2nd MOLIM General Meeting
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Dubrovnik, Croatia

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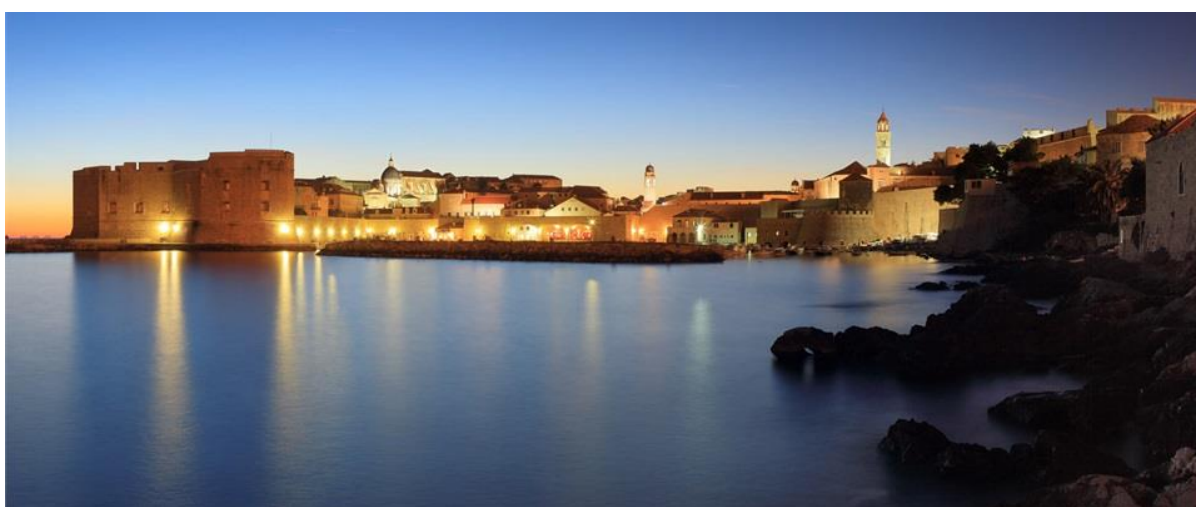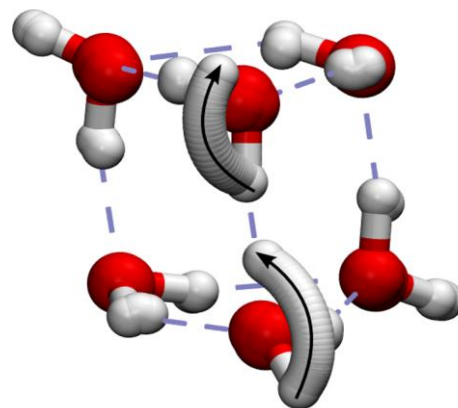
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Dear Friends and Colleagues,

We are pleased to welcome you to the second General Meeting of the COST Action CM1405 *Molecules In Motion* (MOLIM). The MOLIM action is formed by experimentalists and theoreticians working on molecules, clusters, polymers and biological systems in gas phase, condensed phases, nano-confinements or He-droplets. The systems are studied by energy- and time-resolved methods.

The General Meeting is an opportunity to address cutting edge developments in experiment, theory, algorithms and codes that have occurred in recent years and that have helped unravel the complex dynamical behaviour of these systems.

In particular, young researchers will have the opportunity to present results of their work during the Young Scientists Forum (YSF) – a special half-day dedicated to short communications.

The Chairs of the 2nd MOLIM General Meeting: *Marko Cvitaš and Nađa Došlić*

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Attila G. Császár,	Eötvös Loránd University, Hungary
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Martin Quack	ETH Zürich, Switzerland
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Acknowledgments

General Information

Currency

The local currency is kuna (kn or HRK). 1 EUR is approximately 7.50 HRK. Foreign currency is not accepted at most stores in Croatia. Major credit cards are accepted in most hotels, restaurants and shops, but small shops and restaurants may not accept credit cards. Major currencies (EUR, GBP or USD) can be exchanged at airport or banks. On arrival at the airport, it is advisable to exchange or withdraw cash from an ATM, as you will need it for local transport.

Arriving by plane

Dubrovnik is most easily accessible by plane. The International Airport Dubrovnik is situated 22 km from Hotel Lero. The Airport Shuttle Buses operate between the Airport and the city and cost 40 kn on the bus. You should exit at Old Town stop (which is not the last stop) and take the local bus number 4 to Hotel Lero (single ticket is 15 kn on the bus). Alternatively, there are plenty of taxis at Old Town stop, with taxi fare about 50-60 kn to Hotel Lero.

Arriving by car

Hotel Lero is located at 42.6497° N, 18.0890° E

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Invited Talks

New Laser Methods to Access Symmetrical Vibrational States of Acetylene

L. Halonen[1*]

[1]*Department of Chemistry, University of Helsinki, Helsinki, Finland*
[*]*Corresponding author: lauri.halonen@helsinki.fi*

Symmetrical vibrational states in the ground electronic state cannot be accessed by one-photon absorption from the ground vibrational state. Raman spectroscopy and one-photon absorption from an asymmetrical excited vibrational state are possible techniques but become unfeasible for highly excited symmetrical vibrations. I shall discuss laser-induced dispersed vibration-rotation fluorescence within the ground electronic state [1-3], continuous wave infrared stimulated emission pumping [4] and double resonance absorption with cavity ring-down spectroscopy [5] to probe symmetrical vibrations of acetylene. The latest development in locking the double resonance laser/laser type beams to stabilized optical frequency combs is also described.
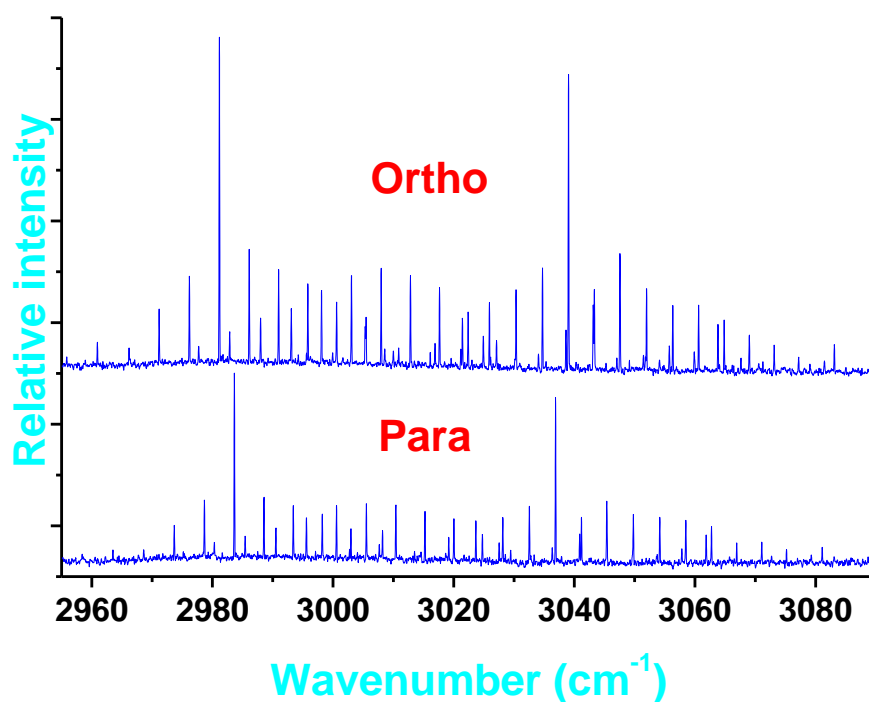
Figure 1: Laser induced dispersed fluorescence spectrum of acetylene

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High resolution spectroscopy of small organic molecules and astrophysical molecules

I. Kleiner

Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), CNRS et Universités Paris Est-UPEC et Paris Diderot, France

This talk will first give a short introduction to the spectroscopy molecules containing one or two methyl internal rotors. One of the goals of our work is to describe with our theoretical method and codes (using effective Hamiltonians describing the rotation-torsion-vibration interactions) the energy levels for this type of molecules. That way we can provide reliable predictions of line positions and intensities for astrophysical molecules containing one internal rotor CH_3, such as the isotopic species of methyl formate $HCOOCH_3$, methanol CH_3OH, acetic acid CH_3COOH, acetaldehyde CH_3CHO or acetamide CH_3CONH_2. The major new facilities, the Atacama Large Millimeter Array (*ALMA*), in Chili, or the NOrthern Extended Millimeter Array (*NOEMA*) in France have now opened the sub-millimeter region up to a few THz for astronomical observations by making investigations with unprecedented high sensitivity and resolution. Molecules which undergo internal rotation of a methyl group present thousands of lines in this spectral range and therefore their spectra are particularly important to model. They are also important tools to help determining the conditions existing in the interstellar medium. I will show some of the recent results in the microwave, millimeter or infrared range for those molecules. In particular I will present recent results for the study of a two-top internal rotor, the methyl acetate molecule CH_3-O-C(=O)-CH_3, which has been very detected in the interstellar cloud Orion thanks our prediction and recent results on the sulfur-containing molecules such as dimethyl sulfide CH_3SCH_3 a potential astrophysical molecule

Another goal is to get some knowledge of the structural properties of small organic molecules or biomimetic molecules. Fourier transform microwave spectroscopy in the gas phase coupled with high level quantum chemical calculations or ab initio calculations has recently led to the precise and detailed determination of molecular structures for the lowest energy conformers of a number of molecules. In this talk, we will show results from molecules which can be considered as prototypes of odorant molecules emitted by plants, such as linalool, an acyclic mono-terpene or methyl jasmonate, a phytohormone.

Photogeneration of Rare Molecules in Cryogenic Matrices

R. Fausto

CQC, Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal.
Corresponding author: rfausto@ci.uc.pt

The "molecular world" is plenty of elusive molecules not easy to observe and exhibiting less usual properties. Experimental approaches are required to efficiently generate and trap such uncommon molecules, making them accessible to investigation. Use of narrowband light sources to selectively produce these species, together with the matrix isolation method (to achieve their stabilization) and infrared spectroscopic probing, offers us, nowadays, the possibility to explore successfully the wonderful world of the rare, most of times high-energy, molecules.[1] Computational chemistry appears also as a fundamental tool to help interpreting the experimental results and providing mechanistic insights for the observed chemical processes.
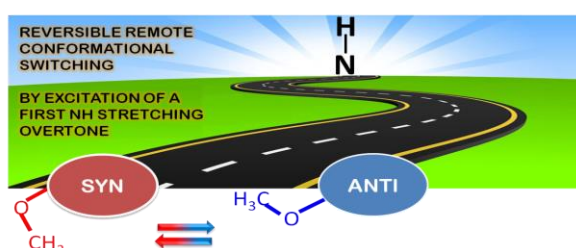
In this talk, recent results obtained in our laboratory in search for elusive reaction intermediates and rare conformers will be presented. Both UV- and IR-induced processes, starting from a stable precursor molecule isolated in cryogenic matrices and giving rise to these species will be considered.

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Anharmonic Theoretical Vibrational Spectroscopy with Localized Modes

Pawel T. Panek[1] and C. R. Jacob[2,*]

[1]*TU Braunschweig, Institute of Physical and Theoretical Chemistry,
Hans-Sommer-Str. 10, 38106 Braunschweig, Germany*
[*]*Corresponding author: c.jacob@tu-braunschweig.de*

Quantum-chemical calculations of the vibrational spectra for large molecules, such as polypeptides or clusters, are usually restricted to the harmonic approximation. However, anharmonic contributions can impact the vibrational spectra significantly and are essential for describing two-dimensional infrared (2D-IR) experiments. Unfortunately, computational methods for treating anharmonicities show a steep increase of the computational cost with system size, which limits their applicability to small molecules.

In this talk, we will present an efficient approach for the calculation of anharmonic vibrational spectra of large systems. We demonstrate that instead of the commonly used normal mode expansion of the potential energy surface, localized modes [1] should be used as starting point for the treatment of anharmonicities. In this space, we perform Local Vibrational Self-Consistent Field (L-VSCF) and Local Vibrational Configuration Interaction (L-VCI) calculations [2]. We show that in this case, many couplings between local modes can be neglected without significant loss of accuracy. This provides a route to the efficient and reliable calculation of anharmonic vibrational spectra of large (bio-)molecules.

