4298 *J. Phys. Chem. A* **1999,** *103,* 4298−4302

# Solvation of $Cu^{2+}$ in Liquid Ammonia: Monte Carlo Simulation Including Three-Body Corrections

**Harno D. Pranowo*,† and Bernd M. Rode**

*Theoretical Chemistry Division, Institute of General, Inorganic and Theoretical Chemistry,*
*University of Innsbruck, A-6020 Innsbruck, Austria*

*Received: January 22, 1999; In Final Form: March 25, 1999*

The $Cu^{2+}-NH_3$ pair potential and the corresponding three-body correction functions have been newly constructed on the basis of ab initio calculations of double-$\zeta$ quality. Monte Carlo simulation results for Cu(II) in liquid ammonia prove the failure of the pair potential approximation, even in the prediction of rough structural properties. Simulation including three-body potentials leads to a first-shell coordination number of 6 for $Cu^{2+}$ in liquid ammonia at 240 K. The structure of the solvated ion is discussed in terms of radial distribution functions, coordination numbers, energies, and angular distributions.

## 1. Introduction

**1.1. Experimental Data.** The structure of the Cu(II)−ammonia system has been the subject of considerable interest, being studied in liquid,[1−4] crystal,[5−7] or gas phase[8] by experimental and theoretical methods.

Valli et al.[1] used extended X-ray absorption fine structure (EXAFS) spectroscopy to determine coordination number and structure of the solvated copper(II) ion in liquid ammonia. The EXAFS data could be fitted with either five or six ammonia ligands, while the X-ray absorption near-edge structure (XANES) spectrum was best reproduced by a model where the copper(II) ion in liquid ammonia is pentacoordinated in a square-pyramidal geometry with the ion lifted above the basis plane of nitrogens. According to this study, the equatorial ammonia nitrogens were located 2.00 Å and the axial nitrogen 2.19 Å away from copper.

Sano et al.[2] have studied a concentrated aqueous ammonia solution of copper(II) sulfate and found that a coordination of four ammonia ligands is predicted by EXAFS, but at the same time they concluded from the XANES spectrum that the complex geometry should be square pyramidal with five ammonias coordinated to copper. Alagna et al.[3] reported an EXAFS study on $[Cu(NH_3)_5](BF_4)_2$ in solution, resulting in five equal Cu−N bonds of 2.04 Å length.

Thus, the conclusions from EXAFS and XANES investigations of solvated Cu(II) in pure and aqueous ammonia are not consistent with each other. On the other hand, they are not consistent with the results from an X-ray diffraction (XRD) study by Yamaguchi and Ohtaki[4] either, which led to an octahedral conformation with an estimate of 1.93 Å for the in-plane Cu−N bond lengths and 2.3 Å for axial Cu−N and Cu−O bonds.

Distler and Vaughan[5] have investigated the crystal structure of the hexammine copper(II) halides by XRD. They found that the structure of these compounds is Jahn−Teller distorted, with four short (2.11 Å) and two long (2.59 Å) copper−nitrogen bonds.

Duggan et al.[6] used XRD to investigate the crystal structure of $K[Cu(NH_3)_5][PF_6]_3$. They found a square-pyramidal molecular structure with strict $C_{2v}$ symmetry with an axial C−N bond length of 2.19 Å and an equatorial one of 2.01 Å.

Elliot and Hatway[7] also examined some hexammine complexes of copper(II) ion by X-ray diffraction. Their results suggested that water and ammonia show similar ligand properties and that the hexaquocopper(II) complexes are Jahn−Teller distorted octahedra.

Walker et al. have studied $[Cu(NH_3)_n]^{2+}$ [8] and $[Cu(H_2O)_n]^{2+}$ [9] complexes in the gas phase by mass spectrometry and found that $[Cu(NH_3)_8]^{2+}$ and $[Cu(H_2O)_8]^{2+}$ complexes appeared to be the most stable compounds, assuming a staggered 8-fold structure.

