Article

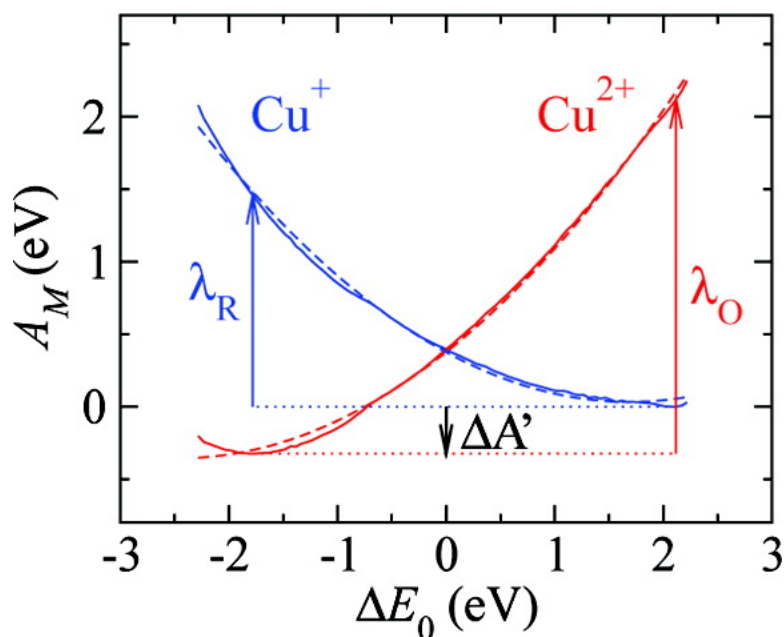## Cu/Cu⁻ Redox Reaction Exhibits Strong Nonlinear Solvent Response Due to Change in Coordination Number

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Cu$_{aq}^{+}$/Cu$_{aq}^{2+}$ Redox Reaction Exhibits Strong Nonlinear Solvent Response Due to Change in Coordination Number

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Abstract: We have carried out extensive Born−Oppenheimer molecular dynamics simulations to characterize the structure and energetics of the Cu$^+$/Cu^{2+} redox pair. Our simulations support recent experimental evidence suggesting that Cu^{2+} adopts a 5-fold coordination in aqueous solution and not the traditionally assumed octahedral coordination. Cu$^+$ forms a linear dihydrate structure with a third water molecule occasionally binding in the equatorial plane. We show that the change in ligand coordination number from 2 for aqueous Cu$^+$ to 5 for aqueous Cu^{2+} leads to marked deviations from the linear response assumption underlying Marcus theory of oxidation. The diabatic free energy curves deviate from parabolic behavior and the reorganization free energies for Cu$^+$ and Cu^{2+} are asymmetric and differ by 1.0 eV. The calculated reorganization free energies can semiquantitatively explain the exceptionally small electron self-exchange rate between Cu$^+$ and Cu^{2+} in aqueous solution.

1. Introduction

The aqueous solution structure of the important redox active ions Cu^{2+}[1−6] and Cu$^+$[7−9] has been the subject of intense discussions over recent years. Aqueous Cu^{2+} was for a long time regarded as the textbook example of a Jahn−Teller distorted octahedral complex.[10] Recent experimental[1−4] and computational studies[1,5,6] indicate, however, that this view is no longer valid. The latest analyses of EXAFS measurements indicate that Cu^{2+} is 5-fold coordinated, forming a distorted square pyramid in aqueous solution.[3] Turning to the solvation structure of Cu$^+$, this ion was often assumed to bind four water molecules.[7,11] However, no direct experimental data for the solvation structure of Cu$^+$ are available because of the short lifetime of this ion in aqueous solution.[8] Recent measurements of IR-photodissociation spectra of gaseous aquo-clusters suggest that Cu$^+$ forms a linear dihydrate[9] analogous to the Cu$^+$ diammine complex.[8] In the present computer simulation study,
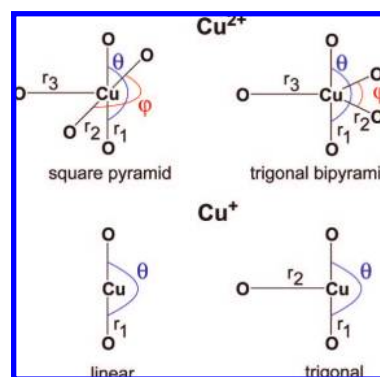