This allows for an efficient inclusion of anharmonic contributions in quantum-chemical calculation of vibrational spectra for small organic molecules [3] and for helical alanine polypeptides [4]. For the latter, anharmonic infrared, Raman, and Raman optical activity spectra are presented and the impact of anharmonicities on the vibrational spectra is discussed.

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Generation of accurate potential energy surfaces of molecular systems of astrophysical and atmospheric interest

M. Hochlaf

Université Paris-Est, Laboratoire Modélisation et Simulation Multi Echelle, MSME UMR 8208 CNRS, 5 bd Descartes, 77454 Marne-la-Vallée, France.
Corresponding author: hochlaf@univ-mlv.fr

We use different *ab initio* methods to compute multi-dimensional potential energy surfaces (PESs) of molecular systems of atmospheric and astrophysical interest. These PESs are incorporated later to solve the nuclear motion problem to deduce the spectroscopy of these species. After benchmarks that include the use of standard coupled cluster, complete active space self consistent field, internally contacted multi reference configuration interaction and the newly developed CCSD(T)-F12 methods, we show that the CCSD(T)-F12/aug-cc-pVTZ approach represents a compromise for good description of the PES and computation cost. This technique leads to results as accurate as those obtained using CCSD(T)/aug-cc-pV5Z whereas the CPU time and the disk used are reduced by ~30 [1,2]. This is valid for monoconfigurational etectronic states. For multi configurational systems and electronically excited states, we should use the costly configuration interaction methods (MCSCF, MRCI). Several examples will be treated including the rigid molecules, charge transfer systems and weakly bound van der Waals molecular systems.

Accurate Evaluation of Intermolecular Potentials and Properties

B. Fernández[1,*]

[1]*Department of Physical Chemistry. University of Santiago de Compostela. E-15782 Santiago de Compostela. Spain*

[*]Corresponding author: berta.fernandez@usc.es

Interaction potentials and properties play a main role in many physical and chemical phenomena and are the subject of a considerable number of experimental and theoretical studies. Weak intermolecular complexes are characterized by an interaction dominated by dispersion, interaction that is essential in processes like the solvation or adsorption of molecules. Taking into account the high accuracy of the experimental results available, the computational study of the dispersion interaction is challenging and difficult, as not only large basis sets, but also high-level correlation methods are mandatory in order to compete with the experiments.

We evaluate accurate potentials and properties in weak intermolecular complexes, using the coupled-cluster singles and doubles (CCSD) and the CCSD including connected triples (CCSD(T)) models and large basis sets extended with sets of midbond functions.[1] We obtain ground and excited state intermolecular potential energy surfaces and calculate the bound states. We compare the results with those of previous theoretical studies and the experimental data available, improving considerably the former, getting a very good agreement with the latter, and in some cases being able to correct and complete the experimental assignments. Results for the ground state of the benzene-Ar, naphthalene-Ar,[2] CO-Ar,[3] HCCH-He,[4] and the CO-N_2 complexes will be presented.

With the CCSD response theory we evaluate interaction induced (hyper)-polarizabilities and the corresponding virial coefficients. Results for the CO-Ar complex will be shown.[5]

References:

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Tensor decomposition in potential energy surface representations

G. Rauhut[1,*]

[1]*Institute for Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55,
70569 Stuttgart, Germany; rauhut@theochem.uni-stuttgart.de*

Sum-of-products representations of multidimensional potential energy surfaces (PES) allow for the fast evaluation of integrals within variational vibrational structure calculations, e.g. vibrational configuration interaction theory (VCI). A new approach for generating such representations using global (polynomal) and local (B-splines, distributed Gaussians) bases relying on a repeated use of Kronecker products will be presented [1].

Once an analytical representation of the potential energy surface is available, the expansion coefficients of high-order coupling terms within multimode expansions of the PES can be decomposed by an alternating least squares approach (CP-ALS). This allows for computational savings in vibration correlation calculations once the rank of the factor matrices can be kept small [2].

Benchmark calculations are provided for single-reference and multi-reference vibrational structure methods.

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Recent Results on the Time Dependent Quantum Dynamics of Mode Selective Intramolecular Energy Flow and Tunnelling in Polyatomic Molecules and Clusters

M. Quack[1,*]

[1]*Physical Chemistry ,ETH Zurich, CH-8093 Zurich, Switzerland*
*Corresponding author: Martin@Quack.CH

We shall introduce the two major experimental approaches towards intramolecular quantum dynamics and kinetics from spectra, (i) the study of time resolved spectra, which has a long history of many decades, and (ii) deriving time dependent quantum dynamics from highly frequency resolved molecular spectra developed largely in the Zurich group over the last three decades [1-5] making use also of developments in the theory of molecular quantum dynamics We shall then report about recent experimental and theoretical results from our group ranging from femtosecond intramolecular energy flow to picosecond and nanosecond tunnelling reactions [6-8], nuclear spin symmetry violation [9-11], and finally time dependent evolution of parity on the time scale of seconds due to electroweak parity violation [3, 12-18] including some recent open problems in molecular quantum dynamics [15]. The role of successive symmetry breakings in defining different time scales of intramolecular primary processes of kinetics will be emphasized [3].

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Photodissociation of HNC and HNC isomers in the UV, from 7 to 13 eV

O. Roncero[1,*]

[1]*Instituto de Física Fundamental, CSIC, Serrano 123, 28006 Madrid, Spain*
Corresponding author: octavio.roncero@csic.es

In regions with high UV flux, photodissociation is a fundamental event destroying molecules. HCN and its isomer HNC are widely detected in space, and in photodissociation regions the HNC/HCN ratio presents anomalies. In order to understand their photostability the photodissociation cross section for both isomers in a wide range of excitation energies will be presented [1,2]. For this purpose, 21 electronic states have been calculated in a three-dimensional grid, 12 ^{1}A' and 9 ^{1}A", at icMRCI level. The individual spectra to each of the excited state are obtained with a wave packet method using the ab initio transition dipole moments.

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Modelling of spectral properties and electron transfer in Re, Ir and Pt organometallic complexes

S. Záliš[1,*], M. Pižl[1,2], J. Heyda[1,2] and A. Vlček, Jr.[1,3]

[1] *J. Heyrovský Institute of Physical Chemistry, v.v.i., Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic,*
[2] *Department of Inorganic Chemistry, University of Chemistry and Technology, Prague 6, Technická, Czech Republic,*
[3] *School of Biological and Chemical Sciences, Queen Mary University of London, UK*
[*]*Corresponding author: zalis@jh-inst.cas.cz*

Femtosecond IR, absorption and emission spectroscopy experiments on a series of Re, Ir and Pt complexes identified excited states which participate to the ultra-fast intersystem crossings (~ps time scale) and mainly contribute to the photophysical properties of these molecules [1]. In order to understand the character and dynamics of optically excited states quantum chemical calculations were performed on $[Re(X)(CO)_3(L)]^n$ (X = Cl, Br, I, im, py, protein chain; L = bpy (2,2'-bipyridine) or phen (phenatroline) systems, tetrakis(pyrophosphito)diplatinate(II) complexes $[Pt_2(BF_2POP)_4]^{n-}$ and for $[Ir_2(1,8\text{-diisocyanomenthane})_4]^n$ (Ir(dimen)^n.

Optimized excited-state geometries were calculated for the lowest singlet and triplet states of each complex by TD-DFT. The lowest excited states were optimized also by the unrestricted Kohn-Sham approach (UKS). DFT calculations employed the hybrid functionals either B3LYP or Perdew, Burke, Ernzerhof exchange and correlation functional (PBE0). The solvent was described by the polarizable continuum model (PCM) (G09 program package) or conductor like screening model (COSMO) (ADF program package). Low-lying excitation energies and coupling elements between low-lying singlet and triplet states were calculated by several quantum chemical approaches which include spin orbit (SO): SO TD-DFT (ADF), SO-RASSI of MOLCAS 8.0 package based on CASSCF/MS-CASPT2.

TD-DFT results on the series of complexes well interpret main spectral characteristic of complexes in different redox states. SO-TD-DFT calculated spectra interpreted experimental UV-vis spectra including the lowest lying singlet – triplet excitations. SO calculations shown the splitting the lowest triplet states and help to understand photophysical properties. Molecular dynamic (MD) simulations on ground and the lowest triplet states followed by time DFT and TDDFT calculations at instant times were used for interpretation of time-dependent experimental data.

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Solved and Unsolved Problems in Modelling Superfluid Helium Nanodroplet-Mediated Synthesis and Soft-Deposition of a New Generation of Metallic Nanoparticles

M. P. de Lara-Castells[1,*], C. Cabrillo[1], R. Fernández-Perea[1], Alexander O. Mitrushchenkov[2], M. Pi[3] , and E. Voloshina[4]

[1]*Consejo Superior de Investigaciones Científicas, C/Serrano 123 E-28006 Madrid, Spain*
[2]*Université Paris-Est Marne-la-Vallée, 5 bd Descartes F-77454 Marne-la-Vallée, France*
[3]*Universitat de Barcelona, Diagonal 645 E-80028 Barcelona, Spain*
[4]*Humboldt-Universität zu Berlin, Unter den Linden 6 G-10099, Germany*
[*]*Corresponding author: Pilar.deLara.Castells@csic.es*

The superfluid helium nanodroplet-mediated synthesis and soft-deposition of metallic nanoparticles [1-6] is attracting the strongest attention nowadays. This is party due to the new fundamental physics revealed, and partly due to their application in producing and depositing onto the target support (in soft-landing conditions), a new generation of stable metallic nano(-photo)catalysts [6], bearing tunable size, shape and composition. We will present both solved and unsolved problems in the theory, modelling and simulation aimed to characterize these exciting molecular processes, including the interphase between the nanoparticle, the fluid helium droplet, and the solid surface. Our first focus will be on ab-initio-based schemes to describe the underlying van-der-Waals dominated interactions, as developed within the framework of the MOLIM COST Action [7-12], including new ab-initio force fields. Our second focus with be on the nuclear dynamics problem: starting with zero-temperature time-dependent density functional theory descriptions of the helium atoms [3], passing through large-scale molecular dynamics simulations of large metallic nanoparticles on corrugated surfaces at finite temperatures [12], and ending with strategies combining both limits.

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Astronomical complex organic molecules in space: the crucial frequency information from rotational spectroscopy

C. Puzzarini[*]

Dipartimento di Chimica "Giacomo Ciamician", Via F. Selmi 2, I- 40126 Bologna
[*]Corresponding author: cristina.puzzarini@unibo.it

Understanding the chemical evolution of interstellar clouds and star-forming regions is a central problem in astrophysics and astrochemistry. The starting point is the identification of the chemical species through their spectroscopic signatures: the frequency information in fact provides the unequivocal proof of the presence of a chemical species. Such identification requires the direct comparison of the frequencies retrieved from the astronomical observations with those obtained in the laboratory, with gas-phase species being mostly discovered via their rotational signatures (with frequencies going from the millimeter-wave region to far-infrared).

The systematic observation of a given astronomical source at all wavelengths leads to line surveys that in principle provide a complete census of the molecular content. The assignment of these line surveys allows for an unbiased picture of the chemical composition that in turn can also be used to infer information on physical conditions (such as temperature and density). The new powerful astronomical facilities (like ALMA, Herschel and SOFIA, just to mention a few examples) opened up to unprecedented resolution and sensitivity as well as frequency coverage, thus offering unique opportunities to extend the chemical inventory, in particular to organic species of increasing complexity (the so-called astronomical complex organic molecules). On the other hand, sensitivity and resolution increase the line confusion in spectral observations, thus requiring a large effort to be taken in laboratory measurements (from both an experimental and computational point of view) to help in unravelling it.

Furthermore, to interpret and analyze the astronomical observations, an important piece of information is provided by the collisional excitation rates of the molecules with the predominant collision partners (like H_2 and He); these rates can be calculated using quantum-chemical methods or measured in the laboratory.

In this contribution, the role played by laboratory (experimental and computational) rotational spectroscopy in the field of astronomical observations and in the investigation of astronomical complex organic molecules will be illustrated through a number of examples and case studies.

