$ trajectory was generated, and the second half was used for computing average properties. The average temperature of the ionic cores was 200 $\text{K}$. The charge distribution in the cluster was quantified in terms of anion and water dipole moments, which were computed based on the centers of the maximally localized Wannier orbitals.\textsuperscript{28–32} In addition, for the purpose of discussing the performance of the electronic structure methodology used in the \textit{ab initio} MD simulations, the geometry of the $\text{NO}_3^-$ ($\text{H}_2\text{O})_3$ complex was optimized. The geometry optimization, \textit{ab initio} MD simulation, and localized orbital transformations were performed using the CPMD program.\textsuperscript{33}

Classical MD simulations were performed for an extended slab consisting of a single $\text{NO}_3^-$ anion and 555 water molecules. Initially, the nitrate anion was put on the surface of a well equilibrated aqueous slab. In order to simulate the air–water interface (actually, two interfaces generated by the slab geometry), periodic boundary conditions were employed with one of the dimensions of the periodic box extended to 100 $\text{A}$. The two remaining box dimensions were set to 26.4 $\text{A}$. The polarizable SPC/POL model for water was employed, with internal degrees of freedom constrained using the standard SHAKE algorithm. Lennard-Jones parameters for the N and O atoms of the nitrate anion were taken from ref. 35, while the values of the partial charges $q_N = +0.95 e$ and $q_O = -0.65 e$, atomic polarizability $\alpha_{\text{O}} = 1.3 \text{Å}^3$, and the N–O distance of 1.269 $\text{Å}$ followed from the present \textit{ab initio} calculations. The cutoff for the intermolecular interactions was set to 12 $\text{Å}$, and the long range electrostatic interactions were accounted for by the smooth particle mesh Ewald sum.\textsuperscript{36} The classical MD simulations were run for 0.4 $\text{ns}$ at a constant temperature of 300 $\text{K}$ with a time step of 1 $\text{fs}$. Classical MD simulations were performed using the program Amber.\textsuperscript{3,16}

4. Results

As a first step, the polarizability of the nitrate ion in the gas-phase, with the geometry optimized at the MP2/aug-cc-pvzd level, has been established using MP2 and B3LYP approaches with different basis sets. The results are summarized in Table 1. We see that the MP2 polarizabilities are slightly larger than those obtained using the B3LYP method, however, the results are converged within less than 10% both with respect to the level of theory and basis set. Also note that the anisotropy of the polarizability tensor is sizable. The in-plane ($\alpha_{\perp}$) polarizability is almost twice the out-of-plane ($\alpha_{\parallel}$) polarizability, the mean value (isotropic polarizability) being around 4.9 $\text{Å}^3$. Phys. Chem. Chem. Phys., 2003, 5, 3752–3757 3753
The results of the AIM partitioning of the NO$_3^-$ polarizability based on the B3LYP/aug-cc-pvdz electron density are presented in Table 2. As expected, the isotropic polarizability of the central atom is predicted to be very small and is even negative (−0.04 Å$^3$). The respective contribution of each of the three equivalent O atoms amounts to 1.57 Å$^3$. The anisotropy of the molecular polarizability is translated to the corresponding atomic contributions and they are additive within the numerical accuracy of the AIM procedure.

In a recent study, it has been shown that three water molecules form the first solvation shell around the nitrate anion. 37 Therefore, we took the NO$_3^-$ (H$_2$O)$_3$ cluster as our entry level system for assessing the effect of aqueous solvation on the polarizability of the ion. Our B3LYP/aug-cc-pvdz optimized geometry and interaction energies are in good agreement with the previous results. 37 However, beside this planar structure, we also found a non-planar stationary point of C$_3$ symmetry. In this isomer, displayed in Fig. 1, each of the three water molecules is involved in three hydrogen bonds, one with the oxygen atom of the nitrate anion and two with the other two water molecules. This isomer, which lies only 0.4 kcal mol$^{-1}$ higher in energy than the planar structure, was confirmed to be a true minimum by a frequency calculation.

