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Structure and ultrafast dynamics of liquid water: A quantum mechanics/molecular mechanics molecular dynamics simulations study

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A quantum mechanics/molecular mechanics molecular dynamics simulation was performed for liquid water to investigate structural and dynamical properties of this peculiar liquid. The most important region containing a central reference molecule and all nearest surrounding molecules (first coordination shell) was treated by Hartree–Fock (HF), post-Hartree–Fock [second-order Møller–Plesset perturbation theory (MP2)], and hybrid density functional B3LYP [Becke's three parameter functional (B3) with the correlation functional of Lee, Yang, and Parr (LYP)] methods. In addition, another HF-level simulation (2HF) included the full second coordination shell. Site to site interactions between oxygen-oxygen, oxygen-hydrogen, and hydrogen-hydrogen atoms of all *ab initio* methods were compared to experimental data. The absence of a second peak and the appearance of a shoulder instead in the $gO-O$ graph obtained from the 2HF simulation is notable, as this feature has been observed so far only for pressurized or heated water. Dynamical data show that the 2HF procedure compensates some of the deficiency of the HF one-shell simulation, reducing the difference between correlated (MP2) and HF results. B3LYP apparently leads to too rigid structures and thus to an artificial slow down of the dynamics. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1888465]

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II. THEORY

A. QM/MM molecular dynamics simulation

In the QM/MM approach the system is divided into the region of major interest; in this case a sphere around a central water molecule, where quantum mechanical techniques are applied, and the rest of the system are treated classically. In order to define the size (radius) of this sphere a classical simulation was performed and according to the resulting O–O radial distribution function (RDF) the size was set to 3.2 Å for HF and B3LYP methods and to 3.4 Å for MP2 as to fully include all molecules that are forming hydrogen bonds (HBs) with the central water molecule. By following the same steps, a full second shell was included in a sphere with radius of 5.6 Å. HF calculations for all forces in these two regions were carried out for a total simulation time of 16 and 40 ps, respectively. First shell forces were calculated by full MP2 for a simulation time of 5.0 ps and B3LYP for a simulation time of 30 ps. All calculations were performed with a Double-ζ plus polarization functions basis set[36] using our own QM/MM MD code implementing TURBOMOLE.[37–39]

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B. Simulation protocol

The density of liquid water is $0.997\,02$ g/cm^3; thus for a sample of 500 water molecules the side length of the cubic elementary box is 24.8 Å. A canonical *NVT* ensemble at 298.16 K was simulated with periodic boundary conditions[40] and the temperature was kept constant using the Berendsen algorithm.[41] Water-water interactions outside the QM spheres were described with the flexible BJH-CF2 model,[8,42,43] consisting of intermolecular and intramolecular potentials. The time step of the simulation was set to 0.2 fs, which allowed for explicit movement of hydrogens. A cutoff of 12 Å was applied for Coulombic interactions, whereas for non-Coulombic interactions it was set to 5.0 and 3.0 Å for O–O and H–H, respectively.

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C. Structural data

All structural details can be obtained by analyzing the MD trajectory files. Intermolecular and intramolecular distances were evaluated by the respective RDFs (i.e., $gO-O$, $gO-H$, $gH-H$). Information about the angles formed between either the oxygen or hydrogens of the central reference molecule, and the hydrogens and oxygens of the surrounding molecules can be gained from the angular distribution functions (ADFs).

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D. Dynamical data

Useful insights into the microscopic dynamics of liquid water can be obtained by computing the velocity autocorrelation function (VACF), which is defined as

$$C(t) = \frac{\sum_i^{N_\tau} \sum_j^N \vec{u}_j(\tau) \cdot \vec{u}_j(\tau + t)}{N_\tau N \sum_i^{N_\tau} \sum_j^N \vec{u}_j(\tau) \cdot \vec{u}_j(\tau)}, \tag{1}$$

where N_τ is the number of "time origins," N is the number of particles, and $\vec{u}_j$ denotes the velocity of a given particle j.[44,45]

Normal-coordinate analysis was used[44,45] for the calculation of the vibrational and librational frequencies of liquid water. Six scalar quantities Q_2, Q_1, Q_3, R_x, R_y, and R_z are defined to describe the bending vibration, symmetric and asymmetric stretching vibrations, and rotations around the three principal axes of the water molecule. The assignment of the bands of the complete spectrum is not a trivial task since they might be overlapping. The desired high resolution of the power spectra can be obtained from the Fourier transformation of VACFs.

All the QM calculated frequencies were multiplied by appropriate scaling factors[46] with amount 0.9051 for HF, 0.9496 for MP2, and 0.9614 for B3LYP. These values were chosen because they had been calculated at the same level of theory and with similar, if not the same, basis set.

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It is also of some importance to know the rate of reorientation of the water molecules around the three principal axes system. These data can be obtained by using the reorientational time correlation functions (RTCFs), defined as

$$C_n(t) = \langle \vec{P}_n[\vec{v}_i(0) \cdot \vec{v}_i(t)] \rangle, \qquad (2)$$

where P_n is the Legendre polynomial of nth order and $\vec{v}_i$ is a unit vector along the three principal axes i used to define the position of the molecule at any given time.