Low Energy Motion of H$_2$ on a Metallic Surface

E. Bernard[1], E. Cances[2], A. Mitrushchenkov[1], M. Guitou[1] and G. Chambaud[1,*]

[1]*Laboratory MSME- University of Paris-Est Marne la Vallée, 77454 Champs sur Marne, France*
[2]*Laboratory CERMICS- Ecole des Ponts et Chaussées, 77454 Champs sur Marne, France*
Corresponding author: chambaud@u-pem;fr

In recent theoretical studies of the H$_2$/Cu system using an embedding approach of a cluster model consisting of 22 Cu atoms, it has been shown that the chemisorption [1] and also the physisorption [2] of H$_2$ can be satisfactorily reproduced. A good test of the accuracy of the potential energy function in the physisorption domain is the comparison with ro-vibrational spectroscopic data obtained with EELS experiments [3]. The large rotational constant of H$_2$ associated with the anharmonic and anisotropic van der Waals potentials, results in a coupling between the rotation of H$_2$ and the stretching along the physisorption well. Such data exist for H$_2$ on Cu(100) and on Ag(111).

Ro-vibrational energy levels of H$_2$ molecules physisorbed on a metallic surface (Ag (111) or Cu(100)) are calculated, using a 5D or 2D potential energy function determined at different levels of theory: periodic (DFT) or cluster representation of the system (highly correlated wavefunction description). Highly correlated electronic calculations on the cluster model have been performed with the code MOLPRO using the MRCI or the coupled cluster CCSD(T) methods. The embedding method has been applied within the ONIOM approach. The periodic calculations have been performed with DFT approach with the code VASP and vdW-DF2 functional.

Two different formalisms are used to study the motion of the H$_2$ molecule considered as a rigid rotor: either a time-dependent dynamic approach or a variational approach using a time-independent Hamiltonian. The relative intensities of the transition lines have been obtained from the calculated dipole moment matrix elements and some widths have been deduced from the corrugation of the surface.
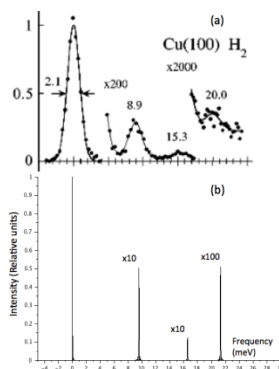
Figure 1: Calculated relative intensities of the ro-vibrational transitions

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Coupled Translation-Rotation Dynamics and Spectroscopy of H_2 and H_2O in C_{60}: Rigorous Quantum Treatment

Z. Bačić[1,*], P. M. Felker[2] and M. Xu[1]

[1]*Department of Chemistry, New York University, New York, NY 10003, USA*
[2]*Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095-1569, USA*
[*]*Corresponding author: zlatko.bacic@nyu.edu*

The behavior of small molecules, H_2 and H_2O in particular, inside the nanoscale cavities of diverse host materials has attracted a great deal of attention in recent years. In nanoscale confinement, the translational center-of mass motions of the caged molecules are quantized and strongly coupled to the quantized molecular rotations. I will first briefly review our rigorous quantum treatment of the translation-rotation (TR) dynamics of $H_2@C_{60}$ [1]. These quantum 5D calculations, assuming rigid monomers, have elucidated the TR level structure and revealed distinct spectroscopic signatures of the TR coupling that were later observed experimentally. Recent perturbation-theory treatment of the TR eigenstates of $H_2@C_{60}$ [2] has allowed connecting specific features of the level structure established in Ref. [1] with specific features of the intermolecular potential energy surface, and provided important new physical insights into the characteristic features of the former.

In another recent study [3], we have reported fully coupled 6D quantum calculations of the TR eigenstates of *para-* and *ortho-*H_2O in C_{60}. They provide a comprehensive description of the dynamical behavior of an asymmetric top, H_2O, inside the fullerene having icosahedral (I_h) symmetry. The calculated TR levels have permitted us to assign tentatively a number of transitions in the measured inelastic neutron scattering (INS) spectra of $H_2O@C_{60}$ [4] that have not been assigned previously.

TR eigenstates of nanoconfined hydrogen-containing molecules can be probed directly by the INS spectroscopy. Several years ago we developed the methodology for accurate quantum simulations of the INS spectra of diatomic molecules in a nanocavity of an arbitrary shape [5]. An unexpected result of this line of work was the discovery and formal proof of the new and surprising selection rule for the INS spectroscopy of H_2 in a near-spherical nanocavity such as that of C_{60} [6], the first ever to be established in the INS of discrete molecular compounds. This INS selection rule was later confirmed experimentally for $H_2@C_{60}$ [7], and subsequently generalized [8].

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Correlated motion in atomic and molecular three-particle systems

H. Cox

Department of Chemistry, School of Life Sciences, University of Sussex, Brighton,
BN1 9QJ, United Kingdom
Corresponding author: h.cox@sussex.ac.uk

High accuracy, non-relativistic, calculations are used to study the electronic and nuclear motion in the ground state of three-particle atomic and molecular systems using a series solution method with a triple orthogonal Laguerre-based wavefunction [1]. This method is adapted to calculate, in a single variational calculation, the critical mass of a third particle required for stable binding to a two-particle system [2] and the critical nuclear charge for binding of two-electrons [3] and, in part, to calculate high-precision Hartree-Fock energies and expectation values.

Accurate determination of fully correlated electron densities is very relevant to those involved in developing correlation functionals for density functional theory. The correlated motion of electrons, including at low nuclear charge Z, is quantified using radial and angular densities and the Löwdin definition of electron correlation [4]. Results confirm the presence of a secondary Coulomb hole for helium, and results for the anionic systems H⁻ and the critical nuclear charge system, indicate that only a primary Coulomb hole exists.

In mainstream quantum chemistry, it is usual to treat molecules within the Born-Oppenheimer approximation, a molecular structure is assumed and the equilibrium structure corresponds to a local minimum structure on a potential energy surface. In the present work no such assumptions are made and atoms and molecules are treated on an equal footing as few-particle quantum systems. Results will be presented demonstrating that the nuclear motion in diatomic ions is strongly correlated; by evaluating the particle density at the centre of mass, it is shown that the spatial distribution/localisation of the like-charged particles depends on the relative masses of the nuclei rather than just their absolute mass, and that molecular structure arises naturally from the analysis of the all-particle wavefunction.
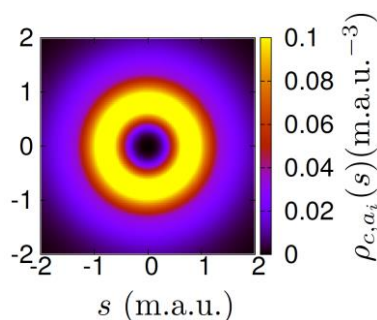
Figure 1: Centre of mass particle density plot for μDT⁺.

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Molecules in motion observed with X-rays

K. B. Møller

Department of Chemistry, Technical University of Denmark, Kemitorvet 207, 2800 Kgs. Lyngby, Denmark
Corresponding author: klaus.moller@kemi.dtu.dk

Progress in our understanding of ultrafast motion in molecules is best achieved through a close combination of experimental and theoretical approaches. Direct comparison is possible if theory is able to calculate experimental observables.

Ultrafast molecular motions are observed experimentally using pump-probe techniques where the processes of interest is initiated and monitored with ultrashort (femtosecond) flashes of electromagnetic radiation. This talk will first review some of our advances on the theory of femtosecond time-resolved x-ray scattering and prescriptions for calculating experimental observables [1,2].

Then, I will present combined experimental investigations and computer simulations of fundamental chemical processes of molecules in solution [3-8]. These involve bond formation [3-5], charge transfer [6-7] as well as intra- and intermolecular energy transfer and solvation dynamics. The experiments were carried out at the x-ray free-electron lasers LCLS (USA) and SACLA (Japan), and the computer simulations are multi-scale QM/MM molecular dynamics (MD) simulations.

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First-quantized relativistic geminal-based many-particle quantum mechanics

M. Reiher[1,*]

[1]ETH Zurich, Lab. f. Phys. Chem., Vladimir-Prelog-Weg 2, 8093 Zurich, Switzerland
*Corresponding author: markus.reiher@phys.chem.ethz.ch

We elaborate on the variational solution of the Schrödinger and Dirac equations of few-body, i.e., small atomic and molecular systems without relying on the Born–Oppenheimer paradigm [1]. The all-particle equations of motion are solved in a numerical procedure that relies on the variational principle, Cartesian coordinates, parameterized explicitly correlated Gaussian functions with polynomial prefactors, and the global vector representation. A stochastic variational optimization of the basis function parameters facilitates the calculation of accurate energies and wave functions for ground and excited states.

We developed a simple strategy for the elimination of the translational kinetic energy contamination of the total energy in such pre-Born–Oppenheimer calculations carried out in laboratory-fixed Cartesian coordinates [2]. The simple expressions for the coordinates and the operators are then preserved throughout the calculations, while the mathematical form and the parametrization of the basis functions are chosen such that translational and rotational invariance are respected.

For semi-classical (first-quantized) relativistic calculations we devised a kinetic-balance condition for explicitly correlated basis functions [3]. We demonstrate that the kinetic-balance condition can be obtained from the row reduction process commonly applied to solve systems of linear equations. The resulting form of kinetic balance establishes a relation between all components of the spinor of an N-fermion system to the non-relativistic limit, which is in accordance with exact-decoupling methods in relativistic orbital-based many-electron theory.

The talk will discuss these developments in the light of spectroscopic results and qualitative concepts such as molecular structure.

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From metrology of spectral line shapes to fundamental physics

R. Ciuryło[1,*]

[1]*Instytut Fizyki, Uniwersytet Mikołaja Kopernika, ul. Grudziądzka 5/7, 87-100 Toruń, Poland*
[*]Corresponding author: rciurylo@fizyka.umk.pl

Search for accurate spectroscopic techniques led us to one-dimensional cavity mode dispersion spectroscopy (1D-CMDS) [1], a spectroscopy technique purely based on frequency measurement. Because the spectrum obtained with this method comes from accurate cavity mode frequency measurement, 1D-CMDS has great potential for minimization of systematic errors in the line shape studies of very week transitions [2]. Nowadays, the ab initio approaches as well as analytical models, allowing to take into account basic effects forming the shape of molecular transitions, make possible the correct interpretation of high accuracy data and testing interatomic potentials [3,4]. All these opens new possibilities for Doppler limited spectroscopy. Especially, molecular hydrogen and its isotopologues are an attractive playground for testing quantum electrodynamics in molecules [5] and search for new physics [6]. The accuracy of measurements can be improved by use of optical atomic clocks [7] as the most stable frequency reference. Going farther, spectroscopy of ultra cold molecules having narrow photoassociation resonances near intercombination transition provides valuable information and new level of control. Narrow optical Feshbach resonances [8] allow efficient control of properties of ultra cold matter [9]. On the other hand analysis of two-colour mass-scaled photoassociation spectroscopy for set of isotopologues of Yb_2 can set bounds for non-Newtonian gravity in the nanometer range [10]. Finally use of optical atomic clocks can help in laboratory search for dark matter [11,12,13,14] and understanding physics beyond Standard Model.

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Multi-way Analysis in Molecular Dynamics Simulations

T. Hrenar

*¹University of Zagreb, Faculty of Science, Department of Chemistry,
Horvatovac 102a, 10000 Zagreb, Croatia
Corresponding author: hrenar@chem.pmf.hr*

The usage of *multi-way* formalism in the analysis of *ab initio* molecular dynamics simulations will be formulated and some preliminaries results presented. Multi-way analysis is well established in some parts of the chemical data analysis (*e.g.* spectroscopy), whereas not so much in quantum chemistry. In particular, the aspect of conformational analysis, which includes collection of structural data from the molecular dynamics trajectories as a sampling method, and tensor decomposition of corresponding multidimensional array of data will be discussed.
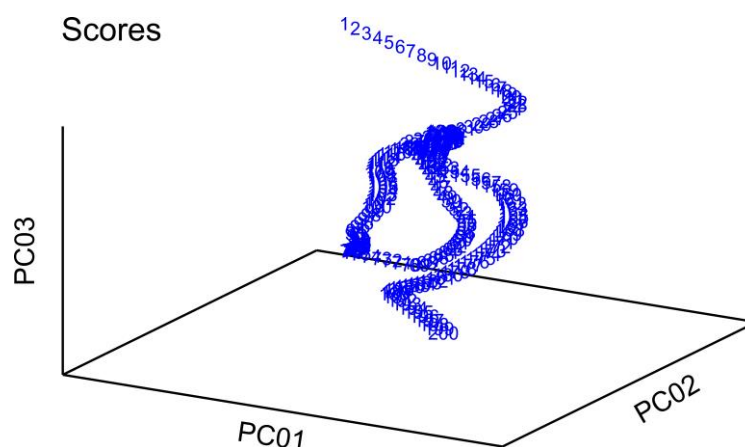
Figure 1: Molecular dynamics trajectory in a reduced space of three principal components.