The anion polarizability within the NO$_3^-$ (H$_2$O)$_3$ cluster was determined in several ways, described in detail in the previous section. First, we computed the total (z$^{\text{tot}}$), solvent (z$^{\text{solv}}$) and solute (z$^{\text{s}}$) polarizabilities for the planar structure at the B3LYP/aug-cc-pvdz level of theory. Note that, since the basis set for the whole cluster is used in the calculation (as in BSSE calculations), z$^{\text{tot}}$ is not exactly equal to the gas phase value given in Table 1. Actually, this value depends on the geometry, i.e., on the position of the ghost orbitals. Hence, only the ratio (z$^{\text{solv}}$ − z$^{\text{tot}}$)/z$^{\text{gas}}$, which for the present system equals 0.956, is a well defined quantity that provides a measure of how much the gas phase polarizability of the ion is reduced upon solvation. Thus, we conclude that in the NO$_3^-$ (H$_2$O)$_3$ cluster the anionic polarizability is reduced by about 5%.

Second, we performed a calculation with water molecules replaced by point charges. The substitution of the water oxygen and hydrogens by fractional point charges of −0.82 e and 0.41 e, 10,11 leads to a value of the NO$_3^-$ isotropic polarizability of 4.43 Å$^3$, which is slightly larger than that of the chloride anion, 10 and about 60% that of the sulfate dianion, 11 in aqueous environments. For the planar minimum, the ratio between this value and the gas phase polarizability (see Table 1) is 0.948, which is very close to the above value of 0.956. For the non-planar C$_3$ isomer the solvent induced reduction of polarizability is slightly smaller, with the polarizability ratio equal to 0.961. The quantitative agreement between the two approaches confirms that the computationally simpler and efficient scheme based on the replacement of water molecules with fractional point charges can be applied for the determination of solute polarizabilities in aqueous systems. The main advantage of this method is that it can be applied to large cluster sizes with a reasonable computational effort. Thus, for MD simulations we have parametrized the polarizable force field for the nitrate ion by assigning the value of 1.49 Å$^3$, i.e., one third of the value of the anionic isotropic polarizability in the C$_3$ symmetric NO$_3^-$ (H$_2$O)$_3$ cluster, to each of the three oxygen atoms. The very small contribution of the nitrogen atom was neglected.

Table 1 Values of parallel, perpendicular and isotropic polarizabilities (Å$^3$) of the NO$_3^-$ anion in the gas phase for several levels of theory

| Method         | $\alpha_{||}$ | $\alpha_{\perp}$ | $\alpha_{\text{iso}}$ |
|----------------|---------------|-------------------|-----------------------|
| B3LYP/aug-cc-pvdz | 5.49          | 3.04              | 4.67                  |
| B3LYP/aug-cc-pvtz | 5.66          | 3.21              | 4.84                  |
| MP2/aug-cc-pvdz  | 5.78          | 3.03              | 4.86                  |
| MP2/aug-cc-pvtz  | 5.89          | 3.19              | 4.99                  |

Table 2 Atoms in Molecules decomposition of the gas phase [NO$_3$]$_3$ parallel, perpendicular and isotropic polarizabilities (Å$^3$). The electron density was computed at the B3LYP/aug-cc-pvdz level

| Method         | $\alpha_{||}$ | $\alpha_{\perp}$ | $\alpha_{\text{iso}}$ |
|----------------|---------------|-------------------|-----------------------|
| Total          | 5.48          | 3.05              | 4.67                  |
| O atoms        | 1.91          | 0.89              | 1.57                  |
| N atom         | −0.25         | 0.38              | −0.04                 |

Table 3 Interaction energies (in kcal mol$^{-1}$) and hydrogen bond lengths (Å) of the NO$_3$ H$_2$O complex

<table>
<thead>
<tr>
<th>Method</th>
<th>$\Delta E$</th>
<th>rO–H$_1$</th>
<th>rO–H$_2$</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP/aug-cc-pvdz</td>
<td>−14.80</td>
<td>1.84</td>
<td>2.58</td>
<td>C$_1$</td>
</tr>
<tr>
<td>MP2/aug-cc-pvdz</td>
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<td>1.85</td>
<td>2.56</td>
<td>C$_1$</td>
</tr>
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<td>Polarizable force field</td>
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<td>2.77</td>
<td>C$_2$</td>
</tr>
<tr>
<td>Non-polarizable force field</td>
<td>−14.37</td>
<td>2.22</td>
<td>2.22</td>
<td>C$_{2v}$</td>
</tr>
</tbody>
</table>
interaction energies and hydrogen bond distances obtained with a polarizable potential are in a very good agreement with the \textit{ab initio} values. Upon employing the non-polarizable potential, not only is the interaction energy slightly underestimated, but also the geometry and symmetry of the minimum is changed from \( C_1 \) to \( C_{2v} \), with each of the water oxygens forming two equivalent hydrogen bonds with an oxygen atom of the nitrate anion. It is interesting that this symmetric structure was assigned as a minimum in earlier \textit{ab initio} studies at the Hartree–Fock level of theory.\textsuperscript{38} Only upon employing correlated \textit{ab initio} methods it has been found that the asymmetric hydrogen bond structure is slightly more stable, by about 0.1 kcal mol\(^{-1}\).\textsuperscript{37–39} which is reproduced by the polarizable force field. For the \( \text{NO}_3^- (\text{H}_2\text{O})_3 \) cluster, neither the non-polarizable nor the polarizable force field give the planar \( C_{3v} \) structure as a global minimum. Rather, both force fields predict a \( C_3 \) geometry (close to the secondary \textit{ab initio} minimum discussed above) and overestimate the stability of the cluster by about 10%.

