Computational Inorganic and Analytical Chemistry

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Abstract. Our research activity in computational chemistry at the university of Fribourg is briefly presented including topics like: Electronic structure calculation of coordination compounds, density functional theory, multiplet structure calculation, modelling the optical and magnetic properties of metal complexes and inorganic materials, molecular dynamics, redox polymers, thin layer cells.

1. Introduction

Basically chemistry is concerned with the structure, spectroscopy, and reactivity of molecules, and our research activity considers the contributions that theoretical methods related to experimental studies can offer to our understanding of these aspects. Starting from first principles or from empirical models, we are able to determine the energy and electronic structure of metal complexes in different electronic states with good accuracy (typically: ±20 kJ). Hence, we can predict their spectra, electronic and magnetic properties, and reaction energies. At the same time the study of potential-energy surfaces and nuclear motion provides information of the dynamic nature of reactivity and reaction probabilities. The determination of the structure and reactivity of an isolated molecule is often only the first step in the development of a quantitative theory whose results can be compared to experimental data. Experimental chemistry, whether in gas phase, in solution, or in solids, involves large numbers of molecules, and we need to use the methods of statistical mechanics to relate the results of a quantum-mechanical treatment of a single molecule to experimental data. Comparison of these predictions with experimental results is essential for two reasons: *i*) to improve and refine the theoretical models; *ii*) to provide information to design new experiments.

The investigation of chemical processes by theoretical methods is a key step for the rationalization and the control of complex chemical systems of practical interest. This area is of immense importance and is rapidly growing, largely as a result of *i*) advances in instrumentation and techniques which stimulate more and more sophisticated experimentation, *ii*) the direct linking of experimental investigations to theoretical models, especially in studies of reactivity and liquid states, and *iii*) the availability in almost all laboratories of ever more powerful computing and computer-graphics facilities, which permit the implementation of theory and the visualisation of its prediction, on a unprecedented scale. Moreover, during the past decade new computational methods have been devised to take advantage of the increased processing speeds, especially the very cost efficient 'workstations' which make decentralized computing most attractive; large core storage, and vector and parallel-processing capabilities of super computers now permit access by numerical methods to chemical information that would be impossible or very difficult to obtain by other means. However, since the field has a truly multidisciplinary nature, the collaboration between experimentalists and theoreticians on specific topics is playing an increasing role. Thus, development in chemical research in the last few years shows clearly the rapidly strengthening interaction between the work of the chemist in the laboratory and theoretical work. Examples are the rapid spread and acceptance of molecular modelling for drug design, the application of theoretical models for interpreting reactivity, and the increasing application of computers for the development of chemical synthesis.

Density Functional (DF) methodology and applications in a broad range of areas is a very promising alternative to the traditional approaches of quantum chemistry and quantum physics: its main advantages lie in the fact that it is faster than the usual *Hartree-Fock* techniques and does not require semiempirical parameters, enabling realistic studies of large systems of practical importance to be performed. It describes with consistent reliability organic, inorganic, metallic, and semiconductor systems. For these reasons, the method has become increasingly important in pharmaceutical, agrochemical, and biotechnology research; materials and polymer science; catalysis, surface, and solid-state research; and electrochemistry and microelectronics.

Within this conceptual frame, we do focus our work to problems for which we have developed good expertise over the years, and for which our colleagues experimentalists have provided us with reliable data. Thus, an important part of our project will be devoted to the description and prediction of the structural, spectroscopic and magnetic properties of coordination compounds using DF methodology which yields good electronic structures for coordination compounds of up to 100 atoms given the actual computer power. In this respect, we plan to develop in Fribourg our own computer program (FRIMOL). This new program will be based on modern numerical methodology and will include the solution of the *Kohn-Sham* equation in magnetic fields [1] providing a new route for the calculation of magnetic properties, especially of chemical shifts. A second point of emphasis is the calculation of multiplet structures based on a method we have recently proposed [2], and which is at the present time rather promising. This latter model will permit a description of the excited-state characteristics of metal complexes, *e.g.* spectroscopic, photophysical, and photochemical properties also in presence of a magnetic field.