Mean residence times (MRTs) of the water molecules of the QM treated coordination shell were calculated by the direct method[47] using t^* values of 0.0 and 0.5 ps. The former value is used as to follow the lifetime of hydrogen bonds and thus the rate of their breaking as well, while the latter is suitable to account for exchanges of ligands in the immediate neighborhood of a given molecule, leaving the coordination shell for a minimal period of 0.5 ps.
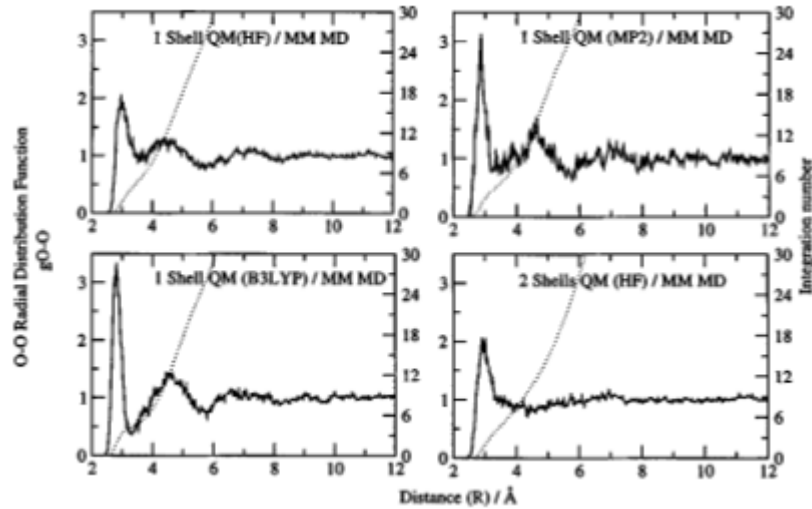
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FIG. 1. Oxygen-oxygen RDFs from HF, B3LYP, MP2, and 2HF simulations.
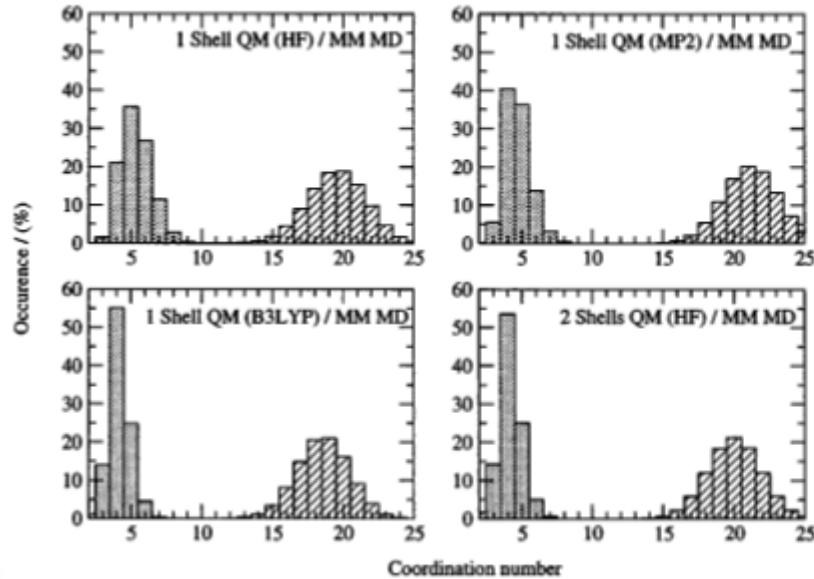
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FIG. 2. Distribution of coordination number from B3LYP, MP2, and 2HF, and simulations.
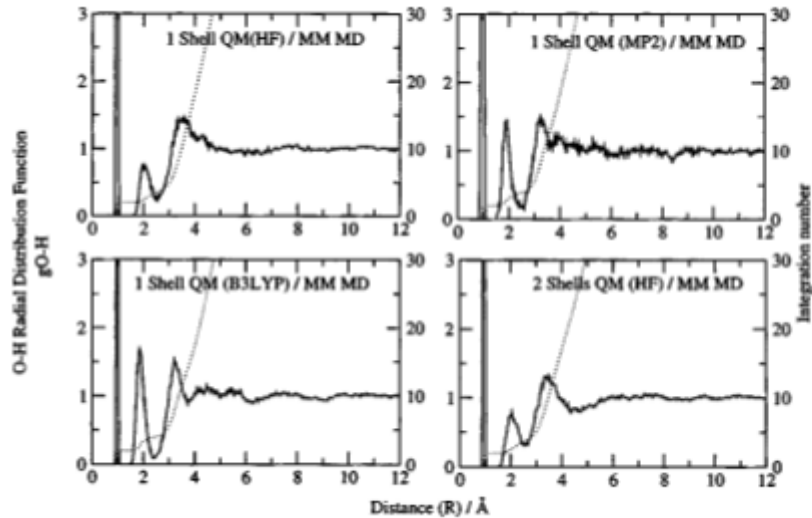
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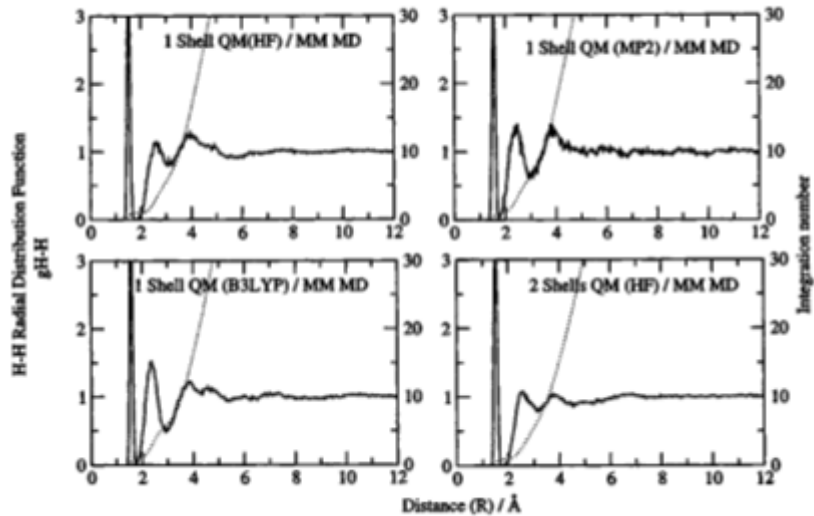FIG. 3. Oxygen-hydrogen RDFs from HF, B3LYP, MP2, and 2HF simulations.

