BOOK OF ABSTRACTS

New avenues in molecular theories: From the lab to beyond the Earth

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EUROPEAN COOPERATION
IN SCIENCE AND TECHNOLOGY

MOLIM
MOLECULES IN MOTION

Универзитет у Београду
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JOINT TRAINING SCHOOL OF THE COST ACTIONS
CM1401 OUR ASTROCHEMICAL HISTORY &
CM1405 MOLIM - MOLECULES IN MOTION

Belgrade (Serbia), August 31 - September 6, 2017

Joint Training School of the COST actions
CM1401 Our Astrochemical History, and
CM1405 MOLIM – Molecules in Motion

New avenues in molecular theories: From the lab to beyond the Earth

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Cover: A view across the River Sava on Belgrade where one of the original four town gates outside of the Kalemegdan Fortress was located. The place remained the kernel of the city till the present day. Towers of St. Michael Cathedral Church (middle, left) and the Seat of Serbian Orthodox Patriarch (middle, right) are visible, as well as other edifices, including some beautiful examples of early 19th century architecture. An old loading dock (bottom) is today a quay for leisure and nightlife.

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Welcome Message

On behalf of the Scientific and Local Organizing Committees, I have a great pleasure in welcoming you to the Joint COST Training School in Belgrade. This school brings together participants from two COST actions: Our Astrochemical History (CM1401), and MOLIM – Molecules in Motion (CM1405). This, at first sight unusual, pairing of the two actions has as one of its principal objects to clearly point out the multitude of connections between Astrochemistry and Chemistry performed in the laboratory (as nicely essentiated in the very title of this school) despite a huge difference in distances between a researcher and the chemical entity of her/his study, as well as in the conditions in which these entities are set. To achieve this goal we have a great team of eminent teachers from Switzerland, France, UK, The Netherlands, Catalonia, Germany, Hungary, and Italy. A glimpse into their lecture summaries reveals that all of them maintain this unifying braid while expounding on their important specific topics. The trainees will therefore have an exquisite opportunity to broaden their horizon, on one hand, and to familiarize themselves with advanced research methods and underlying theories, on the other. As the stage is therefore set for the Training School, we wish to all of you a stimulating and exciting work, and a good time in Belgrade.

Sonja Grubišić

Sonja Grubišić

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Lectures

A Short Introduction to Astrochemistry

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This short introductory course will focus on some factors that make astrochemistry a peculiar brand of chemistry, on the one hand, and will describe some of the types of gases and solids that one has observed in our Galaxy, supporting molecules at various densities and temperatures, on the other hand. In this summary, let us emphasize the physical constraints of astrochemistry, in order to set the scene.

Chemistry in interstellar environments has many peculiarities, that makes it very different from chemistry in environments that are customary for the laboratory chemist. While the basic concepts of physical chemistry evidently remain, the physical conditions are such that many of the usual hypotheses do not hold. Being it interstellar gaseous matter (ISM), gases surrounding Solar System objects like comets and asteroids, the main constraints of the kind of chemistry we are dealing with are: (i) Very dilute conditions, number density $\rho \lesssim 10^{10}\,\mathrm{cm}^{-3}$ (under normal conditions, 298K, 1 atmosphere, the ideal gas has a density of $2.5\,10^{19}\,\mathrm{cm}^{-3}$); (ii) Large range of temperatures, with molecules observed at gas temperatures as low as 5-15 K; (iii) Overwhelming dominance of atomic and molecular hydrogen, which constitute more that 90% (in number) of the whole number density, all other elements but inert He being less than 1% in number. Main elements are O, C, Ne, Fe, N, Si, Ar, Mg, S, and all others present as traces, including alkaline elements, halogens and P.

As a consequence of the physical and chemical conditions, the main differences between laboratory chemistry and astrochemistry, which are relevant for this school could be described as follows:

1. Because of the low density and temperature in the ISM, the chemistry is never at thermodynamical equilibrium. Chemical processes are dominated by the kinetics and branching ratios of the reactions at hand, and are at steady state at best, even if astrophysical timescales are relatively long, characteristic times being of the order of $10^4 - 10^6$ years. Only in planetary atmospheres thermal equilibrium is reached.

2. In space, three-body collisions are absent (or extremely unlikely). This means that reactions like $A + B \to AB$ may only occur with photonic stabilisation, or else on the surface of a grain.

3. The often prevailing low temperatures of interstellar space prevent many reactions to take place, even with modest activation barriers. However, some reactions proceed through tunneling, especially so if involving atomic H (or D).

4. Ion chemistry plays a important role in space, mainly through cations (though anions are also present). Main ions are atomic species (in diffuse clouds) like C^+, and protonated species (in molecular clouds), like HCO^+.

5. In interstellar dilute environments, ionization of trace elements, such as C and S, may proceed by photon with $E < 13.6$ eV, photon of higher energy being absorbed by atomic H. However, cosmic rays (CR) are ubiquitous, even in the denser parts of the ISM and are the main primary source of energy that initiate chemical chains (by the reaction summarized by $H_2 + CR \rightarrow e^- + H_2^+$ followed by $H_2 + H_2^+ \rightarrow H_3^+ + H$).

6. For many environments of very low ionisation fraction, the neutral-neutral reactions are of importance, especially so those involving radicals tend to have higher rates at low temperatures. However, ion/electron chemistry dominates the chemical evolution in many sectors of molecular complexification, like the successive hydrogenation of N^+ or CH^+.

Interstellar grains play a key role in chemistry, although all the intricacies of surface (and solid bulk) chemistry are far from understood. In particular, some key reactions take place on the surface, like the synthesis $H + H \rightarrow H_2$ or else the hydrogenation of CO: $CO + H + H \rightarrow H_2CO + H + H \rightarrow CH_3OH$.

Let us also underline that the chemistry of the ISM is relatively rich, with almost two hundred molecules detected, some of them quite unusual on the point of view of the laboratory: Long carbon chains, $H(CC)_nH$, possibly charged –anions and cations–, and substituted (CH_3, CN); some cyclic molecules (c-C_3H_2), many radicals and protonated species, like the common HCO^+, N_2H^+, H_2O^+ and the all-important $H_3{}^+$. Also, a noticeable part of carbon is taken up in so-called PAH's, polycyclic Aromatic Hydrocarbons, from naphtalene all the way up to poly-coronenes and $C_{60}C_{70}$, along with the charged or O,N once or twice substituted species.

We shall spend also a little time on the ways those molecules are detected—rotational, infra-red spectroscopy—and characterized as unambiguously as possible, by means of careful line analysis and modelling of photon transfers.

Standard Model of Atoms and Molecules

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The "standard model of particle physics" (SMPP) reaches in fact far beyond particle physics and can be considered as the current general quantum physical theory of matter and radiation and their interactions. It also provides a "standard model" for atoms, molecules and clusters as they are formed in astrophysical processes and observed in our immediate environment on Earth. In the lecture we shall start briefly with a broad picture connecting particle physics with molecular physics and astrophysics and we then introduce our current classical and quantum mechanical models of atoms and molecules. We shall discuss basic concepts of molecular structure and dynamics as derived from spectroscopy and kinetics as they are relevant to both "Molecules in Motion" and "Our Astrochemical History" [1].

The general concepts will be illustrated with examples including also quantum mechanical tunneling processes as relevant to our understanding of molecular structure and dynamics of hydrogen bonded complexes as well as chiral and achiral molecules. We briefly discuss most recent progress relating high energy physics to molecular physics through fundamental symmetries and symmetry violations as for example in the very new kinetic process of the time evolution of parity in isolated chiral molecules predicted by theory and perhaps in reach of current experiments. We shall conclude with a brief outlook on "astrobiology" as possibly accessible through spectroscopic observation of chiral molecules. Background reading can be found in [2-9].