Our second field of interest has emerged from a more then ten years old collaboration with Dr. *O. Haas* and Dr. *E. Deiss* from the *Paul Scherrer* Institut (PSI) in Würenlingen. In this respect, we carry out simulations of the electrochemical properties of electrodes covered with redox or conducting polymers using models we have recently developed [3]. More recently, we have extended our modelling to the design of new thin-layer cells to be used as batteries.

In a third part of our research program, we plan to carry out Monte Carlo (MC) an

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Molecular Dynamics (MD) simulations in order to model the interaction between transition-metal ions and macromolecular ligands. The result of this calculation is of great interest with respect to the experimental study of complex formation with macromolecules by my colleague *C.W. Schläpfer* from our Institute (*cf.* article in the same issue of the present journal).

Moreover, we proposed recently in collaboration with Prof. *J. Weber* from the University of Geneva a method of description of reaction potentials between a metallorganic and an electrophilic or a nucleophilic species [4]. This model is quite successful in predicting the site of attack and further developments including solvatation effects are in progress.

2. Density Functional Theory (DFT)

DFT is based on the following theorem due to *Hohenberg* and *Kohn*. Consider an N-electron system moving in an external potential $V(\mathbf{r})$ provided by M nuclei:

$$\hat{H} = \hat{T} + \hat{V} + \hat{U} \tag{1}$$

where

$$\hat{T} = \sum_{i=1}^{N} -\frac{1}{2}\Delta \tag{1a}$$

represents the kinetic energy of the N electrons,

$$\hat{V} = \sum_{i=1}^{N} v(\mathbf{r}_i) = \sum_{i=1}^{N} \sum_{k=1}^{M} \frac{z_k}{|\mathbf{r}_i - \mathbf{R}_k|} \tag{1b}$$

represents the electrostatic attraction of the N electrons due to the M nuclei; $\mathbf{r}_i$ is the position of the i-th electron, $\mathbf{R}_k$ is the position of the k-th nucleus with charge z_k and

$$\hat{U} = \sum_{i<j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{1c}$$

represents the interelectronic repulsion of the N electrons; $\mathbf{r}_i$ and $\mathbf{r}_j$, respectively, are the positions of the i-th and of the j-th electron.

Hohenberg and *Kohn* proved thirty years ago that the full many particle ground state wave function $\Psi(1,2,...,N)$ is a unique functional of the one-particle density $\rho(\mathbf{r})$

$$\rho(\mathbf{r}) = N \int |\psi|^2 \cdot d\mathbf{r}_2 \cdot \ldots \cdot d\mathbf{r}_N \cdot ds_1 \ldots \cdot ds_N \tag{2}$$

This theorem is actually easy to understand from a heuristic point of view. Suppose that the density $\rho(\mathbf{r})$ of an unknown molecule has been obtained to high accuracy by X-ray diffraction and the nuclear positions as well. It is then possible to obtain also the nuclear charges from the M cusp conditions:

$$\left(\frac{\partial\bar{\rho}(\mathbf{R}_k)}{\partial\mathbf{R}_k}\right)_{\mathbf{R}_k=0} = -2\cdot z_k \cdot \bar{\rho}(0) \tag{3}$$

where $\mathbf{R}_k$ is the position of the k-th nucleus, z_k its charge and $\bar{\rho}(\mathbf{R}_k)$ the spherically averaged electron density, and the number of electrons can be obtained by integrating $\rho(\mathbf{r})$. But this is precisely all the informations needed to write down *Schrödinger*'s equation:

$$\hat{H}\psi = E\cdot\psi \tag{4}$$

whose solution yields the ground state wave function ψ, *q.e.d.*!

One year later, *Kohn* and *Sham* provided a route to a set of working equations:

$$\left(-\frac{1}{2}\Delta + v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} + v_{XC}(\rho(\mathbf{r}))\right)\psi_i = \varepsilon_i \psi_i(\mathbf{r}) \tag{5}$$

where

$$v_{XC}(\rho(\mathbf{r})) = \frac{\delta E_{XC}[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})} \tag{6}$$

and the density

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2 \tag{7}$$

These are the well-known *Kohn-Sham* equations which are still exact! All symbols used have been defined earlier except the key term $E_{XC}[\rho]$ which is a functional that contains: exchange + correlation + difference in kinetic energy of interacting and non-interacting particles of density ρ. But unfortunately, $E_{XC}[\rho]$ is not known. To proceed further, approximations have to be introduced in order to represent this latter functional. Three generations of functionals have now succeeded. The first generation was based on *Thomas-Fermi*'s electron gas theory and is usually refered to as Local Density Approximation (LDA). The second one is based on the theory of *Coulomb-* and *Fermi*-holes and does include density gradient corrections. Usually one does refer to functionals of the 2nd generation as Non Local Density Approxima-

tion (NLDA). Whereas the third generation of functionals is still under development, it is based on the Adiabatic Connection Method (ACM) of exact and model exchange potentials.

