The hydration of Cu^{2+}: Can the Jahn-Teller effect be detected in liquid solution?

Jesús Chaboy
Instituto de Ciencia de Materiales de Aragón, CSIC-Universidad de Zaragoza, 50009 Zaragoza, Spain

Adela Muñoz-Páez
Departamento de Química Inorgánica-ICMSE, CSIC-Universidad de Sevilla, 41012 Sevilla, Spain

Patrick J. Merkling
Departamento de Ciencias Ambientales, Universidad Pablo de Olavide, Carretera de Utrera Km. 1, 41013 Sevilla, Spain

Enrique Sánchez Marcos[a)]
Departamento de Química Física, Universidad de Sevilla, 41012 Sevilla, Spain

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The long elusive structure of Cu(II) hydrate in aqueous solutions, classically described as a Jahn-Teller distorted octahedron and recently proposed to be a fivefold coordination structure [Pasquarello *et al.*, Science **291**, 856 (2001)], has been probed with x-ray-absorption spectroscopy by performing a combined theoretical and experimental analysis. Two absorption channels were needed to obtain a proper reproduction of the x-ray-absorption near-edge structure (XANES) region spectrum, as already observed in other Cu(II) complexes [Chaboy *et al.*, Phys. Rev. B **71**, 134208 (2005)]. The extended x-ray-absorption fine-structure (EXAFS) spectrum was analyzed as well within this approach. Quite good reproductions of both XANES and EXAFS spectra were attained for several distorted and undistorted structures previously proposed. Nevertheless, there is not a clearly preferred structure among those including four-, five-, and sixfold coordinated Cu(II) ions. Taking into account our results, as well as many more from several other authors using different techniques, the picture of a distorted octahedron for the Cu(II) hexahydrate in aqueous solution, paradigm of the Jahn-Teller effect, is no longer supported. In solution a dynamical view where the different structures exchange among themselves is the picture that better suits the results presented here. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2165189]

I. INTRODUCTION

Copper(II) ions are present in many biological systems and play a fundamental role in different vital processes. The knowledge of Cu(II) coordination and its local structure in a great number of complexes, its mode of binding to proteins and biomolecules in general, has given rise to a great body of research in different scientific disciplines.[1,2] Surprisingly the structure of the simplest complex, that of Cu(II) in aqueous solution, is a matter of ongoing debate. It has long been described as a six-coordinated Cu–O octahedron, showing an elongation along one of the metal-ligand axes by analogy to that found in the crystalline state. This distortion would be due to the Jahn-Teller (JT) effect expected for a d^9 electronic configuration in an octahedral crystal field.[3] However, the experimental evidence in solution that supports this distorted octahedral geometry turns out rather slippery. After three decades of research, while there is a general agreement concerning the shortest $R(\mathrm{Cu-O})_{\mathrm{eq}}$ interatomic distance in the equatorial plane, neither x-ray or neutron diffraction nor x-ray absorption spectroscopy has provided an unambiguous probe of the loosely bound axial water molecules.[4–7] Salmon and Neilson investigated by neutron diffraction (ND) the coordination of Cu(II) in a concentrated copper nitrate solution, reporting that the radial distribution function (RDF) shows only a single peak that can be associated to the Cu–O pair.[8] Similar results were found by means of x-ray diffraction (XRD) in the case of both copper nitrate solution[9] and aqueous $CuSO_4$ solution:[10] there is no apparent proof of distortion in the nearest-neighbor coordination of Cu(II).[11]

Very recently, it has been proposed that the Cu(II) aquaion adopts a fivefold coordination fluctuating between both a regular square pyramid and a regular trigonal bipyramid configuration.[12] The departure from the generally accepted picture reported by Pasquarello *et al.*[12] causes the appearance of subsequent theoretical and experimental works trying to verify these findings, as reported by Rotzinger in a very recent review.[13] On the theoretical side, contradictory results have been recently provided by molecular-dynamics (MD) simulations. While in one case, Blumberger *et al.*[14] show that the Cu(II) hydrate fluctuates between tetragonally distorted octahedral, square pyramidal, and trigonal bipyramidal coordination, in another case, Schwenk and Rode[15] support a single distorted octahedral structure. In the latter case, the existence of the standard JT distortion was derived from the appearance of a weak shoulder of the asymmetric peak at 2.17 Å in the RDF.[15] Amira *et al.*[16] have recently proposed by means of Car-Parrinello MD computations a

[a)]Electronic mail: sanchez@us.es

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fivefold coordination exhibiting a square pyramid where the axial water molecule is elongated with respect to the four equatorial water molecules.

On the experimental side, contrary to the conclusions of Pasquarello *et al.*[12] proposing a regular structure, claims of a distorted geometry have been recently made by Benfatto *et al.*[17] based on both extended x-ray-absorption fine structure (EXAFS) and x-ray-absorption near-edge structure (XANES) results. In this study, the authors agree with the suggested fivefold coordination of Cu(II) by Pasquarello *et al.*,[12] although they propose a new distorted square pyramidal configuration, discarding both the regular square pyramid and trigonal bipyramid configurations.[17] Frank *et al.*[18] have recently revisited the problem applying a fitting technique, which employs the full multiple-scattering (FMS) approach, including geometrically unconstrained models to the XANES data (MXAN method). They found that the best fit was an elongated square pyramid, although a four-coordinated nonplanar arrangement of D_{2d} symmetry was producing a fit almost as good as the five-coordinated arrangement. A combined large-angle x-ray diffraction (LAXS) and EXAFS analysis performed by Persson *et al.*[19] has been interpreted in terms of the classical distorted sixfold octahedral arrangement that has been assumed by other authors before.[20] The paradox that different studies involving x-ray techniques for structural determination do not lead to the same conclusions indicates that we stand in front of a limit case.