Figure 1. Definition of bond lengths and distances for Cu^{2+} and Cu$^+$. See Supporting Information Table 1 for numerical values.

we find strong support for the latest experimental results that suggest that the aqua-ions of Cu$^+$ and Cu^{2+} are 2-fold[9] and 5-fold[3] coordinated, respectively. Moreover, we show that the change in ligand coordination number from two to five leads to marked deviations from the linear response assumption underlying Marcus theory of oxidation.[12] The computed thermal activation free energy for oxidation is large, due to the drastic change in solvent coordination number, and can semiquantitatively explain the very small rate for electron self-exchange between Cu$^+$ and Cu^{2+}.

2. Results and Discussion

The solvation structure of the Cu$^+$ and Cu^{2+} aqua-ions obtained from 50 ps density functional theory based Born−Oppenheimer molecular dynamics (BOMD) simulation are depicted in Figure 1 (see ref 13 for simulation details). Cu$^+$

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forms a tightly bound approximately linear dihydrate in most configurations, with an average Cu−O distance $r_1 = 1.85$ Å and a O−Cu−O angle $\theta = 172°$ (see Supporting Information for radial distribution functions). The 2-fold coordination of Cu^+ is in agreement with recent IR-spectroscopy data of aquo-clusters in the gas phase.[9] It is also consistent with the successive hydration energies of Cu^+ obtained from experiment and electronic structure calculations. In the experimental study of ref 14, the first two water molecules were found to bind very strongly, whereas the binding energy of the third and fourth water molecule dropped by more than a factor of 2. Static ab initio[15] and DFT calculations[16] in the gas phase could reproduce the experimental hydration energies well and also provided an explanation for this rather peculiar trend: the 4s and 3d levels of Cu^+ are close in energy and mix to form σds orbitals. The mixing removes electron density along the molecular axis of the dihydrate and builds up electron density at the equatorial plane. This makes further water coordination energetically less favorable.

Our simulation shows that the picture for solvation of Cu^+ in the gas phase needs only a slight modification to describe the solvation structure of Cu^+ in aqueous solution under ambient conditions. This is because we also observe that a third water molecule occasionally binds to the dihydrate in the equatorial plane at a rather large distance of 2.6−2.8 Å. This produces a T-shaped structure, where the tight linear coordination of the first two water ligands is retained. A similar T-shaped coordination has recently been reported for an organo-metallic complex of Cu^+ with an elongated water ligand.[17] Our simulations suggest that 2-fold and 3-fold coordination exist at room temperature, with 2-fold coordination being dominant. This finding is consistent with the results of MP2 calculations on the gas phase formation free energy of two $Cu^+(H_2O)_3$ isomers. The isomer forming three Cu−O coordination bonds was found to be only 3.6[18] and 5.5 kcal/mol[19] less stable than the isomer forming two Cu−O coordination bonds and one hydrogen bond between the third water and a first shell water molecule. The small difference in stability indeed suggests that both structures could exist under ambient conditions.

Turning to the solvation structure of the oxidized state, we find that Cu^{2+} binds five molecules in the first solvation shell at an average distance of 1.99 Å (first peak of Cu−O radial distribution function). 5-fold coordination was the only stable coordination observed along the 50 ps trajectory. We have tested this observation by choosing the traditionally assumed octahedral coordination as the initial configuration for Cu^{2+}. Within 60 fs of dynamics, one axial ligand became expelled from the first coordination sphere, leaving Cu^{2+} 5-fold coordinated until the
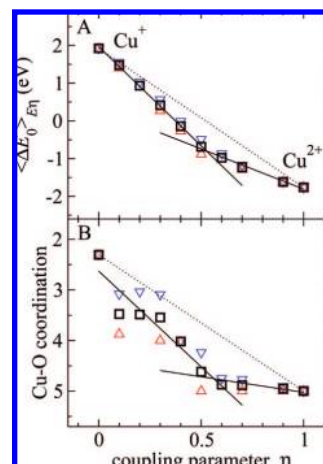

