A Born−Oppenheimer Ab Initio Quantum Mechanical/Molecular Mechanical Molecular Dynamics Simulation on Preferential Solvation of Na$^+$ in Aqueous Ammonia Solution

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We have investigated the structural properties of Na$^+$ in 18.45% aqueous ammonia solution by performing a combined ab initio quantum mechanical/molecular mechanical (QM/MM) molecular dynamics simulation. The first solvation shell of Na$^+$, treated by Born−Oppenheimer ab initio quantum mechanics using the LANL2DZ basis set, contains 3.7 water and 1.8 ammonia molecules, in contrast to the corresponding values of 4.9 and 2.2 obtained by classical pair potential simulation. The results show the effects of many-body interactions on the geometrical arrangement as well as on the coordination number of the solvated Na$^+$. The relative preference for ammonia molecules is discussed in terms of the chemical concept of "hard" and "soft" ions and ligands.

1. Introduction

Characteristics of ions in electrolyte solution are of fundamental scientific interest because these structural and dynamical details can influence a number of chemical processes.[1−4] Such detailed information about solvated ions can be obtained from experiments and, increasingly, also from computer simulations.[5−10] The results from computer simulations can provide even more structural details at the molecular level, in particular for very dilute solutions where experimental results are subject to large errors due to the limitations of experimental techniques.[11,12] As a consequence of the rapid development of computer speed and capacity, more sophisticated simulation techniques using combined quantum mechanical and molecular mechanical (QM/MM) approaches are available for the treatment of condensed-phase systems. Several hybrid QM/MM models combine either semiempirical,[13−16] density functional,[17] valence bond,[18,19] or even ab initio Hartree−Fock[20,21] methodology with commonly used force fields. Consequently, Born−Oppenheimer ab initio QM/MM dynamics have been successfully applied to observe structural and dynamical properties of solvents surrounding solvated ions.[22−27] This technique includes the crucial part of many-body contributions within the whole first solvation shell of ions by considering them quantum mechanically, while the rest of the system is described by classical pair or pair plus-three-body potentials.

The results obtained from this high-level QM/MM technique have shown some new significant features of the role of many-body effects, proving numerous inadequacies of classical pair potential or even three-body corrected simulations. The complexity of many-body contributions is found to especially affect coordination numbers, shifting them to either lower or higher values. In addition, the nonadditivity of interactions due to *n*-body effects was found to play an important role in the orientation of solvent molecules around the solvation sphere of ions. Some characteristic experimental findings concerning ion−

solvent effects—such as the transition from structure-making to structure-breaking effects, which is not observable from classical simulation approach—are also well-reflected.[25]

Besides the investigation of such properties in single-solvent systems, detailed information on ion solvation in mixed solvent systems is also an interesting phenomenon that plays a specific role in solution chemistry and kinetics.[28] Therefore, QM/MM dynamics have been already applied to Li$^+$ in 18.45% aqueous ammonia solution.[26] The QM/MM simulation indicated a tetrahedral structure consisting of three water molecules and one ammonia molecule, compared to the octahedral structure with three water and three ammonia molecules predicted by classical pair potential simulation. The preference for water molecules is in agreement with a qualitative expectation that the "hard" Li$^+$ will prefer the "harder" H$_2$O ligand over the "softer" NH$_3$ molecule. These observations can be seen as proof of the importance of nonadditive many-body effects for a correct description of ions in solution, even if they are only single-charged. As a consequence, the preferential solvation of Na$^+$ in aqueous ammonia solution appeared of interest. The QM/MM molecular dynamics simulations of Na$^+$ in water and in liquid ammonia led to average coordination numbers of 5.6 in H$_2$O[25] and 5.0 in NH$_3$.[29] An earlier Monte Carlo simulation, using pair potentials performed for Na$^+$ in 18.45% aqueous ammonia solution, had predicted a first solvation shell of Na$^+$ containing 2.4 water and 4.0 ammonia molecules.[30] However, this total coordination number (6.4) is rather high, and the preference for ammonia molecules obtained on the basis of classical pairwise additive approximation could not be taken for granted; as in the case of Li$^+$, many-body effects could play a substantial role in Na$^+$ solvation as well. Therefore, a Born−Oppenheimer ab initio QM/MM molecular dynamics simulation was performed to obtain a refined picture of the preferential solvation of Na$^+$ in 18.45% aqueous ammonia solution.