Results obtained from tensor decomposition allow investigation of molecular dynamics trajectories in significantly reduced space (Fig. 1) and their statistical analysis presents a wealth of information, including full conformational space of the investigated system regardless of its structure.

Multilevel Coupled Cluster methods for transient NEXAFS spectroscopy

H. Koch[1,2,*], Rolf H. Myhre[1,2], Ida-Marie Høyvik[1] and Sonia Coriani[3]

[1]*Department of Chemistry, NTNU, Norwegian University of Science and Technology, N-7491 Trondheim, Norway.*
[2]*Department of Chemistry and the PULSE institute, Stanford University, Stanford, California 94305, USA.*
[3]*Dipartimento di Science Chimiche e Farmaceutiche, Università degli Studi di Trieste, I-34127, Italy.*
Corresponding author: henrik.koch@ntnu.no

Coupled Cluster (CC) theory is among the most accurate methods for modelling molecular properties. Recently, we have implemented the core-valence separation (CVS) approximation [1]. In particular, we have combined this with a new implementation of CC3[2], resulting in unrivalled accuracy of core excitations.

Coupled Cluster theory has a high computational cost and steep scaling with system size. In order to overcome this problem, we have developed multilevel CC (MLCC) theory [3] where a smaller part of the molecule is treated with a high accuracy method and the rest more approximately. Local properties such as core excitations are ideally suited for such an approach [4]. Recently we demonstrated two orders of magnitude reduction in computational cost using the MLCC framework.

Recently, the first transient NEXAFS excited state measurements were performed at the Stanford Linear Accelerator Center (SLAC) by The Thymine Collaboration [5]. In the experiment, a new feature appeared after less than 100 fs time delay. In order to characterize this feature, the ground state geometry was optimized at the CCSD(T) level and the excited state geometries at the CCSD level. Excited state UV and X-ray spectra were simulated at the CCSD and CC3 level and show a remarkable agreement with experiment. The source of the new feature is determined to arise from population in the nπ* state. Coupled Cluster dynamic calculations further corroborate this conclusion.

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Ab Initio, Post-Harmonic Vibrational Calculations: Bigger and better?

J. M. Bowman

Cherry L. Emerson Center for Scientific Computation and Department of Chemistry
Emory University, Atlanta, GA 30322
Corresponding author: jmbowma@emory.edu

Progress in the title area has been dramatic over the past ten or so years, as a result of the efforts of many groups. I will review recent work in our group on the two aspects of accurate vibrational calculations, namely accurate potential energy (and dipole moment) surfaces and their use in a variety of VSCF/VCI calculations of vibrational energies and IR spectra. Several recent examples will be presented that illustrate the approaches we have developed in the past ten or so years. They are: potential energy surfaces for the formic acid dimer and nitromethane and 'MULTIMODE' calculations of vibrational energies using them, and many-body, non-covalent interaction potentials for neat water, methane hydrate clathrate, hydrated NaCl and NaF, and 'local monomer' calculations using them. Comparisons with experiment will be made in all the examples presented.

The Gateway Hamilton Operator: Theory and Practice

V. Szalay

Institute for Solid State Physics and Optics, Wigner Research Centre for Physics, Hungarian Academy of Sciences, P. O. Box 49, H-1525 Budapest, Hungary
Corresponding author: szalay.viktor@wigner.mta.hu

I shall explain the gateway Hamiltonian method [1-3] and demonstrate its applicability by calculation of vibrational energy levels.

In particular, it shall be explained and numerically demonstrated that:

- Even when expressed in terms of curvilinear internal coordinates, the gateway kinetic energy operator (KEO) is of an expression nearly identical with the Eckart-Watson operator [4].

- It obviates the need for differentiation of the matrix rotating into the Eckart frame.

- It allows construction of an Eckart ro-vibrational KEO without rotation.

- It leads to defining optimal Eckart displacements.

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Hydrogen Bonding in Water-Methanol and Water-Ammonia Clusters

T. Urbič[1,*]

[1]Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, SI-1000, Slovenija
Corresponding author: tomaz.urbic@fkkt.uni-lj.si

Large molecular clusters can be considered as intermediate states between gas and condensed phases, and information about them can help us understand condensed phases. In this work, ab initio quantum mechanical methods have been used to examine clusters formed of methanol, ammonium and water molecules. The main goal was to obtain information about the intermolecular interactions and the structure of the clusters at the molecular level. The results of the calculations were compared to the available experimental information regarding the liquid methanol/water and ammonium/water mixtures and to the molecular dynamics and Monte Carlo simulations. The structures, energetics, and vibrational spectra of the first few (n ≤6) water, methanol and ammonia clusters obtained from electronic structure calculations will be presented.

Optimizing the Multicycle Rotational Cooling of Diatomic Molecules

Aviv Aroch[1], S. Kallush[2,1] and Ronnie Kosloff[1]

[1]*The Fritz Haber Research Center, The Hebrew University, Jerusalem 91904, Israel*
[2]*Deptartment of Physics and Optical Engineering, ORT Braude College, P.O. Box 78, 21982 Karmiel, Israel*

Cooling the rotational motion of molecules beyond the milikelvin regime is a task that is under extensive research during the last decade. This is usually achieved by controlled processes which involve the use of external electric fields. However, these coherent fields can induce only coherent, purity-conserved transformations, and cannot alter the system's temperature directly. The complementary component to induce cooling is spontaneous emission. This part of the process can create a change in the purity but is uncontrollable. To merge to two components into a single cooling device we employ a field optimized unitary transformation that will stir the system to a situation that will lead to spontaneous cooling. The optimization process is composed by two ingredients: (I) The ergodic theorem is combined with a classical optimization to find a unitary transformation that will lead that system into a pure stead-state after multiple excitation-emission cycles. (II) A quantum-optimal-control theory based algorithm is carried to find the correct field that will produce the desired unitary transformation defined by the former algorithm. The obtained optimal transformation is shown to be capable to cool the AlH^+ ions to sub mili-kelvins, several orders of magnitude below the current experimental state-of-art work [1].

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Nonadiabatic dynamics including intersystem crossing

L. González[1,*]

[1]*Institute of Theoretical Chemistry, Faculty of Chemistry, University of Vienna, Währingerstrasse 17, 1090 Wien, Austria*
Corresponding author: leticia.gonzalez@univie.ac.at

When molecules are electronically excited they can undergo photochemical reactions, exploring different regions of the excited potential energy surfaces. The description of excited state processes is considerably more complicated than ground state chemical reactions because molecules electronically excited can show a high density of states and because potential energy surfaces of same or different multiplicity can cross, breaking the Born-Oppenheimer approximation. Understanding photochemistry also requires a time-dependent analysis of the molecular pathways that a system can follow. In this presentation I will show several examples of photochemical pathways followed after light irradiation revealed with ab initio surface-hopping molecular dynamics. To that aim the locally developed ab initio molecular dynamics code (SHARC) [1], which allows treating on the same footing non-adiabatic and spin-orbit couplings, is employed.
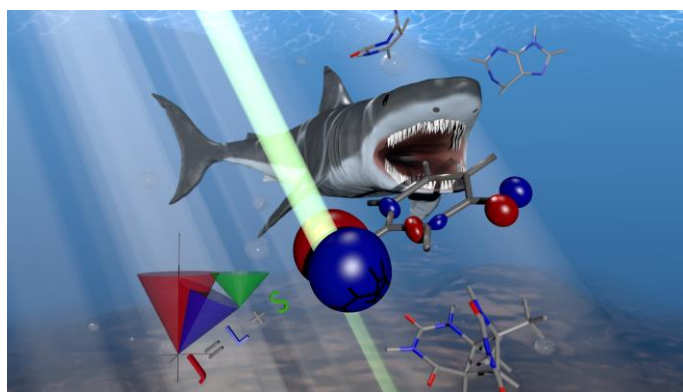
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Concerted hydrogen-bond breaking by quantum tunnelling

J. O. Richardson[1,*]

[1]*Laboratory of Physical Chemistry, ETH Zurich, Switzerland*
[*]*Corresponding author: jeremy.richardson@phys.chem.ethz.ch*

The study of gas-phase water clusters provides a direct experimental probe of the intermolecular forces which also exist in the liquid phase. Hydrogen-bond network rearrangements occurring via quantum tunnelling manifest themselves in the splitting patterns observed by spectroscopy. At low temperature, these tunnelling rearrangements follow pathways which can differ considerably from the minimum-energy pathway. The tunnelling pathways can however be computed using quantum dynamical approaches such as is provided by the ring-polymer instanton method [1].

A recent joint experimental and theoretical study of the water hexamer prism [2] has discovered unexpectedly complex tunnelling pathways showing cooperative behaviour of the water molecules. One of these leads to the simultaneous breaking of two hydrogen bonds (Figure 1). Similar pathways may also exist in the rearrangement of water clusters adsorbed on surfaces, or water in confined or interfacial environments such as at the surface of ice.
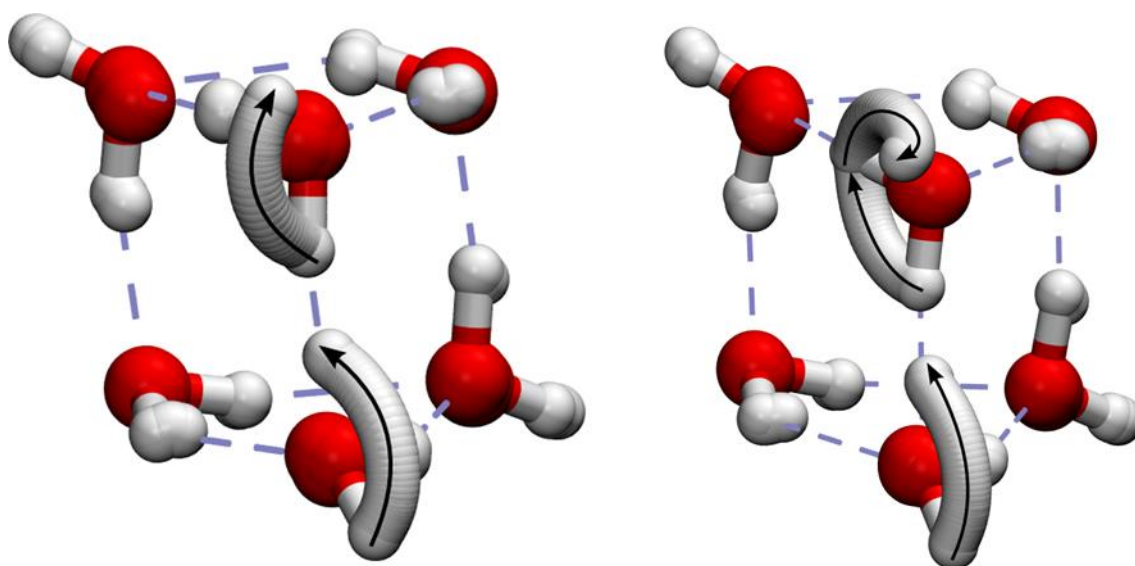
Figure 1: The two feasible tunnelling pathways in the water hexamer prism involving cooperative motion of the water molecules. The first rearrangement breaks only one hydrogen bond whereas the second is able to break two simultaneously.

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Using Direct Quantum Dynamics to Study Non-adiabatic Photochemistry

G. A. Worth[1,*], I. Polyak[2] and G. W. Richings[3]

[1]*School of Chemistry, University College London, 20, Gordon St., London, U.K*
[2]*School of Chemistry, Imperial College London, Exhibition Rd., London, U.K*
[3]*School of Chemistry, Univeristy of Warick, Gibbet Hill, Coventry, U.K*
[*]*Corresponding author: g.a.worth@ucl.ac.uk*

The accurate study of molecular dynamics after photo-excitation requires a full quantum dynamical treatment of the nuclei to correctly describe the flow of energy between vibrational and electronic states. This is particularly true when curve crossing processes, such as internal conversion (IC) through a conical intersection, or inter-system crossing (ISC) are involved. In these cases the coherence of the electronic wavepacket in the different states is key to the time-evolution of the system.

Quantum dynamics simulations are computationally hard problems. Traditional methods use a full direct-product grid basis set and the resources required scale exponentially with the number of degrees of freedom (DOF). The multi-configurational time-dependent Hartree (MCTDH) algorithm is the most efficient grid-based solution to the time-dependent Schrödinger equation (TDSE) [1], and is now able to treat wavepackets with 10s of DOF. Now, however, the bottleneck is obtaining realistic potential energy surfaces (PES) for polyatomic systems as the effort involved in calculating global surfaces also scales exponentially with system size.