At this point it is interesting to recall the early work of Garcia *et al.*, concluding that it is not possible to discriminate if the system is distorted or not from the EXAFS analysis.[21] Sixteen years later, the debate is far from being closed. This controversy on the structure of Cu(II) hydrate in solution is a good test of the limits of the capability of x-ray-absorption spectroscopy to solve the local structure around ions in aqueous solution, since different analysis performed on data recorded by using the same experimental technique does not converge towards the same conclusions.

In some of the works using x-ray-absorption spectroscopy (XAS) to study Cu(II) hydration structure, the XANES part of the spectra is not analyzed, although this region is specially sensitive to coordination polyhedra. The first reason for this exclusion is the lack of a standard fitting procedure to extract structural information from the XANES spectrum similar to that established for EXAFS, although proposals in this direction have appeared recently.[17,22,23] Usually, a structure is confirmed by an *a posteriori* procedure, once the computed XANES spectrum for a given structure resembles that of the experimental one. This procedure is certainly more efficient when a given feature of the spectra changes under the influence of an external parameter (ligand exchange in the reference compound, change of solvent, temperature, etc.). Another way to check the relationship between features of the spectrum and structure can be theoretically achieved when systematic computations of structures either changing the geometry of the environment or adding successive shells around the absorber atom are included to determine the size dependence of the spectrum.

The second reason is that the XANES spectra of Cu(II) compounds are particularly difficult to reproduce. In fact, we have very recently shown the singular behavior of x-ray-absorption spectra of Cu(II) ions in nitrogen-coordinating square-planar complexes,[24] which shows a double channel for the absorption process due to two competitive final states. From this starting point and based upon previous experience in XANES computations of metal cations [Ni(II),[25] Y(III),[26] Cr(III), and Rh(III) (Ref. 27)] and single anions,[28] we carried out an unbiased approach taking into account all the recently proposed structures for the Cu(II) aquaion. To this aim, *ab initio* calculations of Cu *K*-edge XANES region have been performed within the multichannel multiple-scattering framework for four-, five-, and sixfold coordination models. Additionally, analysis of the experimental EXAFS spectrum has been carried out on the same basis, using a procedure similar to that employed in previous studies on the metal cation hydration.[27,29,30]

II. METHODS

Water solutions, 0.2*M*, of the $[Cu(H_2O)_x]^{2+}$ complexes were prepared by dissolving $Cu(ClO_4)\cdot 6H_2O$ in deionized water. X-ray-absorption spectra were recorded at the Cu *K* edge in the transmission mode at beam station 7.1 of the Daresbury Laboratory. The storage ring was operated at 2 GeV with an average current of 200 mA. A double-crystal Si(111) monochromator was used and higher harmonic rejection was achieved by detuning the second crystal. Although no mirrors were used for higher harmonic rejection, the intensity of the beam coming from a bending magnet in this medium energy source is not significant for energies above 15 keV.

The absorption spectra were analyzed according to standard procedures.[31] The origin of the energy scale E_0 was defined to be at the inflection point of the absorption edge. The spectrum was normalized, after background subtraction, at high energy ($\sim$150 eV above the edge) to eliminate the thickness dependence.

The computation of the Cu *K*-edge XANES spectra was performed by using the multiple-scattering CONTINUUM code.[32] A complete description of both the theoretical grounds and the calculation procedures can be found in Refs. 33–35. In the following, only a brief summary of those computational details relevant to our particular case is given. The potential for the XANES calculations has been calculated according to the standard muffin-tin approximation.[35–38] Neutral atomic orbitals were used to build the ground-state potential, while two choices have been tested to generate the final state potential: (i) the screened and relaxed $Z+1$ approximation[39] and (ii) the self-consistent-field (SCF) potential. Regarding the exchange and correlation part of the final-state potential we have used three different types: X_α, the energy-dependent Hedin-Lundqvist (HL) complex potential, and the energy-dependent Dirac-Hara (DH) exchange potential.[35] The calculated theoretical spectra have been further convoluted with a Lorentzian shape function whose width Γ_C accounts for the core-hole lifetime ($\sim$1.5 eV) (Ref. 40) and the experimental resolution ($\sim$1 eV). To improve

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the *ab initio* calculations, SCF potentials were stabilized for both $3d^9$ and $3d^{10}L$ electronic configurations, where L denotes a hole in the coordinating water molecules as described elsewhere.[24] As shown in Ref. 24, the contribution of two absorption channels together with a SCF treatment of the final-state potential is needed to get a correct reproduction of the experimental XANES spectra.

EXAFS fits were carried out taking into account single- and multiple-scattering (SS and MS) contributions using FEFF (v. 8.10) (Ref. 41) and FEFFIT (v. 2.54) (Ref. 42) codes in a procedure similar to that described elsewhere.[27,29,30,43] One SS path was taken into account for the symmetric structure and two for the distorted ones. Relevant MS paths were selected according to an amplitude filter (greater than 4% of the most intense path). Debye-Waller factor for MS paths was derived from those of SS paths according to the independent vibration model.[30,44] The amplitude reduction function, S_0^2, was fixed to 0.81 according to previous spectrum simulations of metal cation aqueous solutions based on molecular dynamics calculations.[27,45] This value has been previously used by us to fit the EXAFS spectra of Cu(II) complexes with nitrogen ligands[43] and is similar to the value used by Stern *et al.*,[42] 0.85, to fit other Cu foil spectra, and by Fulton *et al.*[46] to fit Cu(II) species under hydrothermal conditions. The fit of the EXAFS signal taking the double-channel process into account was carried out calculating two identical EXAFS functions shifted in energy the value obtained from SCF calculations, as described below.