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Atmosphere

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Atmospheric physics is fundamental to the understanding of planet formation and evolution. This is true for our own solar system planets as well as planets far beyond.

In the last two decades we have undergone what could truly be described as a second Copernican revolution. With the discovery of over 3600 exoplanets to date, we can begin to place solar system physics into the grander context of our galaxy.

In order to understand more about these distant worlds, we need to measure their chemistries. As in-situ probes are currently out of question, we must observe these distant worlds remotely using spectroscopy of their atmospheres. Measuring the properties of often hot and highly irradiated atmospheres is a difficult endeavour and very much at the cutting edge of current feasibilities.

In this lecture I will introduce the main concepts of atmospheric spectroscopy for transmission and emission measurements, discuss the intricacies of using high temperature molecular line lists and how clouds and hazes affect the abundance measurements of molecular trace gas species. At the end of the lecture I will discuss current bayesian inverse atmospheric retrieval models and give an overview of some of the most significant discoveries in atmospheric physics of extrasolar planets to date.

Pre-Born-Oppenheimer Molecular Structure Theory

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The lecture is about the direct solution of the full electron-nuclear Schrödinger equation, without the introduction of any kind of separation of the electronic and the nuclear motion. This pre-Born-Oppenheimer (pre-BO) framework allows us to approach the non-relativistic limit arbitrarily close and opens the route for a theoretical assessment of high-order relativistic and QED corrections in molecules. Besides the possibility of achieving an outstanding numerical accuracy in relation with precision spectroscopic measurements, pre-BO theory has its own peculiarities. Most interestingly, the definition of molecular structure is non-trivial if the Born-Oppenheimer (BO) approximation is not introduced. Furthermore, rovibrational states which can be computed as bound states of some excited electronic state in a BO framework, can be obtained only directly as rovibronic resonances with some finite pre-dissociative lifetime. The lecture will start with theoretical foundations about the symmetries, coordinate definition, and Hamiltonians of few-particle quantum systems. Generally applicable basis functions, in particular explicitly correlated Gaussian functions will be discussed and the main steps of the integral calculation will be highlighted. The computation of eigenvalues and eigenfunctions of bound and resonance states is explained and optimization strategies of the basis function parameters, necessary to achieve high accuracy, are reviewed. The lecture ends with the discussion of computational results and open challenges in relation with quantum molecular theory.

Astrophysical Observations

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Molecules started to form early in the history of the universe, allowing the first stars to form. Since then, stellar nucleosynthesis continuously enriches the interstellar medium (ISM) in heavy elements. The evolution of interstellar matter, from molecular clouds to stars, is ruled by non-equilibrium processes in which collisions at the atomic scales play a central role. Our understanding of the evolution of the ISM rests upon remote sensing of photons by means of telescopes across the entire electromagnetic spectrum. Recovering density, temperature, abundances of chemical species, etc, from the detected photons is an inversion problem in which the most detailed knowledge of the collisional (non-reactive and reactive) processes is needed. In this lecture, I will present an overview of the observational methods, biased towards the mm to sub-mm domains. I will also introduce the basic notions of line radiative transfer needed to understand how chemical abundances are estimated.

Solid-state spectroscopy

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The largest molecular reservoir in interstellar space is in the solid state - ices (condensed molecular material) and dust (refractory carbon- and silicate materials). To understand where such materials are found in star-forming regions, as well as elucidate their role in the chemical evolution of stars and planets we need a way to understand their properties and behavior. Spectroscopy is the key. In this lecture I'll focus specifically on solid-state ice spectroscopy. Observational astrochemists use infrared spectroscopy to "find" ices and identify ice species in star-forming regions. Alternatively we can look for THz (or sub-mm) gas phase emission spectra from gaseous molecules desorbed from ices to infer the location, and constituents, of ice in star-forming regions.

Of course observations are only a snap-shot of interstellar materials. Laboratory studies enable us to study ice and dust in a controlled way, to understand how ice spectroscopy is affected by physical and chemical changes in the environment. Laboratory techniques can then be used to determine the structure, physical attributes and chemistry of icy interstellar analogues. In the laboratory we are not limited to electromagnetic radiation:- mass spectrometery and neutron spectroscopy, as well as time-resolved THz and UV spectroscopy, can all reveal more chemical and physical information about ices themselves.

Even then, to fully understand the underpinning physical chemistry, theoretical approaches may be required. Ranging from calculations from molecular dynamics simulations, to ab initio calculations, understanding and linking transition frequencies to ice structure is vital when we are deciphering the chemical processes and dynamics and reactivity of ices. All this feeds back into astrochemical models and builds a picture, from fundamental physical chemistry, to our understanding of astronomical processes on the scale of star and planet formation.

In this lecture I intend to illustrate how fundamental theoretical techniques inform laboratory and observational studies, and how a range of solid-state spectroscopies can be combined to help us understand ice structure and reactivity.

Atomic and Molecular Collisions

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The observation of ro-vibrational bands of molecules such as, e.g., CO, CN, and H_2O, provides detailed information on star-forming regions, protoplanetary disks, and other astronomical environments. In regions of relatively high densities, Local Thermodynamic Equilibrium (LTE) can be assumed, which simplifies the analysis of the data. When the LTE approximation does not apply, collisional rate coefficients are required to model the populations of the molecular quantum states. The dominant species are typically hydrogen and helium atoms, and hydrogen molecules. The major source of rate constants is theoretical calculations. The calculations require potential energy surfaces, which describe the interactions between the collision partners. Potential energy surfaces can be obtained by solving the electronic Schroedinger equation.

Once the PES is known, collisional rate constants for transitions between ro-vibrational quantum states are obtained by solving the Schroedinger equation for the nuclear motion, and this will be the focus of this lecture. I will start with the basics of the time dependent and time-independent formulation of quantum scattering in one dimension and discuss the coupled channels (CC) equation for atom-diatom scattering in three dimensions. Also, the numerical methods used to solve the CC equation will be discussed. The theory will be illustrated by recent work on $H + CO$ scattering.

Symmetry in Computational Molecular Physics

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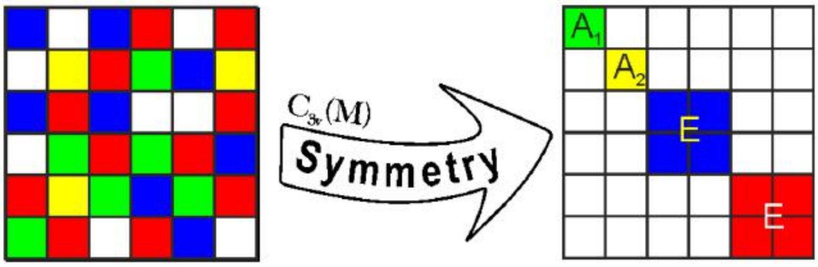
Symmetry is a powerful method in theoretical chemistry and molecular physics. Symmetries together with group theory provide us with a formal method for the description of the properties of molecules by understanding the patterns in their structure. It allows predicting the optical properties of molecules and hence their spectra. This course will introduce some aspects of the group theory using simple, typical examples related to applications of symmetry in computational molecular spectroscopy. The language of the group theory is very formal: CNPI, IRREPS, point groups, characters, projectors, classes, reductions, GOT, improper rotations, isomorphism, homomorphism, feasible operations, representations (faithful and not faithful), symmetry labels, matrix groups, etc. One of aims of this small course is to translate at least some of these terms to 'English'.



Spectroscopy of Weakly Bound Systems

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Information obtainable with rotational spectroscopy on weakly bound systems is discussed.

Energetic and structural features of several non-covalent interactions is presented. We show how rare gases can interact with some molecules generating stable adducts, how some times weak linkages such as halogen bonds or $n \to \pi$ interactions are stronger than competitive hydrogen bonds.