To mitigate for the problem in calculating the potentials, an obvious approach is to use direct dynamics. Here, the potentials are calculated on-the-fly only when required using quantum chemistry calculations [2]. As only information about the PES local to a point in configuration space is obtained from these calculations, most direct dynamics methods rely on classical trajectories to describe the nuclear wavepacket.

We have developed the direct dynamics variational multiconfigurational Gaussian (DD-vMCG) method. Based on the MCTDH algorithm, but using a basis set of time-dependent Gaussian basis functions (GBFs) it is related to the class of methods based on Gaussian Wavepackets (GWPs), such as the multiple spawning of Martinez or coherent states of Shalashilin. Unlike GWP methods, however the vMCG basis functions follow coupled variational trajectories rather than classical trajectories. This makes them better at describing quantum processes as well as providing faster convergence, important in direct dynamics [3]. Combined with an on-the-fy diabatisation procedure [4], this provides an almost black-box approach to quantum dynamics.

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Young Scientist Forum

Ultrafast spin-flip dynamics in transition metal complexes triggered by soft X-ray light

H. Wang[1], S. I. Bokarev[1,*] and O. Kühn[1]

[1] Institute of Physics, University of Rostock, Albert-Einstein-Str. 23-24,18059 Rostock, Germany
*Corresponding author: sergey.bokarev@uni-rostock.de

Recent advances in attosecond spectroscopy open the door to understanding the correlated motion of valence and core electrons on their intrinsic timescales. For valence excitations, processes related to the electron spin are usually driven by nuclear motion. When going, however, to the core-excited states where the core hole has a nonzero angular momentum, a strong spin-orbit coupling starts to play a role [1-3]. In this work, we present a theoretical simulation of an ultrafast spin-flip dynamics driven solely by spin-orbit coupling and electron correlation in the L-edge ($2p \rightarrow 3d$) excited states of a prototypical Fe(II) complex, which occurs faster than the core hole lifetime (about 4 fs) [4]. The non-equilibrium electron dynamics is studied by means of time-dependent restricted active space configuration interaction recast in the form of reduced density matrix propagation. The spin-orbit coupling between electronic states of different multiplicity is considered within the LS-coupling limit employing atomic mean-field integral approximation. Dissipative effects of electronic and vibrational origin are considered as well. A detailed analysis of such phenomena will help to gain a fundamental understanding of spin-crossover processes and build up the basis for their control by light.
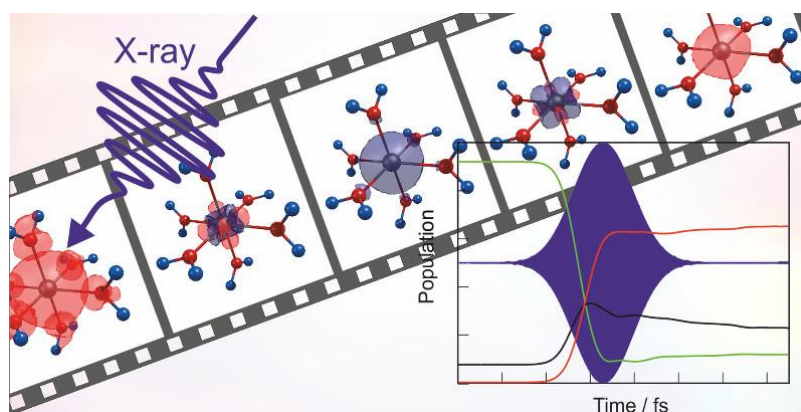
Figure 1: Time-evolution of spin-density and spin-state population for a prototypical Fe(II) complex.

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Exploration of a unified framework for nonadiabatic dynamics and photoelectron spectroscopy

A. Ponzi[1], M. Sapunar[1], N. Došlić[1] and P. Decleva[2]

[1] *Department of Physical Chemistry, Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia*
[2] *Department of Chemical and Pharmaceutical Sciences, University of Trieste, via L. Giorgieri 1, 34127 Trieste, Italy*

The present work concerns the photoionization of prototypical biomolecular chromophores such as furan, pyrrole and tiophene both from the ground state and from the first lowest-lying excited states. The photochemical and photoionization properties of these molecules are of great interest due to an extensive collection of available experimental and theoretical results [1,2].

This work belongs to a wider project focused on a high level theoretical description of Time-resolved photoelectron spectroscopy (TRPES) observables obtained from pump-probe experiments. More specifically, we combined photoionization observables calculation, using Dyson orbitals, with trajectory-based nonadiabatic dynamics calculation of prototype chromophores. We aim at an accurate and computationally efficient simulation of TRPES experiments.

The recently implemented Dyson orbitals [3] are used to describe ionization from excited states at the single channel level, and correlation within the initial and final ionic bound states. The Dyson orbitals were computed with different electronic structure methods, i.e. TDDFT, ADC(2) and CASSCF, typically used in the dynamics simulations.

The high quality calculations of the photoionization dynamical observables are performed through an accurate solution of the continuum one particle wavefunctions in a multicenter B-spline basis, at the DFT and TDDFT levels, which provides an adequate description of the electronic continuum [4]. The approach can be conveniently used to provide results for a series of snapshots along the trajectories generated.

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Laser control of the photodissociation of CO^{2+}

J. Loreau[1,*] and N. Vaeck[1]

[1]*Service de Chimie Quantique et Photophysique, Université libre de Bruxelles (ULB), CP 160/09, 1050 Brussels, Belgium*
Corresponding author: jloreau@ulb.ac.be

The combination of electronic structure calculations by quantum chemistry techniques with wave packet propagation methods provides a powerful way to study reactive processes at a fully quantal level. This approach has been used with success to study charge transfer, photodissociation, or radiative association processes [1-3]. One of its advantages is the possibility to include an electromagnetic field into the dynamics, allowing the control of the outcome of reactions, for example using optimal or local control algorithms. Here we illustrate these methods on the photodissociation of the carbon monoxide dication CO^{2+} into a specific channel. In particular, we show the efficiency of the local control algorithm to find a simple pulse despite the complex nonadiabatic dynamics [4]. This molecular ion also provides an interesting example as it can be produced experimentally in a single vibrational state.

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Calculating the CH$_5^+$ IR Spectrum with the Phase Integration Method

M. Mališ[1,2,*], S. Bonella[1]

[1]*CECAM, EPFL, Avenue Forel 2, 1015 Lausanne, Switzerland*
[2]*Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia*
[*]Corresponding author: momir.malis@epfl.ch

The Phase Integration Method (PIM)[1,2] is a novel approximate quantum dynamical technique developed for computing system's time dependent observables when exact methods become limited due to their exponential scaling on the number of system's degrees of freedom and to simulation times of the order of picoseconds. This method belongs to a class of so-called linearization techniques and it exploits the presence of two propagators in the correlation function to introduce an approximation accurate to second order in an $\hbar$ expansion of the potential. PIM employs an algorithm in which the exact sampling of the quantum thermal density is combined with a linearized approximation of the quantum time propagators represented in the path integral formalism that reduces the evolution to classical dynamics. The quantities of interest can then be computed by combining classical molecular dynamics algorithms with an original generalized Monte Carlo scheme to sample initial conditions. We have applied the PIM for computation of the CH$_5^+$ cation infrared spectrum in gas phase, which is a well now system for its highly anharmonic potential due to the correlated scrambling of its hydrogen atoms around the central carbon atom,[3] in order to further improve the method and its current implementation. Here I represent some of the recent results of our progress.

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Vibration Induced Bond Formation and Breaking

T. Järvinen[1,*], Jan Lundell[1] and Przemysław Dopieralski[2]

[1] Department of Chemistry, University of Jyväskylä, Finland
[2] Faculty of Chemisty, University of Wrocław, Poland
[*]Corresponding author: teemu.j.jarvinen@student.jyu.fi

The high overtone induced processes are initiated by promoting a molecule or a complex to chemically relevant energies in high vibrational excited states through the thermal excitation or direct absorption of visible (VIS) or near-infrared (NIR) radiation. Unlike the thermally induced processes, the reactions initiated by vibrational overtone-pumping of ground electronic state molecule through direct absorption of photon can be treated without the need to consider the collisional activation processes. In general, it is required that the energy is deposited into the initially excited vibrational state and subsequently transferred by intramolecular vibrational redistribution (IVR) to other modes of the molecule including the reaction coordinate. For example, it has been demonstrated that high overtone excitation of OH groups in carboxylic acids isolated in low temperature matrices leads to two different unimolecular processes: isomerization and/or decomposition of the molecules [1-4]. Moreover, overtone pumping was used, for example, in the case of formic acid dimers to produce high-energy conformers within the hydrogen-bonded complexes [5-7].

Studying formic acid-water complex via computational methods hints, that overtone vibrations in formic acid OH-bond induce hydrogen exchange with water molecule. We discuss details of computations and how bonds form and break during the reaction.

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Computational studies of structural and electronic properties in Amyloids: from a single chain in solution to crystals

L. Grisanti[1,*], Jong Kwang Hyok[1], Dorothea Pinotsi[2], Ralph Gebauer[1],

Gabriele S. Kaminski Schierle[2], Ali Hassanali[1]

[1] International Centre for Theoretical Physics (ICTP), Trieste, Italy
[2] Department of Chemical Engineering and Biotechnology, University of Cambridge, Cambridge, UK
*Corresponding author: luca.grisanti@gmail.com

Amyloid fibrils are a result of protein misfolding, associated with the occurrence of neurodegenerative diseases. These aggregates are rich in beta-sheet domains and interconnected by a network of hydrogen bonds [1]. In some Amyloid fibrils, peculiar optical properties, including absorption of low-energy photons (3.5 eV) and fluorescence in the visible range in the absence of aromatic amino acids has been recently measured [2]. At the same time, the hierarchy in the structure when going from single chain, to protofilament and to fibrils, makes the system challenging under the computational point of view – covering different time and space scales and then requiring several levels of theory. With the aim to provide a multi-scale picture of structural, electronic and optical properties we have:

(a) Performed enhanced sampling classical molecular dynamics of a segment of the amyloid protein $A\beta_{1-42}$ in explicit solvent. The conformational landscape of this oligopeptide resembles an intrinsically disordered protein driven by the interplay of polar and hydrophobic interactions and demonstrating the specific role of strong salt-bridges between the N and C termini [3].

(b) Used state-of-the-art ab-initio molecular dynamics simulations of large model systems, to find that in the fibril environment protons can hop along the strong salt-bridges between the N and C termini. The proton transfer events appear to be coupled to subtle changes in the optical properties as gauged by TD-DFT calculations used to characterize the excited states. In addition, we found nuclear quantum effects are likely to play an important role at room temperature [2,4].

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in preparation

Using nonadiabatic surface-hopping dynamics in order to understand the excited state electronic structure of pyrrole

M. Sapunar[1,*], A. Ponzi[1], P. Decleva[2] and N. Došlić[1]

[1]*Department of Physical Chemistry, Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia*
[2]*Department of Chemical and Pharmaceutical Sciences, University of Trieste, via L. Giorgieri 1, 34127 Trieste, Italy*
Corresponding author: msapunar@irb.hr

Pyrrole is a prototype example of a molecule displaying $\pi\sigma^*$ mediated internal conversion. Recent experiments have shown that the time scale of this process is dependent on the wavelength of the initial excitation [1]. To better understand this effect, we have performed nonadiabatic surface-hopping dynamics simulations of the relaxation of pyrrole following excitation in three different energy regions [2].

The primary state populated in the $\approx$200 nm wavelength region is the lowest B_2 state. Historically, this state has been described both as a pure Rydberg $3p_x$ state and as a pure $\pi\pi^*$ state. We have shown in our simulations that the results of the dynamics simulations are highly dependent on the description of this state in the chosen electronic structure method. Specifically, agreement with experiment is only achieved when no Rydberg-valence mixing is present in the description of the state. We also show preliminary simulations suggesting photoelectron spectroscopy as another experimental observable sensitive to the electronic structure of this state.