For more details concerning DFT in general and functionals in particular, see [5].

3. Density Functional Theory Applied to the Excited States of Coordination Compounds

Coordination compounds are usually symmetrical molecules with degenerate orbitals. Hence, the individual multiplet states arising from open-shell configurations can, in general, not be expressed by a single determinant. We have, therefore, exploited symmetry to the largest possible extent in order to simplify the relation between the multiplet splitting and single-determinant energies and, thus, developed a new method based on vector coupling in order to keep the computational effort to a minimum.

A system of computer programs working on both mainframe and personal computers has been developed carrying out for any desired point group the required group theoretical manipulations.

The application of the method is illustrated by considering the Metal to Ligand Charge Transfer (MLCT) states of $[Ru(bpy)_3]^{2+}$ in D_3 symmetry. The method used in this study includes first-order electrostatic multiplet splitting as well as spin-orbit interaction. The results obtained show that there is an important mixing of the excited singlet and triplet states. These first principles results are in good overall agreement with the observed absorption spectra, with respect to both the spread of the excitation energies and the positions of the strong, unambiguously assigned, peaks. Our calculation finds the lowest excited states to be virtually degenerate A_1 and E spin-orbit components of $(d\pi:a_1)\rightarrow(\pi^*:a_2)$ $^3A_2$ state, the former lying few 10 cm^{-1} below the latter one. The next excited triplet *i.e.* $(d\pi:e)\rightarrow(\pi^*:a_2)$ ^3E arises only roughly 1500 cm^{-1} above the $^3A_2$. The MLCT states of $[Ru(bpy)_3]^{2+}$ are depicted in *Fig. 1*, whereas their predicted energies are compared to the experimental values in the *Table*. For more details, see [2][6].

4. Modelling of Time-Dependent Processes at Redox Polymer Electrodes

The electrochemical behavior of redox-polymer-coated electrodes depends on several properties of the polymers. It is mainly the electron-transfer rate at the metal/polymer interface and the electron and counter ion transport within the polymer which characterize the potentiodynamic behavior of these electrodes. For the electrocatalytic behavior, the diffusion and migration of the species towards and in the film as well as the electron-transfer rate between the redox sites of the polymer are possible rate-determining steps. Some of these properties can be manipulated using different preparation techniques or by changing the nature of the electrolyte. Even the thickness of the film may play a important role for the mechanism. The influence of the different rate-determining steps on the overall behavior, however, can only be estimated, if the rather complex electrochemical process of redox-polymer-coated electrodes can be simulated. A general analytical solution of the problem is not possible for the stationary electrocatalytic process. *Albery* and *Hilmann* [7], and *Andrieux* and *Savéant* [8] discussed the system using analytical solutions for special cases. Some years ago, a general numerical solution for this problem was presented including *Tafel*'s law at the electrode polymer boundary. This numerical solution, however, did not take into account migration effects and the *Donnan* equilibrium at the polymer electrolyte interface. Nevertheless, the stationary catalytic processes at rotating redox-polymer-coated electrodes could be simulated satisfactorily [9]. With that program current potential curves of the oxidation of Fe^{II} to Fe^{III} with [Ru(bpy)$_2$Cl-poly(4-vinylpyridine)]Cl-coated electrodes could be simulated by calculating stationary currents at the stepwise increased potentials [9].