For a cluster consisting of a nitrate anion and several water molecules we performed both classical and \textit{ab initio} MD simulations. In such a medium sized cluster the question of surface vs. interior solvation can already be addressed. In Fig. 2 the distance of the nitrate anion to the center of mass of the cluster is shown for a 10 ps classical MD simulation of \( \text{NO}_3^- (\text{H}_2\text{O})_9 \) with the polarizable force field. The starting geometry corresponded to a fully solvated anion. In the simulation with the polarizable force field, it can be seen that the nitrate anion almost immediately moves away from the center of the system and after some 3 ps becomes stabilized at the surface of the cluster. The overall behavior of the cluster during this simulation was similar to that of the \textit{ab initio} MD simulation, which is characterized in more detail below. In contrast, during an analogous run with identical initial conditions, but employing a non-polarizable force field, the nitrate anion remains closer to the cluster center, more completely solvated.

To further strengthen the prediction of the polarizable force field, that the nitrate anion prefers a surface rather than interior location in a water cluster, we carried out an \textit{ab initio} MD simulation of a \( \text{NO}_3^- (\text{H}_2\text{O})_{10} \) cluster. To provide an indication of the quality of the electronic structure methodology used in the \textit{ab initio} simulation, in Fig. 3 we compare geometrical parameters of the minimum energy configuration of \( \text{NO}_3^- (\text{H}_2\text{O})_3 \) obtained previously\textsuperscript{37} in an all-electron calculation at the B3LYP/aug-cc-pvtz level to our results obtained using BLYP with a plane wave basis set and pseudopotentials. The BLYP calculation slightly overestimates the intramolecular distances and the shorter of the two nitrate O-water H distances, and slightly underestimates the intramolecular angle and the longer nitrate O-water H distance.

The time evolution of the structure of the cluster over the first 2 ps of the \textit{ab initio} simulation is depicted by the snapshots shown in Fig. 4. In the initial configuration, the anion is completely solvated. During the first ps the water molecules dramatically rearrange themselves by “flaring out”, and during the second ps they collect on one side of the anion in an asymmetric solvation shell, which remains intact for the duration of the simulation. The evolution of the nitrate ion from an interior to surface location in the cluster is quantified in Fig. 5, where the distance of the N atom from the cluster center-of-mass is plotted as a function of time. It is evident that the anion is rapidly ejected from the interior of the cluster (within 1 ps), and settles down on the surface after

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**Fig. 2** Time evolution of the distance of the nitrate anion to the center of mass of the \( \text{NO}_3^- (\text{H}_2\text{O})_9 \) cluster from a classical molecular dynamics simulation. Full line—polarizable force field, dashed line—non-polarizable force field.

**Fig. 3** Minimum energy geometry \((D_{3h} \text{ symmetry})\) of the \( \text{NO}_3^- (\text{H}_2\text{O})_3 \) complex. Selected geometrical parameters obtained from an energy minimization using the density functional scheme employed in the \textit{ab initio} MD simulations (BLYP exchange-correlation functional, and plane wave basis set expansion of valence orbitals to 70 Ry) are given, along with the corresponding values (in parentheses) from a B3LYP/aug-cc-pvtz optimization.\textsuperscript{37}

**Fig. 4** Snapshots at 0.5 ps intervals depicting the evolution of the structure of \( \text{NO}_3^- (\text{H}_2\text{O})_{10} \) during the first 2 ps of the 5 ps \textit{ab initio} MD simulation at 200 K.