In addition, the peculiar propensity of water to have a high internal dynamic activity in its molecular complexes with organic molecules is described. Often, the corresponding large amplitude motions are reflected in the tunnelling splittings of the rotational transitions which, in turn, provide information for the determination of the potential energy surfaces and of the non covalent interactions of water with a variety of atoms and/or functional groups. A classification of this kind of molecular complexes is given, also in relation to the tunnelling features of the rotational spectra.

Finally, we describe the results of the rotational investigations of dimers of carboxylic acids, and of mixtures of formic acid with several alcohols, ethers, esters and ketones. Conformational shapes and geometries of these adducts, the topologies of their intermolecular hydrogen bonds and the effects of the internal dynamics on the rotational spectra are presented. An explanation is given of the failure of the assignments of the rotational spectra of the adducts of formic acid with some alcohols.

Reactivity

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This lecture gives an introduction into the quantitative characterization of the kinetics of elementary chemical reactions, such as they are of relevance for the dynamics of interstellar molecular clouds, but also of planetary atmospheres. Examples for the processes considered are the formation and the subsequent radiative or collisional stabilization of reactive pairs of atoms, molecules and ions. Direct or complex-forming bimolecular reactions, photolysis and thermal dissociation processes are discussed as well. Experimental laboratory studies are compared with theoretical models.

Solid State Reactivity (Modeling of Surfaces and Reactivity in Astrochemical Context)

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Spectroscopic observations show that the ordinary matter of the interstellar medium consists of gas and submicron sized grains mixed together. Such a matter is not distributed evenly but aggregates in clouds that settle in the disk of spiral galaxies. In clouds where the atomic densities are about 1-10 H atoms cm^{-3} (the so-called diffuse clouds) grains consist of dust of Mg/Fe-silicates and carbonaceous materials, whereas in clouds with atomic densities of about 10,000 cm^{-3} (the so-called dense clouds) dust grains are covered in ices of volatile species. The current knowledge of this interstellar matter is mostly based on observational measurements, supported by the comparison with laboratory experiments and astrochemical models. The combination of these three approaches has provided important information such as the chemical composition of grains and their chemical activity. However, atomic-scale information such as the detailed structure of the grain particles or precise reaction mechanistic steps is still lacking, which is a serious limitation to fully understand the physico-chemical steps leading to the increase of the chemical complexity in space. This information gap can partly be filled in by using theoretical calculations based on quantum mechanical approaches. This training session aims to provide and exhaustive overview of the different computational techniques for the modelling of surfaces mimicking the solid phases present in the interstellar medium. The session will give insights on: i) surface modeling adopting periodic and cluster approaches, ii) the Bloch theorem, which is the quantum mechanical formalism for periodic calculations, iii) surface properties; iv) simulation of adsorption processes and calculation of adsorption energies, v) simulation of point and surface defects, and vi) simulation chemical reactions on surfaces. Several numerical exercises are also planned as practices.

High Resolution Molecular Spectroscopy

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This class is dedicated to a more detailed description of molecular spectroscopy in the gas phase. More precisely, it will address some advanced theory connected with high resolution rotational spectroscopy in the microwave, millimeter and sub-millimeter, and (far)-infrared spectral range. The first part will be dedicated to a brief summary of the experimental state-of-the-art methods, then I will describe the theoretical principles based on effective Hamiltonians treating the various effects present in molecules (rotation, centrifugal distortion, hyperfine structure…). Then, in the second part I will apply the theory to a number of examples from recent or on-going research projects connected with species of astrophysical (or astrobiologial) interest. A particular emphasis will be given to the description of the theory and spectral analysis connected with the presence of large amplitude motions in various molecular systems, such as internal rotation of methyl group(s). I also will explain the connection between the molecular parameters provided by the experimental analysis of the rotational spectra by effective Hamiltonians and the parameters calculated by quantum chemical methods, and finally the implications for the detection and for the abundance determination in the interstellar medium.

Ions in Astrophysical Media

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Very early, ions were considered in astrochemical models because of the assumed importance of ion-molecule collision processes in astrophysical media (Dalgarno & Cray 1973, Herbst 1981). Nowadays, several positive and relatively few negative molecular ions were identified there. This motivated new surveys as well as theoretical and laboratory studies to determine their role and influence on the composition of extraterrestrial sources, where mostly gas phase ion-molecule reactions are taking place (Cernicharo et al. 2011, Bierbaum et al. 2011). These investigations showed that these ions play crucial roles, as reactants and intermediates, in gas phase physical and chemical processes occurring in these media. For instance, H_3^+ cation (Oka 2006) is strongly involved in this complex chemistry as proton donor. Also carbon chain anions are known to be important precursors for neutral prebiotic molecules.

In my lecture, I will review the molecular ions, both positively and negatively charged, detected in astrophysical media. I will also focus on the up-to-date theoretical and experimental studies and observations (Roueff & Lique 2013; Hochlaf 2017). Mostly, I will point out that discoveries are infrequent and very recent due to the lack of experimental data and since the abundances of such species seem to be very low. Moreover, I will present the needed thermochemical and spectroscopic and collisional data for the identification of such species. Some models for potentially detectable ionic species will be given (Senent & Hochlaf 2013).

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Astrophysical Modelling

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The physical conditions in space can be vastly different from laboratories and I will briefly revisit the typical conditions ranging from dilute gases in the interstellar medium to dense protoplanetary disks around young stars and planetary atmospheres. Astrophysical models of these environment vary in complexity and I plan to discuss in more detail models of photodissociation regions (PDRs), models of disks and atmosphere models with special attention to how the atomic/molecular data enters into the heating/cooling balance of the gas and the chemistry of those regions. The role of dust, which is ubiquitous in space, also plays a crucial role by acting as a surface for atoms/molecules to adsorb, but also as a sink and source of radiation that can influence the excitation state of atoms/molecules. Using a few examples I will show how atomic/molecular data is the key in the interpretation of astrophysical observations such as line emission and line ratios.

Trainees' Posters

Study of a cometary atmosphere: Evolution of halogen species in the coma of 67P/Churyumov-Gerasimenko

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It is nowadays commonly accepted that comets are good indicators of the conditions reigning during planet formation 4.6 billion years ago, considering their storage, since then, within the cold extended confines of our solar system.

The European Space Agency's ROSETTA mission, aiming at the *in situ* study of comet 67P/Churyumov-Gerasimenko (67P/C-G), brought back a never-seen-before data collection both of its nucleus and the composition of its atmosphere while entering the inner parts of the solar system. The unprecedented *in situ* detection of the halogen halides HF, HCl and HBr [1], made possible with the presence of the on-board Double Focusing Mass Spectrometer ROSINA/DFMS [2], allowed the derivation of their abundances in the atmosphere of the comet (or coma).

We use the astrochemistry package KROME [3] to generate relevant kinetic databases best describing the coma of 67P/C-G, and to solve the related ordinary differential equations (ODE) based on the calculated abundances of important molecules such as H_2O, CO_2, CO, and O_2, as well as halogen species including F, HF, $^{35/37}$Cl, H$^{35/37}$Cl, $^{79/81}$Br and H$^{79/81}$Br.

We show the evolution of these species of interest taking into account environmental conditions from different stages of the mission.