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FIG. 4. Hydrogen-hydrogen RDFs from HF, B3LYP, MP2, and 2HF simulations.
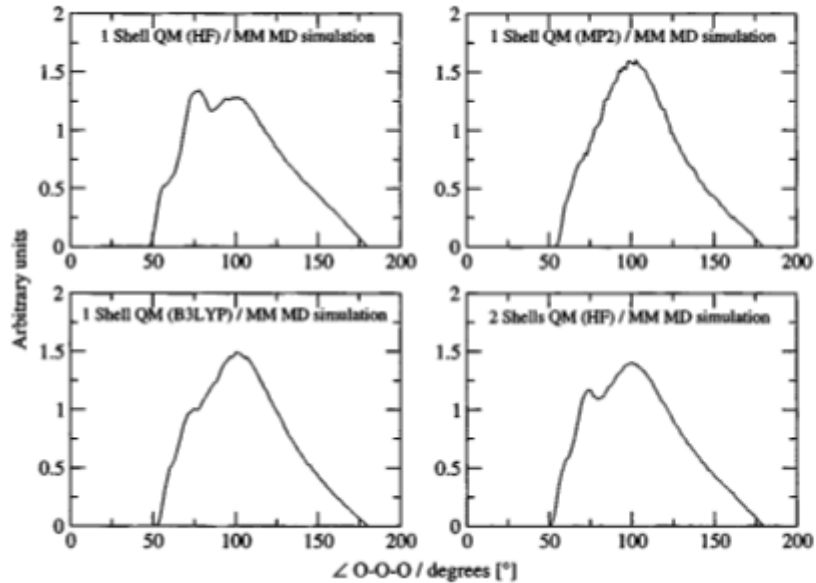
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FIG. 5. Distribution of O–O–O angle from HF, B3LYP, MP2, and 2HF simulations.
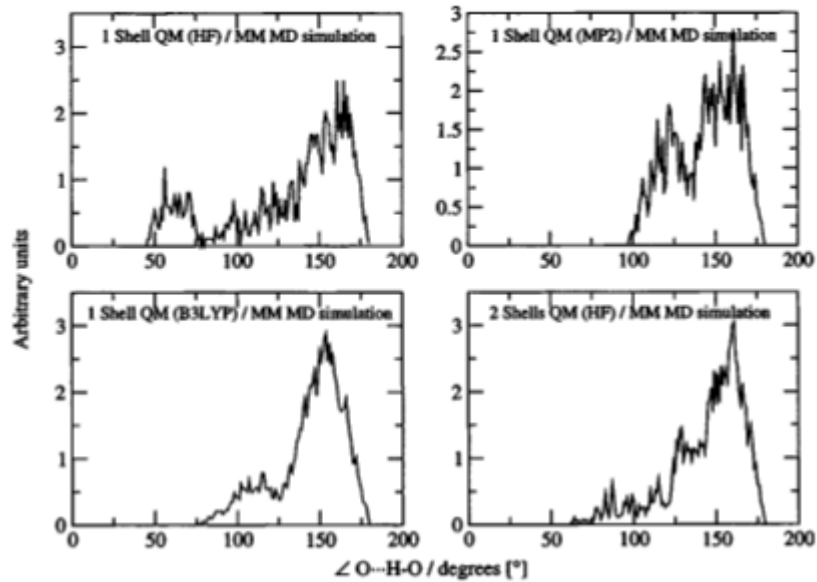
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FIG. 6. Distribution of O···H—O angle from HF, B3LYP, MP2, and 2HF simulations.
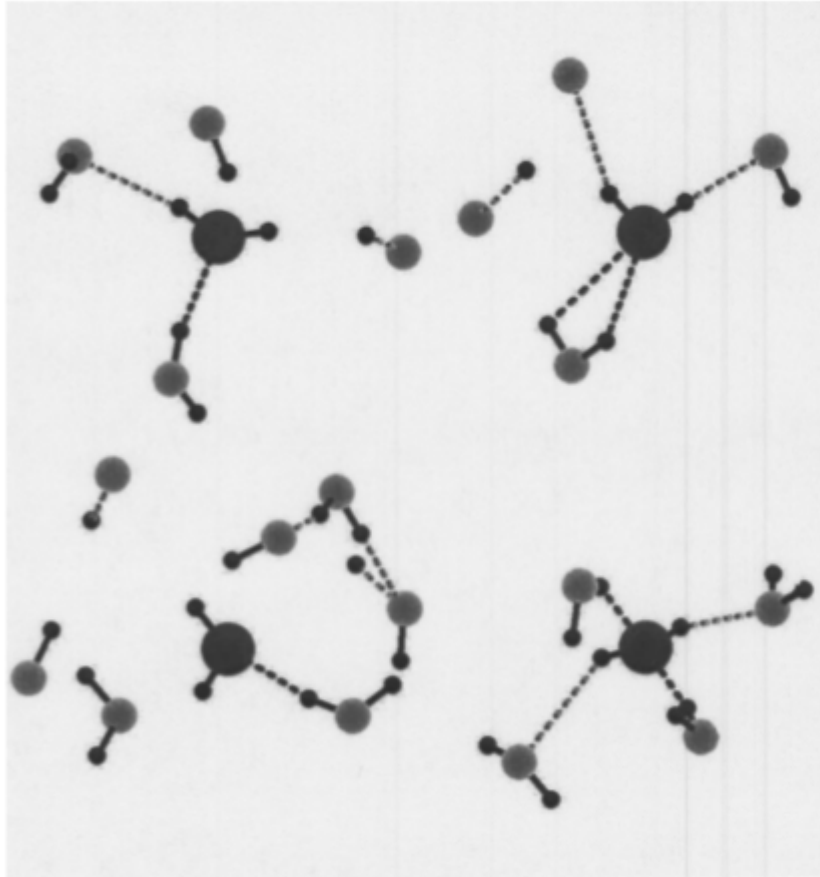
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FIG. 7. Different types of bonds in liquid water obtained from evaluation of the same trajectory file with MOLVISION 4D program (the large full black circle denotes the oxygen atom from the central water molecule).

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TABLE III. Complete structural parameters obtained from RDFs graphs produced by simulations at HF, B3LYP, and MP2 levels of theory (all distances in angstroms and angles in degrees, numbers in parentheses are second shell estimates).

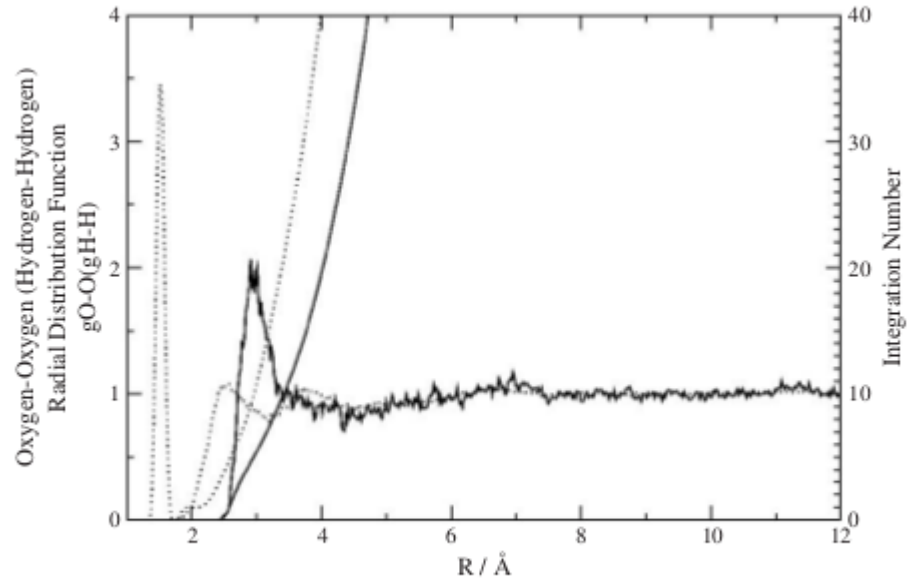|	R_{O-O}		R_{O-H}		R_{H-H}		$\angle O^a-O^c-O^a$	$\angle O\cdots H-O$	CN
	R_{max}	R_{min}	R_{max}	R_{min}	R_{max}	R_{min}			
HF	2.97(4.41)	3.59(5.77)	2.05(3.59)	2.53(4.82)	2.63(3.95)	3.09(5.71)	101	165	4.9(21.23)
MP2	2.87(4.67)	3.43(5.85)	1.93(3.24)	2.61(4.29)	2.44(3.76)	2.95(5.20)	103	167	4.7(22.78)
2HF	2.92($\cdots$)	3.41($\cdots$)	2.06(3.47)	2.53(4.33)	2.59(3.77)	3.24(4.65)	101	161	4.2(19.26)
B3LYP	2.81(4.45)	3.31(5.79)	1.85(3.21)	2.42(3.73)	2.33(3.87)	2.89(5.37)	102	154	4.2(22.05)

