

THEORETICAL METHODS FOR THE STUDY OF THE ELECTRONIC STRUCTURE OF MOLECULES

Nowadays the correct description of the electronic structure of molecules still remains a great challenge, particularly for systems of large chemical interest, such molecules during bond breaking/formation, radicals, transition metal complexes, and electronically excited states. To get a thorough understanding of these complex systems innovative theoretical means are required. The activity of the group of theoretical chemistry has developed new methods to efficiently couple quality and computational effort.

GOALS

The research aims at the development of new theoretical methods for the description of molecular systems, wherein the electronic structure cannot be describe with a single configuration, their implementation within efficient calculation codes, and their application towards the study of complex chemical problems. The main efforts are devoted towards the development of "Multireference perturbation theory" methods which will be applied towards the study of metal-metal bonds, the description of electronic excited states, and the understanding of magnetic coupling in polynuclear complexes based on transition metals.

INSTRUMENTS AND METHODS

Methods: formal development of theory in the field of quantum chemistry, implementation of calculation codes by using FORTRAN programming language, high level calculations on computer clusters.

Instruments: quad-core computer clusters for parallel calculation within Linux operating system.

MAIN SUBJECTS

Physical chemistry, Theoretical chemistry, Computational chemistry

RESEARCH GROUP

Prof. C. Angeli, Prof. R. Cimiraglia

STUDY AND CHARACTERIZATION OF MOLECULAR MAGNETS

The project deals with the study of the interactions between metal centers within polynuclear molecular complexes. Polynuclear complexes are multi-functional materials and, among them, those containing copper are particularly interesting due to their multiple properties. Indeed, they can mimic active sites of natural biomolecules, they can interact with DNA, or they can be used as innovative materials in chemistry and in nanotechnologies thanks to their featuring electronic, magnetic, and redox properties.

GOALS

The main goal is to start a systematic study of the magnetic properties of bi- and tri-nuclear copper and nickel complexes. The interest towards these systems arises from the fact that oxygen atoms of specific ligands can act as bridges between copper centers. Since there is a strong relationship between the molecular structure (particularly metal coordination and structure of bridges) and the nature and intensities of the magnetic interactions between unpaired electrons in the metal centers, an accurate choice of organic ligands may induce a direct modulation of the magnetic properties.

INSTRUMENTS AND METHODS

- Development of synthetic strategies for the preparation of polynuclear complexes;
- Structural characterization with X-ray diffraction techniques;
- Study of the magnetic properties via SQUID (Superconducting Quantum Interference Devices);
- EPR spectroscopy;
- Application of theoretical and computational strategies for the appropriate description of the electronic structure and the magnetic properties.

MAIN SUBJECTS

Physical chemistry, Inorganic chemistry, Spectroscopy, Theoretical chemistry

RESEARCH GROUP

Dr. V. Ferretti, Prof. C. Angeli, Prof. V. Bertolasi

COLLABORATIONS

- Dr. F. Spizzo (Department of Physics and Earth Sciences, UNIFE)
- Prof. C. J. Calzado (Departamento de Química Física, Universidad de Sevilla, Spain)
- Prof. R. P. Sharma (Department of Chemistry, Punjab University, Chandigarh, India)
- Prof. J. Jezierska (Institute of Chemistry, Wroclaw University, Poland)
- Prof. A. Ozarowski (National High Magnetic Field Laboratory, Florida State University, USA)
- Prof. S. Chandra Manna (Department of Chemistry and Chemical Technology, Vidyasagar University, Midnapore, India)
- Prof. D. Ray (Department of Chemistry, Indian Institute of Technology, Kharagpur, India)

HIGH-PERFORMANCE ELECTRODIC AND ELECTROLYTIC MATERIALS FOR THE DEVELOPMENT OF NEW GENERATION ENERGY STORAGE SYSTEMS

The increasing energy demand requires the exploitation of clean energy sources and sustainable energy storage systems. Nowadays, lithium-ion batteries are the most efficient devices for the electrochemical storage of energy thanks to their unique properties, such as high specific energy, high efficiency, and durability. However, towards a thorough exploitation of this energy storage systems innovative electrode materials, for both the cathode and the anode, as well as new electrolytic components are required. This research project targets the development of lithium-ion batteries based on new electrodic components, featuring higher energy density, extended lifetime, and higher specific capacity. The aim of the project is therefore the research of new high-performance material for the preparation of anodes, such as materials that work through a conversion reaction mechanism (e.g., Fe_2O_3 , CuO) and graphene, as well as the quest of low-cost and environmentally-friendly cathodic materials, such as olivine-type compounds (e.g., LiFePO_4 , LiMnPO_4). Part of the research activity is also dedicated to the development of new electrolytes such as ionic liquids (ILs). Moreover, new-generation charge accumulators are also considered based on the reaction with sulfur and oxygen (e.g., lithium sulfur and lithium-air batteries).