The present simulation program is more general, it includes the possibility to simulate potentiodynamic processes which involves also the kinetics of the *Donnan* equilibrium the transport (migration and diffusion) of the counter ion in the film and in the diffusion layer. It also takes care for the fact that electroneutrality in the polymer and diffusion layer is not hurt. An electron-hopping mechanism has been introduced to simulate the electron transport within the film. It should also allow the simulation of more complicated redox polymers with two electron-exchanging centres including protonation equilibria.
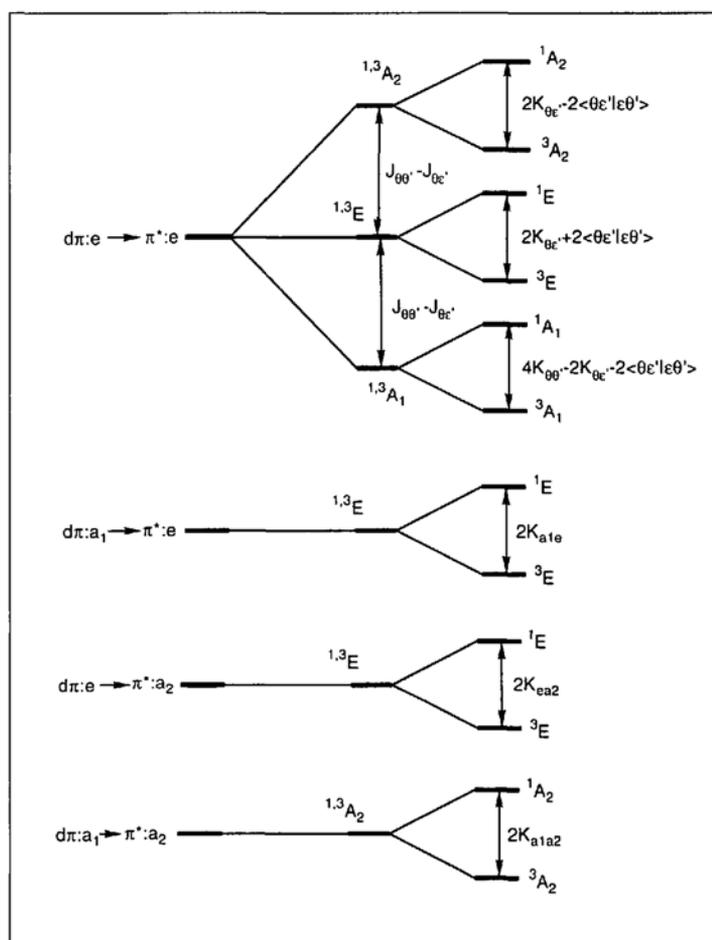