III. RESULTS AND DISCUSSION

Being our aim to determine the local structure of the Cu(II) aquaion, we have calculated the Cu K-edge XANES for different four-, five-, and sixfold coordination models. The following structures have been considered:

- the classical sixfold octahedral geometry around Cu: axially distorted [d-O_h(JT)] and regular (O_h) octahedron;
- the distorted fivefold geometry proposed by Benfatto *et al.*,[17] i.e., four oxygen atoms and Cu lie in the plane while the fifth oxygen atom occupies the apical position of the square pyramid (d-SPy); the regular fivefold structures proposed by Pasquarello *et al.*,[12] i.e., a regular trigonal bipyramid with Cu at the center (TBPy); and a regular square pyramid (SPy); and
- a square-planar geometry (SPl) has also been considered because it is representative of the common arrangement formed by a set of four water molecules defining a plane which contains the metal cation.

Average distances for copper-oxygen have been taken from the literature, thus R_{eq}=1.96 Å and R_{ax}=2.34 Å for the distorted structures, whereas the shortest distance was employed in the case of structures with only one type of Cu–O coordination.

As shown in Fig. 1, the experimental XANES spectrum shows an asymmetric peak (A) centered at ~6 eV above the edge whose high-energy tail (B) extends up to the first absorption minimum (C) lying at ~30 eV above the edge. In a first approach, *ab initio* calculations have been performed by considering the d-O_h(JT) structural arrangement, i.e., the distorted octahedral geometry, as it has long been addressed as corresponding to that of Cu(II) in water solution. The computation does not correctly reproduce neither the shape nor the relative energy separation between the different features of the absorption spectrum (A–D). The main disagreement is found at the white-line region, i.e., in the first 20 eV above the absorption edge. This feature is narrower in the computed spectrum than in the experimental one. Subsequently other representative structures were checked. As shown in Fig. 1, none of the calculations performed for the geometries described above yields a good reproduction of the experimental XANES spectrum. In all cases the width of peak A in the calculated spectrum is about one-half of the experimental width. The disagreement of the computed spectra in reproducing both the shape and the relative energy separation between the different features of the absorption spectrum is independent of the exchange-correlation potential (ECP) used for the calculation. As shown in Fig. 2, no improvement

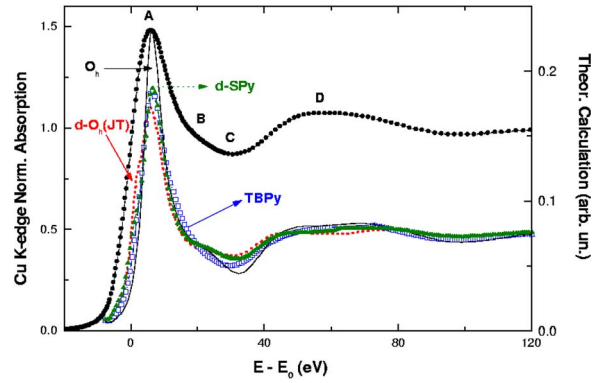

FIG. 1. Comparison of the experimental XANES spectrum at the Cu K edge in Cu(II) aqueous solution (●) and computed spectra for different coordination models: [d-O_h(JT)] distorted octahedron (small ●), (TBPy) regular trigonal bipyramid (□), (O_h) regular octahedron (solid line), and (d-Spy) distorted square pyramid (▲).

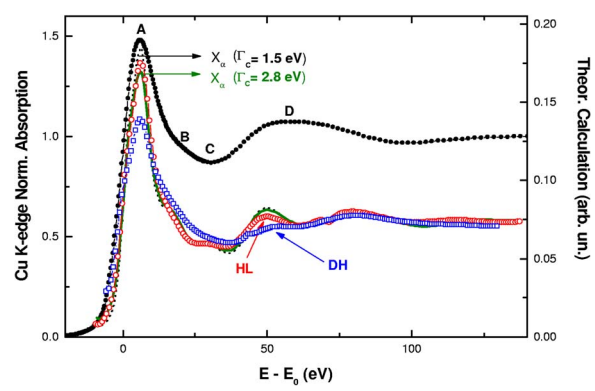

FIG. 2. Comparison of the experimental XANES spectrum at the Cu K edge in Cu(II) aqueous solution (●) and the theoretical spectra calculated for the distorted octahedron geometry [d-O_h(JT)] by using X_α potential and different convolution parameter: Γ_C=1.5 eV (small ●) and 2.8 eV (solid line). Computations performed with different ECP potentials are also shown: complex Hedin-Lundqvist (○) and complex Dirac-Hara (□).