Figure 2. Thermal average of the ionization energy ΔE_0 (A) and of the Cu−O coordination number (B) as a function of the coupling parameter η. Data points obtained for increasing values of η (= oxidation of Cu^+) are denoted by triangles pointing downward, and data points obtained for decreasing values of η (= reduction of Cu^{2+}) are denoted by triangles pointing upward. Average values for oxidation and reduction are denoted by squares. The prediction of linear response theory is shown in dotted lines in (A). Linear fit functions for data points in the intervals $\eta = [0, 0.5]$ and $\eta = [0.5, 1]$ are shown in solid lines.

end of the simulation. The coordination geometry of Cu^{2+} is highly dynamic fluctuating between distorted square pyramidal and trigonal bipyramidal (see the Supporting Information for a quantitative analysis). These two coordination geometries were in fact the only ones that could not be excluded in any analyses of EXAFS, neutron diffraction or large-angle scattering studies of aqueous Cu^{2+}.[3] Latest fits to EXAFS data gave best agreement with an elongated five-coordinated square pyramid[3] with bond distances that are remarkably similar to the ones obtained in the present simulation (see Table 1 in the Supporting Information).

To investigate the energetics for the redox reaction $Cu^+ \rightarrow Cu^{2+}+1e^-$, we have carried out BOMD simulations[20] on the composite potential energy surface $E_\eta = \eta E_O+(1 - \eta)E_R$, where E_R and E_O are the N and $N - 1$ electron DFT-ground-state potential energy surfaces (PES) of the reduced and oxidized states, respectively, and η is a linear parameter (using the system specification of ref 13). Note that in our approach, the excess electron in state O is simply removed from the system and not transferred to the solvent. Simulation on the PES E_η is necessary because configurations that connect the reduced and oxidized state would not be sampled during the simulation of the two end states. Thus, the system was slowly transferred from the reduced to the oxidized state by carrying out a series of 10 BOMD simulations (each at fixed η) for increasing values of η from 0 to 1 in steps of 0.1. The reverse reaction, reduction of Cu^{2+}, was simulated by decreasing η in 8 steps from 1 to 0. The ionization energy $\Delta E_0 = E_O-E_R$ averaged over these trajectories, $\langle\Delta E_0\rangle_{E_\eta}$, is shown in Figure 2 A. In case of linear response, $\langle\Delta E_0\rangle_{E_\eta}$ should be a linear function over the entire range of η values. As one can see in Figure 2 A, this is not the case for the Cu^+ /Cu^{2+} redox pair. $\langle\Delta E_0\rangle_{E_\eta}$ decreases faster in the range $\eta = 0-0.5$ than for $\eta = 0.5-1$. However, each of the two regions can be fit to a linear function with R^2 values of 0.9991 for $\eta = 0-0.5$ and 0.9872 for $\eta = 0.5-1$.

(13) Solutions contain 1 Cu ion and 32 water molecules, simulated under periodic boundary conditions at $T = 300$ K using the BLYP exchange-correlation functional, code: CPMD Version 3.10, The CPMD consortium, http://www.cpmd.org, MPI für Festkörperforschung and the IBM Zurich Research Laboratory 2005, see Supporting Information for further details.

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The change in Cu–O coordination number corresponding to the change in ionization energy is illustrated in Figure 2 B. The coordination number successively increases with increasing η from 2.3 at $\eta = 0$ to 4.2 at $\eta = 0.5$. At this stage, all four water molecules forming the equatorial ligands of square pyramidal Cu^{2+} are bound. Then, at $\eta = 0.6$, a fifth water molecule penetrates the coordination sphere and forms a very weak coordination bond with Cu. Further increase of η merely leads to a tighter binding of the water ligands and of the fifth, axial ligand in particular. Reduction of Cu^{2+} does not follow exactly the same route in terms of coordination number, although the averages in ionization energies for reduction and oxidation are very similar (see Supporting Information for discussion). Comparing panels A and B of Figure 2, we find that the change in slope for ionization energy at $\eta = 0.5$ coincides with the formation or decay of the 5-fold coordinated Cu ion. This implies that the two slopes observed for ionization energy are the consequence of two different types of solvent reorganization: the branch with the larger slope ($\eta = 0-0.5$) is caused by addition of three solvent molecules to the coordination sphere of Cu, while the branch with the smaller slope ($\eta = 0.5-1$) is due to tighter binding of first shell ligands and reorganization of solvent in the second coordination shell.

