Excited-state solvation structure of transition metal complexes from molecular dynamics simulations and assessment of partial atomic charge methods

In this work, we investigate the excited-state solute and solvation structure of \([\text{Ru(bpy)}_3]^{2+}\), \([\text{Fe(bpy)}_3]^{2+}\), \([\text{Fe(bmip)}_2]^{2+}\) and \([\text{Cu(phen)}_2]^+\) (bpy = 2,2'-bipyridine; bmip = 2,6-bis(3-methyl-imidazole-1-ylidine)-pyridine; phen = 1,10-phenanthroline) transition metal complexes (TMCs) in terms of solute-solvent radial distribution functions (RDFs) and evaluate the performance of some of the most popular partial atomic charge (PAC) methods for obtaining these RDFs by molecular dynamics (MD) simulations. To this end, we compare classical MD of a frozen solute in water and acetonitrile (ACN) with quantum mechanics/molecular mechanics Born-Oppenheimer molecular dynamics (QM/MM BOMD) simulations. The calculated RDFs show that the choice of a suitable PAC method is dependent on the coordination number of the metal, denticity of the ligands, and type of solvent. It is found that this selection is less sensitive for water than ACN. Furthermore, a careful choice of the PAC method should be considered for TMCs that exhibit a free direct coordination site, such as \([\text{Cu(phen)}_2]^+\). The results of this work show that fast classical MD simulations with ChelpG/RESP or CMS PACs can produce RDFs close to those obtained by QM/MM MD and thus, provide reliable solvation structures of TMCs to be used, e.g. in the analysis of scattering data.

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Theoretical Evidence of Solvent-Mediated Excited-State Dynamics in a Functionalized Iron Sensitizer

The solvent-mediated excited-state dynamics of the COOH-functionalized Fe-carbene photosensitizer [Fe(bmicp)₂]²⁺ (bmicp= 2,6-bis(3-methyl-imidazole-1-ylidine)-4-carboxy-pyridine) is studied by time-dependent density functional theory, as well as classical and quantum dynamics simulations. We demonstrate the crucial role of the polar acetonitrile solvent in stabilizing the metal-to-ligand charge transfer (MLCT) states of the investigated molecule using the conductor polarizable continuum model. This leads to dynamics that avoid sub-ps back electron transfer to the metal and an exceptionally long-lived 1MLCT state that does not undergo sub-ps 1MLCT → 3MLCT intersystem crossing as it is energetically isolated. We
identify two components of the excited-state solvent reorganization process: an initial rotation (∼300 fs) and diffusional dynamics within the local cage surrounding the rotated solvent molecule (∼2 ps). Finally, it is found that the relaxation of the solvent only slightly affects the excited-state population dynamics of [Fe(bmicp)2]2+. 

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Anisotropy enhanced X-ray scattering from solvated transition metal complexes

Time-resolved X-ray scattering patterns from photoexcited molecules in solution are in many cases anisotropic at the ultrafast time scales accessible at X-ray free-electron lasers (XFELs). This anisotropy arises from the interaction of a linearly polarized UV-Vis pump laser pulse with the sample, which induces anisotropic structural changes that can be captured by femtosecond X-ray pulses. In this work, a method for quantitative analysis of the anisotropic scattering signal arising from an ensemble of molecules is described, and it is demonstrated how its use can enhance the structural sensitivity of the time-resolved X-ray scattering experiment. This method is applied on time-resolved X-ray scattering patterns measured upon photoexcitation of a solvated di-platinum complex at an XFEL, and the key parameters involved are explored. It is shown that a combined analysis of the anisotropic and isotropic difference scattering signals in this experiment allows a more precise determination of the main photoinduced structural change in the solute, i.e. the change in Pt-Pt bond length, and yields more information on the excitation channels than the analysis of the isotropic scattering only. Finally, it is discussed how the anisotropic transient response of the solvent can enable the determination of key experimental parameters such as the instrument response function.

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Photoinduced Molecular Dynamics in Solution: Multiscale Modelling and the Link to Ultrafast Experiments

Recent advancements in X-ray source technologies have opened up the possibility for directly observing photoinduced chemical reactions as they unfold on the femtosecond time scale. An increasing number of time-resolved X-ray scattering experiments are being directed toward uncovering the light-induced ultrafast dynamics of photocatalytic metal complexes in solution. In this scenario, theory and modelling are brought into play to offer assistance to the interpretation and analysis of intricate measured data. Besides, theoretical modelling is the key to the fundamental understanding of the atomistic mechanisms behind reaction dynamics in solution.

The work presented in this thesis deals with extending, benchmarking and applying a novel multiscale atomistic modelling strategy for simulating the structural dynamics of complex molecular systems. The method is based on the direct Born-Oppenheimer Molecular Dynamics (BOMD) propagation of the nuclei and treats solvent effects within a quantum mechanics/molecular mechanics (QM/MM) framework.

The first part of the thesis shows how the QM/MM scheme is augmented to include electronic excited states with arbitrary spin multiplicity using a ΔSCF approach. We describe the testing and implementation of the method in the GPAW DFT code, providing all prerequisite theoretical background. The robustness of the implementation and the computational expediency of GPAW allow fast configurational sampling, overcoming the problem of statistical accuracy in excited-state BOMD simulations of systems as large as transition metal complexes.