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Modelling of ammonia in the circumstellar envelopes of AGB stars

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HIFI instrument onboard the Herschel satellite provided unprecedented number of detections of the lowest rotational transitions of ammonia in circumstellar envelopes of evolved stars including massive red supergiants, AGB, and post-AGB stars. Chemistry of ammonia formation in the circumstellar envelopes of evolved stars is poorly understood. The proposed mechanisms for its formation are processes behind the shock front, photochemistry in the inner part of the clumpy envelope, and formation of dust grains. We present results of the non-LTE radiative transfer modelling of ammonia transitions, mainly of the ground-state rotational one NH_3 $J_K = 1_0 - 0_0$ transition at 572.5 GHz, in selected AGB stars, aiming at the quantitative estimation of the NH_3 abundance. The model of ammonia includes IR radiative pumping via ν_2=1 vibrational band at 10 μm.

Mysterious formation of diatomic molecules in space: Radiative association of CH

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When new stars are born, matter is contracting towards their center of mass during a so called gravitational collapse. The gravitational energy is then transformed into kinetic energy, similar to a falling object. For the star formation to continue efficiently, some of the kinetic energy must be removed, which can occur by emitting electromagnetic radiation [1]. Emission of electromagnetic radiation can be efficiently done by molecules. Therefore knowing which molecules are present in the interstellar media, how they are created and destroyed, is of importance when considering star formation.

This work is focused on the radiative association reaction of the CH molecule. Radiative association is the process where a molecule is formed from two atoms or smaller molecules, while emitting a photon (i.e., electromagnetic radiation). The CH molecule was chosen for this study because of its occurrence in several chemical reactions in the interstellar medium, the sun, and comets [2].

The aim of the study was to calculate the reaction cross sections and reaction rates for the CH molecule and its isotopes. The reaction cross section is a measure of how frequently the atoms will collide and form a molecule. The cross section is then used to obtain the reaction rate constant, thereby giving an understanding of the formation process of the molecule.

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NMR spectra of imidazolium based ionic liquids: Insights from large-scale QM/MD calculations

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Nuclear magnetic resonance spectroscopy, most commonly known as NMR spectroscopy, can provide detailed information about the structure, dynamics, reaction state, and chemical environment of molecules. Differences between isotropic values of nuclear magnetic shielding tensors, the so-called chemical shifts, are most common observables in NMR spectroscopy. Room-temperature ionic liquids (RTILs), which are salts in liquid state at ambient temperatures and pressures, provide desirable features such as very low vapor pressure, thermal stability, high ionic conductivity, non-flammability, and a large temperature range for which they remain liquid. One of the many advantages of RTILs is the ability to tune physicochemical properties such as density, viscosity, conductivity, and hydrogen bonding ability by selecting appropriate cations, anions, and polar or non-polar solvents. Experimentally, a curious behavior of the ^{1}H NMR spectra of 1-decyl-3-methyl-imidazolium ([DMim]) molecule – a popular cationic component of imidazolium based ionic liquids – dissolved in solvents of varying polarity was recorded: the increasing shielding of the proton at the 2nd position of the imidazolium ring was observed with the rising polarity of the solvent.

In this work, we present a systematic study of the proton NMR chemical shifts prediction of ion pair of 1-decyl-3-methyl-imidazolium chloride ([DMim][Cl]) in solvents of different polarity: dichloromethane, acetonitrile, and water. We have applied two approaches – DFT method with polarizable continuum model (PCM) to account for solvent effect, and conjugated QM/MM model combined with a statistical mechanical scheme based on classical molecular dynamics simulations. To conclude, the DFT results showed that the ^{1}H NMR spectra of [DMim] cation in dielectric continuum turned out to be almost identical irrespective of the solvent, what contradicts experimental results. Therefore, the explicit hydrogen bonding partner needs to be included into the PCM. The results for [DMim] cation with an anion or solvent molecule revealed that 2nd position proton chemical shift does not depend on polarity of the solvent, but it depends on Cl anion. To improve accuracy of the results a good description of the electrostatic solute-solvent interactions and non-electrostatic interactions is important, thus the calculations with combined QM/MM method have been performed. The results confirmed that Cl anion is strongly influencing the chemical shift of the hydrogen at the 2nd position. In the ^{1}H NMR spectrum of [DMim] the chemical shift of the proton in 2nd position revealed that ionic pair can dissociate in highly polar solvents. Eventually, we have reproduced the results for the chemical shifts in conformity with the experimental data, and explained the unusual behaviour of the chemical shifts for the 2nd position proton of [DMim] cation.

Reactive collisions between electrons and H_2^+: Dissociative recombination-state-to-state cross section and rates

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Dominant elementary processes in numerous cold ionized gases are dissociative recombination (DR), elastic collisions (EC), vibrational excitation (VE) (inelastic collisions), vibrational de-excitation (VdE) (superelastic collisions), and dissociative excitation [1, 2]:

$$\mathrm{AB}^+(N^+,v^+)+e^- \to \mathrm{A}+\mathrm{B},\ \mathrm{AB}^+(N^{+\prime},v^{+\prime})+e^-,\ \mathrm{A}+\mathrm{B}^++e^- \tag{1}$$

where N^+/v^+ stand for the rotational/vibrational quantum numbers of the cation. Using a stepwise method based on Multichannel Quantum Defect Theory (MQDT), cross sections and rate coefficients have been obtained for reactions induced on H_2^+ [3]. Full rotational computation considerably improves the accuracy of the resulting dissociative recombination cross sections and Maxwell isotropic rate coefficients, for H_2^+. In order to model the very cold environments involved in the chemistry of the early Universe we explored the rotational dependence of DR of HD^+ [4].

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Applications of Reactive Molecular Dynamics on Systems of Astrochemical Interest

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The combination of quantum and classical methodologies is a winning strategy for studying astrochemical phenomena, making it possible to explain telescopic observations. In this work two reactive events are studied in this way, using Reactive dynamics performed using MS-ARMD (Multi-Surface Reactive Dynamics) module present in CHARMM.

The first study regards the formation of O_2 in the Interstellar Media (ISM): this species is considered to be the first reservoir of atomic Oxygen, but there are only few observations that support this hypothesis. Mass-spectrometric observations of comet colas suggest that O_2 is highly correlated with water ice grains. After characterizing the ice structure at ISM temperature regime, 50 K, reactive simulations are performed inside the ice bulk and on top of its surface, using a MRCI Potential Energy Curve to describe O_2. The majority of the reactions are observed within the first 5 ps of simulation, showing the ability of the ice morphology to catalyze the reaction. The scarce interaction between O_2-H_2O has as a consequence a slow relaxation of the newly formed molecule that is estimated on the 100 ns time scale. In the meanwhile it acts as a heat source for the bulky ice increasing the temperature by 15 K during a 5 ns time interval.

In the second example the interaction of fullerene cations with hydrogen ($C_{60}H+$ and $C_{60}H_2^+$) is investigated. Its results are of particular interest both in astrochemical (as can be used to trace the fullerene contributions to the Carbon abundance in the Universe) and technological (due to a high capacity of these species for storing of Hydrogen) fields. The energetic profiles are characterized via B3LYP/6-31g(d) calculations. The chemisorption of one hydrogen atom on a fullerene results in 85.87 kcal/mol stabilization, and consequent possibility of diffusion on top of the adsorbate specie (barrier of 29.45 kcal/mol). Nanosecond MD simulations show the equivalence between the different adsorption sites. In agreement with previous studies on Carbon nanotubes, H_2 bond is broken during the chemisorption.

In both example the use of MS-ARMD technique shows to be important: *ab-inito* levels results can be easily reproduced at a cost of classical simulations. The inclusion of possible diabatic crosses between PES is planned as a further improvement of this module, opening the possibility to study more complicated photochemical processes.