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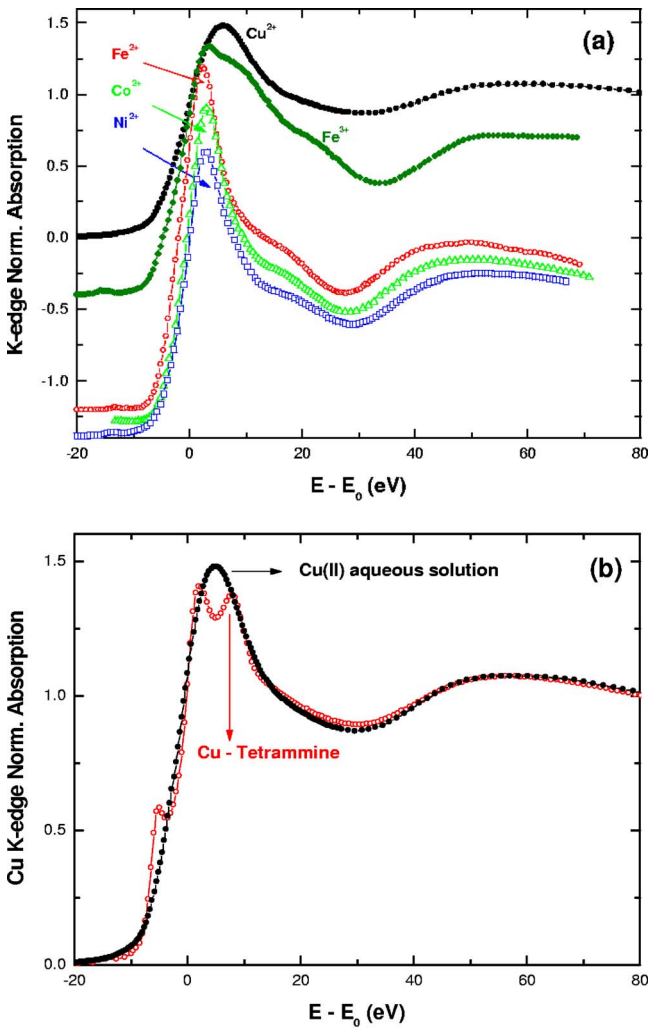

FIG. 3. (a) Experimental *K*-edge XANES spectra of different transition metals in aqueous solution, Cu(II) (●), Fe(II) (○), Co(II) (△), Ni(II) (□), and Fe(III) (♦). Data of Ni(II) and Co(II) are taken from Ref. 48 whereas those of Fe(II) and Fe(III) are extracted from Ref. 47. All the spectra are displayed in the same scale although vertically shifted for the sake of clarity. (b) Comparison of the experimental Cu *K*-edge XANES spectra of Cu(II) aqueous solution (●) and aqueous solution of tetramminecopper(II) (○) taken from Ref. 24.

is found by changing the ECP used for the theoretical calculation. Similarly, increasing the constant parameter Γ_C used to account for the experimental resolution and the core-hole lifetime through the convolution of the theoretical spectrum does not improve the comparison. This unsatisfactory result is obtained for all the structural arrangements considered. Even more, the comparison of the computed spectra for the different proposed structures reported in Fig. 1 shows that differences among them, due to the different contribution of the multiple-scattering paths, are very subtle.

These results point out the need of obtaining an accurate reproduction of the whole XANES spectrum, specially of the edge region, prior to get a reliable conclusion regarding the structure of Cu(II) hydrate in aqueous solution. To this respect, it is interesting to note that the width of peak A for the calculated Cu(II) spectrum in Fig. 1 is rather similar to the experimental spectra for Fe(II), Co(II), and Ni(II) cations in water[47,48] reported in Fig. 3(a). These experimental spectra were well accounted for by single-channel MS computations.[47,48] In contrast, peak A is much wider for the Fe(III) and Cu(II) hydrates included in the same figure. Whereas the Fe(II) spectrum is well accounted for by a single-channel calculation, two excitation channels are needed to reproduce the Fe(III) experimental spectrum.[47] This comparison points to the possibility that Cu *K*-edge XANES spectrum of Cu(II) aquaion is due to the superposition of two different excitation channels. Moreover, a recent work performed on the Cu *K* edge of Cu(II) complexes with N-coordinating ligands forming a square-planar arrangement around metal cation also supports this hypothesis.[24] Indeed, the comparison of the experimental Cu *K*-edge XANES spectra of the Cu(II) aqueous solution and that of tetramminecopper(II) reported in Fig. 3(b) shows that the width of the main absorption line is similar in both cases. The differences in the coordinating ligands (H_2O instead of NH_3) modify the shape of each absorption channel and render it wider in the aquocomplex in such a way that both signals merge and the double peak in the aminocomplex collapses to a broad peak in the aquocomplex. This is a direct consequence of using the SCF procedure. As a result, the projected density of states (DOS) is different and this result leads to the differences at the main absorption line, which is mainly due to atomiclike transitions to the empty DOS. This comparison strongly suggests the need of considering the addition of two absorption channels to account for the experimental XANES spectrum of Cu(II) aqueous solution.

Therefore, two absorption channels have been considered by assuming two different electronic configurations: $3d^9$ and $3d^{10}L$. According to self-consistent-field calculations, these configurations give rise to two absorption edges shifted in energy by $\Delta E = 6.06$ eV, as shown in Fig. 4(a). The XANES spectrum was then computed by considering that the total cross section can be written as the weighted sum of the contributions of both $3d^{10}L$ and $3d^9$ electronic configurations present in the final state.[49] The weighting factors for the $3d^{10}L$ and $3d^9$ electronic configurations have been fixed to 0.68 and 0.32, respectively, as already described in Ref. 24. No free parameters were used in the computations of the XANES spectra of the proposed structures for the Cu(II) hydrates.

Figure 4(b) shows the result of this calculation performed for all the structures. The use of both $3d^{10}L$ and $3d^9$ absorption channels improves the agreement with the experimental spectrum, being the width of the white line well accounted for by the computation. The HL ECP leads to a good reproduction of the relative energy separation between features A, B, and C. To the best of our knowledge, these computations are the best reproduction, in the absence of free parameters and fitting procedures,[17,50] of the experimental XANES spectrum of the Cu(II) hydrate. It should be noted that the damping associated with the inelastic losses of the photoelectron have been *ab initio* accounted for by using the complex Hedin-Lundqvist potential. Benfatto *et al.*[17] take into account these losses by using an energy-dependent broadening function that was considered as a fitting parameter.