Fig. 1. *MLCT states of* $[Ru(bpy)_3]^{2+}$

Table. *Energies of the MLCT States Including Spin-Orbit Coupling*

Composition[a])	State	Predicted energy [10^3 cm^{-1}]	Observed energy [10^3 cm^{-1}]
85% $^3A_2(d\pi_{a1}\rightarrow\pi^*_{a2})$ + 14% $^3E(d\pi_e\rightarrow\pi^*_{a2})$	A_1	19.877	
87% $^3A_2(d\pi_{a1}\rightarrow\pi^*_{a2})$ + 7% $^3E(d\pi_e\rightarrow\pi^*_{a2})$	E	19.896	18.47
77% $^3E(d\pi_{a1}\rightarrow\pi^*_{a2})$ + 22% $^3E(d\pi_e\rightarrow\pi^*_{a2})$	A_2	20.213	18.95
85% $^3E(d\pi_{a1}\rightarrow\pi^*_{a2})$ + 14% $^3A_2(d\pi_e\rightarrow\pi^*_{a2})$	A_1	21.439	
77% $^3E(d\pi_{a1}\rightarrow\pi^*_{a2})$ + 22% $^3A_2(d\pi_e\rightarrow\pi^*_{a2})$	A_2	21.513	20.45
66% $^3E(d\pi_{a1}\rightarrow\pi^*_{a2})$ + 21% $^3E(d\pi_e\rightarrow\pi^*_{a2})$	E	21.534	
99% $^3E(d\pi_e\rightarrow\pi^*_{a2})$	E	21.938	
57% $^3A_1(d\pi_e\rightarrow\pi^*_e)$ + 40% $^3E(d\pi_{a1}\rightarrow\pi_e)$	A_2	22.056	
60% $^3A_1(d\pi_e\rightarrow\pi^*_e)$ + 34% $^3E(d\pi_{a1}\rightarrow\pi^*_e)$	E	22.103	
72% $^1E(d\pi_e\rightarrow\pi^*_{a2})$ + 27% $^3E(d\pi_e\rightarrow\pi^*_{a2})$	E	22.125	21.5 (strong)
88% $^3E(d\pi_{a1}\rightarrow\pi^*_e)$ + 8% $^3E(d\pi_e\rightarrow\pi^*_e)$	E	22.399	
92% $^3E(d\pi_{a1}\rightarrow\pi^*_e)$ + 5% $^1A_1(d\pi_e\rightarrow\pi^*_e)$	A_1	22.450	
46% $^3E(d\pi_{a1}\rightarrow\pi^*_e)$ + 20% $^3A_1(d\pi_e\rightarrow\pi^*_e)$	E	22.566	
58% $^3E(d\pi_{a1}\rightarrow\pi^*_e)$ + 41% $^3A_1(d\pi_e\rightarrow\pi^*_e)$	A_2	22.923	24.74
56% $^1E(d\pi_{a1}\rightarrow\pi^*_e)$ + 19% $^3A_1(d\pi_e\rightarrow\pi^*_{a2})$	E	23.201	
72% $^3E(d\pi_e\rightarrow\pi^*_e)$ + 22% $^1E(d\pi_{a1}\rightarrow\pi^*_e)$	E	23.948	
78% $^3E(d\pi_e\rightarrow\pi^*_e)$ + 11% $^1E(d\pi_{a1}\rightarrow\pi^*_e)$	E	24.000	
99% $^3E(d\pi_e\rightarrow\pi^*_e)$	A_1	24.348	
99% $^3E(d\pi_e\rightarrow\pi^*_e)$	A_2	24.354	25.60
89% $^1A_1(d\pi_e\rightarrow\pi^*_e)$ + 4% $^3A_2(d\pi_e\rightarrow\pi^*_e)$	A_1	24.362	
85% $^1E(d\pi_e\rightarrow\pi^*_e)$ + 14% $^3E(d\pi_e\rightarrow\pi^*_e)$	E	24.766	23.3 (strong)
97% $^3A_2(d\pi_e\rightarrow\pi^*_e)$ + 1% $^1E(d\pi_{a1}\rightarrow\pi^*_e)$	E	25.623	
93% $^3A_2(d\pi_e\rightarrow\pi^*_e)$ + 5% $^1A_1(d\pi_e\rightarrow\pi^*_e)$	A_1	25.663	
99% $^1A_2(d\pi_e\rightarrow\pi^*_e)$	A_2	26.089	26.13

[a]) Only the major parent states are reported.

The set of partial differential equations thus obtained are transformed into ordinary differential equations using the method of lines with cubic *Hermite* polynomials. The time integration is performed by a semiimplicite method and the stepsizes are quality controlled. Calculated and measured data of cyclic voltammograms of a ruthenium-polymer-coated electrode are compared and demonstrate the reliability of the model (*cf. Fig. 2*). For more details, see [3].

This general method is now extended in order to simulate the electrochemical processes taking place in thin layer cells. As an example, a cell containing two polymer coated electrodes is described by using the mechanisms shown above. To prevent physical contact between the electrodes, an inert material is used in the experimental cells as spacer. Its cavities are filled by the electrolyte solution. In the simulation program, this system is taken into account by introducing the condition of charge compensation for the two half cells. Therefore, one obtains the necessary conservation of electron flux. Presently, the model is tested and improved for a symmetric concentration cell, whose redox species follow *Nernst*'s law. The transport of the electrons within the polymer layer is accomplished by a diffusion-equivalent hopping mechanism, whereas for the mass transport the diffusion laws hold. In
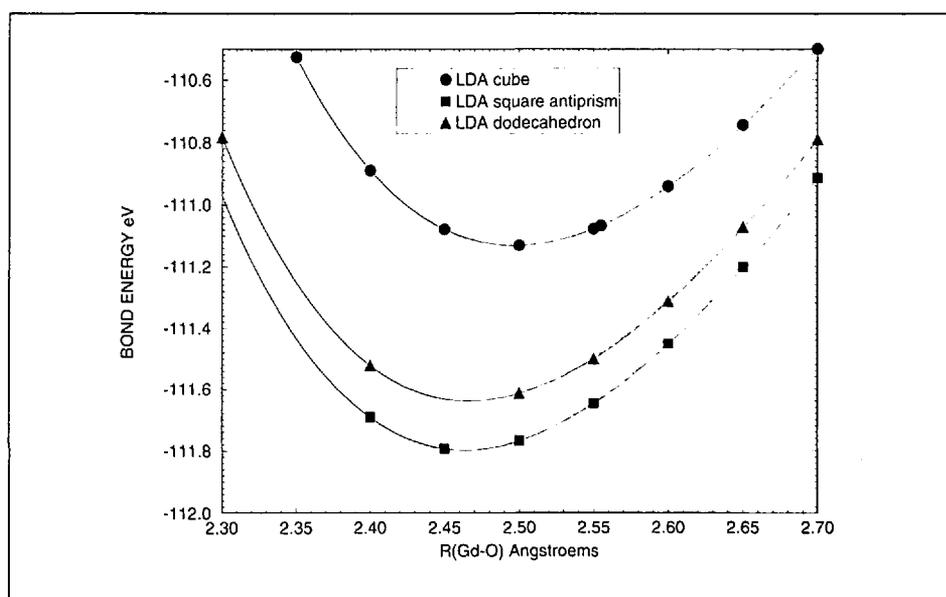
addition to the behavior of the redox species in the polymer the concentration profiles of the electrolyte are calculated. They are considered in the resulting current and potential profiles obtained during the simulated charge and discharge cycles. The influence of the polymer characteristics on the charge-storage properties of batteries containing these electrode systems is an important part of modelling thin-layer cells. More results on modelling of thin layer cells will be presented at the fall