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Fig. 1. Oxygen–oxygen (full line) and hydrogen–hydrogen (dotted line) RDFs.
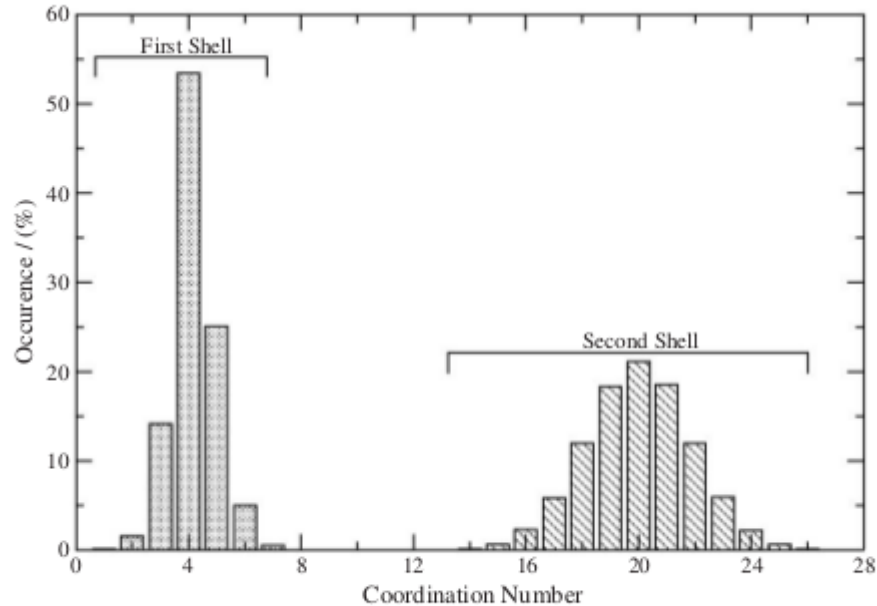
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Fig. 2. Distribution of coordination numbers within the QM region of the simulation. Limits for 1st and 2nd shell were set to 3.4 and 5.6 Å.
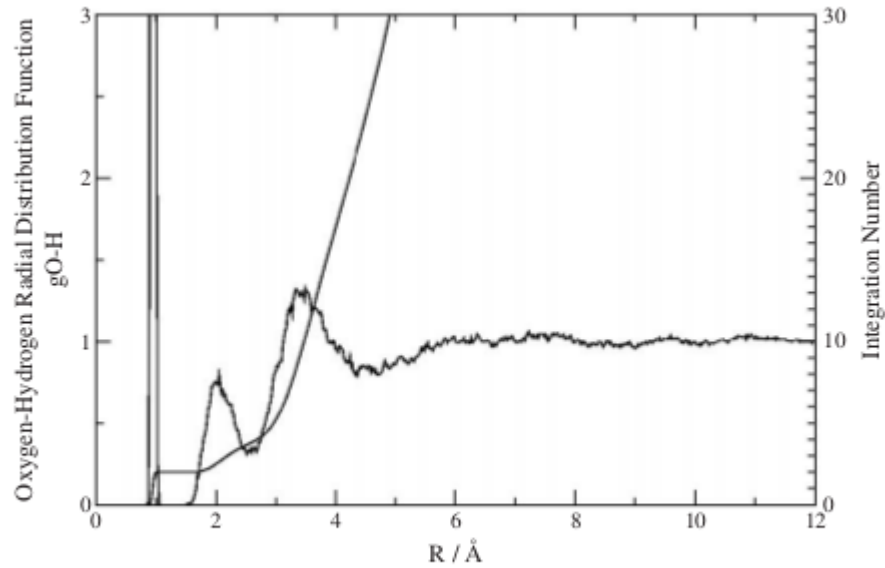
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Fig. 3. Oxygen–hydrogen RDF from a HF simulation.
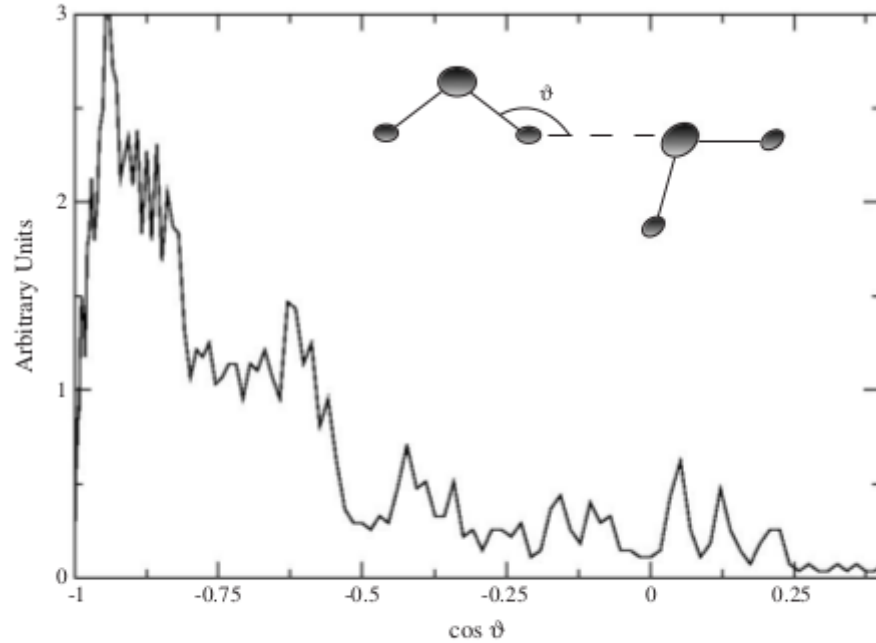
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Fig. 4. Cosine distribution of O–H–O (ϑ) angle from a HF simulation.
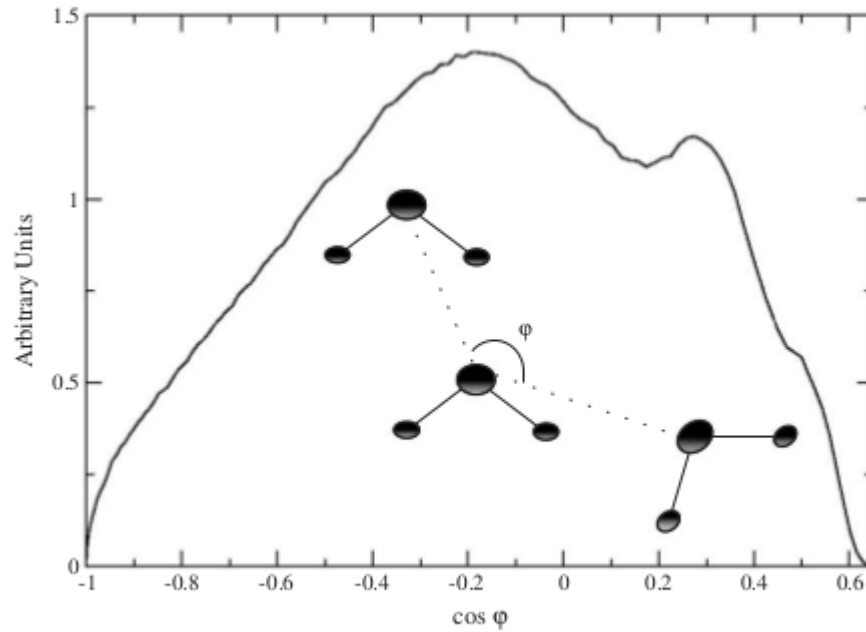
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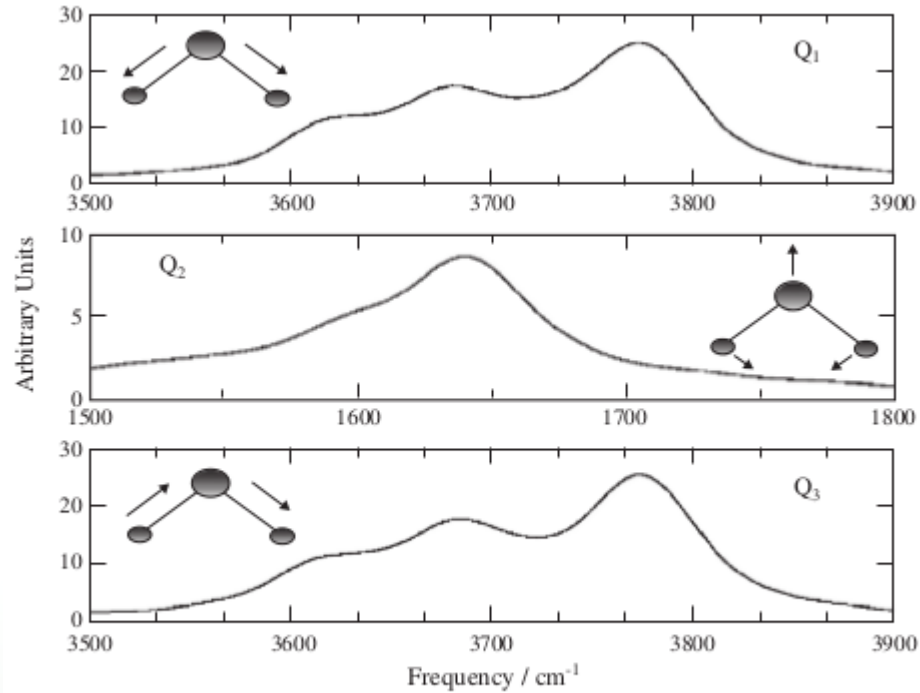Fig. 5. Cosine distribution of O−O−O (φ) angle from a HF simulation.