With the inclusion of the two-channel calculation the

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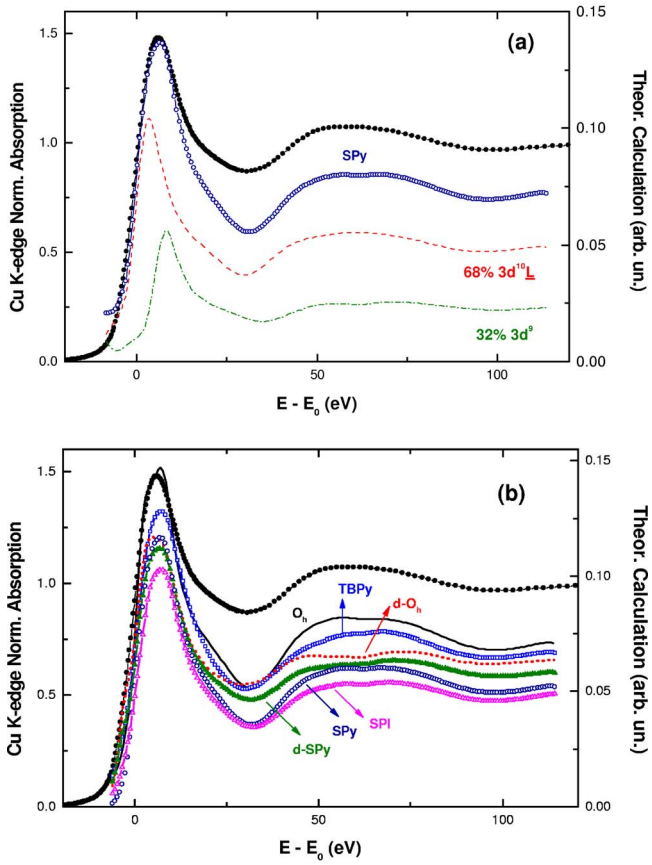

FIG. 4. (a) Comparison of the experimental XANES spectrum at the Cu K edge in Cu(II) aqueous solution (●) and the theoretical spectra obtained for the regular square pyramid arrangement (Spy) (○) as the weighted sum of the $3d^9$ (32%) and $3d^{10}L$ (68%) contributions calculated by using the Hedin-Lundqvist ECP (see text for details). For the sake of clarity the single contributions of both $3d^9$ (dot-dashed) and $3d^{10}L$ (dashed) electronic configurations are also shown. (b) Comparison of the experimental XANES spectrum at the Cu K edge in Cu(II) aqueous solution (●) and the theoretical calculation on the double-channel approximation performed for the different structures discussed in the main text: regular octahedron (O_h) (solid line), distorted octahedron [d-O_h(JT)] (small ●), regular square pyramid (Spy) (○), distorted square pyramid (d-Spy) (▲), trigonal pyramid (TBPy) (□), and square planar (SPl) (△). All the spectra are displayed in the same scale although vertically shifted for the sake of clarity.

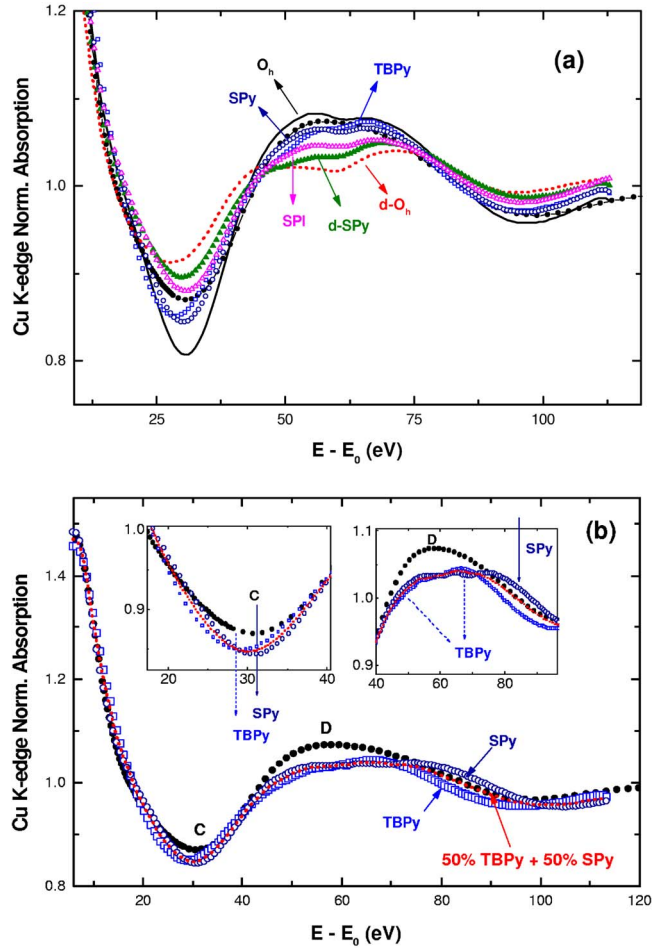

FIG. 5. (a) Detailed comparison of the experimental XANES spectrum at the Cu K edge in Cu(II) aqueous solution (●) and the theoretical calculation on the double-channel approximation performed for the different structures discussed in the main text: regular octahedron (O_h) (solid line), distorted octahedron [d-O_h(JT)] (small ●), regular square pyramid (Spy) (○), distorted square pyramid (d-Spy) (▲), trigonal pyramid (TBPy) (□), and square planar (SPl) (△). (b) Similar comparison is shown for a regular trigonal pyramid (TBPy) (□), a regular square pyramid (Spy) (○), and its weighted sum (small ●). The insets show detailed views of this comparison in the regions of features C and D.