Fig. 3. *Bond energy of [Gd(H₂O)₈]³⁺ as a function of metal-water distance for the three following coordination geometries: cube, square antiprism, and dodecahedron*

session 1994 of the *New Swiss Chemical Society*.

5. Modelling of Nucleophilic and Electrophilic Additions and Substitutions Using Semi-Empirical Reaction Potentials

A new formalism has been developed in order to evaluate intermolecular interaction energies for organometallic complexes including electrostatic, polarization and orbital contributions based on semiempirical molecular-orbital theory. The electrostatic interaction is evaluated using *i*) a multipolar expansion of charge density, or *ii*) by calculating directly the electrostatic integrals in the basis of atomic orbitals. The polarization effects are evaluated by introducing a perturbation into the effective hamiltonian. The orbital interaction is calculated by considering a supermolecule made of the organometallic substrate and a model electrophile or nucleophile. To provide the shortest possible response time on an interactive computer graphics facility, this model should require the minimum amount of computer time, which explains why approximate procedures are used to evaluate the dominant contributions to the interaction energies. Preliminary results show that these interaction energies lead to reaction potentials in good agreement with experiment for a broad series of nucleophilic and electrophilic addition or substitution reactions involving organometallic complexes. In addition, it is shown that the method can easily be extended for the calculation of solvent effects. To this end, developments considering the supermolecule sur-
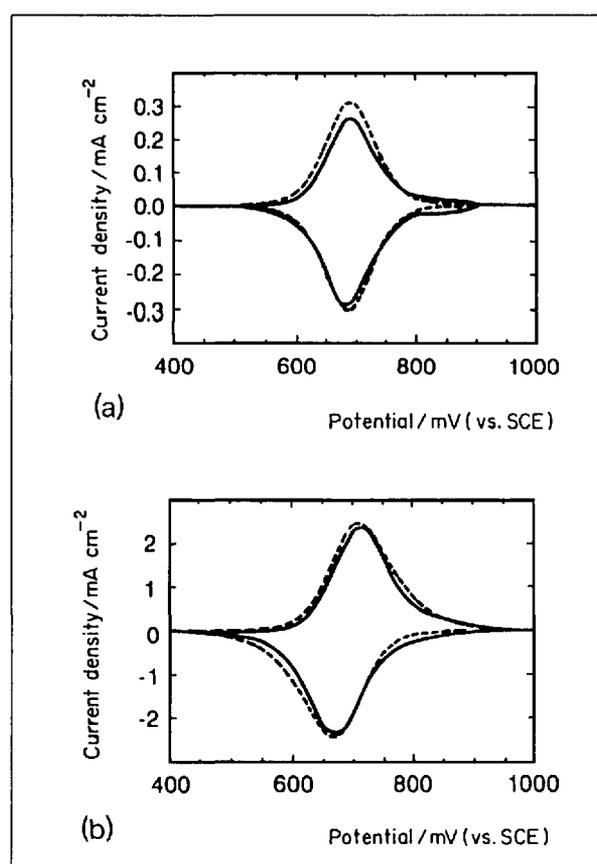

Fig. 2. *Observed (—) and predicted (----) cyclic voltammograms of ruthenium polymer caotings for a sweep rate of a) 0.11 V·s⁻¹ and b) 1.1 V·s⁻¹*

rounded by a polarizable continuum are in progress. For more details, see [4].