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Fig. 7. Vibrational Q_1, Q_2, Q_3 modes from a HF simulation.

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https://youtu.be/Zl74NCVbA5A

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Influence of Electron Correlation Effects on the Solvation of Cu^{2+}

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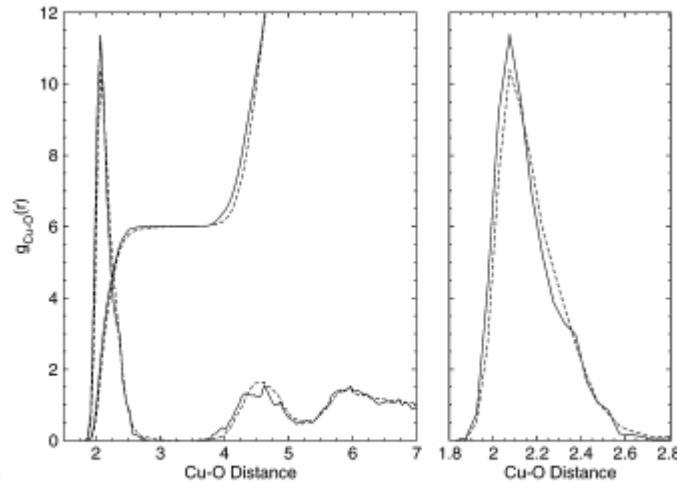
Figure 1. Cu−O radial distribution function (RDFs) obtained from MP2/MM (solid line) and HF/MM (dashed line) QM/MM MD simulations with their running integration numbers.
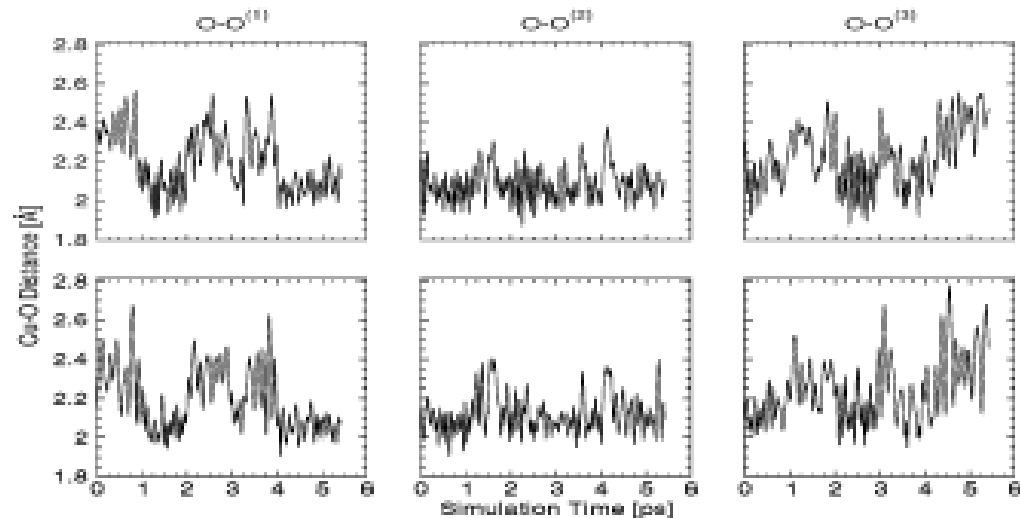
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Figure 2. Ion—oxygen distance plots during the MP2/MM simulation, showing three pairs of synchronal moving trans-positioned water molecules.

I. INTRODUCTION

Aqua complexes of transition metal ions are of particular interest as they frequently serve as basic models for theoretical and experimental investigations of more complicated transition metal complexes.[1,2] These transition metal complexes are also regarded as prototypes for biological systems[3] because they serve to elucidate the electronic structure of various metallocenters of the active sites of enzymes. Aqua complexes of numerous transition metal ions have been well attended by both theoreticians and experimentalists to fully understand their geometric and electronic structures as well as other significant properties.[4] Nevertheless, the hydration behavior of transition metal ions can only be pursued when an aqueous solution of such metal ions is carefully examined.[5,6] The above statements also apply in the case of copper Cu(II); one of the transition metal ions that has great significance in many areas that range from chemistry to biology and other disciplines.[3,7] The knowledge of local environment of the hydrated copper(II) ion will certainly be helpful to understand its underlying reaction dynamics and to guide reaction mechanisms occurring in many biological and other systems.[8,9] Therefore, the dynamic behavior of the first coordination sphere of the Cu(II) aqueous system has been extensively studied via both experimental and theoretical techniques.[10–14] However, the structural and dynamics behavior of the Cu(II) ion in aqueous solution have been poorly explored even though various sophisticated experimental techniques have been employed for its characterization.

In the past, it was almost believed that Cu(II) ion generally exists only in six coordinated form in aqueous solution, which for the first time was challenged by Pasquarello *et al.* who presented a five coordinated model based on Car-Parinello molecular dynamics (CPMD) simulation and neutron diffraction.[15] Five equal Cu–O bonds were found in that model with frequent exchanges of coordination geometries which coexist as square pyramidal and trigonal bipyramidal. The concept of 5-coodinated structure of the Cu(II) ion in aqueous solution was contradicted by extensive extended X-ray absorption fine structure (EXAFS) and large angle X-ray scattering (LAXS) experiments performed by Persson *et al.* who again suggested the existence of 6-fold coordinated geometry of this aqueous system.[16] In these experiments, various copper-water clusters were modeled and it was assessed that the experimental data for the Cu(II) ion in aqueous solution is best fitted with distorted octahedron. *Ab initio* QM/MM MD simulation studies were also reported on the hydration behavior of Cu(II) ion in aqueous solution which also supported the idea of 6-fold coordination geometry along with an explanation of the Jahn–Teller effects of the first hydration shell.[14] CPMD simulation and X-ray absorption near-edge structure (XANES) study suggested again a five coordinated square pyramidal structure of aqueous Cu(II) ion but with one elongated axial water molecule. Moreover, EXAFS and XANES spectroscopy were recently employed to elucidate the structure of aqueous Cu(II) ion that also gave a