computed spectra for the different structures proposed are rather similar, although several small differences can be addressed, as shown in Fig. 5(a). It should be noted, however, that the effect of static and dynamic disorders (Debye-Waller factors) has not been included in the calculations. The occurrence of these effects can slightly influence the calculated spectral shape, as shown in previous work.[27,51] Consequently, none of the considered geometries may be proposed unambiguously as the *single* preferred structure in solution. Bearing in mind this fact, we discuss in the following the performance of the calculation for each computed geometry. With the exception of the regular octahedron geometry (O_h) which does not properly account for the shape of the white line [see Fig. 4(b)], calculations performed for regular structures yield a good reproduction of the XANES spectrum, while the distorted ones [d-O_h(JT) and d-SPy] worsen the reproduction of the XANES structures beyond the first 30 eV above the edge. It is interesting to note that the performance of the calculation for the simple square-planar geometry (SPl) is better than that obtained for the distorted geometries. These results show that both regular fivefold coordination models (TBPy and SPy) yield the best reproduction of the XANES spectrum.

Finally, we have also tested the model proposed by Pasquarello *et al.* regarding the dynamics in the first solvation shell of the Cu(II) aquaion. To this respect, we have simulated the average spectrum which would be obtained under the assumption of a dynamic behavior where both trigonal bipyramid (TBPy) and square pyramid (SPy) arrangements were equally contributing to the whole signal. Then, the XANES spectrum would be the result of adding their computed XANES signals weighted at 50%. This theoretical XANES represents some improvement over both XANES spectra it is made of [see Fig. 5(b)] and provides an argument in support of several structures in equilibrium, for example, through a fast rate of the water exchange process of Cu(II) aquaion as proposed by Pasquarello *et al.*[12] and Blumberger *et al.*[14] Without additional source of information concerning

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TABLE I. Best fit $\mathcal{R}^2$ (minimum of the sum of squares as defined in Ref. 42), distances, Debye-Waller factors, and edge energy around the copper in water obtained from the analysis of an experimental EXAFS spectrum. SPl=square planar, O_h=octahedral, d-O_h(JT)=Jahn-Teller distorted octahedron, d-SPy =distorted square pyramid, TBPy=regular trigonal bipyramid, and SPy=regular square pyramid. The double-channel fit has the same degrees of freedom since the energy separation is fixed to 6 eV and the intensities to 68% (lower energy) and 32% (higher energy). 2.8 $\text{Å}^{-1} \leqslant k \leqslant 13\ \text{Å}^{-1}$, 1 $\text{Å} \leqslant R \leqslant 5$ Å, S_0^2 =0.81, and EXAFS was fitted to $\chi(k)k^2$.

	$\mathcal{R}^2$	R_1 (Å)	σ_1^2 (Å^2)	R_2 (Å)	σ_2^2 (Å^2)	E_0 (eV)
			Single-channel process (conventional fit)			
SPl	0.015	1.96(1)	0.0056(4)	⋯	⋯	−2.8(5)
O_h	0.105	1.94(2)	0.0129(14)	⋯	⋯	−5.7(18)
d-O_h(JT)	0.007	1.96(1)	0.0051(3)	2.40(4)	0.033(5)	−2.0(6)
d-SPy	0.007	1.96(1)	0.0051(3)	2.37(3)	0.015(4)	−2.0(5)
TBPy	0.043	1.95(1)	0.0086(7)	⋯	⋯	−4.1(10)
SPy	0.055	1.95(1)	0.0090(8)	⋯	⋯	−4.3(11)
			Double-channel process			
SPl	0.009	1.96(1)	0.0052(3)	⋯	⋯	−2.7(4)
O_h	0.083	1.95(2)	0.0119(11)	⋯	⋯	−5.3(16)
d-O_h(JT)	0.006	1.96(1)	0.0048(3)	2.36(5)	0.040(8)	−1.8(6)
d-SPy	0.006	1.96(1)	0.0048(2)	2.35(4)	0.021(6)	−1.9(5)
TBPy	0.034	1.95(1)	0.0081(6)	⋯	⋯	−3.9(10)
SPy	0.040	1.95(1)	0.0084(7)	⋯	⋯	−4.0(10)

the relative weights of each structure, no further calculations have been done in this sense, because they should be speculative. Nevertheless, it is clear from Fig. 5 that in the experimental spectrum the specific features corresponding to a given structure are averaged out. Further XANES computations, averaging structural information derived from statistical simulations of Cu(II) in water (e.g., Refs. 14 and 16), are required to shed light on this point, as already shown in the XAS study of other single ions.[27,28,51–55] Related to these XANES computations, a further point to be investigated is the analysis of the efficiency of the FMS approach when the asymmetric structures, resulting from the fluxional behavior of the aquaion and its close environment, were considered to provide an average spectrum. The efficiency of alternative methods, such as finite-difference method,[56] should be explored.