2. Methods

In the QM/MM technique,[22,23,27] all particles within the first solvation shell of Na$^+$ are treated by means of quantum mechanics, and the rest of the system is described by classical

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Solvation of Na⁺ in Aqueous Ammonia Solution

J. Phys. Chem. A, Vol. 105, No. 2, 2001 **507**

TABLE 1: Optimized Parameters of the Analytical Pair Potential for the Interaction of Ammonia with Na^{+a}

pair	A (kcal mol^{-1} Å^6)	B (kcal mol^{-1} Å^7)	C (kcal mol^{-1})	D (Å^{-1})
Na–N	−22169.844	25126.098	46378.265	2.8712794
Na–H	−1711.2562	2303.0311	393.37514	1.5726892

^{a} Interaction energies in kcal mol^{-1}; distances in Å.

pair potentials. The interactions between QM and MM regions are calculated using classical pair potentials, and the forces at the boundary between the regions are smoothed. The selection of the size of the QM region and the quality of the basis set used in the QM part (the most expensive computational part, which takes approximately 200−300 times longer than that of the classical simulation) are crucial to the quality of simulation results. Because the computational effort for ab initio force calculations is rather expensive, the diameter of the first solvation shell of ion obtained from the traditional pair potential simulation is used to define the size of this region. The LANL2DZ basis sets[31,32] were selected because ab initio geometry optimizations using these basis sets reproduce structural properties rather well with respect to calculations using larger basis sets (such as the D95V+(d,p) basis set).[25,33,34] Including the electron correlation can improve the quality of the results, but it is very time-consuming. Thus, this effect is assumed to be small and negligible.[33,34] The pair potential function for Na⁺−H₂O interactions was obtained from our previous work;[24] for Na⁺−NH₃ interactions, the potential function was newly constructed using DZV+P basis sets[31] for NH₃ and the Los Alamos ECP plus DZ basis set[32] for Na⁺ (the same basis sets as employed for Na⁺−H₂O). We fitted 1300 Hartree−Fock interaction energy points, obtained from Gaussian 94[35] calculations, to the analytical form

$$\Delta E_{\text{Na}^+-\text{NH}_3} = \sum_{i=1}^{4} \left(\frac{A_{ic}}{r_{ic}^6} + \frac{B_{ic}}{r_{ic}^7} + C_{ic} \exp(-D_{ic} r_{ic}) + \frac{q_i q_c}{r_{ic}} \right) \quad (1)$$

where A, B, C, and D are the fitting parameters (see Table 1), r_{ic} denotes the distances between Na⁺ and the ith atom of ammonia, and q are the atomic net charges. The charges on Na⁺, and N and H of ammonia were set to 1.0, −0.8022, and 0.2674, respectively. Flexible models for intra- and intermolecular interactions were employed for water[36,37] and ammonia.[38] The pair potential function for water−ammonia interactions was adopted from the work of Tanabe et al.[39]