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All these applications indicate a complicated nature of the Cu(II)–water system which is expected to be explored only including its dynamics and with high level *ab initio* methods. In the current study, the *ab initio* quantum mechanical charge field molecular dynamics (QMCF-MD) simulations[21, 22] were performed for Cu(II) in water with two different ratios of cation and water molecules (Cu(II)/499 and Cu(II)/999 water molecules). Not only the composition of the systems was different, but also the size of the quantum mechanics (QM) region was varied; one with a conventional QM radius while the other system had a considerably extended QM radius to check the sensitivity on the choice of the QM region, with the expectation that an enlarged QM region might be useful in particular to fully understand the dynamics of exchange events which involve ligands at longer distances and depend on the Jahn-Teller distortions of the aqueous Cu(II)
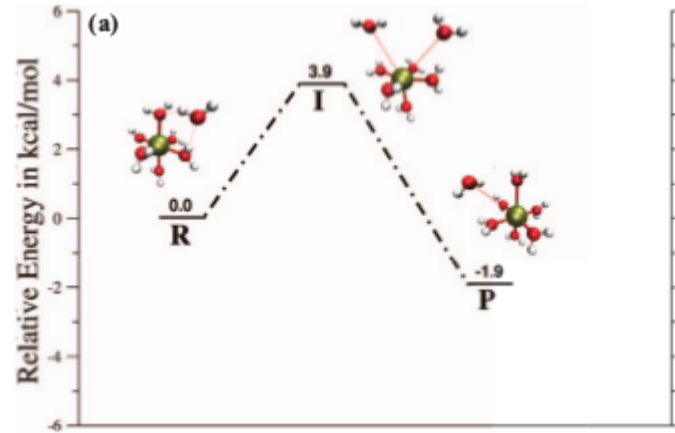
TABLE II. Characteristic data for the solvent dynamics for second shell water ligands of Cu(II) and pure water (N_{ex} is the number of exchange events, R_{ex} is the number of attempts needed to produce one lasting exchange, and CN the average Coordination Number.

Method	CN	$N_{ex}^{0.5}$	$N_{ex}^{0.0}$	$\tau_{0.5}$ (ps)	$\tau_{0.0}$ (ps)	R_{ex}
Cu(II) (QMCF-MD; 499 water)	11.5	118/34.5	1026/34.5	3.4	0.4	8.7
Cu(II) (QMCF-MD; 999 water)	11.6	294/50 ps	2001/50 ps	2.0	0.3	6.8
Cu(II) (QM/MM MD)[38]	11.7	46/30.1 ps	660/30.1 ps	7.7	0.5	14.3
H_2O[34]	4.1	20	131	1.3	0.19	6.6

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The structure of the hydrated copper(II) ion in aqueous solution has been debated intensively in recent years. It is, however, difficult to draw a clear conclusion as the interaction in the axial position is very weak, and the color of copper(II) complexes with Jahn–Teller distorted octahedral and tetragonally distorted square-pyramidal are pale blue, while four- and five-coordinated complexes with oxygen donor ligands are green. In the solid state, a very large majority of the reported structures display a Jahn–Teller distorted structure with mean Cu–O bond distances of 1.975 and 2.35 Å in the equatorial and axial positions, respectively [8,9]. A limited number of solid-state structures contain penta-aquacopper(II) complexes in distorted square-pyramidal configuration with the axial position at the same distance as found in the six-coordinate Jahn–Teller distorted complexes [69–74], and only one penta-aquacopper(II) complex with trigonal bipyramidal configuration [75], and one tetra-aquacopper(II) complex with square-planar configuration [76] are reported in the solid state. Pasquarello et al. proposed some years ago that the hydrated copper(II) ion is five-coordinate in aqueous solution [77], a view which has been supported by theoretical simulations and EXAFS/XANES studies [78,79]. EXAFS and LAXS studies did, however, give physically unrealistic Debye–Waller factors with on average only one water in the axial positions, supporting a Jahn–Teller distorted octahedral configuration [42]. Another EXAFS/XANES study concluded that it is not possible to distinguish between four-, five-, and six-coordinate hydrate structures of copper(II) [43], and a recent theoretical simulation showed that the energetic difference between five- and six-coordination is very small (ca. 5 kJ/mol) supporting co-existence in aqueous solution [44]. It is not possible from the present experimental or theoretical simulation data to unambiguously determine if the hydrated copper(II) ion is five- or six-coordinated or if they co-exist in aqueous solution, but five-coordination in trigonal bipyramidal fashion and four-coordination can be ruled out as copper(II) complexes in these configurations have a different color, green [8,9]. However, it is a striking fact that the number of six-coordinate copper(II) aqua complexes in the solid state is much larger than the number of five-coordinate, in spite of the much lower water activity at the formation of a solid phase than in aqueous solution.

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https://www.youtube.com/watch?v=ccR9dblai2I

https://www.youtube.com/watch?v=ZiZsEAtbyaY&app=desktop

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Structure and Dynamics of Sulfate Ion in Aqueous Solution—An *ab initio* QMCF MD Simulation and Large Angle X-ray Scattering Study

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The hydrated sulfate ion has been characterized in aqueous solution in structural and dynamic aspects using *ab initio* quantum mechanical charge field (QMCF) molecular dynamics (MD) simulation and large angle X-ray scattering (LAXS) methods. The LAXS data show an average coordination number of the sulfate ion of up to 12 water molecules bound through hydrogen bonding, while the QMCF MD simulation displays a wide range of coordination numbers between 8 and 14 with an average value of ~11. The $O_s \cdots O_w$ distance cannot be distinguished from the $O_w \cdots O_w$ distance in the LAXS experiment; the weighted mean $O \cdots O$ distance is 2.880(10) Å. In the simulation, the $O_s \cdots O_w$ and $O_w \cdots O_w$ distances are found to be very similar, namely, 2.86 and 2.84 Å, respectively. The $S-O_s$ bond and $S \cdots O_w$ distance have been determined by the LAXS experiment as 1.495(6) and 3.61(2) Å, respectively, indicating an average nearly tetrahedral $S-O_s \cdots O_w$ angle. The ~5% deviations of simulation distances (1.47 and 3.82 Å) from the experimental ones can probably be ascribed to the neglect of correlation energy in the quantum mechanical method. The mean residence time of water ligands at O atoms, 2.57 ps, is longer than that in pure water, 1.7 ps, characterizing the sulfate ion as a weak structure maker.