Kinetics of the Reaction Between But-2-yn-1-yl Radical and Molecular Oxygen

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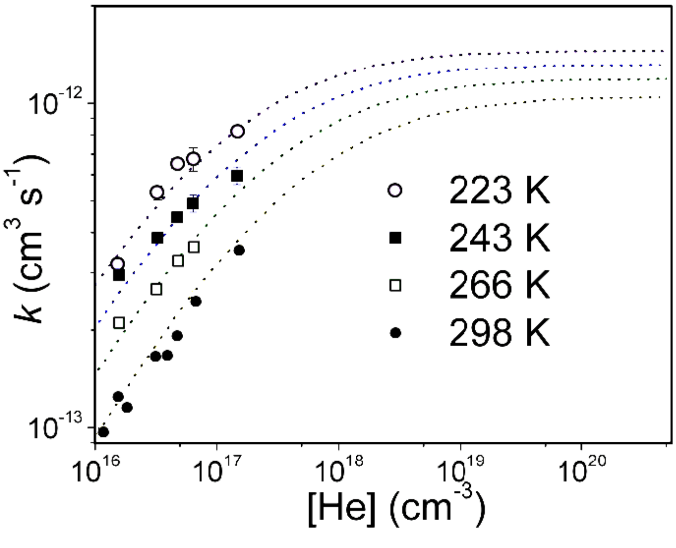
We have directly measured the rate coefficients for the reaction of but-2-yn-1-yl (1-methylpropargyl) radical with molecular oxygen as a function of temperature and pressure. The experiments were performed at low pressures (0.3–5.0 Torr) in the temperature range 223–681 K. The measurements were done in a tubular flow reactor coupled to a laser-photolysis/resonance-gas-discharge-lamp photoionisation mass spectrometer(LP-PIMS). In the temperature range 223–298 K, the rate coefficients exhibited negative temperature dependence and depended on the bath gas concentration. Between temperatures 340 K and 395 K, the radical signal did not decay to signal background, indicating that an equilibrium reaction was taking place. In this temperature range, equilibrium constants were measured. At even higher temperatures ($T > 465$ K), the radical signal again decayed to signal background, allowing us to measure rate coefficients. At high temperatures, the rate coefficients exhibited *positive* temperature dependence and were independent of bath gas concentration. At temperatures above 350 K, we were able to detect a formation signal for ketene.



The experimental results were combined with Master Equation modelling and quantum mechanical calculations. Master Equation modelling requires knowledge about the potential energy surface of the reaction system. By experimentally adjusting two barrier heights in the potential energy surface, the Master Equation model was able to reproduce our experimental results.

Ab initio study of the vibronic spectrum in the $X^2\Pi_u$ electronic state of ion C_6^- : Variational approach

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Over the last three decades carbon chain molecules (C_n) have been of great interest in astrophysics, interstellar and combustion chemistry. It was proposed that they are responsible for the Diffuse Interstellar Bands and they also appear as intermediate species in astrochemical models of reactions involving carbon molecules and polycyclic aromatic hydrocarbons [1]. The aim of the present study is to calculate the vibronic spectrum of linear C_6^- ion in $X^2\Pi_u$ electronic state by means of multireference *ab initio* calculations. Anion C_6^- ion is particularly interesting because in its ground electronic state $X^2\Pi_u$ exhibits the Renner-Teller effect, which along with the spin-orbit coupling complicates its vibrational spectrum.

The corresponding potential energy surfaces are computed by the SA-CASSCF + MRCI method. The vibronic spectrum is computed variationally with a simple model for *ab initio* handling of the Renner-Teller effect (and spin-orbit coupling) in molecules with linear equilibrium geometry and with arbitrary number of nuclei [2]. The program for the variational treatment of Renner-Teller effect in hexatomic molecules is written in Python programming language and the obtained low-bending vibronic spectrum is compared with the one previously calculated using peturbative formulas and based on DFT approach [3].

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The nuclear kinetic energy operator for a triatomic molecule using distance-dependent masses and a single potential energy surface

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Small non-adiabatic effects in nuclear motion can be simulated using effective distance-dependent nuclear masses (DDM). The kinetic energy operator for triatomic molecules with nuclear DDM has been derived. Two different types of nuclear DDM have been considered: (i) distance-dependent masses of the individual nuclei; (ii) reduced distance-dependent masses, which describe the relative motion of the nuclei. By a combination of the chain rule method and the analysis of infinitesimal variations of molecular coordinates, a simple and general technique for the construction of the kinetic energy operator has been proposed. The asymptotic properties of the Hamiltonian have been investigated with respect to the ratio of the electron and proton mass. It has been demonstrated that an ad-hoc introduction of distance-dependent nuclear masses in Cartesian coordinates preserves the total rotational form-invariance of the problem. With the help of Wigner rotation functions, an effective Hamiltonian for nuclear motion can be derived. In the derivation, the effective trinuclear Hamiltonian has been considered. All necessary matrix elements are given in closed analytical form.

Electronic and reactive collisions in edge fusion plasma and interstellar space: Application to H_2^+ and BeD^+

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Dissociative recombination, ro-vibrational excitation, and dissociative excitation of molecular cations with electrons are major elementary process in the kinetics and in the energy balance of astrophysically-relevant ionized media (supernovae, interstellar molecular clouds, planetary ionospheres, early Universe), in edge fusion, and in many other cold media of technological interest.

The Multichannel Quantum Defect Theory (MQDT) [1, 2] has been employed in computing cross sections and Maxwell rate coefficients for reactions induced on HD^+ [3], H_2^+ [4] and BeD^+ [5]. These data are used in the modelling of the kinetics of various cold ionized media of fundamental and applied interest.

Our calculations resulted in good agreement with the CRYRING (Stockholm) and TSR (Heidelberg) magnetic storage ring results, and our approach is permanently improved in order to face the new generation of electrostatic storage rings, such as CSR (Heidelberg), and DESIREE (Stockholm).

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The gas-phase structure of dimethyl peroxide

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There has been a disagreement amongst experimentalists and between experimentalists and theoreticians as to the gas-phase structure of dimethyl peroxide. We have investigated this problem with a high-level MRCI procedure. There can be no doubt anymore that, at the minimum of the potential energy surface, the COOC fragment has a trans-structure. The dynamical structure of the molecule can, however, be different and may be explained by a very slow torsional motion. We have analyzed the dynamical structure using numerical wavefunctions of the torsional motion and a fully optimized potential curve of MP2/aug-cc-pVTZ quality [1]. Computational and all experimental results are shown to be in complete agreement. The problem that has persisted for more than thirty years, highlighted in a recent review article by Oberhammer entitled “Gas phase structures of peroxides: experiments and computational problems" [2], has thus been resolved.

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Potential Energy Surface and Dynamics of the $H_2CO + OH$ reaction

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H_2CO has been known to be one of the most abundant "complex organic molecules" (COMs) found in the interstellar medium (ISM) [1]. That is why it is of paramount importance to understand its chemistry in the conditions found here. In this work we focus on the $H_2CO + OH \rightarrow H_2O + HCO$ reaction for its interesting kinetic behaviour in the low temperature range. Highly accurate *ab initio* calculations carried for this reaction are in good agreement with previous results for the stationary points of the potential [2]. Also, an analytic potential energy surface (PES) for this reaction, obtained by fitting high level *ab initio* points is provided.

Over this PES, quassi-classical dynamics are carried out in order to calculate the reaction rates for the reaction at different temperatures.

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The Probabilistic Potential Energy Surface of a Water Molecule

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To overcome the unfavourable memory cost and the scaling with the system size, the stochastic methods are being used and developed for the calculation of the electronic ground state energies. However, due to the stochastic nature of the calculations, the estimated energies have stochastic errors associated with them. The aim of the project was to probabilistically describe the potential energy surface mapped out by the electronic energies with errors.

To demonstrate the method, the potential energy surface of a single water molecule with a fixed bond angle of 104.48° was fitted probabilistically. The probabilistic potential energy surface aimed to capture the Gaussian errors associated with the complete basis set extrapolation of the coupled cluster energies.