GOALS

Development of new-generation materials for charge accumulators, such as lithium-ion, lithium-air, lithium-sulfur, and sodium-ion batteries and devices with ionic liquids and graphene. Development of batteries for automotive engines, electronic devices, and charge accumulation from photovoltaic plants.

INSTRUMENTS AND METHODS

Argon glove box, high-performance multichannel galvanostatic cyclers, electrochemical impedance spectroscopy (EIS), cyclic voltammetry, Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS).

MAIN SUBJECTS

Electrochemistry, Material science, Sustainable energy

RESEARCH GROUP

Prof. Jusef Hassoun

COLLABORATIONS

- Prof. J. Garche (University of Ulm, Ulm, Germany)
- Prof. S. Passerini (Helmholtz Institute, Ulm, Germany)
- Prof. Y.-K. Sun (Hanyang University, Seoul, South Korea)
- Prof. S. Greenbaum (Hunter College of CUNY, NY, USA)
- External collaborations with BMW, Volkswagen, Samsung, and Evonik

SYNTHESIS OF CO-CRYSTAL RELEVANT TO PHARMACEUTICAL APPLICATIONS

Pharmaceutical co-crystals are composed of an active pharmaceutical ingredient (AI), either as a neutral or an ionic species, and another component (bioactive or not), held together by means of non-covalent, reversible interactions. With respect to the active component alone, co-crystals show different physico-chemical properties (stability, solubility, bioavailability) which can be very interesting from the pharmaceutical viewpoint.

GOALS

In principle, the formation of a co-crystal can be predicted on the basis of the structural properties of the interacting molecules, provided that the type of interactions are known. The detailed study of the intermolecular interactions between the active ingredient and the partner molecules in a series of co-crystals targets the identification of the “ideal partner”. This study is completed by an investigation of pharmaceutically important co-crystal properties such as solubility, bioavailability and permeation through biological membranes.

INSTRUMENTS AND METHODS

Room temperature crystallization by slow vapor evaporation, X-ray diffraction techniques (both single crystal and powder) crystallographic databases.

MAIN SUBJECTS

General chemistry, Physical chemistry, Structural chemistry

RESEARCH GROUP

Prof. V. Bertolasi, Dr. V. Ferretti, Dr. P. Gilli

COLLABORATIONS

- Prof. A. Dalpiaz (Department of Chemical and Pharmaceutical Sciences, UniFe)
- Dr. B. Pavan (Department of Life Sciences and Biotechnologies, UniFe)

INTERACTION AND RECOGNITION IN MOLECULAR CRYSTALS

Molecular crystals are ideal models for the study of molecular interaction forces that are responsible for the different aggregation states of matter and which are important for supramolecular recognition processes relevant in chemistry, material science and biochemistry of the drug-receptor and enzyme-substrate interactions. The study of crystal packing within extended series of crystals (either designed ad hoc or derived from systematic investigation of crystallographic databases, also possibly integrated with thermodynamic and spectroscopic data as well as computational calculations) allows for the identification of intermolecular recognition forces that enable molecule to be part of stable aggregated species. The data analysis is performed with LFER (linear free-energy relationships) and structural correlation methods aimed at the definition of the reaction pathways and the identification of structure/properties relationships.

GOALS

(a) Systematic study of hydrogen bonding, its classification in chemical classes and formulation of general models capable of predicting the properties, with particular regard to structure and energetic. (b) Application of strong hydrogen bonding in chemistry, biochemistry, and material science. (c) Systematic study of charge transfer interactions in molecular crystals. Their importance in the determination of the crystal packing and in the definition of a general theoretical basis for molecular interactions. (d) Application of the understanding of the molecular interactions towards crystal engineering, with particular regard towards functional materials and co-crystals of pharmaceutical interest.

INSTRUMENTS AND METHODS

Systematic use of crystallographic and thermodynamic databases. Simulation of model molecules by quantum chemistry with either “ab initio” or DFT methods. Preparations of molecular crystals and co-crystals for the study of molecular interactions and their structural determination by X-ray diffraction technique at both room and cryogenic temperature.

MAIN SUBJECTS

Structural chemistry, Physical chemistry, General chemistry

RESEARCH GROUP

Dr. P. Gilli, Prof. V. Bertolasi