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Applying Direct Quantum Dynamics to Photo-Excited Processes: Proton Transfer and Charge Migration

K. E. Spinlove[1,2,*] and Graham Worth[3,**]

[1]*School of Chemistry, University of Birmingham, Birmingham, B15 2TT*
[2]*Department of Chemistry, Imperial College London, London, SW7 2AZ*
[3]*Department of Chemistry, University College London, London, WC1E 6BT*
* *kes714@bham.ac.uk*
** *g.a.worth@ucl.ac.uk*

In order to understand photo-excited processes it has been proven to be important to describe significant quantum effects such as tunnelling and conical intersections. A method of direct quantum dynamics for the study of such photo-excited processes has recently been implemented in the Quantics software package. The DD-vMCG (direct dynamics by the variational multi-configurational Gaussian) method promises to be fast, efficient, and with better convergence properties than previous methods based on classical trajectories [1]. As it is in the development phase, testing is required.

The underlying physical processes by which mutagenesis occurs in DNA/RNA, whether by UV radiation or spontaneous occurrence, has been the subject of extensive chemical and biological research. Prototypically the inter- and intra-molecular proton-transfers in excited states of 2-pyridone/2-hydroxypyridine and Formamide/Formamidic acid have been used as analogues to the description of mutagenesis. They present an interesting system to study with the DD-vMCG method as they may demonstrate competition between proton-transfer and non-adiabatic curve crossing [2,3].

Another photo-excited process of interest is the competition between charge-transfer and charge-migration. A new direct dynamics method, based on the Ehrenfest approach, has been used previously to study charge-migration in the Toluene cation [4]. A model Hamiltonian for the Allene (C_3H_4) radical cation has been used as a test in previous Quantics studies on charge-transfer [5], and presents an ideal system to test the Ehrenfest approach.

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Theoretical Study of the Nature of S-π Interactions, Their Role in Activation Process of Dopamine D₂ Receptor and Comparison with Se-π Systems

M. Senćanski[1,*] and S. Grubišić[2]

[1]*Center for Multidisciplinary Research and Engineering, Institute of Nuclear Sciences Vinča, University of Belgrade, Mike Petrovića Alasa 12-14, 11001 Belgrade, Serbia*
[2]*Center for Chemistry, Institute for Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia*
[*]Corresponding author: sencanski@vin.bg.ac.rs

Amino acids Cysteine (Cys) and Methionine (Met) are frequent in proteins and responsible for their stability (e.g. cysteine disulphide bridges) and activity. They play major roles in catalytic sites of the enzymes, and form SH-π (or S-π) interactions with aromatic amino acid residues in protein which also highly contribute to the stability of structure. Although SH-π and S-π interactions were widely described [1-3], there is still much unknown about the nature of their interactions if substituents are present on aromatic ring. This research of the nature of S-π interactions in case of substituted aromatic systems has been stimulated by the recent experiments with fluorine substitution in phenylalanine and tryptophan of D₂ receptor [4]. Analogously to the research of CH-π interactions [5], DFT calculations were used to study substituted benzenes in complex with H_2S, CH_3SH, and CH_3SCH_3, as models for Cys and Met. The results of calculations showed that SH-π interactions had lower energy than S-π interactions. Opposite trends in changes of interaction energies between SH-π and S-π cases were observed with increasing electronegativity of the substituent on benzene ring. We also investigated the model system of Cys···Trp interaction in D₂ receptor, as well as adjacent cluster of aromatic amino acids in its active site by constructing the ideal model system of adjacent benzene rings. The results showed that fluorination of benzenes in aromatic cluster transmits electrostatics influence through space and enhances the Cys···Trp interaction. This effect is enhanced when transmission occurs through the rest of benzene rings, which suggests possible explanation in mechanism of D₂ receptor activation. [6] In order to interpret difference in nature of S-π and Se-π interactions, we also report extensive DFT calculations of dispersive and electrostatic contributions in Se-π interactions and comparison with S-π calculations. The results show larger contribution of dispersive interactions in case of Se-π systems rather than S-π, which mainly originate from the interaction of Se and substituent groups.

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Modeling of multiple conical intersections in adiabatic single-sheeted potential energy surfaces: the case of ground-state C_3

C. M. R. Rocha and A. J. C. Varandas

Departamento de Química, and Centro de Química, Universidade de Coimbra 3004-535 Coimbra, Portugal.

Homonuclear triatomic (X_3-type) molecules have enjoyed a great theoretical interest for many decades, and still provide a challenging target for electronic structure calculations. At high-symmetry configurations, such elemental clusters assume equilateral triangular geometries with some of the electronic states transforming according to the E'(E'') irreps of the D_{3h} point group. Not surprisingly, therefore, symmetry-required conical intersections (CIs) between the associated potential energy surfaces (PESs) are often realized for such molecules [1].

Apart from the well-studied linear E $\otimes$ e Jahn-Teller (JT) systems, the locus of CI can be of remarkable intricacy. Referred to as small linear parameter (SLP) JT molecule [1,2], besides the usual D_{3h} seam, the title species shows three additional symmetry-allowed CIs along the line of C_{2v} symmetry which lie close to the D_{3h} one [3,4].

In previous work [3], we have reported a single-sheeted DMBE PES for ground-state $C_3(1^1A')$. We first outlined there the presence of the 4 CIs and because a third electronic state of $^1A'_1$ symmetry comes close in energy to the $^1E'$ pair, such unusual topological attributes have been ascribed to a combined JT plus pseudo-JT (PJT) case. Most recently, the (E' + A'$_1$) $\otimes$ e' problem in C_3 has been further exploited [4] and the results so obtained clarified. Accordingly, the three additional C_{2v} seams are not static objects with respect to the D_{3h} CI but instead fluctuates as a function of the perimeter of the molecule.

Ongoing work to devise a form capable of accurately modeling the three C_{2v} disjoint seams, in addition to the D_{3h} one, will also be briefly addressed. It also includes, a simplified version of the multiple energy switching scheme (ES) [5] to improve the PES in the vicinity of its linear global minima such as to attain near spectroscopic accuracy. The global form so obtained will then be commended for both spectroscopic and reaction dynamics.

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Posters

Probing an Electronic Wavepacket in Real Time

J. Ajay[1*], R. D. Levine[1,2]

[1]The Fritz Haber Research Center for Molecular Dynamics, The Hebrew University of Jerusalem, Jerusalem 91904, Israel
[2]Department of Chemistry and Biochemistry and Department of Molecular and Medical Pharmacology and Crump Institute for Molecular Imaging, The University of California Los Angeles, CA 90095-1569, USA
[*]Corresponding author: jay@fh.huji.ac.il

We are developing pump-probe schemes for assessing the evolution of a system with non-equilibrium electron distribution as it moves in space and time. In such a system, the electronic wavefunction will be distributed over several electronic states. We are investigating the evolution following excitation by an ultrafast XUV pulse. In the Nitrogen molecule for example this excitation leads to a non-equilibrium distribution of electrons over two Rydberg states and a valence state. These states are diabatic in character and are electronically coupled[1]. The couplings between the diabatic states can have a significant influence in the excitation process as well as the time propagation[2]. We find that for quite a number of vibrations the nuclear motion does not dephase the electronic disequilibrium. One probe of this is how the nuclear motion modulates the dipole of the homonuclear molecule, a dipole that should vanish at electronic equilibrium. This arises from the nuclear wave packets on different electronic states moving in and out of the Franck−Condon region. We also examine the quadruple moment as it evolves in time. The motion of the electrons further out of the center of charge in the Rydberg states and the contraction of the charge cloud in the valence excited state is reflected in oscillations that also do not dephase for an appreciable time.

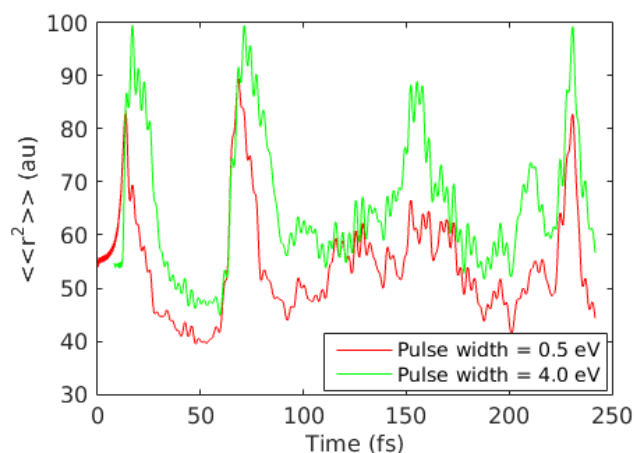Figure 1: Variation of the normalized quadrupole for $^1\Sigma_u^+$ excited states of the homonuclear Nitrogen molecule as a function of time in fs during and following excitation by two ultrafast VUV pulses with different widths.

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[1] D. Spelsberg, W. Meyer, *J. Chem. Phys.* 2001, **115**, 6438-6449
[2] J. Ajay, J. Smydke, F. Remacle, R. D. Levine, *J. Phys. Chem. A* 2016, **120**, 3335-3342

Theoretical spectroscopic investigations of HNS^q and HSN^q (q = 0, +1, −1) in the gas phase

S. Ben Yaghlane[1], N.-E. Jaidane[1], C. E. Cotton[2], J. S. Francisco[2], M. M. Al Mogren[3], R. Linguerri[4] and M. Hochlaf[4]

[1]*Laboratoire de Spectroscopie Atomique, Moléculaire et Applications - LSAMA, Université de Tunis El Manar, Tunis, Tunisia*
[2]*Department of Chemistry and Department of Earth and Atmospheric Science, Purdue University,West Lafayette, Indiana 49707, USA*
[3]*Chemistry Department, Faculty of Science, King Saud University, PO Box 2455, Riyadh 11451,Kingdom of Saudi Arabia*
[4]*Laboratoire Modélisation et Simulation Multi Echelle, Université Paris-Est, MSME UMR 8208 CNRS,5 bd Descartes, 77454 Marne-la-Vallée, France*

We performed accurate *ab initio* investigations of the geometric parameters and the vibrational structure of neutral HNS/HSN triatomics and their singly charged anions and cations. We used standard and explicitly correlated coupled cluster approaches in connection with large basis sets. At the highest levels of description, we show that results nicely approach those obtained at the complete basis set limit. Moreover, we generated the three-dimensional potential energy surfaces (3D PESs) for these molecular entities at the coupled cluster level with singles and doubles and a perturbative treatment of triple excitations, along with a basis set of augmented quintuple-zeta quality (aug-cc-pV5Z). A full set of spectroscopic constants are deduced from these potentials by applying perturbation theory. In addition, these 3D PESs are incorporated into variational treatment of the nuclear motions. The pattern of the lowest vibrational levels and corresponding wavefunctions, up to around 4000 cm^{-1} above the corresponding potential energy minimum, is presented for the first time.

QM/MM protocol for studying interactions in ionic liquids: optimization of charges

D. Lengvinaite[1], S. Grubisic[2], K. Aidas[1], I. Cvijetic[3], A. Laaksonen[4], F. Mocci[5]

[1] Department of General Physics and Spectroscopy, Faculty of Physics, Vilnius University, Lithaunia
[2] Center for Chemistry, IHTM, University of Belgrade, Belgrade, Serbia
[3] Innovation Center of the Faculty of Chemistry, University of Belgrade, Serbia
[4] Division of Physical Chemistry, Arrhenius Laboratory, Stockholm University, Sweden
[5] Department of Chemical and Geological Sciences, University of Cagliari, Italy
[*] Corresponding author: fmocci@unica.it

Ionic liquids (ILs) are organic salts, characterized by a remarkably low melting temperature (<100°), and by many useful properties (e.g. electrical conductivity, high thermal stability, high solvating capability, etc.) which can be tuned by modifying the anion or cation. The need of designing ILs with desired properties had stimulated a large amount of investigations. Among the experimental techniques used to this purpose, we are interested in the nuclear magnetic resonance (NMR) signal of the quadrupolar nuclei, particularly of the halides which are common anions in ILs.