The potential energy surface was based on an analytic potential energy function with five adjustable parameters and the joint probability distribution of the parameters was sampled using Bayesian statistics. The discrepancy function which accounts for the inadequacy of the model was optimised using the Gaussian process regression.

The coupled cluster calculations were done up to CCSDTQ with cc-pCVXZ basis sets. The energies of 24 arbitrarily selected geometries of a water molecule were calculated and the potential energy surface was fitted to the complete basis set limit energies.

The nuclear Schrödinger equation of a water molecule with a fixed bond angle was solved in real space using a grid based method to demonstrate the performance of the fitted potential energy surface and the ability to propagate the sampled errors.

Theoretical studies on the dynamics of the HO + HBr → H_2O + Br reaction

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The reaction HBr + OH → H_2O + Br is an excellent model for complex-forming barrierless bimolecular reactions. Given its central role in the chemistry of atmosphere, many measurements have been conducted over the years. A highly accurate full dimensional *ab initio* potential energy surface has recently been published, so it is now possible to perform reaction dynamical calculations not only for comparison with experiments but also for learning about the details of the reaction's dynamics.

We have calculated reaction rates over a wide range of temperatures and found a strong non-Arrhenius behaviour: the activation energy is negative at low temperatures, zero at about 600 K, and positive at higher temperatures. We suggest that this is caused by a difference in reactivity of different rotational states of the reactants. The reaction cross section first rapidly decreases when the rotational quantum number of the reactants increases, but after reaching a minimum reactivity at around $J=15$, it increases again. The reaction rate was also calculated using the ring polymer molecular dynamics (RPMD) method, which accounts for quantum mechanical effects.

The lifetime of the collision complex was also examined. Multiple algorithms for lifetime calculations were compared, and it was found that the collision complex can not be considered as statistical. This, together with the fact that recrossing over the barrier is non-negligible, shows that transition state theory (TST) should only be applied to this reaction cautiously.

A concept for stimulated proton transfer in 1-(phenyldiazenyl)naphthalen-2-ols: Theory vs. experiment

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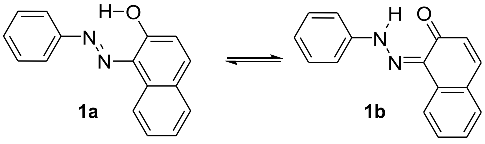
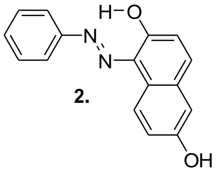
A series of arylazoderivatives of naphthols (**1**-**3**) were studied by means of UV-Vis spectroscopy in different solvents as well as by quantum chemical calculations (MO6-2X/TZVP). Previous studies have shown that 1-(phenyldiazenyl)naphthalene-2-ol (commonly known as Sudan 1 (**1**) exists as a tautomeric mixture. The effect of solvents is minimized by the existing intramolecular hydrogen bond. In general in non-polar solvents such as i-octane and tetrachloromethane **1a** form predominates, whilst in more polar solvents (methanol and formamide) the opposite holds true (**1b**) [1].

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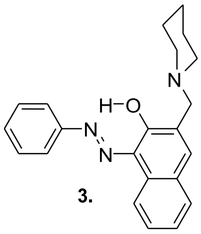
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The aim of the current study is to investigate how structural modifications can influence the tautomeric proton exchange. Structure 2 contains an additional OH-group which is expected to deprotonate easily and to affect the position of the tautomeric equilibrium by changing the electronic properties of the substituent (from OH to O^-).

The implementation of a sidearm in **3** is expected to create a condition for competition between nitrogen from azo group and from piperidine unit for the tautomeric proton. In analogy with already existing tautomeric switching systems, developed by us [2] the use of acids as stimuli for controlling the tautomeric process could be foreseen.

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Towards Modeling Atmospheric Kinetics with Microcanonical Instanton Theory

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Instantons describe the tunneling pathways that dominate molecular dynamics at low temperatures [1]. They provide a link between the classical and quantum mechanical descriptions of chemical kinetics in so called semi-classical transition state theory (SCTST) [2]. This theory is useful because it allows for efficient computation of rate constants in systems where the full quantum description would be too demanding. The new formulation of SCTST takes a microcanonical approach and gives more accurate dynamics near the cross-over temperature, which was a failure of the initial canonical model [1]. Our work aims to use this new SCTST model to calculate cumulative reaction probabilities P(E) for molecular systems and to identify thermal rates k(T) that are valid at all temperatures.

So far, this method has been tested on a model system with coupled degrees of freedom and has produced accurate P(E) values for all energies. We are in the process of applying this formulation to the collinear H + H_2 chemical reaction which has a well-characterized potential energy surface (PES) [3]. Quantum mechanical rate constants for this BKMP surface provide exact solutions for which we can compare our results. Overall, the new SCTST method gives rate constants that are within an order of magnitude of the quantum results and do not diverge at the cross-over temperature. Future work will consist of extending this microcanonical instanton method to calculate thermal rates for interesting atmospheric chemical reactions.

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Efficient thermoelectric response from perovskite interface: role of electronic structure and spin dynamics

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The possibility to grow perovskite oxides layer by layer has lead to the discovery of exotic electronic phenomena. For instance, magnetism has been found at the $CaRuO_3/CaMnO_3$, $BiMnO_3/SrTiO_3$ interfaces [1, 2] and metallicity/super-conductivity at the $LaAlO_3/SrTiO_3$ interface. In magnetic interfaces, induced orbital reconstruction results in modified exchange interaction, and thus substantially affects spin transport and associated dynamics, making them important test-beds for ultrafast manipulation of magnetization and optomagnetism. Interestingly, in between layers of such oxides it is possible to intercalate water molecules; thus both hydrated and non-hydrated phases are feasible. Such interlayer modification through water molecule gating and associated charge transfers [3] often results in enhanced surface reactivity and modified performance. Reports have shown substantial enhancement of the figure of merit of hydrated oxides where the value exceeds 34% in comparison to the non-hydrated phase [4].

In this work we investigate the formation of a $BiMnO_3/SrTiO_3$ interface with a pseudo-halfmetallic state as a possible route to enhance the thermoelectric behaviour of $SrTiO_3$-based oxide materials, using first principles calculations within pseudo-potential-based density functional theory. We study the effects of O vacancy and water molecule on the local electronic structure and demonstrate for n-type interface, a substantially high figure of merit. O vacancy at MnO_2 site shows a positive effect on the thermoelectric performance. We identify the underlying spin transfer through ferromagnetic dynamics in this class of materials, and associate spin currents through the transport channels in response to a thermoelectric bias. We examine how the interplay and dynamics of interface spin plays a major role in the performance of such interfaces. Furthermore we attempt to understand the possibility of intercalation of water molecules in between layers of $BiMnO_3/SrTiO_3$ interface and resulting modification in the electronic structure and transport.

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Combined studies towards the aggregation of trimethine cyanine dyes

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Over the past couple of decades, cyanine dyes have attracted a significant medicinal, biological and biochemical scientific interest, due to their unique photophysical properties, such as their low toxicity and remarkable fluorescence enhancement upon binding to bio-objects. These favourable characteristics, along with their long-wavelength absorption/emission bands and outstandingly high molar extinction coefficients (>100.000 $M^{-1}cm^{-1}$), define the importance of their use as diagnostic tools for the recognition of polynucleotides. Our recent studies [1] revealed that trimethine cyanine dyes AK3-4 and AK3-9 (Figure 1.) possess a highly selective response to specific DNA/RNA sequences. This observation was a consequence of the dye molecules self-association into H-dimers.