A classical pair potential molecular dynamics simulation was performed first. After that, a Born−Oppenheimer ab initio QM/MM dynamics simulation was carried out, starting from the equilibrium configuration resulting from the pair potential simulation. Long-range interactions were treated using the reaction-field procedure.[40] The diameter of 7.6 Å of the first solvation shell of Na⁺, obtained from the pair potential simulation, was selected as the size of the QM region. To ensure a continuous change of forces at the transition between the QM and MM regions, we applied a smoothing function[41] within an interval of 0.2 Å (i.e., between 3.8 and 4.0 Å). Both simulations were carried out in a canonical ensemble at 293 K with a time-step size of 0.2 fs. This canonical ensemble was realized by coupling to an external temperature bath. The cubic box employed in the simulations, with a box length of 18.56 Å, contained one Na⁺, 37 ammonia, and 163 water molecules, assuming the experimental density of 18.45 mol % for aqueous ammonia solution (0.9353 g.cm^{-3}). The classical molecular dynamics simulation started from a random configuration and
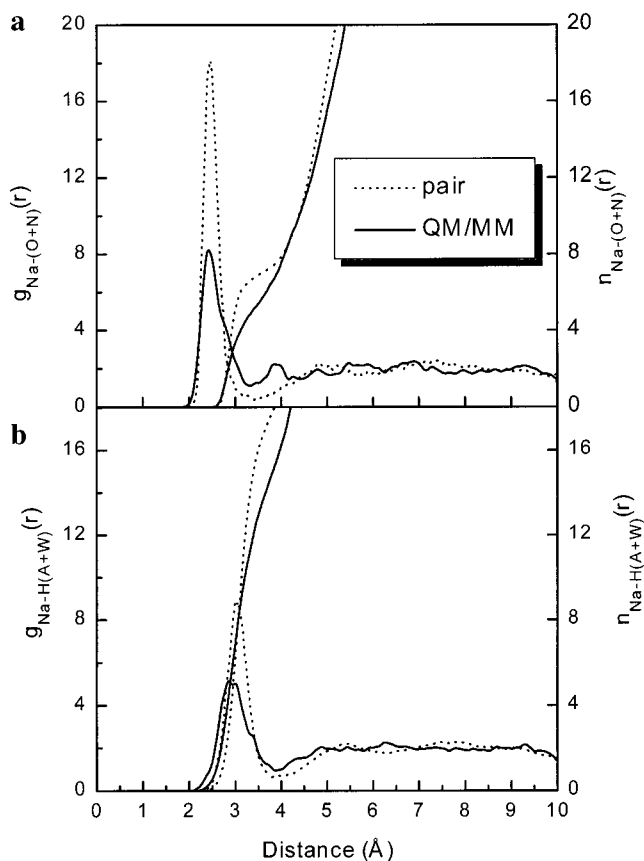

Figure 1. (a) Na−(N+O) and (b) Na−H(A+W) radial distribution functions and their corresponding integration numbers.

was equilibrated for 50 000 time steps. The simulation was continued for 80 000 time steps to collect configurations every 10th step. The combined QM/MM molecular dynamics simulation started with a reequilibration for 20 000 time steps, followed by another 30 000 time steps to collect configurations every fifth step.

3. Results and Discussion

The total radial distribution functions (RDFs) for Na−(N+O) and Na−H (from both water and ammonia molecules) and their corresponding integration numbers, obtained from both classical pair potential and combined QM/MM simulations, are shown in Figure 1. The pair potential simulation gives a sharp first Na−(N+O) peak at 2.49 Å and the first solvation shell is rather well separated from the outer region, leading to the average coordination number of 7.1 ± 0.1. In the QM/MM simulation, a broader, less pronounced first peak is observed at 2.38 Å. The first solvation shell is not so distinctly separated from the outer region, indicating an easy interchange of ligand molecules with the bulk. The average coordination number is 5.5 ± 0.2. The broadness of the first peak means that the molecular arrangement of ligands in the first solvation shell of Na⁺ is more flexible than was observed in the pair potential simulation. A distinct second Na−(N+O) peak is not found. The Na−H₂O and Na−NH₃ RDFs and their corresponding integration numbers are depicted in Figures 2 and 3, respectively. In the pair potential simulation, the first Na−O and Na−N peaks are centered at 2.37 and 2.49 Å, giving average coordination numbers of 4.9 and 2.2 for water and ammonia, respectively. The corresponding peaks in the QM/MM simulation are located at shorter Na−O and Na−N distances of 2.30 and 2.41 Å, leading to the average of 3.7 and 1.8 water and ammonia ligands, respectively. A
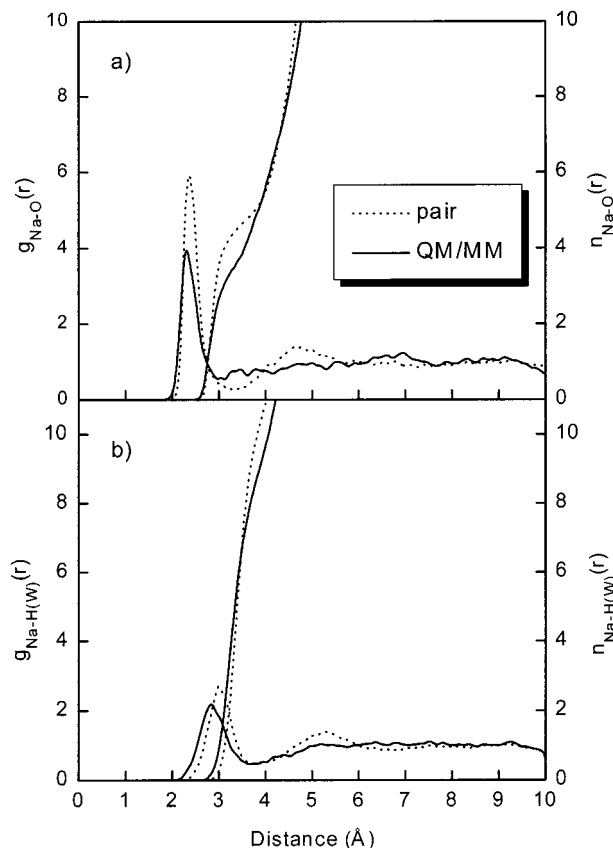
Figure 2. (a) Na−O and (b) Na−H(W) radial distribution functions and their corresponding integration numbers.

