

Influence of Electron Correlation Effects on the Solvation of Cu²⁺

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Strongly solvated metal cations such as copper(II), titanium(III), and chromium(II) dissolved in polar liquids show a Jahn–Teller distortion^{1–3} of the six-fold-coordinated complex which is well known to occur in solids. The most popular Jahn–Teller distorted cation is the d⁹ ion copper(II) intensively studied by theoretical as well as experimental methods.^{4–7}

To observe the Jahn–Teller distortions, the very fast dynamics (low picosecond or even femtosecond time scale) makes experimental measurement a challenging task, often leading to an averaged, apparently undistorted configuration. EXAFS and diffraction techniques are on a much shorter time scale than vibrational motions, thus yielding reliable values for the average structure of the complex, but without giving any indication about the dynamics of this effect.^{4–6} ¹⁷O NMR line width measurements (usually restricted to a time scale above 10^{–8} s) were used to investigate the dynamics of the Jahn–Teller effect, yielding estimates for the lifetime of a given distortion of 5.1 ps and a mean residence time of water molecules in the first shell of 230 ps.¹

On the other hand, classical simulations, even including three-body potentials, fail to describe the Jahn–Teller effect.⁸ Treating the whole system quantum mechanically, thereby including all necessary *n*-body effects to describe the Jahn–Teller behavior, is still by far not feasible. Combined quantum mechanical/molecular mechanical (QM/MM) molecular dynamics (MD) simulations, including the crucial first solvation shell in the quantum mechanical region, offer a suitable compromise. These hybrid techniques have proven to yield very reasonable results.^{8–14} Several different simulations have been carried out for solvated Cu²⁺, already providing a quite accurate picture of the solvation structure. However, the level of theory had been restricted so far to HF and B3LYP simulations with varying size of the QM region,⁷ as until now it was not possible to perform simulations beyond the HF level including electron correlation effects. Detailed information on the QM/MM technique and the intermolecular potentials as well as the simulation protocol can be found in earlier publications^{7,8} and the Supporting Information.

QM/MM simulations at MP2 level of theory allow one to estimate the influence of electron correlation on structural and dynamical properties and the Jahn–Teller distortion. Furthermore, it offers the possibility to assess the quality of our previous simulations in this field. However, the computational demand of the simulation is increased to nearly 150 days of CPU time on 10 Athlon 2.4 GHz processors for 5 ps simulation time (plus 1 ps equilibration), in contrast to the previous HF simulation, consuming 40 days on two 1.0 GHz processors for the same simulation time.

The main structural properties of the system are summarized and compared with an identical simulation at the HF level in Table 1, and the results of two, two-shell QM/MM simulations at the HF and B3LYP levels, analyzed in detail in our previous work,⁸ are listed in this table, too. The two, one-shell QM/MM simulations (MP2/MM as well as HF/MM) use a three-body corrected classical

Table 1. Hydration Structure Parameters of Cu²⁺ in Water, Determined by QM/MM MD Simulations at the MP2 and HF Levels, and Comparative Data of HF and B3LYP QM/MM MD Simulations, Including the First and Second Hydration Shells in the QM Region⁷

	MP2/MM	HF/MM	HF-2shell	B3LYP-2shell
<i>r</i> _{1,max} (Å) ^a	2.07/2.35/(2.5) ^b	2.07/2.2 ^c	2.03/2.15/(2.3)	2.02/2.29
<i>r</i> _{2,max} (Å) ^a	4.6	4.62	4.22	4.13
CN 1st ^d	6.0	6.0	6.0	6.0
CN 2nd ^d	10.4	11.7	12.7	11.9
O–M ²⁺ –O (°)	88/174	89/173	90/172	88/173
θ (°) ^e	166	170	162	136
tilt (°) ^f	0–60	0–50	0–70	0–90
α(O–H–O) (°)	107	106	107	106
<i>d</i> (O–H) (Å)	0.982	0.962	0.957	0.983

^a First (second) peak maximum of Cu²⁺–O–RDF. ^b Shoulder of the first (second) peak of the Cu²⁺–O–RDF and a small second shoulder in parentheses. ^c Resolved by Gaussian peak analysis. ^d First (second)-shell coordination number. ^e Angle between ion–O and dipole vector. ^f Angle between ion–O vector and water plane.

potential to describe the non-QM part of the system. The radius of the QM region was 3.2 Å, and double-ξ basis sets with additional polarization functions were used for all atoms.

The first peak maxima are identical and located at 2.07 Å, slightly larger than the two-shell QM/MM results, and especially in the MP2 case a clearly defined shoulder of the first peak was observed located at 2.35 Å. The shoulder caused by the Jahn–Teller distortion of the six-fold-coordinated complex was much weaker in the HF simulation, indicating an influence of electron correlation effects on the Jahn–Teller behavior.

The MP2 result is also in good agreement with both available EXAFS studies^{4,15} for the “axial” value; for the “equatorial” one it fully agrees with ref 15, but differs by 0.09 Å from the value reported in ref 4. Compared to our previous two-shell QM/MM simulations, it shows less well defined shoulders of the first peak.

The first-shell coordination number of 6 is in agreement with nearly all experimental data.^{4,6,15} The average coordination number in the second solvation shell of the MP2 simulation (10.4) is slightly smaller compared to the HF and the two-shell QM/MM simulations. Several angle distributions, such as angular distribution functions, tilt, and θ angles, show similar results for all simulations (see Table 1). The electron correlation influence on water molecules in the QM region can be seen from the comparison of bond lengths and bond angles (see Table 1).