**1.2. Theoretical Investigation.** Ion−ammonia pair potentials derived from ab initio molecular orbital theory have been used in molecular dynamics and Monte Carlo simulations of metal cations in aqueous ammonia with varying degrees of success because of problems with nonadditivity. In most cases of divalent and trivalent ions, the assumption of pairwise additive intermolecular potentials results in seriously wrong structural and energetic data for the solvate. Nonadditivity has been studied, therefore, for a number of ion−ammonia interactions. Most of this work has concentrated on main group metal ions including $Li^+$,[10] $K^+$,[11] $Na^+$,[12] and $Mg^{2+}$ [13] but also on the transition metal cation $Zn^{2+}$.[14] The influence of nonadditivity effects on the structure of copper hydrates has been investigated by ab initio calculations[15] and Monte Carlo methods,[16−18] proving that three-body or even higher terms are of major importance to describe this ion in solution.

Simple possibilities to correct some of the inherent inadequacies of the assumed additivity of pair interactions are the use of the nearest-neighbor ligand correction (NNLC) algorithm[19,20] or of effective pair potentials. Floris et al.[21] proposed a method for the construction of such effective pair potentials, incorporating some *n*-body effects implicitly. The advantage of such approaches is the possibility of performing improved simulations of the liquid state without handling explicitly the computer-intensive three-body or higher-order terms, but at the same time, accuracy and the possibility of a detailed analysis of the *n*-body effects are lost.

In this work, attention is focused on the role of three-body effects in the first solvation shell of $Cu^{2+}$ in liquid ammonia.

---

† Permanent address: Austrian−Indonesian Centre for Computer Chemistry, Gadjah Mada University, Yogyakarta, Indonesia.

10.1021/jp990264b CCC: $18.00

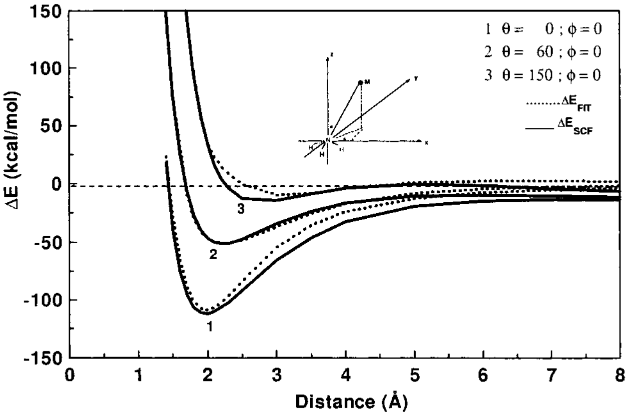

**Figure 1.** Comparison of the energies obtained from the SCF calculations, $\Delta E_{SCF}$, and from the analytical potential function, $\Delta E_{FIT}$, using the final values of the fitting parameters as given in Table 1 for values of $\theta = 0°$, 60°, and 150° and $\phi = 0°$.

The corresponding analytical potential functions were constructed, and subsequently, Monte Carlo simulations were performed for $Cu^{2+}$ in liquid ammonia with and without three-body corrections.

## 2. Details of the Calculations

**2.1. Construction of Two- and Three-Body Potentials.** The quantum chemical calculations were carried out at the unrestricted Hartree–Fock (UHF) level using the double-$\zeta$ valence (DZV) basis set developed by Schäfer et al.[22] for copper(II) ion. Initial guesses for the eigenvectors were obtained from calculations of the Cu(II)–ammonia system using the modified[23] ECP-DZP basis set of Hay and Wadt.[24] For ammonia, the double-$\zeta$ plus polarization (DZP) basis set from Dunning[25] corresponding to D95V* in the Gaussian 94 program[26] was used. The experimental gas-phase geometry of the ammonia molecule, with N–H distance of 1.0124 Å and HNH angle of 106.67°, was taken from literature[27] and kept constant throughout the calculations. A global minimum of −111.7 kcal/mol was found for the $C_{3v}$ dipole-oriented configuration of the Cu(II)–$NH_3$ adduct at a Cu–N distance of 2.00 Å.