The marked deviations from linear response have important consequences with regard to calculation of redox potential and reorganization free energy. The reaction free energy for the oxidation reaction $Cu^+ \rightarrow Cu^{2+} + 1e^-$, as obtained by integrating $\langle \Delta E_0 \rangle_{E_\eta}$ over the coupling parameter η (thermodynamic integration), is $\Delta A = \int_0^1 \langle \Delta E_0 \rangle_{E_\eta} d\eta = -0.32$ eV, while the linear response approximation gives $\Delta A = 1/2(\langle \Delta E_0 \rangle_{E_0} + \langle \Delta E_0 \rangle_{E_1}) = 0.08$ eV. The oxidation free energy is therefore severely overestimated in the linear response approximation, and this is caused by the convex shape of $\langle \Delta E_0 \rangle_{E_\eta}$ with respect to η. We would like to emphasize that the absolute redox potential obtained in this way cannot be compared with experiment due to the finite size of our simulation cell (containing not more than 32 molecules). However, we have shown that relative redox potentials between two iso-Coulombic redox reactions can be compared to experiment because the finite size effects cancel to a very good approximation.[5,21] This is because the redox potential difference between two iso-Coulombic reactions is a short-range effect. Adopting the $Ag^+ \rightarrow Ag^{2+} + 1e^-$ reaction as an iso-Coulombic reference system ($\Delta A = 1.16$ eV),[20] we obtain a reaction free energy of $-0.32-1.16 = -1.48$ eV for the total reaction $Cu^+ + Ag^{2+} \rightarrow Cu^{2+} + Ag^+$. The experimental value is -1.83 eV. The deviation of about 0.3 eV is in the typical range of errors for estimation of aqueous phase redox free energies with density functional methods.[22]

The diabatic free energy curves of Cu^+ and Cu^{2+}, $A_M(\Delta E_0)$, were calculated from the probability distributions of ΔE_0, p_M, $M = R,O$, according to $A_M = -k_B T \ln p_M(\Delta E_0) + \text{const.}$ The probability distributions were obtained from the BOMD simulations on the PES E_η by collecting for each η-window the values ΔE_0 in bins of width 0.05 eV, followed by combination and reweighting of the data according to WHAM.[23] According to Marcus Theory, the two diabatic curves are parabola with equal
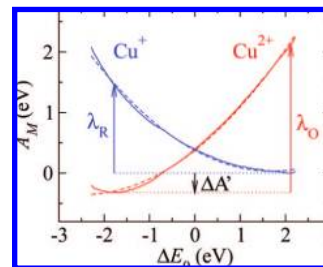

Figure 3. Diabatic free energy curves for Cu^+ and Cu^{2+} in aqueous solution (solid lines) and parabolic fit functions (dashed lines). The reorganization free energies of Cu^+ and Cu^{2+} are denoted λ_R and λ_O. The free energy difference between the two minima of the curves, $\Delta A'$, is identical with the full reaction free energy ΔA within the accuracy of our calculations (see ref 27 for an explicit relation of these two quantities).