We use classical MD, coupled with QM and QM/MM calculations, to understand how the structure and dynamics of ILs at the atomistic and sub-atomistic level affects the NMR signal of quadrupolar nuclei [1] and what information can be extracted from the experimental signals. The work presented in this symposium concerns stages 1-3 of the scheme in Fig.1, and is focused on the improvement of the currently used force field parameters in order to improve the description of the interactions between anions and cation of 1-decyl-3-methyl-imidazolium chloride (DMimCl). To this aim we improved the partial and total charges by performing QM calculations and varying the van der Waals parameters. The atomic charges were calculated using Gaussian 09 program, with the restrained electrostatic potential (RESP) approach by fitting the electrostatic potential grid computed at the B3LYP DFT level on the optimized geometries. The new set of AMBER parameters has been validated by comparing the structural and dynamical behavior of investigated systems by means of MD simulations with QM data and experimental evidence. A very good agreement with reference data (ab initio [2] and experimental) has been obtained for all of the investigated structural and dynamical properties.
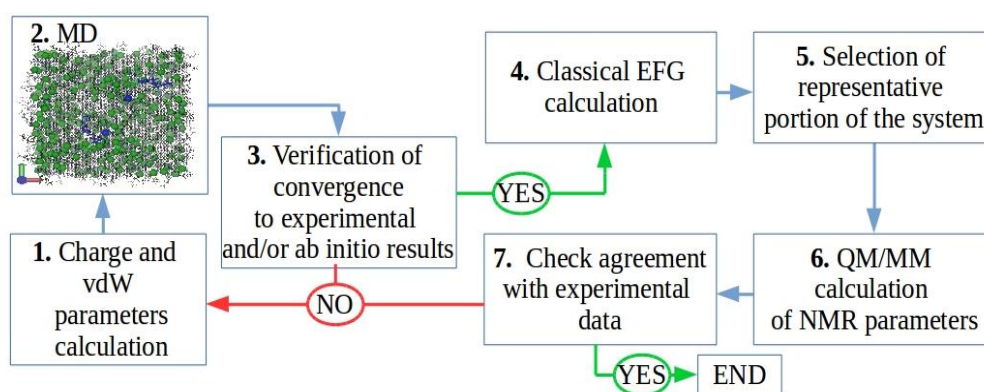

Figure 1: Proposed scheme for calculation of NMR parameters of some ionic liquid

References
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Ytterbium basis set considerations

D. Kędziera

Faculty of Chemistry, Nicolaus Copernicus University in Torun, Gagarina 7, 87-100 Torun,Poland
*Corresponding author: teodar@chem.umk.pl

The great development of the experimental methods of modern molecular physics particularly in the field of ultra-cold gas physics, results in possibilities of obtaining of the previously unprecedented precision in the experimental measurements of the properties describing small molecular systems such as length scattering in the inter atomic collisions, bond energies, polarizabilities, time of life in the resonant states and many others. As a consequence, the theoretical investigations get the unique chance of testing new theories and methodologies, that more and more accurately describe systems of interest of chemistry and physics of cold molecules. Among many possible molecules, the ytterbium dimer was chosen for the current study. What makes Yb_2 molecule so interesting, is its usefulness for investigations of limitations of the non-Newtonian gravity.

Calculations of the most accurate ytterbium dimer ground-state curve require taking into account the following contributions: electronic correlation, relativistic effects, finite nucleus size and DBOC corrections. Moreover, apart from quite demanding approaches, one faces also the problem of relatively small number of basis set representatives for Yb element. Their different behavior is investigated, and further on some attempts of creating a new, superior basis set are presented.

Selectivity of Imidazole for CO_2 Capture in a Rich Atmosphere in the pollutants: CO_2, NH_3, SO_2 and CO and N_2O.

S. Dalbouha[1,2], R. Boussessi[1,3], N. Komiha[2], N. Jaidane[3], and M. L. Senent[1]

[1]Departamento de Química y Física Teóricas, Instituto de Estructura de la Materia, CSIC, Serrano 121, Madrid 28006, Spain

[2]LS3ME-Equipe de Chimie Théorique et Modélisation, Faculté des Sciences, Université Mohammed V, 1014 RP, Rabat, Maroc.

[3]Laboratoire de Spectroscopie Atomique, Moléculaire et Applications-LSAMA LR01ES09, Faculté des Sciences de Tunis, Université de Tunis El Manar, 2092, Tunis, Tunisie.

Corresponding author: ml.senent@csic.es

Due to the problem of global warming caused from mass emissions of greenhouse gas and pollutants, such as CO_2, NH_3, SO_2, CO and N_2O new gas capture and gas sequestration materials need to be designed. The aim of this work is the study of the Van-der-Walls complexes of these gases with imidazole, considering the imidazolate rings simplest models for the study of the nature of host-guest interactions in Zeolitic Imidazolate Frameworks (ZIF's) [1-2] . With this objective, we try to study the interaction between imidazole and the different gases, such as NH_3, SO_2, CO and N_2O using accurate ab initio methods. The electronic structure calculations were performed using second order Möller- Plesset theory (MP2) in combination with large augmented bases set. Results are compared with those of the CO_2 [2], the most abundant greenhouse effect gas. Selectivity for gas capture and gas separation is discussed.

We present all the possible structures of the imidazole-NH_3, imidazole-SO_2, imidazole-N_2O, and imidazole-CO complexes, as well as, the binding energies and the interaction potential energy surfaces. Harmonic frequencies are provided to demonstrate the minimum energy character of the structures. Further work on studying the three-body systems type NH_3-imidazole-CO_2, SO_2-imidazole-CO_2, N_2O-imidazole-CO_2 and CO-imidazole-CO_2 confirms the probability of simultaneous attachments.
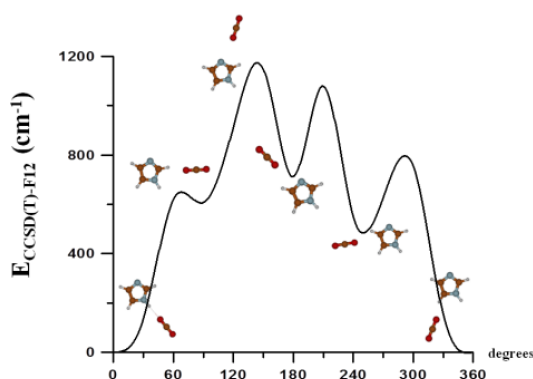
References

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Matrix Effects on the Stability of High-Energy Conformers of Matrix-Isolated Asymmetrically *ortho*-Fluorosubstituted Benzoic Acid

N. Kuş[1,2] and Rui Fausto[1]

[1]*CQC, Department of Chemistry, University of Coimbra, P3004-535 Coimbra, Portugal*
[2]*Department of Physics, Anadolu University, TK-26470 Eskişehir, Turkey*

DFT(B3LYP)/6-311++G(d,p) calculations on 2-fluorobenzoic acid show that the molecule has four conformers (see Figure 1): two low energy conformers (forms **1** and **2**) with the carboxylic acid group assuming the *cis* configuration (O=C–O–H dihedral equal to 0º) and two higher-energy conformers (**3**, **4**) with a *trans* carboxylic group configuration. Isolation of 2FBA monomers in argon or nitrogen matrices allows for the efficient trapping of both low-energy conformers initially present in the gas phase room temperature equilibrium.

Narrowband selective near-infrared (NIR) excitation of 2νOH mode of **1** in both argon and N_2 matrices allows its efficient conversion into conformer **3**, which is stabilized by an intramolecular
O–H⋯F interaction. On the other hand, upon identical selective vibrational excitation of **2** no changes could be noticed in the argon matrix spectra at the time-scale of the preformed experiments, while experiments carried out on N_2 matrices showed conversion of **2** into **3**.

In conformer **4** (the expected direct product resulting from NIR pumping of **2**), the stabilizing O–H⋯F interaction existent in 3 is replaced by a O–H⋯H repulsive interaction, which leads to a barrier separating this form from **2** that is about half that separating **3** from **1**. Under these circumstances, once formed by vibrational excitation of **2**, conformer **4** can easily convert to the reactant species by fast tunneling, justifying the apparent inefficiency of the **2** → **4** conversion upon vibrational excitation of **2** in an argon matrix. On the other hand, the stabilization of the initially formed conformer **4** by the N_2 matrix (due to OH⋯N_2 interactions) allows this species to survive long enough to allow the **4** → **3** over-the barrier conversion to be competitive with the **4** → **2** tunneling, justifying the observed net conversion of the NIR excited conformer **2** into form **3** in N_2 matrix.

These results demonstrate in a very clear way the relevance of the size of the torsional barrier about the C–O bond in determining the *trans* → *cis* tunneling rate in carboxylic acid compounds, and show also as the intramolecular local topology may decisively influence the intrinsic kinetic stability of different conformers of the same molecule. They are also a clear additional evidence of the stabilization of higher-energy conformers of carboxylic acids by the N_2 matrix medium, that has been found for other molecules of the same family.
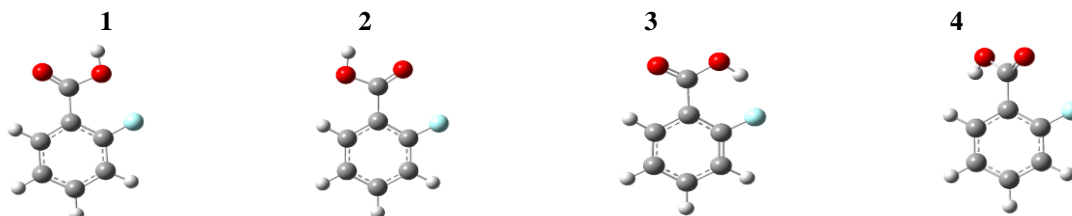
A New Efficient Method for the Calculation of Interior Eigenspaces and its Application to Vibrational Structure Problems

T. Petrenko[1,*] and G. Rauhut[1]

[1]*Institut für Theoretische Chemie, Universität Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany*
*Corresponding author: petrenko@theochem.uni-stuttgart.de

Vibrational configuration (VCI) theory and its multireference variants are common methods for calculating vibrational levels and associated IR and Raman spectra of small and medium-sized molecules. When combined with appropriate configuration selection procedures, the method allows the treatment of VCI problems with up to 10^9 configurations. In general, this approach pursues the construction of the eigenspaces involving eigenstates with significant contributions of physically relevant configurations. The corresponding eigenfunctions are evaluated in the subspace of selected configurations. However, it can easily reach the dimension which is not feasible for conventional eigenvalue solvers. Although Davidson and Lanczos methods are the methods of choice for calculating exterior eigenvalues, they usually fall into stagnation when applied to interior states. The latter are commonly treated by the Jacobi-Davidson method. This approach in conjunction with the matrix factorization for solving the correction equation (CE) is prohibitive for larger problems, and it has limited efficiency if the solution of the CE is based on the Krylov's subspace methods.

We propose the iterative subspace method that is based on the optimality condition for the residual norm. The subspace extraction and expansion are modified according to this principle which allows very efficient calculation of interior vibrational eigenspaces with a strong multireference character for different vibrational structure problems.

The convergence behavior of the method and its performance in comparison with aforementioned algorithms is investigated in a set of benchmark calculations.

Stark deflection of nitromethane in CW beams

A. Rebelo[1], T. Cunha[1], P. Limao-Vieira[1], R. Pandey[2], S. Eden[2]

[1]Laboratório de Colisões Atómicas e Moleculares, CEFITEC, Departamento de Física, FCT - Universidade NOVA de Lisboa, P-2829-516 Caparica, Portugal
[2]Department of Physical Sciences, Open University, Walton Hall, Milton Keynes, MK7 6AA, United Kingdom
[*]Corresponding author: afc.rebelo@campus.fct.unl.pt

Distributions of different species within neutral target beams can present a major challenge in analyzing radiation-induced processes and drawing rigorous comparisons with theory. A series of experiments by Küpper, Meijer, and their respective co-workers have demonstrated that the Stark effect can be exploited to select specific tautomers [1] and clusters [2] from rotationally-cold beams produced in pulsed supersonic expansions. Pulsed molecular beams are suitable for action spectroscopy experiments but are much less applicable to studies of collision-induced processes with relatively low cross sections. Therefore we are developing an experiment at the Open University that uses a Stark deflector built by Küpper and co-workers to manipulate CW beams. Figure 1 shows that *high-field seeking* deflections of 2 mm of nitromethane (CH_3NO_2) can be achieved in a helium beam without any loss of molecules and negligible *low-field seeking* deflection. Initial comparisons with Stark curves (calculated using the CMIStark [3] package) indicate that the majority of the molecules were in J states ≤ 3. While further optimization is in progress, this level of rotational cooling bodes well for the deflection of more complex species. Our ultimate aim is to carry out electron attachment experiments on selected tautomers of biological building blocks (e.g. nucleobases) and their clusters. Dissociative electron attachment is known to contribute to radiation damage in DNA [4] but the effects of intermolecular bonding on the fundamental mechanisms are still quite poorly understood.
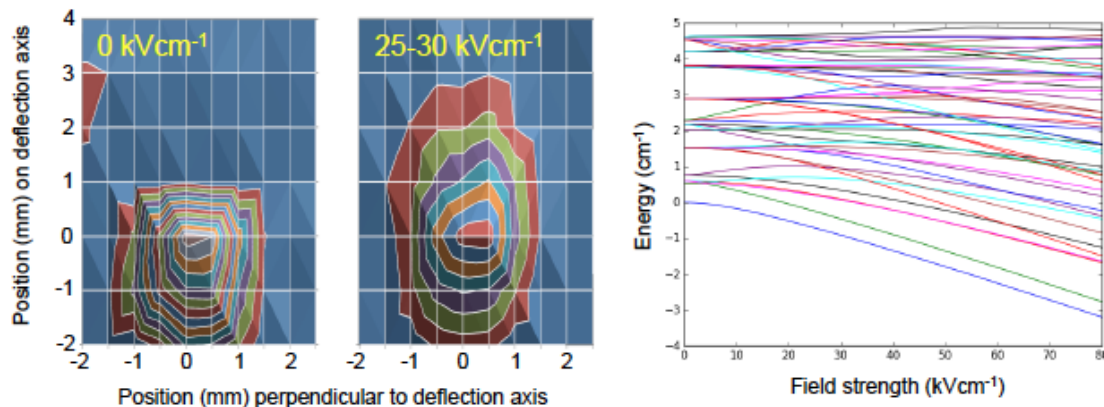

Figure 1: (Left) Electron impact ionization profiles of undeflected and deflected (25-30 kVcm^{-1}) nitromethane in CW helium beams; (Right) Stark curves for nitromethane in J states ≤ 3.