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QM region
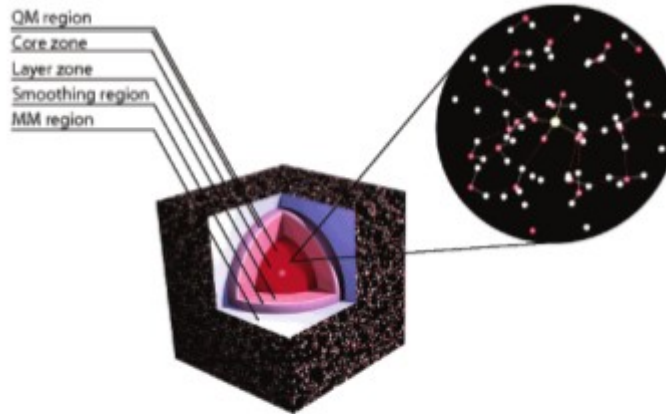Core zone
Layer zone
Smoothing region
MM region

Figure 1. Definition of the quantum mechanical (QM) and molecular mechanical (MM) regions in the QMCF approach: the QM region is separated into the core zone and the layer zone.
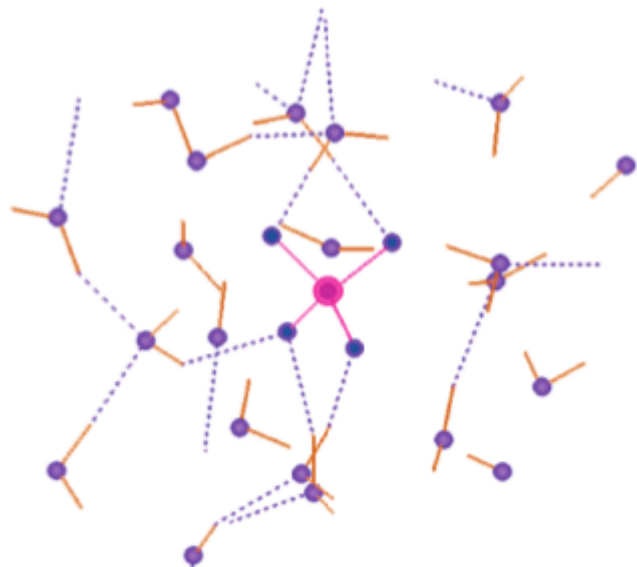
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Figure 7. Snapshot picture from the QMCF MD simulation, illustrating the structure of the hydrated sulfate ion.

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Al(III) Hydration Revisited. An ab Initio Quantum Mechanical Charge Field Molecular Dynamics Study

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To assess the novel quantum mechanical charge field (QMCF) molecular dynamics (MD) approach, two simulations of hydrated Al(III) have been carried out, as this system proved to be a well-suited test case for hybrid ab initio/molecular mechanics simulations. Two different population analysis schemes according to Mulliken and Löwdin have been applied to evaluate the atomic charges in the QM region. It is shown that the QMCF MD approach yields a substantially improved description of the system and that, due to the fact that solute−solvent potentials can be renounced, the QMCF MD framework is a more convenient approach to investigate solvated systems compared to conventional ab initio QM/MM MD approaches.
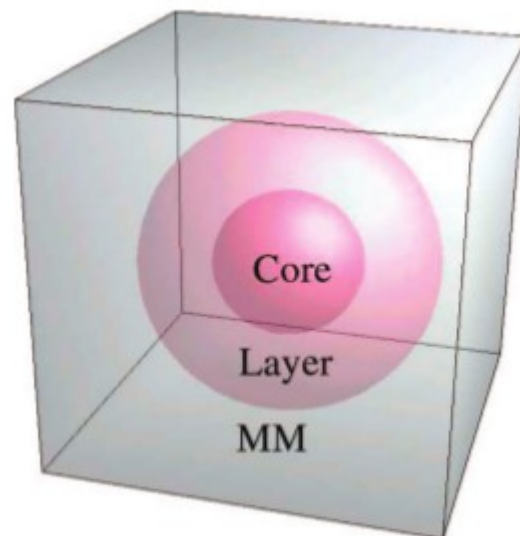
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Figure 1. Partitioning of the simulation box in the QMCF approach.
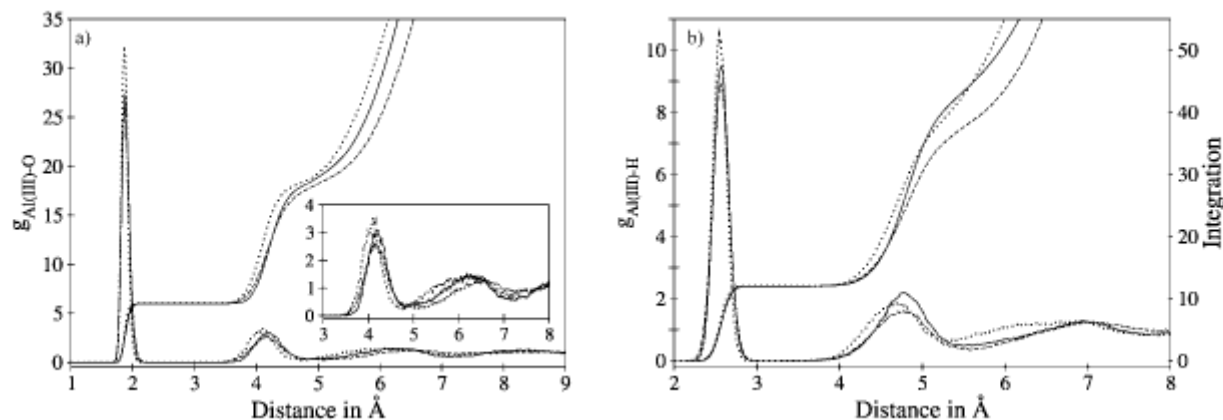
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Figure 2. (a) Al−O and (b) Al−H radial distribution functions and their running integration numbers for QMCF MD simulations with Mulliken (solid line) and Löwdin (dashed line) charges and a conventional QM/MM MD simulation (dotted line) of Al(III) in aqueous solution.

TABLE 2: Maxima (r_M, Å) and Minima (r_m, Å) of the Al(III)−O Radial Distribution Function ($g_{Al(III)-O}$) and Average Coordination Numbers (CNs) of the Respective Shells

|	r_{M1}	r_{m1}	r_{M2}	r_{m2}	r_{M3}	r_{m3}	$CN_{av,1}$	$CN_{av,2}$	$CN_{av,3}$
QMCF (Mulliken)	1.88		4.15	4.85	6.25	7.20	6.0	12.8	31.6
QMCF (Löwdin)	1.88		4.15	5.05	6.6	7.25	6.0	13.0	28.8
two-shell QM/MM[5]	1.86		4.10	4.75	6.25	7.15	6.0	12.2	37.3
exptl value[45−47]	1.87−1.90		3.98−4.15				6.0	12−14	
Al(III) MM MD[38]	1.9	2.6	4.0	4.6	~6.2	~7.2	6.0	~14	
AlCl₃ MM MD[36]	2.0	2.5	4.3/4.5	~5.3	~6.8	~7.5	6.0	~19	
Al(III) CP MD[39]	1.92		4.09				6	11.2	
AlCl₃ CP MD[40]	1.92		4.09				6	12	
Al(III) CP MD[41]	1.93		4.08				6	12	