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\textsuperscript{1} Phys. Chem. Chem. Phys., 2003, 5, 3752–3757
approximately 2 ps, which is similar to the behavior noted above in the simulation with the polarizable force field. While in the surface location, the nitrate anion maintains a preferred orientation, with plane of the ion normal to the surface of the cluster formed by the water molecules. This is demonstrated by the inset to Fig. 5, where we have plotted the angle between a vector normal to the plane of the anion and the vector connecting the N atom and the cluster center-of-mass (the latter essentially defines the surface normal, to the extent that it may be defined in a small cluster). The angle oscillates around a value near \(90^\circ\), which is characteristic of an orientation of the molecular plane parallel to the surface normal. This orientation is expected if polarizability is primarily responsible for the interfacial propensity of the nitrate anion, because the in-plane component \(\alpha_{||}\) of the polarizability tensor is the dominant component.

Electronic polarization effects on the solvation of the nitrate anion are manifested in the charge distribution of the \(\text{NO}_3^-\) complex. In Fig. 6 we have plotted histograms of the dipole moment of the nitrate anion and water molecules computed during the last 2.5 ps of the \textit{ab initio} MD simulation. The dipole moment of the anion vanishes in the gas phase, but in the asymmetric solvation shell on the surface of the water cluster, the nitrate anion is predicted to have a dipole moment of \(\approx 1.5\) D on average. This is roughly twice as large as the dipole moment induced on a chloride ion in a cluster of six water molecules.\(^{31}\) Thus, it appears that the surface location of the nitrate anion is significantly stabilized by the resulting induction energy (dipole–induced dipole). The distribution of dipole moments of the water molecules is similar to that observed previously in \textit{ab initio} simulations of aqueous ionic clusters;\(^{31,32}\) water molecules near the ion, which participate simultaneously in ion–water and water–water interactions have dipole moments characteristic of bulk water (\(\approx 2.9\) D),\(^{50}\) while water molecules on the edges of the cluster have dipole moments characteristic of the water dimer (\(\approx 2\) D).\(^{50}\)

In order to further check the solvation effect on the polarization of the nitrate anion, we have taken 20 snapshots from the classical MD simulation of the \(\text{NO}_3^-\) cluster with the polarizable force field and computed the average value of the anionic polarizability, again using the fractional point charges model to the water molecules. The average value of 4.47 \(\text{Å}^3\), incidentally, exactly coincides with the effective value in aqueous solutions suggested by Pyper \textit{et al.}\(^{40}\) It is also very close to the value of 4.49 \(\text{Å}^3\) obtained for the \(\text{NO}_3^-\) cluster at the \(\text{C}_3\) geometry, optimized using the polarizable force field. This result indicates that the first three water molecules are responsible for the dominant part of the solvent induced decrease of the polarizability of the anion from its gas phase value. Thus, the polarizable force field parametrization derived from results for the \(\text{NO}_3^-\) cluster is adequate for the description of the aqueous solvation of the anion. As a last step, we performed a 0.4 ns run at 280 K of an extended aqueous slab containing a single nitrate anion. Putting a polarizability of 1.49 \(\text{Å}^3\) on each of the nitrate oxygens resulted in a numerical instability due to which the MD simulation after a certain period crashed (this is the so-called "polarization catastrophe" which can occur in the case of proximal, strongly polarizable centers\(^{41}\)). In order to stabilize the MD propagation we had to slightly reduce the value of the oxygen polarizability to 1.3 \(\text{Å}^3\). Nevertheless, even with this lower polarizability we obtained essentially the same result, namely, that the nitrate anion clearly prefers surface over interior solvation. This is demonstrated in Fig. 7, which
shows the distance of NO$_3^-$ from the center of the slab during the simulation. We see that the nitrate anion spends almost all the simulation time in the interfacial layer. Note that, with the polarizability “switched off”, NO$_3^-$ “dives” into the aqueous bulk (see Fig. 7). This clearly demonstrates the principal role that polarizability plays in determining the surface propensity of the nitrate anion, as previously noted for the halogen anions.\(^3\) Finally, as a check of self-consistency, we used 10 snapshots from the polarizable force field MD run to re-evaluate the NO$_3^-$ polarizability at the B3LYP/aug-cc-pvdz level, replacing water molecules by fractional point charges. The resulting values of the NO$_3^-$ isotropic polarizability of 4.4-4.6 Å$^3$ corroborate the claim made above that small water clusters already account for the dominant part of the solvent reduction of the anionic polarizability.

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References