6. Modelling the Coordination Sphere of Lanthanides

Hydrated lanthanides(III) ions $Ln^{3+}(H_2O)_x$ ($x = 8$, 9) with $Ln^{3+} = Gd^{3+}$, Sm^{3+} and Dy^{3+} are currently studied using DFT and the results are in agreement with similar *Hartree-Fock* results [10]. The calculations are related to experimental results in order to elucidate the hydration behavior of lanthanide(III) ions. It has been established that the coordination number of the lanthanides changes in the middle of the serie: Nd^{3+}, Sm^{3+}, Eu^{3+} [11].

The energies between different structures (*i.e.*, cube, square antiprism, and dodecahedron) of the first solvation sphere are compared. The bond energy as a function of ion-water distance obtained in the local density approximation (LDA) is pre-

sented in *Fig. 3*. It is seen that the square antiprism has energetically the most favorable coordination geometry. This result is in good agreement with MD simulations of NMR data obtained by *Foglia, Helm, Kowall* and *Merbach* in Lausanne [12].

The charge polarization of the coordinated water molecules at different geometries is also being studied in order to design better interaction potentials to be used in molecular dynamics (MD) simulations of such systems. More results will be presented at the fall session 1994 of the *New Swiss Chemical Society*.

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Molecular Devices Based on Bridged Transition-Metal Complexes

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Abstract. The article from *A. von Zelewsky*, in this issue gives a broad survey about some scientific activities at the Institute of Inorganic Chemistry of the University of Fribourg. The present contribution will be rather focused on a detailed study of the photophysical and photochemical behavior of a molecular device that is capable to undergo energy- and/or electron-transfer processes.

1. Introduction

The scientific field of supramolecular chemistry [1–3] means that such complicated systems have the potential to achieve much more capabilities than simple molecules. A simple molecule has only the possibility to participate in chemical reactions. Supramolecular systems can per-

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form functions and have, therefore, the potential to behave as *molecular devices*. Photochemical molecular devices are those that use light to achieve their functions.

The development of photochemical molecular devices for different applications (*e.g.*, artificial photosynthesis and information processing) [4] is based on the design of molecular species in which photoinduced energy- or electron-transfer processes can take place over a long distance with high efficiency.

To elucidate the role played by various factors in determining the occurrence of photoinduced energy- and electron-transfer processes, we have designed and synthesized different bridged polynuclear metal complexes [5][6]. The requirements for the construction of such a molecular device for charge separation are (*Fig. 1*):
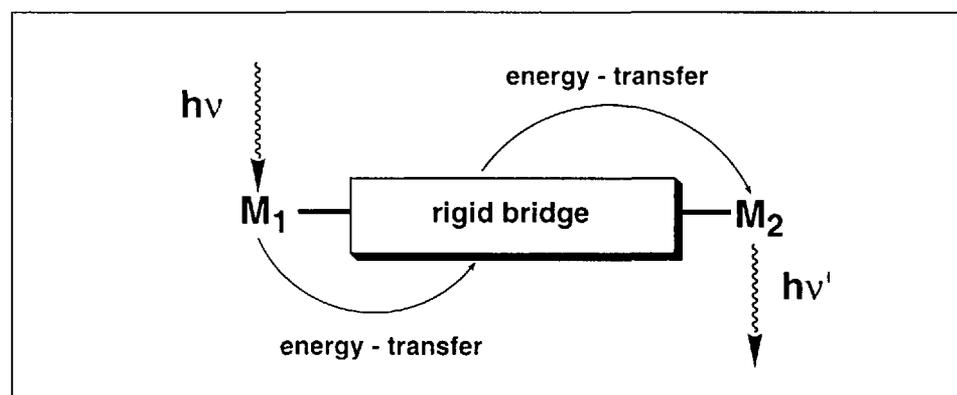

Fig. 1. *Block diagram of a molecular device that is capable for an energy-transfer process*