Figure 1 shows Cu–O radial distribution functions of both simulations, clearly demonstrating the high similarity of the curve shapes. However, analyzing the first peak shape exhibits a significantly better resolved shoulder in the MP2 case, indicating a more distinct [4+2] distortion of the complex due to the Jahn–Teller effect. The running integration number is exactly 6, proving the six-fold-coordinated species to be the exclusive one in the first hydration shell.

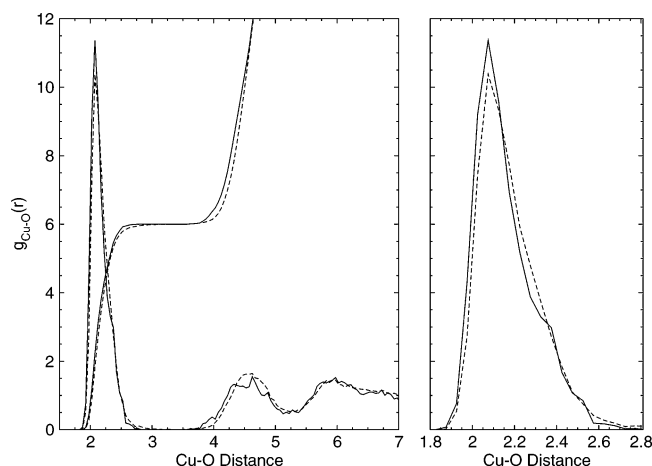


Figure 1. Cu–O radial distribution function (RDFs) obtained from MP2/MM (solid line) and HF/MM (dashed line) QM/MM MD simulations with their running integration numbers.

The stretching frequencies from MP2/MM and HF/MM simulations are 327 (215) and 303 (180) cm^{-1} , showing lower flexibility due to stronger bonds in the MP2 case. The two-shell QM/MM results are even higher, amounting to 356 (250) cm^{-1} in the HF case and 388 (280) cm^{-1} in the B3LYP case. The Jahn–Teller distortion is well visible in the power spectra⁸ as well, and numbers in parentheses give the values for the two elongated bonds of the [4+2] configuration.

The theoretical model of the Jahn–Teller distortion is consistent with a [4+2] configuration, as has already been shown in our previous HF and B3LYP QM/MM simulations. However, in agreement with these previous works, the MP2/MM simulation confirms that several other configurations with one, three, and even four elongated Cu–O bonds occur during the simulation.

The most interesting aspect of the Jahn–Teller behavior is its dynamic change of configurations with longer (“axial”) and shorter (“equatorial”) bonds, mostly in the relation 2:4. The lifetime of the distorted species, called inversion time, was estimated experimentally (¹⁷O NMR line widths at 298 K) to be 5.1 ps,¹ which, however, has to be considered with caution as the NMR technique is not suitable to accurately measure events in the low picosecond range.

Oxygen–oxygen distance plots are suitable to analyze the changes of the [2+4] configuration during the simulation time. Figure 2 shows the three pairs of trans-located oxygen pairs (O–O¹, O–O², and O–O³) involved in the dynamical distortion process. Similar results have been obtained from our previous QM/MM simulations at HF and B3LYP levels,⁷ but introducing electron correlation effects yields much better defined concurrent movements of trans-located water molecules.

The distance plots, together with detailed analysis using the MOLVISION visualization software, have clearly shown the inversion times to be 100–200 fs, proving the experimental value of 5.1 ps to be a strong overestimation. This is in agreement with the value of ~ 200 fs estimated from our previous QM/MM simulations, proving the reliability of HF/MM and B3LYP/MM simulations in this case. In addition to these very fast axial/equatorial inversions, an overlapping oscillation with a larger wavelength of 1–2 ps can be recognized.

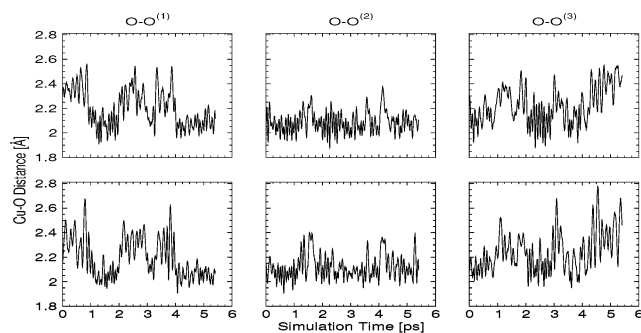


Figure 2. Ion–oxygen distance plots during the MP2/MM simulation, showing three pairs of synchronous moving trans-positioned water molecules.

No first-shell exchange processes were observed, as expected from the experimental mean residence time of a water molecule in the first shell of Cu^{2+} (230 ps).¹ The calculation of mean residence times of the classically treated second hydration shells with the direct method and a t^* value of 0.5 ps¹⁶ yielded similar values in the MP2 and HF cases, namely 10 and 8 ps, respectively.

QM/MM MD simulations at the HF and B3LYP levels give accurate results for structural and dynamical data. However, there is a detectable influence of electron correlation effects, especially on the Jahn–Teller behavior of the solvated Cu^{2+} ion. Our study also indicates that, for some data, the inclusion of the second shell into the QM region may be equally important as the inclusion of electron correlation. The data presented here also seem to be the most accurate theoretical treatment of the Jahn–Teller effect in solution so far.

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Supporting Information Available: Details of QM/MM MD simulations, construction of two- and three-body potential functions, and calculation of ion–oxygen frequencies and mean residence times. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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