Figure 3. (a) Na−N and (b) Na−H(A) radial distribution functions and their corresponding integration numbers.

comparison between the structural parameters from this work and the data from an earlier Monte Carlo simulation is summarized in Table 2. As can be seen from the QM/MM RDFs, placement and orientation of both water and ammonia molecules around Na$^+$ are not so rigid as those found in the pair potential simulation. The broader first Na−H(W) and Na−H(A) RDF peaks in the QM/MM simulation confirm this statement. The exchange of water molecules in the first solvation shell of Na$^+$ seems to occur more easily than for ammonia molecules, as can be seen from the RDF values in the region between first shell and outer region. The lower total coordination number of 5.5, compared to 7.1 from the pair potential simulation, obviously confirms the failure of the pairwise-additive approximation to describe the properties of solvated ions in solution; it also proves that the many-body effects are not negligible, even concerning single-charged ions.

According to the composition of the solution, which consists of 163 water and 37 ammonia molecules, the statistical average distribution of ligands around Na$^+$ should be 4.4:1 for water and ammonia, respectively. In this work, pair potential and QM/MM simulations clearly indicate that Na$^+$ is preferentially solvated by ammonia molecules, yielding the corresponding water-to-ammonia ratios of 2.2:1 and 2:1, respectively. The general concept of "hard" and "soft" acids and bases[42−45] predicts that "soft" Lewis acids prefer to bind to "soft" (i.e., more easily polarized) Lewis bases. Hence, the soft acid Na$^+$ is expected to prefer NH$_3$ over H$_2$O as ligand, which is in full agreement with the results of our study. Although the preference for ammonia molecules is also well-reflected in the pair potential simulation (as well as in an earlier MC simulation, where the corresponding ratio was even 1:1.6), the actual number of ligands in the first solvation shell of Na$^+$ is incorrect. Because the results of such simulations rely on the pairwise additivity
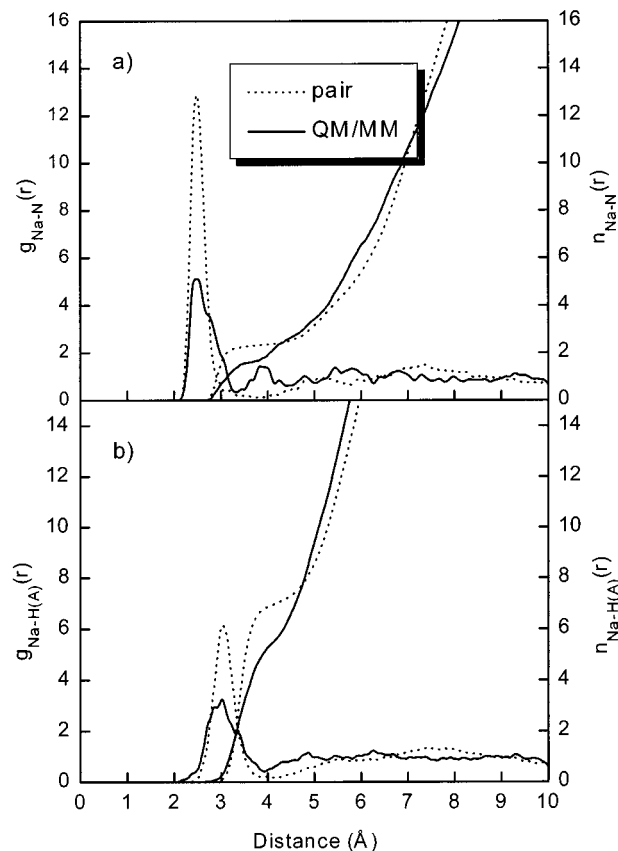
TABLE 2: Comparison of Solvation Parameters for Na$^+$ in 18.45 mol % Aqueous Ammonia Solution, Obtained from Pair Potential and QM/MM Simulations