To develop the $Cu^{2+}$–$NH_3$ pair potential, the ammonia molecule was fixed at the origin of the coordinate system and the $Cu^{2+}$ ion moved in the field of this ammonia molecule, varying geometrical parameters within $1.5\ \text{Å} \le r_{Cu-N} \le 10.0\ \text{Å}$, $0° \le \theta \le 180°$, and $0° \le \phi \le 60°$ (Figure 1). The interaction energy $\Delta E_{2b}$ between ammonia and copper is computed by subtracting the ab initio energies of the isolated species $E_{Cu}{}^{2+}$ and $E_L$ from those of the monosolvates $E_{CuL}{}^{2+}$, where L denotes $NH_3$.

$$\Delta E_{2b} = E_{CuL}{}^{2+} - E_{Cu}{}^{2+} - E_{L} \tag{1}$$

The $Cu^{2+}$–ammonia pair potential was constructed from more than 600 SCF energy points, covering the whole configuration space around the ammonia molecule. Fitting of these data to a functional form was performed by a least-squares method with Levenberg–Marquart algorithm and, after testing various potential types in order to describe all electrostatic and van der Waals interactions, resulted in the function

$$\Delta E = \sum_{i=1}^{4} A_{iM} r_{iM}{}^{-5} + B_{iM} r_{iM}{}^{-8} + C_{iM} \exp(-D_{iM} r_{iM}) + q_i q_M r_{iM}{}^{-1} \tag{2}$$

**TABLE 1: Final Optimized Parameters for the Interactions of N and H Atoms of Ammonia with $Cu^{2+}$** [a]

| atom | $q_i$ | $A$ | $B$ | $C$ | $D$ |
|---|---|---|---|---|---|
| N | −0.8022 | −5532.8613 | 2710.5409 | 122 573.1805 | 3.4670 |
| H | 0.2674 | −3018.4696 | 2721.8126 | 13 181.3449 | 2.4732 |

[a] The atomic net charges are given in au, interaction energies and distances in kcal mol$^{-1}$ and Å, respectively.

where $A_{iM}$, $B_{iM}$, $C_{iM}$, and $D_{iM}$ denote the fitting parameters, $r_{iM}$ are the distances between the $i$th atom of $NH_3$ and $Cu^{2+}$, $q_i$ are the atomic net charges of the $i$th atom of $NH_3$ taken from Mulliken population analysis, and $q_M$ is the charge of Cu(II). A weight factor was introduced to give special emphasis to values near the global and local energy minima ($f = \Delta E/(-111.7)$); values above 30 kcal/mol were excluded. This analytical potential function form is similar to the form of functions for solvated metal ions used previously.[11,12,28] The final parameters of the function are given in Table 1. The standard deviation of the fitted values from SCF data was ±6.8 kcal/mol for the whole region and ±4.5 kcal/mol for the region between the global minimum and 0 kcal/mol.

For the system consisting of one copper ion and two ammonia molecules, 1200 configurations have been generated in the configuration space around the copper ion. Orientations where one of the hydrogen atoms is closer to the ion than the corresponding nitrogen need not be considered, since their highly repulsive two-body energy values prevent the occurrence of such orientations during the simulation process. The three-body interaction energy $\Delta E_{3bd}$ for each configuration was computed by subtracting the two-body interaction $E_{2b}$, calculated with the help of the pair potential functions for copper–ammonia and ammonia–ammonia, from the ab initio energies in the following way:[16,29]

$$\Delta E_{3bd} = E_{ML_1L_2} - E_M - E_{L_1} - E_{L_2} - E_{2bML_1} - E_{2bML_2} - E_{2bL_1L_2} \tag{3}$$

where M, $L_1$, and $L_2$ denote copper, the first ammonia, and the second ammonia, respectively. All three-body data points were fitted to an analytical function to be used as correction for the pair potential. The form of this correction function was

$$\Delta E_{3bd} = 0.000364[13.606286 + (\pi - \theta_{L_1ML_2})^2]^2 \times \exp(-0.204528 r_{ML_1}{}^2) \exp(-0.157809 r_{ML_2}{}^2) \times |[(CL^2 - r_{ML_1}{}^2)(CL^2 - r_{ML_2}{}^2)]| \tag{4}$$