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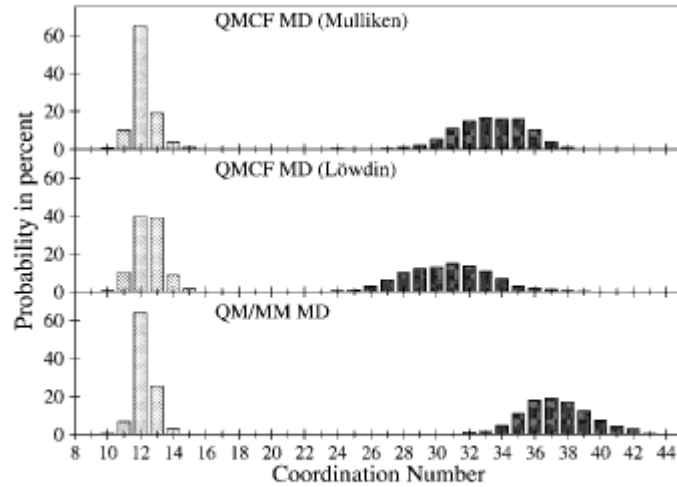
Figure 3. Coordination number distributions obtained from QMCF MD simulations with Mulliken and Löwdin charges and a conventional QM/MM MD simulation of Al(III) in aqueous solution.
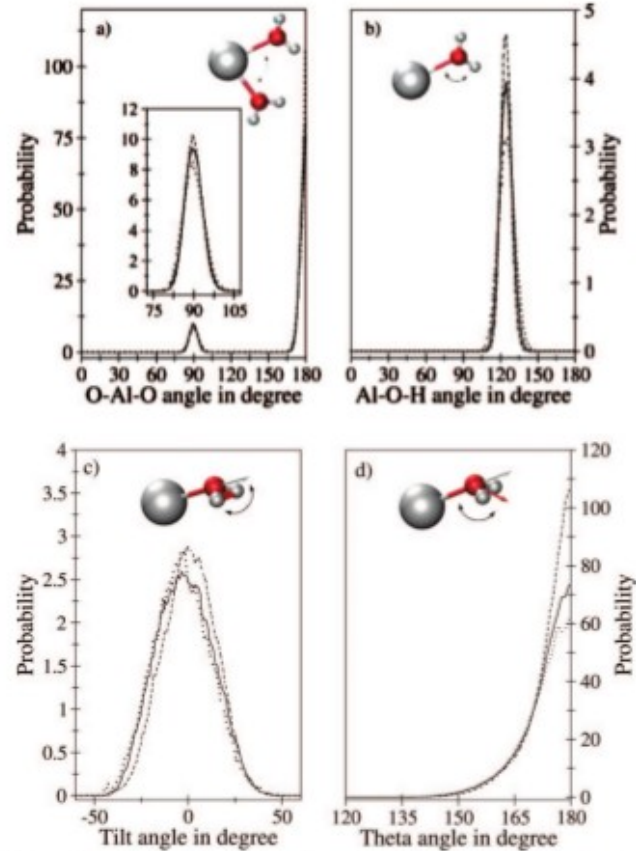
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Figure 4. Angular distribution functions of the first hydration shell of Al(III) in aqueous solution obtained from QMCF simulations with Mulliken (solid line) and Löwdin (dashed line) charges and a conventional QM/MM MD simulation (dotted line).
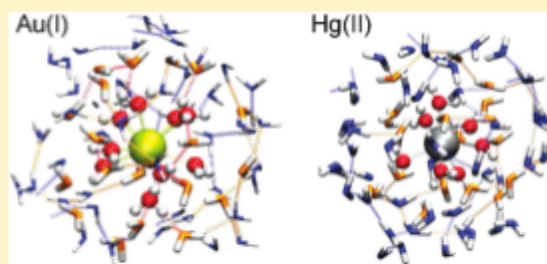
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Gold(I) and Mercury(II)—Isoelectronic Ions with Strongly Different Chemistry: Ab Initio QMCF Molecular Dynamics Simulations of Their Hydration Structure

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ABSTRACT: The hydration structure of the isoelectronic Au(I) and Hg(II) ions was determined by means of ab initio quantum mechanical charge field molecular dynamics (QMCF MD) simulations. The two hydrates proved as very labile but entirely different in their structural features. While Hg(II) forms two distinct hydration shells, Au(I) is characterized by an additional extended first shell (meso-shell) which has a considerable influence on all data extracted from the simulation trajectory, namely, radial and angular distribution functions, coordination number distribution, and dynamical data such as mean ligand residence times (MRT) and vibrational frequencies. The short MRT values of the first shell ligands, amounting to a few picoseconds, lead to the simultaneous presence of a number of hydrate complexes with differing geometries, which explains the difficulties in assigning structural data to spectroscopic measurements. The results presented here demonstrate that isoelectronic transition metal ions can show strongly different chemical properties, which cannot be explained on the basis of their different charge alone. The importance of including the second hydration shell and thus the intershell hydrogen bonds in the quantum mechanical treatment of the simulation is clearly proven.
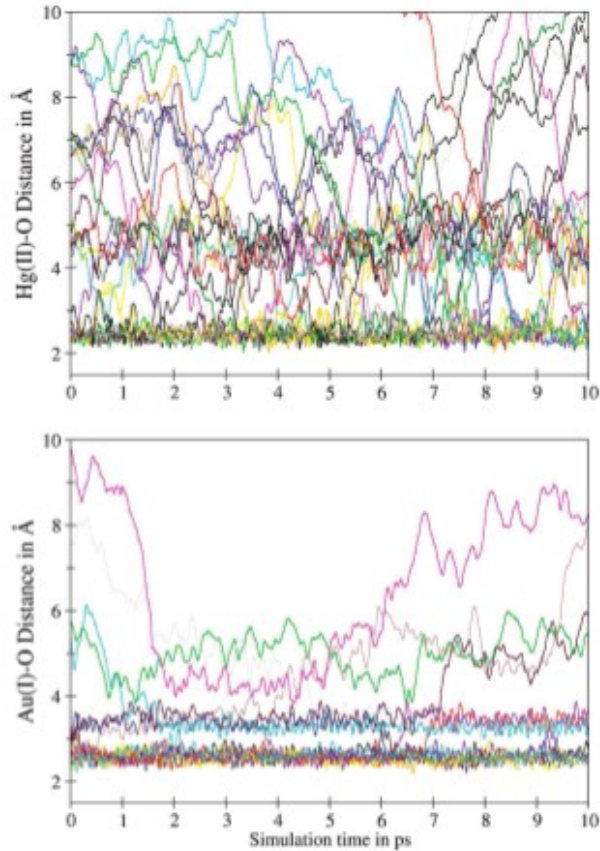
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Figure 5. Ion–ligand distance plots for Hg(II) (upper panel) and Au(I) (lower panel) illustrating exchange processes in the course of the simulations.
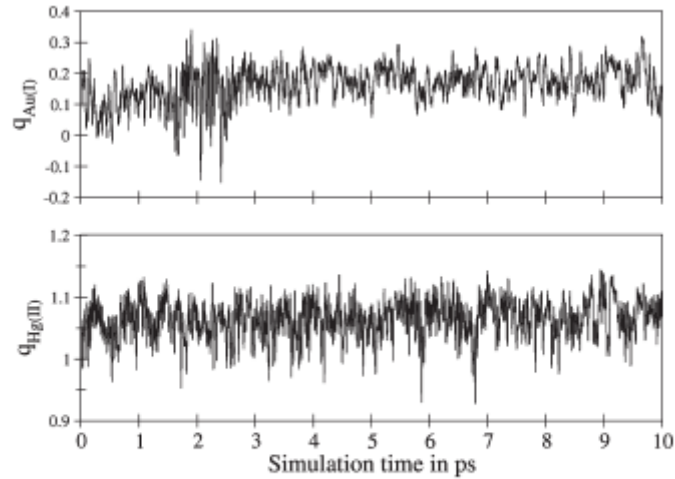
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Figure 6. Fluctuation of the atomic partial charge according to Mulliken population analysis of Hg(II) and Au(I) during the QMCF MD simulation .

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Περισσότερα videos προσομοίωσης

http://mw.concord.org/modeler/