	$r_{max}{}^a$	$r_{min}{}^b$	$n_{min}{}^c$	method	ref
Na−O	2.37	3.23	4.9	pair potential MD	this work
	2.30	2.98	3.7	QM/MM MD	this work
	2.36		2.4	pair potential MC	30
Na−H(W)	2.98	3.81	10.9	pair potential MD	this work
	2.86	3.66	9.1	QM/MM MD	this work
Na−N	2.49	3.77	2.2	pair potential MD	this work
	2.41	3.24	1.8	QM/MM MD	this work
	2.46		4.0	pair potential MC	30
Na−H(A)	3.02	4.11	7.1	pair potential MD	this work
	3.03	3.91	5.4	QM/MM MD	this work

^{a} Denotes the first maximum of the radial distribution functions, in Å. ^{b} Denotes the first minimum of the radial distribution functions, in Å. ^{c} Average number of ligand molecules obtained by integration up to r_{min}.

of ion−ligand interactions, an overestimation of stabilization energies due to the neglect of many-body terms can be expected to be the main source of the incorrect structural properties predicted for the solvated Na$^+$.

Figure 4 shows the probability distributions of ligands in the first solvation shell of Na$^+$, calculated up to the ion−ligand separation of 3.2 Å. A main coordination number of 7 (in addition to 8 and 6 in decreasing amounts) is predicted by the pair potential simulation, whereas the preferred value of 6 (followed by 5 in a comparable amount and 7 in a small amount) is observed in the QM/MM simulation. Obviously, given that the neglect of many-body contributions results in incorrect coordination numbers, the geometrical arrangement of the ligands in the solvation should also be erroneous. As can be seen from Figure 4b,c, the QM/MM simulation detects only
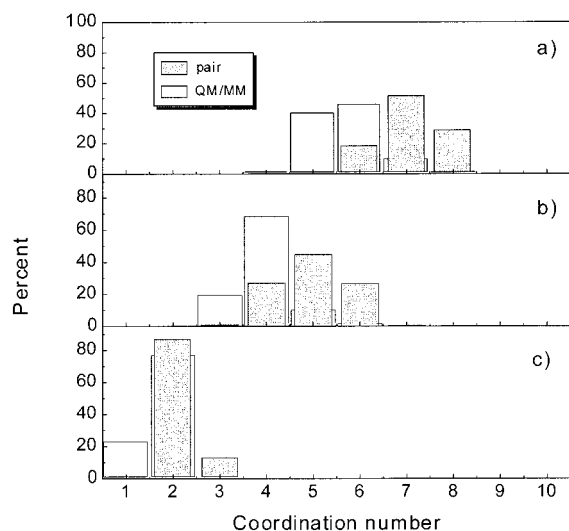
Solvation of Na$^+$ in Aqueous Ammonia Solution