where $L_i$ denotes the $i$th ammonia molecule, $\theta_{L_1ML_2}$ is the $NH_3$–Cu–$NH_3$ angle, and $r_{ML_i}$ the distance between the center of mass of ammonia molecule $L_i$ and copper(II). CL represents the cutoff limit to be used in the simulation, beyond which three-body effects can be neglected. In our case CL was set to 6.0 Å. The parameters of the three-body correction function were obtained by fitting with the Levenberg–Marquart algorithm, and the fitted values show a standard deviation of ±4.6 kcal/mol.

**2.2. Monte Carlo Simulations.** The Monte Carlo simulations were carried out with an *NVT* ensemble containing one Cu(II) and 215 ammonia molecules at 240 K using the Metropolis algorithm.[30] The experimental density of pure liquid ammonia of 0.682 g cm$^{-3}$ at this temperature results in an elementary box length of 20.855 Å. Periodic boundary conditions and a cutoff at half the box length were employed;[31] the starting configuration was randomly generated. All quantities were evaluated from two million configurations of the system sampled after energetic equilibrium was reached after three million

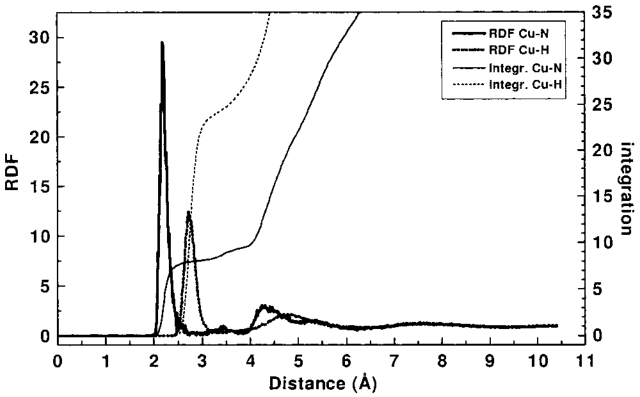

**Figure 2.** Cu−N and Cu−H radial distribution functions and their running integration numbers obtained by using the pair potential only.

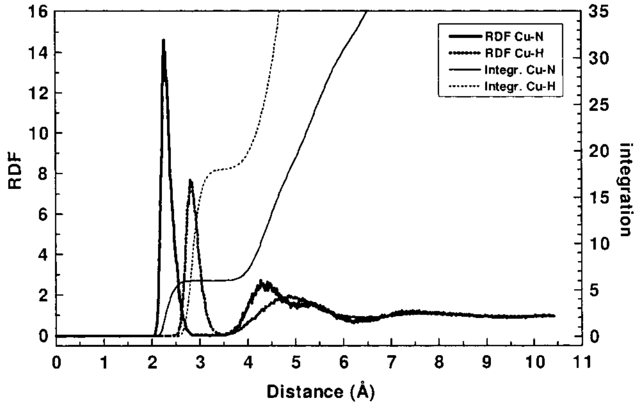

**Figure 3.** Cu−N and Cu−H radial distribution functions and their running integration numbers obtained after inclusion of the three-body correction function.

configurations. For ammonia−ammonia interactions, the same potential function as in previous studies[10−12] has been employed. For a charged system like the one treated here, long-range corrections by Ewald summation are not possible. However, comparison of similar single ion−solvent systems[18−19,29] and related systems containing a balanced amount of cation and anion,[20,32,33] for which Ewald corrections have been performed, shows that the differences appear to be marginal at lower salt concentrations.

## 3. Results and Discussion

In Figure 1 the stabilization energies obtained from the SCF calculations ($\Delta E_{\mathrm{SCF}}$) and from the fitted potential function ($\Delta E_{\mathrm{FIT}}$) are compared for some orientations. The function exhibits a stabilization energy of −108.7 kcal/mol at a Cu−N distance of 2.00 Å with the copper ion located on the dipole moment vector of ammonia.

