TA01 10:00 – 10:50

TOWARD A ROBUST AND USER FRIENDLY MULTI-FREQUENCY VIRTUAL SPECTROMETER

Vincenzo Barone

Scuola Normale Superiore, piazza dei Cavalieri 7, 56126 Pisa, Italy

Within the plethora of modern experimental techniques, vibrational, electronic, and resonance spectroscopies are uniquely suitable to probe static and dynamic properties of molecular systems under realistic environmental conditions and in a non-invasive fashion. However, the outcome of spectroscopic studies is rarely interpretable without the support of theoretical treatments providing a link between chemical/electronic structure and spectroscopic properties. Furthermore, the development of more and more sophisticated experimental techniques poses correspondingly stringent requirements on the quality of the models employed to interpret spectroscopic results, and on the accuracy of the underlying chemical-physical descriptions.

The predictive and interpretative ability of computational chemistry experiments can be clearly demonstrated by state-of-the-art quantum mechanical approaches to spectroscopy, which at present yield results comparable to the most accurate experimental measurements. However, the highly accurate methods available for small molecular systems are not transferable directly to the study of large, complex molecular systems. Clearly, the definition of efficient computational approaches aimed at spectroscopic studies of macro-systems is in general a non-trivial task, and the basic requirement is that such effective models need to reflect a correct physical picture. Then, appropriate schemes can be introduced even for challenging cases, retaining the reliability of more demanding computational approaches for molecular systems of drug design, materials science, nanotechnology, etc. interest.

On these grounds, the present contribution aims to present and analyze several examples illustrating the current status of computational spectroscopy approaches applicable to medium-to-large molecular system in the gas phase and in more complex environments. Particular attention is devoted to theoretical models able to provide data as close as possible to the results directly available from experiment, in order to avoid ambiguities in the interpretation of the latter. The examples range from anharmonic frequencies and IR-Raman intensities of medium size systems [1], to vibrationally resolved UV-Vis [2] and Resonance Raman [3] spectra of molecules in solution. The point is also made that computational spectroscopy studies of more complex macro-systems are becoming feasible, provided that the new capacities offered by the constant increase in computer performances are exploited by developing suitable multi-scale approaches.

[1] V. Barone, M. Biczysko, J. Bloino, PHYSICAL CHEMISTRY CHEMICAL PHYSICS **16**, 1759-1787 (2014).
[2] A. Baiardi, J. Bloino, V. Barone, JOURNAL OF CHEMICAL THEORY AND COMPUTATION **9**, 4097-4115 (2013).
[3] F. Egidi, J. Bloino, C. Cappelli, V. Barone, JOURNAL OF CHEMICAL THEORY AND COMPUTATION **10**, 346-363 (2014).

TA02 11:20 – 12:10

SENSITIVE CHIRAL ANALYSIS VIA MICROWAVE SPECTROSCOPY

David Patterson

Department of Physics, Harvard University, Cambridge, MA 02138, USA

Chirality plays a fundamental role in the activity of biological molecules and broad classes of chemical reactions; for example, most drugs developed in the last decade are of a specified chirality. Despite this importance, methods to unambiguously determine the species and the handedness of a chemical sample remain elusive. Of particular interest is a method that can identify enantiomers within complex mixtures. Here we present recent progress on our microwave 3-wave mixing technique, which can identify enantiomers by mapping the enantiomer onto the phase of microwave radiation when the molecules are exposed to two resonant, orthogonal fields. In contrast to conventional circular dichroism methods, only electric dipole allowed transitions are used in this method. Proposed extensions of the technique will be presented, including combining the technique with state selective molecular guides, allowing for physical separation of enantiomers from a racemic sample.

TA03 12:10 – 13:00

STRUCTURE AND DYNAMICS OF THE HYDRATION SHELL OF BIOLOGICAL IONS AT THE MOLECULAR LEVEL PROBED BY IR SPECTROSCOPY

Otto Dopfer

Institut für Optik und Atomare Physik, TU Berlin, Germany

Hydration of biomolecular structures and proteins is well known to strongly contribute to their function. Thus, a description of the structure, energetics, and hydrogen-bonded hydration layer around biomolecules at the molecular level is of fundamental importance for understanding biomolecular function. This hydration layer is often called *biological* or *interfacial* water. Unfortunately, it is difficult - if not impossible - to experimentally probe directly the interaction of individual water molecules around biomolecular structures in the condensed phase because of averaging effects within the first solvation layers in most spectroscopic approaches.

Microhydrated clusters composed of biomolecules and a controlled number of solvent molecules isolated in the gas phase are thus ideal model systems to investigate the structure, energetics, and dynamics of microhydration shells around biomolecules under controlled hydration conditions. Such clusters can readily be prepared in molecular beams and characterized by size- and isomer-selective spectroscopic techniques. In the past two decades, we have aimed at the IR and UV spectroscopic characterization of the vibrational and electronic structure of microsolvated aromatic (bio)molecules, their radical cations, and their protonated ions. The positive charge has a dramatic impact on the interaction potential, with respect to both the interaction strength and the geometry of the global minimum structures [1]. This ionization-induced switch in the preferred recognition motif between the aromatic (bio)molecule and the solvent often triggers an intermolecular isomerization reaction, whose dynamics may be probed in real time by picosecond time-resolved pump-probe spectroscopy [2]. Such benchmark experiments have recently probed for the first time the dynamics of intermolecular isomerization reactions in molecular clusters, including the motions of individual water molecules around peptide bonds [3] and aromatic molecules with several functional groups. The analysis of such time-resolved spectra by molecular dynamic simulations provides valuable and unprecedented insight into fundamental properties of such dynamical isomerization processes, including time scales, reaction potential profiles, intermediates, and reaction pathways.

[1] O. Dopfer, Z. Phys. Chem. **219**, 125(2005).
[2] M. Fujii and O. Dopfer, Int. Rev. Phys. Chem. **31**, 131(2012).
[3] K. Tanabe, M. Miyazaki, M. Schmies, A. Patzer, H. Sekiya, M. Sakai, O. Dopfer, M. Fujii, Angew. Chem. Int. Ed. **51**, 6604 (2012).