J. Phys. Chem. A, Vol. 105, No. 2, 2001 **509**

Figure 4. Coordination number distributions: (a) Na$^+$−(H$_2$O+NH$_3$), (b) Na$^+$−H$_2$O, and (c) Na$^+$−NH$_3$.
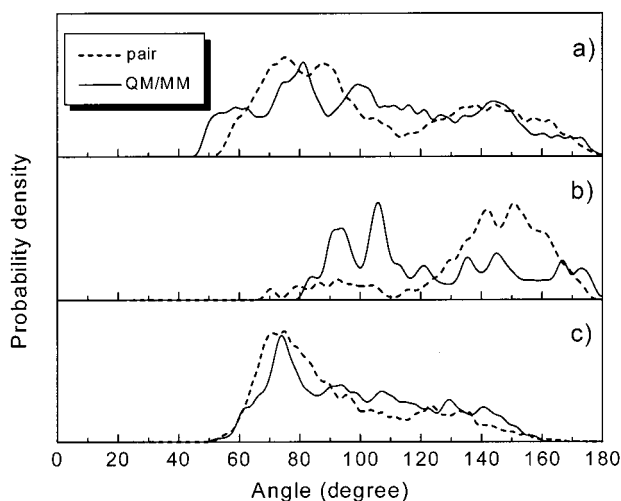

Figure 5. (a) O−Na−O, (b) N−Na−N, and (c) O−Na−N angular distributions, calculated up to the first minimum of the Na−(N+O) RDFs.

four water molecules (compared to five in the pair potential simulation) which are located close to Na$^+$, whereas two ammonia ligands are found in the first shell in both simulations.

Figure 5 shows the O−Na−O, N−Na−N, and O−Na−N angular distributions, calculated up to the first minimum of the Na−(N+O) RDFs. An approximately octahedral arrangement can be recognized from both pair potential and QM/MM simulations, from the two broad peaks between 60 and 100°, and between 130 and 170°. In the QM/MM simulation, an increased flexibility in the angular orientation of water molecules is obviously related to the preferred lower coordination number-(s) in comparison to the pair potential simulation. A significant difference is found for the arrangement of ammonia molecules. Although the number of ammonia molecules in the first solvation shell of Na$^+$ is not changed in either simulation, the QM/MM simulation places them in a cis arrangement, whereas a trans arrangement results from the pair potential simulation. This arrangement can be seen from the dominant peaks between 130 and 170°, and between 80 and 120° (see Figure 5b) observed in pair potential and QM/MM simulations, respectively, and serves as another proof of the significant role of many-body contributions in describing the proper arrangement of ligands around solvated ions.
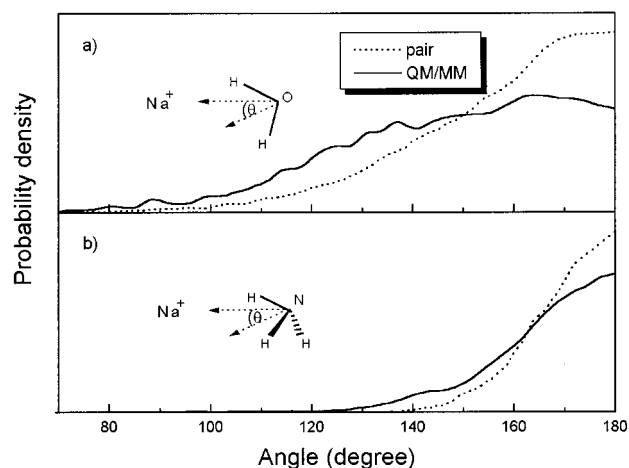

Figure 6. Distributions of θ in the first solvation shell of Na$^+$. (a) water; (b) ammonia.

Figure 6 provides some more detailed information concerning the orientation of ligand molecules (the distribution of the angle θ, defined by the dipole vector of the ligand molecule and the Na$\cdots$O and Na$\cdots$N vectors, respectively) around Na$^+$. In both pair potential and QM/MM simulations, the orientation of ammonia molecules sticks more rigidly to the dipole-oriented arrangement than does that of the water molecules. This behavior is due to the higher binding energy of Na$^+$−NH$_3$ compared to that of Na$^+$−H$_2$O, amounting to 28.0 and 26.3 kcal mol^{-1}, respectively, when Na$^+$ is located at the global minimum of the corresponding pair potential functions. In the QM/MM simulation, the higher flexibility of ligand orientation can be ascribed to the lower coordination number, which reduces steric hindrance and repulsion effects between ligands in the first solvation shell of Na$^+$. The binding of ligand molecules in the first solvation shell with those of outer region is also influenced by this effect, as can be seen from the QM/MM RDFs.