Figures 2 and 3 show the radial distribution functions (RDFs) for $\mathrm{Cu^{2+}}$−N and $\mathrm{Cu^{2+}}$−H together with the corresponding running integration numbers, with and without three-body corrections, respectively. The characteristic values are summarized in Table 2. The Cu(II)−N RDF without three-body corrections shows a sharp peak centered at 2.21 Å, with a corresponding integration number of 8.0. This value agrees with the number of ammonia molecules observed by Walker et al. for $[\mathrm{Cu(NH_3)_8}]^{2+}$ [8] in the gas phase but disagrees with all experimental investigations for Cu(II) in aqueous or pure ammonia.[1−4]

**TABLE 2: Characteristic Values of the Radial Distribution Functions $g_{\alpha\beta}(r)$ for the Cu(II)−Ammonia Solution**

| α | β | $r_{\mathrm{M1}}$ | $r_{\mathrm{m1}}$ | $n_{\alpha\beta}$(m1) | $r_{\mathrm{M2}}$ | $r_{\mathrm{m2}}$ | $n_{\alpha\beta}$(m2) |
|---|---|---|---|---|---|---|---|
| | | | | Pair Potential | | | |
| Cu | N | 2.21<br>(3.52) | 2.90<br>(3.94) | 8.00<br>(1.97)[b] | 4.29 | 6.09 | 28.55 |
| Cu | H | 2.76 | 3.23 | 24.03 | 4.93 | 6.00 | 91.01 |
| | | | | Pair + Three-Body Potential | | | |
| Cu | N | 2.26 | 2.98 | 5.99 | 4.44 | 6.30 | 28.39 |
| Cu | H | 2.82 | 3.46 | 17.95 | 4.98 | 6.53 | 100.35 |

[a] $r_{\mathrm{M1}}$, $r_{\mathrm{M2}}$ and $r_{\mathrm{m1}}$, $r_{\mathrm{m2}}$ are the distances in Å, where $g_{\alpha\beta}(r)$ has the first and second maximum and the first and second minimum, respectively. $n_{\alpha\beta}$(m1) and $n_{\alpha\beta}$(m2) are the running integration numbers integrated up to $r_{\mathrm{m1}}$ and $r_{\mathrm{m2}}$, respectively [b] There is a peak between 3.2 and 3.94 Å corresponding to two ammonia molecules.

Of particular interest in the Cu−N RDF plots is the small peak beyond the first coordination shell within the range 3.1−3.9 Å. This additional peak contains another two ammonia molecules. Similar peaks were found in the simulations of $\mathrm{Mg^{2+}}$ [12] and $\mathrm{Zn^{2+}}$ [13] in liquid ammonia and have been shown to be an artifact of the simulation involving pair potentials only.

After inclusion of three-body corrections, the first maximum is shifted to 2.26 Å, 0.05 Å beyond the Cu−N distance obtained by the pair potential, and a first-shell coordination number of 6 is obtained. The coordination number of 6 is in agreement with some X-ray and EXAFS data but in contradiction to the pentacoordinated complex postulated by Valli et al.[1] on the basis of the XANES spectrum. It should be mentioned, however, that this interpretation was reached with the help of some theoretical DV-Xα calculations, whose reliability can be questioned. Neutron diffraction with isotope substitution (NDIS) spectroscopy could probably be of great help for a decision between the disputed coordination numbers but has not been performed so far. Among simulation methods, a combined quantum mechanical−molecular mechanical (QM/MM) simulation as performed recently for $[\mathrm{Cu(H_2O)}]^{2+}$ [34] could be equally capable of finally solving this question. Since a simulation including no higher than three-body effects cannot account for Jahn−Teller distortion in principle, our value of 2.26 Å appears to be a reasonable average of the experimentally determined values between 2.0 and 2.6 Å.[1−6]

