Copper Cation Interactions With Water

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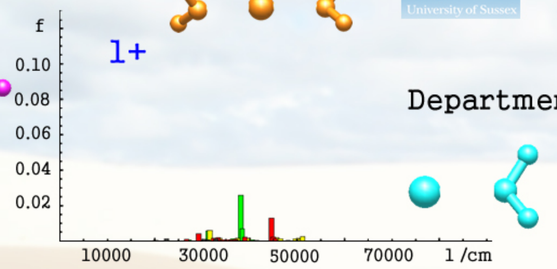
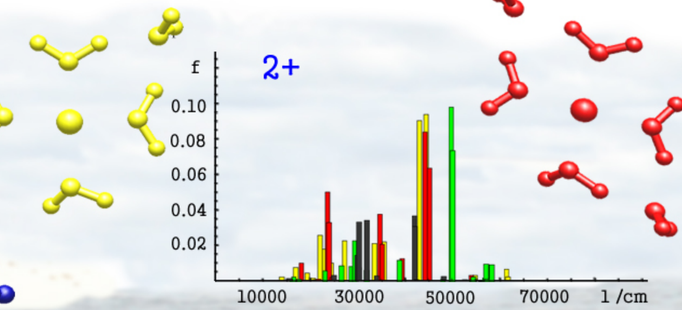
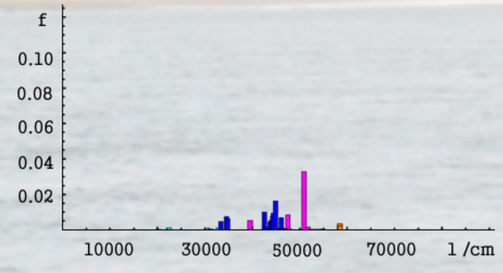


2) Spectra of monovalent structures with 4 coordinated primary solvation shell - n=5 to 8 (LB94)

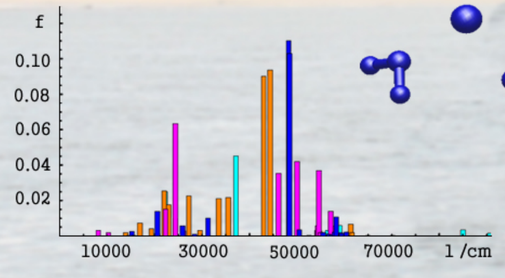


2) Spectra of divalent structures with 4 coordinated primary solvation shell - n=5 to 8 (LB94)

Excitation spectra



3) Spectra of monovalent complexes with n= 1 to 4 (LB94)



4) Spectra of divalent complexes with n= 1 to 4 (LB94)

Spectra of $Cu^{2+}(H_2O)_n$ are colour coded:

n=1 cyan; n=2 orange; n=3 purple; n=4 blue; n=5 green; n=6 yellow; n=7 red; n=8 grey

Introduction

Water is the most important solvent, it is the matrix of life. A knowledge of hydration patterns of cations such as Cu is important from a theoretical perspective and also to explain a range of biological phenomena and the results of gas phase experiments where new solvation patterns have been discovered by Stace, Firth and Wright [1,2]. These structures have also been the subject of their latest experiments [3].

The interconversion of Cu(I) – Cu(II) is at the heart of important biochemical electron transfer pathways [4] which include respiration. A knowledge of how the ionisation energies of Cu(I) change under different ligand environments and geometries relates to the functioning of copper proteins and metalloproteins in general.

Following the work of Berces and Ziegler [5], who have determined the unusual structures of the divalent complexes, structures have been calculated for the monovalent complexes. In addition, the Lande g constant have been calculated (for divalent complexes based on the 4 coordinated structure and octahedral) and excitation energies and IE's have been calculated for all complexes.

Computational Details

Calculations have been performed using the Amsterdam Density Functional (ADF 2006.01) program [6]. A TZ2P basis set or better was used in all calculations.
Geometry optimisations employed the Local density Approximation (LDA) [7]. The corresponding energies included post SCF gradient corrections based on the Becke exchange [8] and Perdew correlation [9].Binding energies were calculated with and without relativistic scalar (ZORA) [10] corrections.
Excitation energies were calculated non-relativistically using time dependent density functional theory (TDDFT) with adiabatic LDA (ALDA). The SCF step of the calculations was carried out using the LDA and the LB94 [11] potentials and the TZ2P basis set.
ESR g values have been calculated using the TZ2P basis set and the ZORA approximation including spin orbit effects and employing LDA, BP86 and LB94 potentials.

Ionization Energies

IE's calculated using the LDA post SCF Becke Perdew and the TZ2P basis set. Vertical IE's are based on the same structure–for 1+ and 2+ states – and adiabatic energies are based on the geometries optimised for the 1+ and 2+ cases (Koopman IE = $-E_{homo}$).