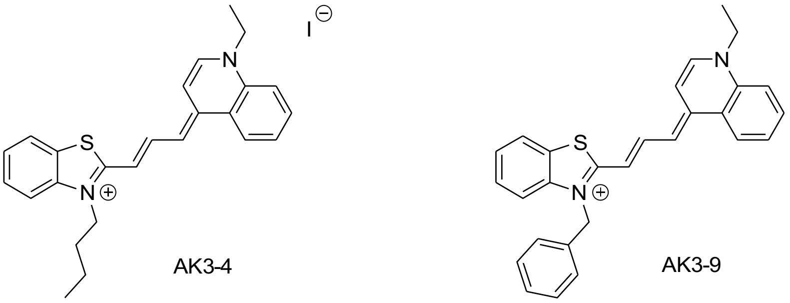

Figure 1. Chemical structures of the compounds under investigation.

Therefore, the former results inspired us to shed more light into the aggregation process of the title compounds. To that end, we employed chemometric analysis [2], crystallographic studies, and quantum chemical calculations, aiming at fully profiling the dimeric species, and the equilibria between the monomers and dimers. In this work our concept was achieved by: (i) the investigation of the photophysical properties of trimethine cyanines in aqueous media adjusting the temperature, the concentration, varying the path length, and introducing a polar aprotic solvent (DMSO); (ii) advanced processing of the experimental data, which provided information on the strength of the dimer assembly; (iii) verification of the experimental results by X-ray crystallography; and (iv) quantum chemical calculations.

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Experimental investigations and theoretical calculations: Molecular rotors based on ground state proton transfer

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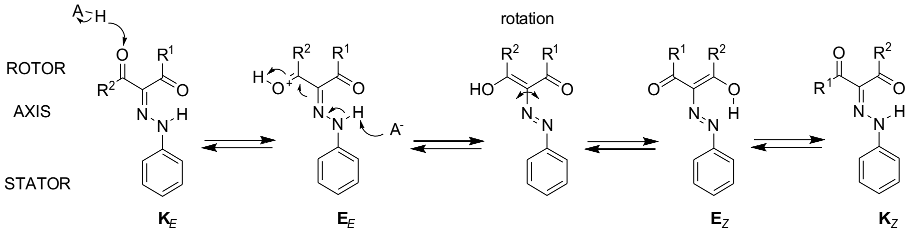
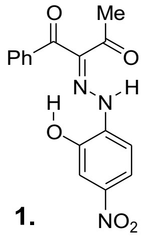
Rotor switches (molecules, containing defined parts: rotor—axis—stator) are one of possible perspective platforms for development of molecular switching systems. They can be used not only as switches, but also as molecular cranes and motors. The action is based on intramolecular, acid-catalysed, proton transfer. 1,2,3-tricarbonyl-2-arylhydrazones represent a typical example for a molecular rotor, which exists in solution as an equilibrated mixture of intramolecularly hydrogen bonded E/Z isomers.



The main problem in this system is the inability to provide conditions to obtain pure isomeric forms in solution (being the main requirement in the design of molecular devices).



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For this reason the aim of the current investigation was to design molecular rotor containing one additional tautomeric functionality (an OH group) in the stator to trace how it will affect the rotation. The possible tautomeric forms and the effects of the solvents and acidity have been investigated theoretically and experimentally. According to quantum chemical calculations (M06-2X/TZVP) in DMSO four tautomeric forms are possible in **1**. However, the spectral measurements (NMR and UV-VIS spectroscopy) and crystallographic data show that only one tautomeric form is presented in solution.

Light-induced dynamics and time-resolved photoelectron imaging of organic radicals

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The ultrafast photodynamics and nonradiative relaxation of organic radicals has been investigated in the framework of the quantum-classical field-induced surface-hopping method (FISH) [1]. This approach allows for the simulation of dynamical processes under the influence of arbitrarily shaped laser fields, providing insights at the molecular level. In order to establish the connection between the theoretical results and experimental data, the dynamics simulations were utilized to calculate the time- and angle-resolved photoelectron imaging spectra based on computing Dyson orbitals for the ionization along the nuclear trajectories [2]. The above described methodology was employed to study the photodynamics in selected organic radicals which are of interest in the context of combustion processes and astrochemistry.

As an example of a small unsaturated system, the 2-methylallyl radical was investigated [3]. Its nonradiative relaxation is characterized by significant involvement of low-lying s- and p-Rydberg states, from which the ground state is nonradiatively reached within several 100 fs, in agreement with experimental results [3]. Returned to the ground state, the main part of the molecules is vibrationally hot but chemically intact. However, as a minor deactivation pathway, also a cyclization reaction has been observed.

When analyzing the complex mechanisms and reactive molecular species in combustion chemistry, one cannot ignore the importance of arylic structures. As a relevant combustion product of toluene found e.g. in diesel fuel, the benzyl radical has been studied [4], as well as its constitutional isomer, the tropyl radical, which may be formed from benzyl in combustion processes. These species exhibit similar absorption patterns involving intense Rydberg states and $\pi\pi^*$ states between 4 and 5 eV, indicating that the two molecules are not only structurally but also electronically closely related. The photodynamics of benzyl is characterized by initial excitation of a $\pi\pi^*$ state, followed by the transition to an s-Rydberg state within about 200 fs [4].

In an attempt to systematize the arylic systems relevant to combustion, the influence of adding a second methylen group to the phenyl ring, leading to para-xylylene, has been investigated. Although a biradical electronic structure could be expected, the system was shown to have predominantly closed-shell character. Light-induced excitation to the lowest-lying intense absorption band at 4.1 eV is followed by fast nonradiative relaxation to the ground state within 500 fs. The excited states involved in this process are mainly of $\pi\pi^*$ character. The characteristics of para-xylylene's electronic structure were compared to related molecules such as ortho-xylylene to discover trends in the reactivity and deactivation pathways of such systems.

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A docking study of potential caspase-3 inhibitor

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The apoptosis is the genetically programmed death of a cell. It is a physiological process during fetal development, in the tumors prevention, and all those processes that affect homeostatic tissue. The process is led by lithic enzymes called caspases which divide themselves into initiator caspases (8, 9, 10) and execution caspases (3, 6, 7). Excessive and uncontrolled activation of the apoptotic process is implicated, for example, in myocardial infarction, cerebral ischemia, Alzheimer's disease and tumors. Therefore execution caspases are an important therapeutic target. Current inhibitors are peptides that covalently bind caspase-3. These are very reactive compounds that are difficult to convey to the active site as they react with other proteins. The purpose of our study is to detect inhibitors that do not covalently link caspase-3.

For this study we use computational molecular docking methods, i.e., we simulate the interaction between the inhibitor and the target in the receptor pocket. Several different levels of theory can be used in the docking process, and previous studies have shown that to obtain accurate prediction of the binding free energy and of the inhibition constant the combined use of quantum mechanic and molecular mechanics methods leads to the best results [1]. The procedure planned for our master thesis comprises different stages, the first of which is checking the docking protocol on different known inhibitors and then applying to candidate molecules potentially capable of inhibiting Caspase-3. The docking protocol can be schematized as follow: protein and ligand preparation, docking – done keeping the protein active site either rigid or flexible. The polarization effect in the binding process should also be taken into consideration. To take into account this effect it was necessary to perform quantum mechanics/molecular mechanics (QM/MM) using a QM polarized ligand docking protocol [2].