The second part is dedicated to an investigation of the structure and dynamics of a model photocatalyst, the diplatinum(II) complex [Pt2(P2O5H2)4]4−, abbreviated PtPOP. In doing that we make extensive use of the computational tools presented in the first part. First, we show how ΔSCF for the first time provides computational evidence that the lowest-lying singlet and triplet excited states have parallel potential energy surfaces (PESs) along the Pt-Pt coordinate. Then we highlight the synergy between time-resolved experiments and simulations in unravelling the photoinduced ultrafast dynamics of the complex in water.

QM/MM BOMD simulations are used to guide the analysis of X-ray Diffuse Scattering (XDS) data measured at an X-ray free electron laser (XFEL), and to elaborate a semi-classical picture of ground-state hole dynamics that explains the experimental outcome. Finally, we take a step forward in the understanding of the excited-state vibrational relaxation in solution. We show, through the simulations, that PtPOP after excitation does not retain the symmetry of the ground state, as so far believed; and that excess Pt-Pt vibrational energy is first directed towards vibrational modes involving the ligands, while the role of the solvent is to favour intramolecular vibrational energy redistribution (IVR) in the complex.

Solution Structure and Ultrafast Vibrational Relaxation of the PtPOP Complex Revealed by ΔSCF-QM/MM Direct Dynamics Simulations

Recent ultrafast experiments have unveiled the time scales of vibrational cooling and decoherence upon photoexcitation of the diplatinum complex [Pt2(P2O5H2)4]4− in solvents. Here, we contribute to the understanding of the structure and dynamics of the lowest lying singlet excited state of the model photocatalyst by performing potential energy surface calculations and Born–Oppenheimer molecular dynamics simulations in the gas phase and in water. Solvent effects were treated using a multiscale quantum mechanics/molecular mechanics approach. Fast sampling was achieved with a modified version of delta self-consistent field implemented in the grid-based projector-augmented wave density functional theory code. The known structural parameters and the PESs of the first singlet and triplet excited states are correctly reproduced. Besides, the simulations deliver clear evidence that pseudorotation of the ligands in the excited state leads to symmetry lowering of the Pt2P8 core. Coherence decay of Pt–Pt stretching vibrations in solution was found to be governed by vibrational cooling, which is in agreement with previous ultrafast experiments. We also show that the flow of excess Pt–Pt vibrational energy is first directed toward vibrational modes involving the ligands, with the solvent favoring...
intramolecular vibrational energy redistribution. The results are supported by thorough vibrational analysis in terms of
generalized normal modes.

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Mechanism and Thermochemistry of Coal Char Oxidation and Desorption of Surface Oxides

The present study investigates the coal char combustion by a combination of thermochemical and X-ray photoemission spectroscopy (XPS) analyses. Thermoanalytical methods (differential thermogravimetry, differential scanning calorimetry, and temperature-programmed desorption) are used to identify the key reactive steps that occur upon oxidation and heating of coal char (chemisorption, structural rearrangement and switchover of surface oxides, and desorption) and their energetics. XPS is used to reveal the chemical nature of the surface oxides that populate the char surface and to monitor their evolution throughout thermochemical processing. XPS spectra show the presence on the carbon surface of three main components. It is shown that the most abundant oxygen functionality in the raw char is epoxy. It decreases with preoxidation at 300°C and even more at 500°C, where carboxyl and ether oxygen functionalities prevail. The rearrangement of epoxy during preoxidation goes together with activation of the more stable and less reactive carbon sites. Results are in good agreement with semi-lumped kinetic models of carbon oxidation, which include (1) formation of "metastable" surface oxides, (2) complex switchover, and (3) desorption into CO and CO2.
Grid-Based Projector Augmented Wave (GPAW) Implementation of Quantum Mechanics/Molecular Mechanics (QM/MM) Electrostatic Embedding and Application to a Solvated Diplatinum Complex

A multiscale density functional theory-quantum mechanics/molecular mechanics (DFT-QM/MM) scheme is presented, based on an efficient electrostatic coupling between the electronic density obtained from a grid-based projector augmented wave (GPAW) implementation of density functional theory and a classical potential energy function. The scheme is implemented in a general fashion and can be used with various choices for the descriptions of the QM or MM regions. Tests on H2O clusters, ranging from dimer to decamer show that no systematic energy errors are introduced by the coupling that exceeds the differences in the QM and MM descriptions. Over 1 ns of liquid water, Born-Oppenheimer QM/MM molecular dynamics (MD) are sampled combining 10 parallel simulations, showing consistent liquid water
structure over the QM/MM border. The method is applied in extensive parallel MD simulations of an aqueous solution of the diplatinum [Pt2(P2O5H2)4]- complex (PtPOP), spanning a total time period of roughly half a nanosecond. An average Pt-Pt distance deviating only 0.01 Å from experimental results, and a ground-state Pt-Pt oscillation frequency deviating by...
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Projects:

**Light-induced electronic and structural dynamics**
Levi, G., PhD Student, Department of Chemistry
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