Once the existence of two competitive final states for the absorption process has been established, their influence on the fitting procedure of the EXAFS spectrum has to be investigated. A primary question that arises from the double-channel phenomena is whether the EXAFS fitting procedure based on the assumption of a single channel, as already done by many research groups for the last 30 years,[5,6,17,19,21] would be affected of some bias as a consequence of neglecting the existence of a second channel absorption. If this was the case a new question would appear: Might the splitting of the Cu–O distances, which supports the Jahn-Teller distortion of Cu(II) hydrate, be an artifact of the fitting procedure to compensate for the lack of the second absorption channel? To explore this possibility two parallel fitting procedures were carried out: one on the hypothesis of a single channel and the other taking into account two absorption channels shifted by 6.06 eV with relative weights 0.68 and 0.32. In the second fit procedure, two EXAFS signals shifted by 6.06 with the above-indicated weights were computed and added without using any additional free parameter. In both procedures three free parameters (ΔE_0, σ_{eq}^2, and R_{eq}) were used in the analysis of the regular polyhedra and five parameters (ΔE_0, σ_{eq}^2, R_{eq}, σ_{ax}^2, and R_{ax}) in the case of the distorted ones. The results obtained from both approaches have been summarized in Table I, which reports the optimized fit parameters and minimum of the sum of squares $\mathcal{R}^2$ under the assumption of both single- and double-channel processes.

The first noticeable fact is the close similarity of the results obtained in both approaches: coordination distances are the same for all structures; there is only a small difference in the quality of the fit, slightly better in the case of double channel (see $\mathcal{R}^2$ values), and in the values of the Debye-Waller (DW) factors, slightly smaller in the double-channel fit. Hence, our results indicate that there is no significant difference with the computations taking into account the double channel. There are two reasons for this similarity: first, while 6.06 eV in the region close to the edge (XANES) represents a significant shift, this value is rather small compared to the EXAFS frequencies; second, when passing from eV scale (used in XANES) to Å^{-1} scale (used in EXAFS), this shift shrinks noticeably: at $k=3\ \text{Å}^{-1}$ above the edge, $\Delta E=6.06$ eV corresponds to $\Delta k=0.25\ \text{Å}^{-1}$, but at $k=12\ \text{Å}^{-1}$ corresponds to $\Delta k=0.065\ \text{Å}^{-1}$. Additional computations showed that a shift of 15 eV was needed to see noticeable changes in the EXAFS region. Figure 6 illustrates the changes in computed EXAFS spectrum with different values of ΔE. These computed spectra were obtained for the model structure corresponding to the square planar (SPl) assuming that the EXAFS function is the linear combination (with weights 68% and 32%) of two channel processes separated ΔE in energy. Therefore, the comparison of the fitting values for the single and double channels shows that the introduction of such a peculiar factor not only does not worsen the fit but it improves it. This general behavior confirms the previous XANES conclusions for the existence of the double channel and supports both the possibility to get reasonable EXAFS results for different structures and the

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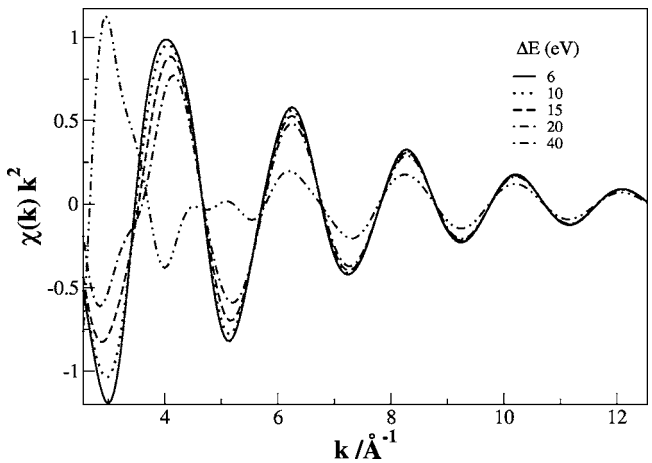

FIG. 6. Computed k^2-EXAFS spectra at the Cu K edge assuming the Cu(II) aquaion structure of the square planar complex and a double channel process (with weights 68% and 32%) with an energy separation ΔE.

slight distortion of the analysis results caused by the contribution of two channels to the EXAFS signal.

Once the double-channel approach has been chosen, comparative plots of the experimental spectrum and the best fit for each structure have been included in Fig. 7. As deduced from the visual examination of this figure, and by checking $\mathcal{R}^2$ values included in Table I, good reproductions were obtained for all structures except for the regular octahedron, as in the case of XANES region where this geometry does not correctly reproduce the shape of the white line. The best reproductions of the spectrum are attained for the distorted structures d-O_h(JT), as already observed by Persson *et al.*,[19] and d-SPy, as already observed by Benfatto *et al.*[17] and Frank *et al.*[18] The obvious reason for this improvement is the inclusion of two additional free parameters for the axial water molecules. Astonishingly, an almost equally good fit was achieved for the square-planar structure, SPl [see Fig. 7(a)] including one type of water molecule, and only two structural free parameters, as in the cases for SPy, TBPy, and O_h structures. This finding has been pointed out by Frank *et al.*[18] from the fit of the XANES spectrum. From the analysis of the EXAFS spectra it can be concluded that there is a set of four Cu(II)$-O_{eq}$ strong bonds with short distances (R_{eq} $=1.96$ Å) and small mean-square deviations (σ_{eq} $\simeq 0.005$ Å^2). In addition, there are some additional loosely bound water molecules ($R_{ax}=2.35-2.36$ Å and σ_{ax} $=0.02-0.04$ Å^2) responsible for its fast solvation dynamics (estimated exchange time of 200 ps), for which EXAFS is much less sensitive.