curvature. As one can see in Figure 3, the best parabolic fit functions of A_M approximate the region around the minimum of Cu^+ very well, and also the region of high free energies for Cu^{2+}. However, the same parabola do not fit the minimum of Cu^{2+}, because the curvature is higher than for Cu^+. As a consequence, the reorganization free energy for Cu^{2+}, $\lambda_O = 2.44$ eV, is significantly larger than for Cu^+, $\lambda_R = 1.46$ eV. (Note that according to Marcus Theory, they should be equal.) The asymmetry of the free energy curves is consistent with the nonlinearity of $\langle \Delta E_0 \rangle_{E_\eta}$ and a further indication that the Cu^+/Cu^{2+} redox pair is not in the linear response regime. However, the Cu^+/Cu^{2+} redox pair can be well described by a two-Gaussian model, see ref 24 for details. The remarkably large reorganization free energy for Cu^{2+} can be explained by the high stability of the four equatorial water ligands of Cu^{2+}. In order to form the dihydrate structure of Cu^+, two of the four tightly bound equatorial ligands have to unbind at a very large energetic cost.

The reorganization free energies for Cu^+ and Cu^{2+} are significantly larger than the values that we have previously calculated for aqueous Ru^{2+} and Ru^{3+}, 0.78 eV for both oxidation states.[25] This is in line with the very small reaction rate for electron self-exchange between Cu^+ and Cu^{2+} in aqueous solution (estimated upper bound is $5 \times 10^{-6} M^{-1}s^{-1}$),[11] when compared to electron self-exchange between Ru^{2+} and Ru^{3+}, 20 $M^{-1}s^{-1}$.[26] Estimating the activation free energy for electron self-exchange from the single ion reorganization free energies, $\Delta A^\ddagger = (\lambda_R + \lambda_O)/4$, the ratio of the rate constants of the two reactions is predicted to be $k_{Cu}/k_{Ru} = exp[-(\Delta A_{Cu}^\ddagger - \Delta A_{Ru}^\ddagger)/k_B T)] = 10^{-10}$, as compared to the experimental estimate of $\leq 10^{-7}$. Clearly, this is only a rough estimation, since the pre-equilibrium constant, coupling matrix element, and donor–acceptor distance are assumed to be equal for both reactions. However,

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(24) The diabatic curves in Figure 3 can be fit to two parabola, one for the region 2.2 to -0.8 eV (1) and one for -0.8 to -2.3 eV (2). These two regions coincide with the two approximately linear segments between $\eta = 0-0.5$ and $\eta = 0.5-1$ in Figure 2A. The width of the corresponding Gaussian distributions is $\sigma_1 = 0.20$ eV and $\sigma_2 = 0.37$ eV, predicting a slope $\partial \langle \Delta E_0 \rangle_\eta / \partial \eta = -\beta \sigma_i^2 = 5.39$ ($i = 1$) and 1.59 eV ($i = 2$) to be compared with the slopes from the linear fits of the two segments in Figure 2A, 5.26 and 2.13 eV. The fairly good agreement between these two sets of numbers shows that the Cu(I)/Cu(II) system can be well described by a two-Gaussian model. However, there is some deviation for the slope of segment 2 induced by moderate nonlinearities in this segment (which is consistent with the smaller R^2 value of the linear fit of segment 2 in Figure 2A).

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our estimation shows that the computed reorganization free energies can at least semiquantitatively account for the very small self-exchange rate between Cu^+ and Cu^{2+}.

3. Conclusions

In conclusion, we have given support to the latest experimental evidence suggesting that Cu^+ forms a dihydrate structure and Cu^{2+} a distorted square pyramidal structure in aqueous solution. Moreover, we have identified the change in first shell coordination number of a transition metal ion as a possible source for strong deviations from the linear response assumption underlying Marcus theory of oxidation. We hope that the asymmetry in the energy gap fluctuations of Cu^+ and Cu^{2+} can be confirmed experimentally in the near future, for example by measurement of energy resolved photoelectron spectra.

Note Added in Proof. After submission of this manuscript a computational study of the Cu^{2+} aqua ion was published.[28] It was shown that the five-coordinate ion is more stable than either the six- or four-coordinate ion in agreement with present results.

Supporting Information Available: Relevant formulas for the free energy calculations, simulation details, a more detailed discussion of the structure of Cu^{2+} and the nonlinear solvent response, a table summarizing structural data, and a figure showing the radial distribution functions of Cu^+ and Cu^{2+}. This material is available free of charge via the Internet at http://pubs.acs.org.

JA805471A

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