The QM/MM technique includes not only the crucial many-body contributions for the whole first solvation shell of Na$^+$, but also the polarization effects. To understand the importance of the different polarizability of water and ammonia for the preferential ammonia solvation, we compared the Mulliken charges on solvent molecules inside the QM region resulting during the simulation and the charges used in the classical potential for the Coulomb terms. In the QM/MM simulation, ligands in the first solvation sphere are strongly polarized by Na$^+$, leading to higher atomic charges of the ligands by about 22% and 18% for water and ammonia, respectively, compared to the values employed in the classical simulation. This observation shows that a much stronger interaction will take place not only between ion and ligands, but also between the ligands in the same sphere. This actually reflects the importance of QM treatment for the first solvation sphere. The pair potential (and even three-body correction) would not account for this change in charges of the molecules, because these potentials, by definition, use fixed partial charges for the atoms.

Because the internal pressure is usually related to the atomic forces acting in the system, one might think that the pressure difference between the classical and QM/MM simulations could in part lead to the different results. To analyze this point, we observed the magnitude of difference in forces inside the QM region; forces were calculated both quantum mechanically and classically. We found a difference in forces of about 10%. Because the QM part is only a small region, namely a sphere of around 3−4% of the overall volume, this difference could

be considered a slight deviation that does not much affect the relative internal pressure.

4. Conclusion

The results from the Born−Oppenheimer ab initio QM/MM molecular dynamics simulation presented here confirm once again the severe limitations of simulations that use only pair potentials for the treatment of electrolyte solutions. Therefore, a correction for three-body and higher nonadditive contributions, although time-consuming, seems to be inevitable and compulsory for an accurate description even of simple, single-charged ions in solution. This seems to be particularly important when ligands other than water are involved in the solvation process. Because experiments are often prone to large errors when very dilute solution systems are studied, and no experimental data are available for such systems under investigation, it is reasonable to believe that the QM/MM studies can give the correct trend.

References and Notes

(1) Frank, H. S. *Chemical Physics of Ionic Solutions*; John Wiley & Sons: New York, 1956; p 60.

(2) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed.; Butterworth: London, 1959.

(3) Kay, R. L. In *Water, A Comprehensive Treatise*; Franks, F., Ed.; Plenum Press: New York, 1973; Vol. 3.

(4) Harned, H. A.; Owen, B. B. *The Physical Chemistry of Electrolyte Solutions*; American Chemical Society Monograph; Reinhold Publishing Corporation: New York, 1950.

(5) Neilson, G. W.; Enderby, J. E. *Adv. Inorg. Chem.* **1989**, *34*, 195.

(6) Neilson, G. W.; Tromp, R. H. *Annu. Rep. Phys. Chem. C* **1991**, *88*, 45.

(7) Bopp, P. A.; Kohlmeyer, A.; Spohr, E. *Electrochim. Acta.* **1998**, *43*, 2911.

(8) Impey, R. W.; Madden, P. A.; McDonald, I. R. *J. Phys. Chem.* **1983**, *87*, 5071.

(9) Koneshan, S.; Rasaiah, J. C.; Lynden-Bell, R. M.; Lee, S. H. *J. Phys. Chem. B* **1998**, *102*, 4193.

(10) Obst, S.; Bradaczek, H. *J. Phys. Chem.* **1996**, *100*, 15677.

(11) Hewish, N. A.; Neilson, G. W.; Enderby, J. E. *Nature* **1982**, *297*, 138.

(12) Howell, I.; Neilson, G. W. *J. Phys.: Condens. Matter* **1996**, *8*, 4455.

(13) Warshel, A.; Levitt, M. *J. Mol. Biol.* **1976**, *103*, 227.