The small intermediate Cu−N RDF peak at 3.5 Å disappears. The fact that the Cu−N RDF is now near zero after its first peak and stays at this value for more than 0.6 Å suggests that the first shell is quite stable and that ligand exchange with the second shell should be marginal. The coordination number distribution analysis for the first solvation shell of Cu(II) leads to 99.4% for 6 and 0.6% for 5, which also indicates a low but not negligible exchange rate for the first solvation shell ligands. Recently, QM/MM methods have been applied proving the importance of higher nonadditive terms for the description of several cations.[28,35,36] For example, a tetrahedral structure with four ammonia molecules in the first solvation shell of $\mathrm{Li^+}$ was found by QM/MM molecular dynamics, in contrast to the octahedral structure obtained by a traditional simulation using pair potentials[28] and even three-body-corrected potentials.[37] Such QM/MM methods have not yet been applied to the Cu(II)−ammonia system, but for the hydration of Cu(II) the QM/MM Monte Carlo method predicts a coordination number of 6 and Cu−O distances in the first hydration shell of Cu(II)[34] clearly demonstrating Jahn−Teller distortion.

The Cu−H RDFs of our simulations also show a sharp first peak located at 2.76 and 2.82 Å, containing the 24 and 18 hydrogen atoms corresponding to the 8 and the 6 ammonia molecules predicted for the first solvation shell with and without three-body corrections, respectively. The small artificial peak in the Cu−N RDF representing two intermediate ammonia

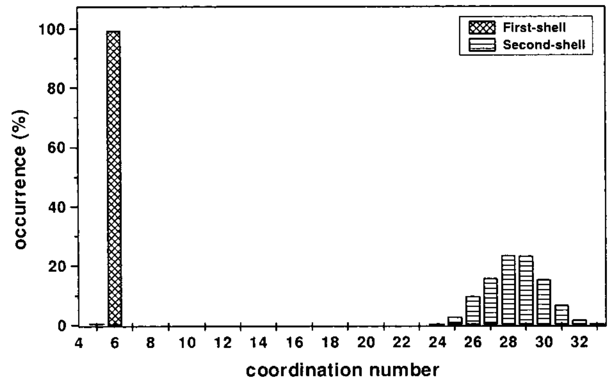

**Figure 4.** First- and second-shell coordination number distribution of $Cu^{2+}$ in liquid ammonia using the three-body-corrected function.

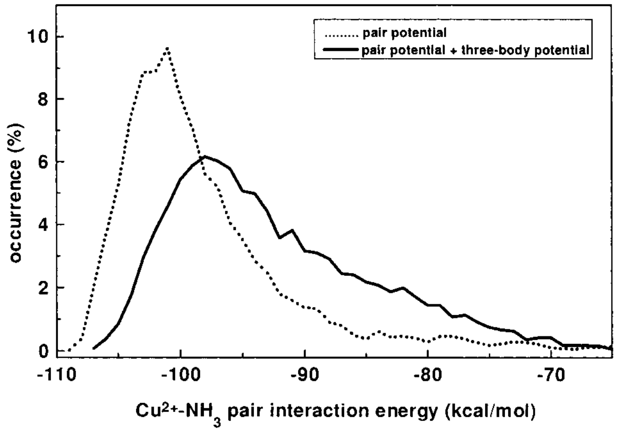

**Figure 5.** Comparison of pair interaction energies of Cu(II)−$NH_3$ in the first solvation shell obtained from the simulations with (solid line) and without (dashed line) three-body corrections.

molecules obtained without three-body correction is also well reflected in the Cu−H RDF (six hydrogen atoms).

The second peak of the Cu−N RDFs of the simulation including three-body corrections, representing the second shell, is clearly separated from the first shell. The average coordination number is 28.4. Both RDF and coordination number distribution of the second solvation shell (Figure 4) reveal that orientation and binding of these ammonia molecules are not exclusively determined by hydrogen bonding, since on average more than four ammonia molecules in the second shell interact with one ammonia molecule in the first shell.

The distribution of pair interaction energies (Figure 5) also demonstrates the impact of three-body effects on the ion−ligand interaction. Implementation of three-body correction shifted the peak maximum of the pair interaction energy to a higher value, namely, to −92.4 kcal/mol from −98.0 kcal/mol for the six and eight ammonia ligands. The three-body effects seem to weaken the ion−ligand interactions, giving more flexibility to their coordination as expressed by the wider energy range observed.