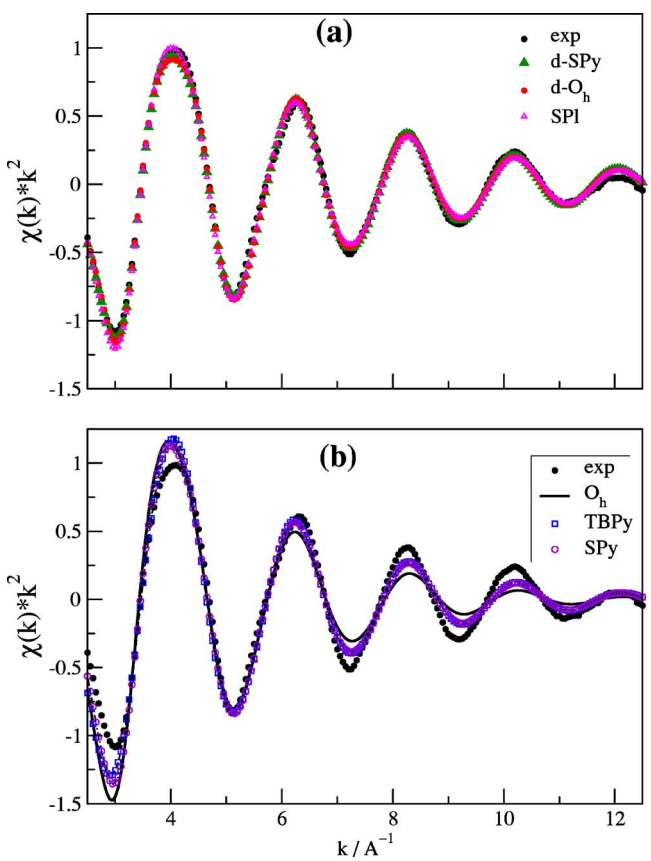

FIG. 7. Comparison of the experimental k^2-EXAFS spectrum at the Cu K edge in Cu(II) aqueous solution and the fitting results obtained assuming a double channel separated by 6 eV and with weights 68% and 32%, taking as model structure the different Cu(II) arrangements discussed in the main text: (a) structures d-O_h(JT), d-Spy, and SPl and (b) structures O_h, Spy, and TBPy.

Summarizing, unlike what is observed in the majority of metal cations for which EXAFS has provided detailed information concerning its local structure,[6,27,29,30,43,57] this technique cannot discard nor support a unique solvation structure for Cu(II). This is the root of the open controversy concerning this point, as very recently emphasized by Rotzinger.[13,58] XANES can go further, but it does not yield a unique answer: the simple idea of a stable well-defined coordination geometry in solution does not work in this case. On the basis of this hypothesis, the question on which is the structure adopted by Cu(II) aquaions in solution is meaningless. The high intrinsic dynamics of the copper hydrate allows the coexistence of six- and fivefold hydration numbers, regular and distorted. Even more, the striking fact that the square-planar arrangement is capable of supplying a fair representation for both the EXAFS and XANES spectra must be regarded as an additional fact supporting this reasoning line. The pattern of a set of water molecules defining a plane bearing the metal cation is the common and persistent motif of the set of structures compatible with the highly dynamic behavior of the system. Therefore, the main conclusion of this work is that Jahn-Teller in solution must be better understood as a dynamical effect as earlier proposed by Curtiss *et al.*,[59] based on classical MD, and later by Blumberger *et al.*[14] based on *ab initio* MD. When trying to project this dynamical behavior on a representative structure, experimental x-ray-absorption spectra provide a structural answer which is an average of many of them. The classical Jahn-Teller distortion, well established in solid state, cannot be associated to a given structure in solution. Frank *et al.* have recently pointed out how for the preferred Cu(II) aquaion arrangement should not be cached in the crystal structure geometries alone.[18] As proposed by Curtiss *et al.*[59] JT effect should be understood as a kind of dynamical symmetry breaking which is only appearing on short time scales, being washed out at longer time scales. We believe that the spectroscopical peculiarities associated to the double channel appearing in the ionization pro-

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cess of the Cu(II) hydrate in water provide a fairly good background to further XAS molecular-dynamics combined studies.[27,28,51–55] Thus, the microscopic representation of the dynamics of this hydration would allow the computation of simulated EXAFS and XANES spectra from a statistically significant set of structures, and then to extract additional conclusions about the relative importance of the different structures contributing to the XAS spectra, the double-channel spectroscopic peculiarity being simultaneously considered.

IV. CONCLUDING REMARKS

Extensive *ab initio* computations of the Cu *K*-edge XANES spectra of Cu(II) aquaion, considering the different structures proposed in the literature, have been performed. The comparison between experimental data and *ab initio* computations revealed that two absorption channels, corresponding to both $3d^9$ and $3d^{10}L$ electronic configurations of Cu(II), were needed to reproduce the experimental XANES spectrum. It is worth mentioning that the *ab initio* computed spectra presented here are in closer agreement to the experimental one than any other previously reported in the absence of free parameters and fitting procedures. We can now be fairly confident to have captured adequately the spectroscopic and electronic details of the XANES calculation for this system and to have checked that the EXAFS analysis was virtually unaffected by the existence of two absorption channels of different energies, since the energy gap between the two channels is small enough. Neither the classical Jahn-Teller geometry nor other six- or fivefold-coordinated geometries may be proposed unambiguously as the *single* preferred structure in solution. XANES is compatible with the existence of all of them. As in the XANES case, the EXAFS analysis did not lead to a clearly preferred structure for the Cu(II) aquaion.

The high fluxionality of this system invoked by several authors from theoretical examination of the dynamics of the system[12,14,59] provides a rationalization of the results obtained, according to which six-, five-, and four-coordinated structures would coexist dynamically in solution.

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