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Theoretical Spectroscopic Characterization at low Temperatures of C_2H_3NO and its Isomers

S. Dalbouha[1-2], M. L. Senent[1], N. Komiha[2], and R. Dominguez-Gómez[3]

[1]*Departamento de Química y Física Teóricas, Instituto de Estructura de la Materia, CSIC, Serrano 121, Madrid 28006, Spain*

[2]*LS3ME-Equipe de Chimie Théorique et Modélisation, Faculté des Sciences, Université Mohammed V, 1014 RP, Rabat, Maroc*

[3]*E.T.S. de Ingeniería Civil, Universidad Politécnica de Madrid, Alfonso XII, 3-5, Madrid 28014, Spain*

Corresponding author: ml.senent@csic.es

Relevant astrophysical molecules of empirical formula C2H3NO are characterized using explicitly correlated coupled cluster methods (CCSD(T)-F12/AVTZ-F12). We present results for four species: the most stable methyl isocyanate (CH_3NCO), as well as, methyl cyanate (CH_3NCO), acetonitrile oxide (CH_3CNO) and hydroxyacetonitrile ($HOCH_2CN$).

Whereas acetonitrile oxide is a linear C_{3v} structure, the remaining isomers are non-rigid species derived from methyl or OH group torsions. The recently detected methyl isocyanate shows a very low torsional energy barrier (V_3=16.2 cm-1). All the torsional energy levels lye over the barrier. Thus, the methyl group can be considered a free rotor. The ground vibrational state rotational constants have been calculated to be A_0 =76164.32 MHz, B_0 =4411.89 MHz and C_0 =4254.58 MHz. Although, the rotational parameters are really dependent of the skeletal motions, our parameters are in a very good agreement with the experimental ones [1].

Methyl cyanate shows a more conventional behavior. In this case, V_3= 364.84 cm^{-1}. The rotational constants A_0 =39089.80 MHz, B_0 = 5314.78 MHz and C_0 = 4816.35 MHz were determined in a very agreement with the experimental ones [2]. Hydroxyacetonitrile show two different conformers which energy separation is 1.5 kcal/mol. The hydroxyl group display internal rotation restricted by two energy barriers (V_t=540 cm-1 and $V_{g \to g}$=446.4 cm^{-1}).

Finally, we provide anharmonic frequencies, predicting possible Fermi interactions, centrifugal distortions constants and torsional transitions. These last were calculated variationally using a CCSD(T)-F12 potential energy surface.
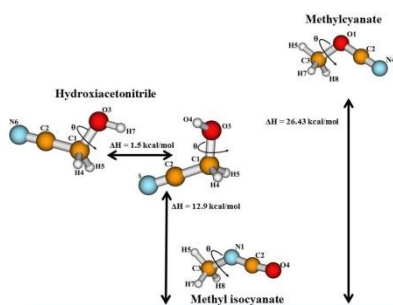
References

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[2] L. Kolesnikova, J.L.Alonso, C.Bermúdez, E.R.Alonso, B.tercero, J.Cernicharo and J.C.Guillemin, Astron&Astrophys (2016)

Hydrogen bond strength dependence on electronegativity of atoms

M. Simončič[1] and T. Urbič[1]

[1]*Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, SI-1000, Slovenija*
Corresponding author: tomaz.urbic@fkkt.uni-lj.si

The hydrogen bond is the strongest intermolecular interaction. It occurs when a molecule with a hydrogen atom bonded to an electronegative atom donates the hydrogen to another electronegative element. This interaction is also of paramount importance for the development of life on Earth as we know it, for it plays a major role in the formation of Watson-Crick base pairs in the DNA and RNA molecules. It is the reason for more than 70 anomalous properties of water [1]. All this makes the hydrogen bond important to research and we want to know the strength of the hydrogen bond and the correlations with the properties of atoms involved in making it.

In this work, we have calculated the strength of the hydrogen bond between different hydrides of the upper right part of the periodic table (HF, H_2O, H_2S, NH_3 etc.), altogether 90 different dimmers using the Gaussian 09 [2] program suite, employing MP2 (full) method [3] with the Aug-CC-pVTZ basis set [4]. Energies of hydrogen bonds were calculated and then correlation checked between the strength of the interaction and the electronegativity of the participating atoms as well as connections with geometries of molecules and charges distributions.

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An efficient fitting procedure for high-dimensional potential energy surfaces

B. Ziegler[1,*] and G. Rauhut[1]

[1]*Institute for Theoretical Chemistry, Universität Stuttgart,*
Pfaffenwaldring 55, D-70569 Stuttgart, Germany
[*]*Corresponding author: ziegler@theochem.uni-stuttgart.de*

Many quantum chemical calculations, e.g. dynamics calculations or anharmonic frequency calculations, require an accurate representation of the multi-dimensional potential energy surface (PES). For our purpose, namely the calculation of anharmonic frequencies of polyatomic molecules, a grid-based multimode expansion of the PES is a proper choice. To speed up variational vibrational calculations, it is recommendable to transform the grid representation to an analytical one. Within the framework of linear least squares fitting, a highly efficient algorithm is presented, which relies on a direct product representation of the PES and an iterative use of Kronecker products. In comparison to customary linear least squares fitting algorithms, this algorithms leads to significant speed-ups and memory savings by several orders of magnitude. Furthermore different fitting bases, like polynomials, B-splines and distributed Gaussians, are tested.

List of participants

Liudmil	Antonov	lantonov@orgchm.bas.bg
Jayanth K.	Ajay	jayanth.ajay@mail.huji.ac.il
Zlatko	Bačić	zlatko.bacic@nyu.edu
Saida	Ben Yaghlane	saidayagh@gmail.com
Sergey	Bokarev	sergey.bokarev@uni-rostock.de
Joel	Bowman	jmbowma@emory.edu
Gilberte	Chambaud	gilberte.chambaud@u-pem.fr
Roman	Ciuryło	rciurylo@fizyka.umk.pl
Sonia	Coriani	coriani@units.it
Hazel	Cox	h.cox@sussex.ac.uk
Attila G.	Császár	csaszar@chem.elte.hu
Marko	Cvitaš	mcvitas@irb.hr
Maria Pilar	de Lara-Castells	Pilar.deLara.castells@csic.es
Nađa	Došlić	nadja.doslic@irb.hr
Rui	Fausto	rfausto@ci.uc.pt
Berta	Fernández	berta.fernandez@usc.es
Leticia	González	leticia.gonzalez@univie.ac.at
Luca	Grisanti	luca.grisanti@gmail.com
Sonja	Grubišić	grubisic@chem.bg.ac.rs
Magnus	Gustafsson	magnus.gustafsson@ltu.se
Lauri	Halonen	lauri.halonen@helsinki.fi
Majdi	Hochlaf	hochlaf@univ-mlv.fr
Tomica	Hrenar	hrenar@chem.pmf.hr
Christoph	Jacob	c.jacob@tu-braunschweig.de
Nejm-Eddine	Jaidane	nejmeddine.jaidane@fst.rnu.tn
Teemu	Järvinen	teemu.j.jarvinen@student.jyu.fi
Shimshon	Kallush	shimshonkallush@braude.ac.il
Dariusz	Kędziera	teodar@chem.umk.pl
Isabelle	Kleiner	isabelle.kleiner@lisa.u-pec.fr
Henrik	Koch	henrik.koch@ntnu.no
Najia	Komiha	komiha@fsr.ac.ma
Nihal	Kuş	nkus@anadolu.edu.tr
Jérôme	Loreau	jloreau@ulb.ac.be
Momir	Mališ	momir.malis@epfl.ch
Jordan	Miles	jmiles02@qub.ac.uk
Klaus	Møller	klaus.moller@kemi.dtu.dk
Jurica	Novak	jurica.novak@irb.hr
Gunnar	Nyman	nyman@chem.gu.se
Alec	Owens	alec.owens.13@ucl.ac.uk
Taras	Petrenko	petrenko@theochem.uni-stuttgart.de
Aurora	Ponzi	aurora.ponzi@irb.hr
Cristina	Puzzarini	cristina.puzzarini@unibo.it

Martin	Quack	martin@quack.ch
Guntram	Rauhut	rauhut@theochem.uni-stuttgart.de
Andre	Rebelo	afc.rebelo@campus.fct.unl.pt
Markus	Reiher	markus.reiher@phys.chem.ethz.ch
Heribert	Reis	hreis@eie.gr
Jeremy	Richardson	rjeremy@ethz.ch
Carlos M. R.	Rocha	carlosmurilorocha@hotmail.com
Octavio	Roncero	octavio.roncero@csic.es
Marin	Sapunar	marin.sapunar@irb.hr
Milan	Senćanski	sencanski@vin.bg.ac.rs
Maria Luisa	Senent	senent@iem.cfmac.csic.es
Kaite	Spinlove	kes714@student.bham.ac.uk
Viktor	Szalay	szalay.viktor@wigner.mta.hu
Tomaz	Urbič	tomaz.urbic@fkkt.uni-lj.si
Ad	van der Avoird	avda@theochem.ru.nl
Jirí	Vanícek	jiri.vanicek@epfl.ch
Graham	Worth	g.a.worth@bham.ac.uk
Stanislav	Záliš	zalis@jh-inst.cas.cz
Benjamin	Ziegler	ziegler@theochem.uni-stuttgart.de

Conference Timetable

	Monday, October 10		Tuesday, 11 October	Wednesday, 12 October
08:15 – 08:30	Opening			
08:30 - 09:00	Lauri Halonen		Zlatko Bačić	Joel Bowman
09:00 - 09:30	Isabelle Kleiner		Hazel Cox	Viktor Szalay
09:30 - 10:00	Rui Fausto		Klaus Møller	Tomaž Urbič
10:00 - 10:30	Christoph Jacob		Markus Reiher	Shimshon Kallush
10:30 - 11:00	Coffee Break		Coffee Break	Coffee Break
11:00 -.11:30	Majdi Hochlaf		Roman Ciurylo	Leticia González
11:30 - 12:00	Berta Fernández Rodríguez		Tomica Hrenar	Jeremy Richardson
12:00 - 12:30	Guntram Rauhut		Henrik Koch	Graham Worth
12:30 - 14:00	Lunch		Lunch	Closing
				Lunch
14:00 – 14:30	Martin Quack		Young Scientists Forum: S. Bokarev, A Ponzi, J. Loreau, M. Mališ,T. Järvinen	Leaving
14:30 - 15:00	Octavio Roncero			
15:00 - 15:30	Stanislav Záliš			
15:30 - 16:00	Coffee Break		Coffee Break	
16:00 - 16:30	Maria Pilar de Lara-Castells		Young Scientists Forum: L. Grisanti, M. Sapunar, K. Spinlove, M Senćanski, C. Rocha	
16:30 - 17:00	Cristina Puzzarini			
17:00 – 17:30	Gilberte Chambaud			
17:30 – 19:30	Posters	MC Meeting	Posters	
19:30 -	Dinner		Dinner	