The three-body energy distribution for $[Cu(NH_3)_6]^{2+}$ (Figure 6) shows a broad peak between 3 and 16 kcal/mol corresponding to a rather uniform distribution of energies rather independent of the relative orientation of the two ammonia molecules. Hannongbua[37] observed that the rotation of the ammonia molecules around their dipole axes in the tetrahedral and octahedral clusters causes only slight changes in the three-body energies. This behavior of the pyramidal $NH_3$ ligand is in contrast to that from the simulation of hydrated $Zn^{2+}$, where the distribution of three-body interaction energies shows two peaks corresponding to staggered and eclipsed orientations for the two planar water molecules.[29]

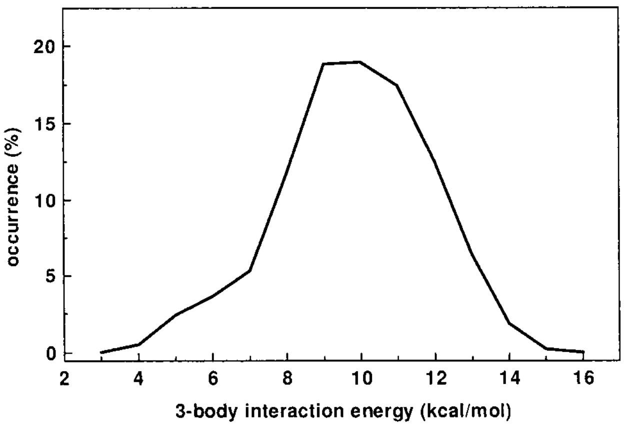

**Figure 6.** Distribution of three-body interaction energies in the first shell.

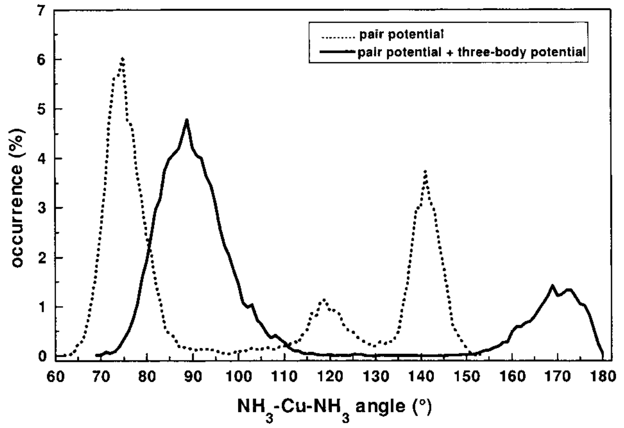

**Figure 7.** Comparison of $NH_3$(I)−Cu−$NH_3$(II) angles in the first solvation shell obtained from the simulations with (solid line) and without (dashed line) three-body corrections.

In the distribution plots of the $NH_3$−Cu−$NH_3$ angles, the expected drastic changes are found after the three-body corrections have been included (Figure 7). The distribution for the $[Cu(NH_3)_8]^{2+}$ complex shows three maxima at 75°, 119°, and 141°. No peak is found beyond 153°. With the three-body terms included, the N−Cu−N angle distribution of $[Cu(NH_3)_6]^{2+}$ displays two peaks centered at 89° and 173°, corresponding to a distorted octahedral complex.

## 4. Conclusion

The ab initio $Cu^{2+}$−$NH_3$ pair potential is inadequate to describe the structure of the copper(II) ion in liquid ammonia and leads especially to an overestimation of the coordination number and of stabilizing energies.

The inclusion of three-body interactions markedly improves the agreement with experimental data. It should be expected that higher terms of interaction included in a more sophisticated but extremely time-consuming simulation method such as the QM/MM approach may have a slight influence on the coordination number in the first solvation shell of the Cu(II)−ammonia system and may allow a decision of whether the small amount of $[Cu(NH_3)_5]^{2+}$ found in our work is significant or even an indication that a large amount of the species is present in reality.