		Koopman		Vertical	Adiabatic
		LDA post SCF BP	LB94		
$[Cu(H_2O)]^+$		12.40	19.05	17.44	17.40
$[Cu(H_2O)_2]^+$		11.11	17.28	15.58	15.53
$[Cu(H_2O)_3]^+$	3+0	9.44	15.70	14.52	13.62
	2+1	10.36	16.35	14.39	*
$[Cu(H_2O)_4]^+$	4+0	8.09	14.60	12.91	12.25
	3+1	8.70	14.85	13.02	12.86
	2+2	9.40	15.51	13.46	*
$[Cu(H_2O)_5]^+$	4+1	8.08	14.15	11.77	11.38
	3+2	8.24	14.26	+	*
$[Cu(H_2O)_6]^+$	4+2	7.70	13.83	11.74	10.83
$[Cu(H_2O)_7]^+$	4+3	6.86	12.96	10.74	10.16
$[Cu(H_2O)_8]^+$	4+4	5.47	11.74	9.60	9.53

* An optimised geometry couldn't be obtained for the divalent complex
\+ The divalent calculation using the monovalent structure failed to converge

Incremental Binding Energies

$$Cu^+(H_2O)_n \rightarrow Cu^+(H_2O)_{n-1} + H_2O$$

IBE's (kcal / mol) have been calculated and compared to experimental results and to high level *ab initio* calculations. All data presented is in good agreement with experiment. Inclusion of relativistic effects does not improve agreement with experiment. The energies (both with and without inclusion of relativistic effects) appear fairly converged even at the TZ2P basis set level. Thus this level of methodology appears adequate for the purposes of this work.

		Calculated								Exp.	Ref.
		DFT							CCSD(T)	[13]	
		non-relativistic				relativistic			[12]		
		post SCF BP86				post SCF BP86					
Complex	Config.	TZ2P	TZ2P+	ET-pVQZ	ET-QZ3P	TZ2P	TZ2P+	QZ4P			
$[Cu(H_2O)]^+$	1	43.4	42.1	45.9	46.1	46.9	45.2	46.6	39.0	36 ± 3	[14]
										38.4 ± 1.4	[15]
$[Cu(H_2O)_2]^+$	2	43.4	42.2	44.0	44.5	46.6	45.6	47.0	43.8	40 ± 3	[14]
										40.7 ±1.6	[15]
$[Cu(H_2O)_3]^+$	2+1	18.4	18.5	17.7	17.8	18.7	18.6	18.0	16.6	16.4 ± 0.2	[14]
										17.6 ± 2	[14]
										13.7 ± 1.8	[15]
$[Cu(H_2O)_4]^+$	2+2	16.2	16.2	16.0	16.7	16.6	16.4	16.0	15.0	16.7 ± 0.2	[13]
										16 ± 2	[15]
										12.8 ± 1	[13]
$[Cu(H_2O)_5]^+$	3+2	6.2	6.1	6.0	7.1	5.1	5.6	5.0	9.0	14 ± 0.1	[13]

ESR g values

Calculated ESR g values are compared to experimental results obtained in solid glass matrices and also to previous high level *ab initio* calculations. LDA seems to provide the best results among the 3 functionals employed. The results displayed below suggest that the octahedral structure (OCT) has values that differ slightly from all the 4-coordinated structures. The values $g_{\parallel}$ / $g_{\perp}$ are displayed below:

	DFT						MRSDCI [12]	Exp. [17]
	4+0	4+1	4+2	4+3	4+4	6+0 (OCT)	(OCT)	(OCT)
LDA	2.17 / 2.04	2.16 / 2.04	2.15 / 2.04	2.14 / 2.04	2.14 / 2.04	2.20 / 2.06	2.30 / 2.09	2.40 / 2.10
BP86	2.15 / 2.04	2.17 / 2.03	2.14 / 2.04	2.13 / 2.04	2.13 / 2.04	2.17 / 2.05		
LB94	2.14 / 2.03	2.13 / 2.03	2.12 / 2.03	*	*	2.16 / 2.05		

* LB94 calculations didn't converge for these large systems

Conclusions

For both mono- and divalent Cu-water complexes, a strong preference for second shell coordination via double acceptor hydrogen bonds to the primary solvation shell was found for n greater than 3.

As expected, the Koopman ionization energies (IE) using LDA were underestimated, however, the LB94 Koopman IE were overestimated, when compared with the calculated vertical IE. Furthermore, there was surprisingly good agreement between the adiabatic IE and the vertical IE. Interestingly, for n > 4, the IE of the singly charged complex is less than that of water (12.61 eV).

The TDDFT study revealed that for Cu(II) complexes with n > 4, the dominant transition energies were around 40000 and 50000 wavenumebers (5-6 eV). All transitions are LMCT and terminate at the beta lumo. The dominant transitions in the Cu(I) complexes have much smaller oscillator strengths and are primarily MLCT arising from a homo-lumo transition.
The LB94 energies are lower than the ones obtained using the LDA for the divalent complexes. For monovalent complexes the situation is reversed: LDA yields lower excitation energies.

Calculated g values seem to be suitable to distinguish 4-coordinated (4+2) from 6-coordinated structures. Agreement to experimental result is not very close , which may indicate different degrees of Jahn-Teller distortion on the solid and gas phases.

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Acknowlegments

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