(14) Field, M. J.; Bash, P. A.; Karplus, M. *J. Comput. Chem.* **1990**, *11*, 700.

(15) Cummins, P. L.; Gready, J. E. *J. Comput. Chem.* **1997**, *18*, 1496.

(16) Gao, J. *Rev. Comput. Chem.* **1996**, *7*, 119.

(17) Stanton, R. V.; Hartsough, D. S.; Merz, K. M., Jr. *J. Comput. Chem.* **1995**, *16*, 113.

(18) Bernardi, F.; Olivucci, M.; Robb, M. A. *J. Am. Chem. Soc.* **1992**, *114*, 1606.

(19) Åqvist, J.; Warshel, A. *Chem. Rev.* **1993**, *93*, 2523.

(20) Singh, U. C.; Kollman, P. A. *J. Comput. Chem.* **1986**, *7*, 718.

(21) Muller, R. P.; Warshel, A. *J. Phys. Chem.* **1995**, *99*, 17516.

(22) Kerdcharoen, T.; Liedl, K. R.; Rode, B. M. *Chem. Phys.* **1996**, *211*, 313.

(23) Tongraar, A.; Liedl, K. R.; Rode, B. M. *J. Phys. Chem. A* **1997**, *101*, 6299.

(24) Tongraar, A.; Liedl, K. R.; Rode, B. M. *Chem. Phys. Lett.* **1998**, *286*, 56.

(25) Tongraar, A.; Liedl, K. R.; Rode, B. M. *J. Phys. Chem. A* **1998**, *102*, 10340.

(26) Tongraar, A.; Liedl, K. R.; Rode, B. M. *J. Phys. Chem. A* **1999**, *103*, 8524.

(27) Marini, G. W.; Liedl, K. R.; Rode, B. M. *J. Phys. Chem. A* **1999**, *103*, 11387.

(28) Gutmann, V. *The Donor−Acceptor Approach to Molecular Interactions*; Plenum Press: New York, 1978.

(29) Kerdcharoen, T.; Rode, B. M. *J. Phys. Chem. A* **2000**, *104*, 7073.

(30) Rode, B. M.; Tanabe, Y. *J. Chem. Soc., Faraday Trans.* **1988**, *2*, 1779.

(31) Dunning, T. H., Jr.; Hay, P. J. *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum: New York, 1976.

(32) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270.

(33) Kerdcharoen, T. Hot-Spot Molecular Dynamics. Ph.D. Thesis, University of Innsbruck, Innsbruck, Austria, 1995.

(34) Tongraar, A. *Ab Initio QM/MM Dynamics Simulations of Cations in Aqueous Solution*. Ph.D. Thesis, University of Innsbruck, Innsbruck, Austria, 1998.

(35) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stafanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 94*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(36) Bopp, P.; Jancsó, G.; Heinzinger, K. *Chem. Phys. Lett.* **1983**, *98*, 129.

(37) Stillinger, F. H.; Rahman, A. *J. Chem. Phys.* **1978**, *68*, 666.

(38) Hannongbua, S.; Ishida, T.; Spohr, E.; Heinzinger, K. *Z. Naturforsch.* **1988**, *43a*, 572.

(39) Tanabe, Y.; Rode, B. M. *J. Chem. Soc., Faraday Trans. 2* **1988**, *84*, 679.

(40) Adams, D. J.; Adams, E. H.; Hills, G. J. *Mol. Phys.* **1979**, *38*, 387.

(41) Brooks, B. R.; Bruccoleri, R. E.; Olafson, B. D.; States, D. J.; Swaminathan, S.; Karplus, M. *J. Comput. Chem.* **1983**, *4*, 187.

(42) Schwarzenbach, G. *Experentia Suppl.* **1956**, *5*, 163.

(43) Ahrland, S.; Chatt, J.; Davies, N. *Quart. Revs.* **1958**, *12*, 265.

(44) Pearson, R. G. *Structure and Bonding*, Vol. 80; Springer-Verlag: Berlin and Heidelberg, Germany, 1993.

(45) Komorowski, L. *Structure and Bonding*, Vol. 80; Springer-Verlag: Berlin and Heidelberg, Germany, 1993.