**Acknowledgment.** Financial support for this work from the Austrian Science Foundation (FWF), P 11683-PHY, and an

Austrian Government Scholarship for H.D.P. are gratefully acknowledged.

## References and Notes

(1) Valli, M.; Matsuo, S.; Wakita, W.; Yamaguchi, T.; Nomura, M. *Inorg. Chem.* **1996**, *36*, 5642.

(2) Sano, M.; Maruo, T.; Masuda, Y.; Yamatera, H. *Inorg. Chem.* **1984**, *23*, 4466.

(3) Alagna, A.; Prosperi, T.; Tomlinson, A. A. G.; Vlaic, G. *J. Chem. Soc., Dalton Trans.* **1983**, 645.

(4) Yamaguchi, T.; Ohtaki, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 415.

(5) Distler, T.; Vaughan, P. A. *Inorg. Chem.* **1967**, *6*, 126.

(6) Duggan, M.; Ray, N.; Hathaway, B. J.; Tomlinson, A. A. G.; Brint, P.; Pelin, K. *J. Chem. Soc., Dalton. Trans.* **1980**, 1342.

(7) Elliott, H.; Hathaway, B. J. *Inorg. Chem.* **1966**, *5*, 885.

(8) Walker, N. R.; Firth, S.; Stace, A. J. *Chem. Phys. Lett.* **1998**, *292*, 125.

(9) Stace, A. J.; Walker, N. R.; Firth, S. *J. Am. Chem. Soc.* **1997**, *119*, 10239.

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

(11) Tongraar, A.; Hannongbua, S.; Rode, B. M. *Chem. Phys.* **1997**, *219*, 279.

(12) Hannongbua, S. *J. Chem. Phys.* **1997**, *106*, 6076.

(13) Hannongbua, S.; Rode, B. M. *Chem. Phys.* **1992**, *162*, 257.

(14) Hannongbua, S.; Kerdcharoen, T.; Rode, B. M. *J. Chem. Phys.* **1992**, *96*, 6945.

(15) Curtiss, L. A.; Jurgens, R. *J. Phys. Chem.* **1990**, *94*, 5509.

(16) Texler, N. R.; Rode, B. M. *J. Phys. Chem.* **1995**, *99*, 15714.

(17) Rode, B. M.; Islam, S. M. *Z. Naturforsch.* **1991**, *46a*, 357.

(18) Cordeiro, M. N. D. S.; Gomes, J. A. N. F.; Gonzales-Lafont, A.; Lluch, J. M.; Bertran, J. *Chem. Phys.* **1990**, *141* 379.

(19) Rode, B. M.; Islam, S. M. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 417.

(20) Rode, B. M. *J. Phys. Chem.* **1992**, *96*, 4170.

(21) Floris, F.; Persico, M.; Tani, A.; Tomasi, J. *Chem. Phys. Lett.* **1992**, *199*, 518.

(22) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.

(23) Krömer, R. T.; Michopoulos, Y.; Rode, B. M. *Z. Naturforsch.* **1991**, *45a*, 1303.

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

(25) Dunning, T. H., Jr. *J. Chem. Phys.* **1970**, *53*, 2823.

(26) 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.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, 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. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 94*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(27) Benedict, W. S.; Plyler, E. K. *Can. J. Phys.* **1985**, *35*, 890.

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

(29) Marini, G. W.; Texler, N. R.; Rode, B. M. *J. Phys. Chem.* **1996**, *100*, 6808.

(30) Metropolis, N.; Rosenbluth, A. W.; Teller, A. H.; Teller, E. *J. Chem. Phys.* **1953**, *21*, 1087.

(31) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Oxford University Press: Oxford, U.K., 1987.

(32) Vizoso, V.; Rode, B. M. *Chem. Phys.* **1996**, *213*, 77.

(33) Texler, N. R.; Rode, B. M. *Chem. Phys.* **1997**, *222*, 281.

(34) Marini, G. W.; Rode, B. M. Manuscript in preparation.

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

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

(37) Hannongbua, S. *Chem. Phys. Lett.* **1998**, *288*, 663.