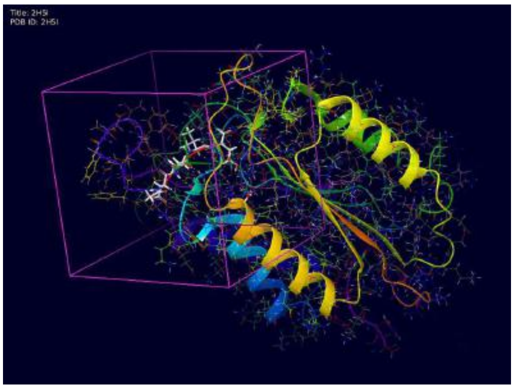

Figure 1: Caspase-3

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Study of mutual neutralization in various collisions

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Modelling of stellar atmospheres requires various detailed and accurate data on different processes such as the mutual neutralization (MN) of cation-anion pairs that can affect atomic species of interest. Indeed, neutralization reactions play an important role in atmospheric and astrophysical environments.

Our merged-beam setup [1] was modified in order to be able to study the mutual neutralization of ^{7}Li$^+$ + ^{2}D$^-$ $\rightarrow$ Li*(nl) + D(1s) and determine which states of the neutral lithium atom are predominant in the total cross section. Preliminary measurements at 7 meV average collision energy have been performed and compared with theoretical calculations [2]. Our apparatus gives access to the branching ratio among accessible neutral channels of the lithium atom and could discriminate between the Li(3p) and Li(3d) channels which are separated by only 44 meV. The measured total cross section of this study agrees with the results of Croft et al. However, our measured branching ratio suggests higher proportions of the 3d (by approximately 6%) and 3s (by approximately 5%) channels at the expense of the Li(3p). Using the MRCI+Q method, new theoretical calculations have been performed which cover various basis sets, i.e., Slater Type Orbitals or even-tempered basis sets, in order to look at their influence on the avoided crossings and the non-adiabatic coupling matrix elements. Thus, using a Landau-Zener methodology, partial and total cross sections have been computed, showing a good agreement with the experimental values.

We present also experimental KER-spectra and absolute mutual neutralization cross section for O$^-$ colliding with N$^+$ and O$^+$ in the 0.005–10 eV energy range. Based on a multi-channel Landau-Zener methodology and an asymptotic model for the ionic-covalent coupling matrix element [3], cross section and branching ratio are also computed. Good agreement is found for the O$^+$ + O$^-$ system, but the excitation channel of an *s*- to a *p*-orbital of N is highly underestimated in the N$^+$ + O$^-$ system unless if this coupling element is modified using atomic results.

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Enhanced photo-electron emission from illuminated phosphorene surface

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Phosphorene is a recently well-studied two-dimensional allotrope of phosphorus and has the great mechanical stability and flexibility of graphene. While, like graphene its carrier mobility is very high, it possesses a structural anisotropy, and demonstrates inherent, direct and appreciable band-gap, which is a function of its number of layers [1]. Thus, under laser irradiation, owing to its high carrier mobility and intrinsic easy tunability of its band structures, there would be coexisting and competing thermionic emission, and photo-excited emission. The intrinsic response of phosphorene can further be altered by its surface engineering through adsorption of molecules on the surface [2] and associated charge transfer and electronic level alignment.

Based on density functional theory calculations, we study the tunable band structure of phosphorene under different physical conditions. From the locations of the electronic bands, and band edges, we estimate the Fermi level, work function, Fermi velocities. Using these results to define the useful parametric space, we establish a formalism to address co-existing and complementing thermionic and photoelectric emission from illuminated phosphorene structures operating at a finite temperature. Taking into account the Fermi-Dirac statistics, the electron energy redistribution due to thermal agitation via laser irradiation, and Fowler's approach of the electron emission, along with Born's approximation to evaluate the tunneling probability, the expressions for the photoelectric and thermionic emission flux have been derived. The cumulative emission flux is observed to be sensitive to the parametric tuning of the laser and material specifications. Based on the parametric analysis, the photoemission flux is noticed to dominate over its coexisting counterpart thermionic emission flux for smaller values of the material work function, surface temperature, and laser wavelength. How the materials work function, and associated emission can be tuned through absorption of molecules on the phosphorene surface is discussed. Our results suggest efficient utilization of phosphorene towards energy conversion schemes applicable to the alternative power sources like photo-detectors and thermionic converters.

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The influence of gold(III) complexes on the Na/K-ATPase activity

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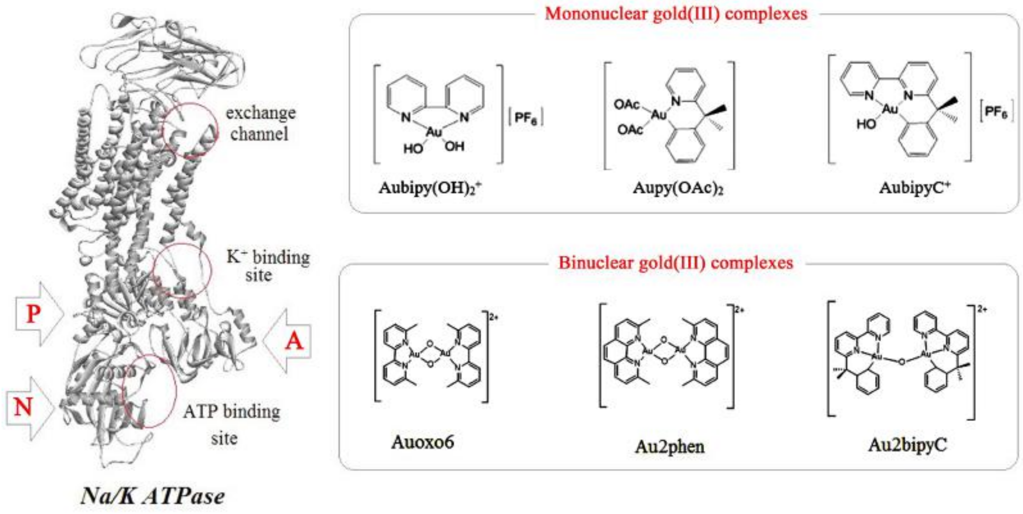
The mechanisms of anticancer action of gold(III) complexes are still largely unexplored but appear to differ profoundly from cisplatin. There are several reports that some anticancer gold(III) complexes inhibit Na/K-ATPase activity.

The docking studies predicted the binding sites for tested mononuclear and oxo-bridged binuclear gold(III) complexes (Figure) in the enzyme structures, in good accordance with the results obtained by experimental measurements. All gold complexes inhibited the enzyme activity in a concentration-dependent manner achieving IC_{50} values in the low micromolar range. The mechanism of Na/K ATPase inhibition by AubipyC and Aubipy(OH) is similar to that of cardiotonic steroids (Na/K exchange channel), while Aupy(OAc)2 appears to block the K^+ binding site. The inhibitory actions of oxo-bridged binuclear complexes are related to E2-P enzyme conformation, by binding to exchange channel and intracellular part between N and P subdomains.



Theoretical study of Co(III) complexes with selenazoles and thiazoles

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The study of thiazole Co(III) complexes has been inspired by a broad range of their biological properties. Comparative investigation of cobalt(III) complexes with (1,3-thiazol-2-yl)hydrazones and their Se analogues has also been done due to possible consequences of S to Se substitution on their biological activity. In order to study electronic characteristics of these isostructural complexes, the singlet excited state energies and HOMO-LUMO energy gap were calculated with time-dependent density functional theory (TD-DFT), using the Polarisable Continuum Model (PCM) for simulation of the effect of dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) solvents. Density functional theory (DFT) calculations provided yet another way to assess the reactivity of the complexes – through the Fukui functions, which point to the reactive centers most susceptible for nucleophilic, electrophilic, or radical attacks. The results showed a very good agreement between experimental and calculated structural, electrochemical, and spectroscopic data [1]. Theoretical calculation provide more detail and some explanation for experimentally observed properties of Co(III) complexes with selenazoles and thiazoles.

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The Nature of C–F Bond in Fluorinated Graphenes

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Fluorinated graphenes show a huge variability of C–F bond characteristics. This means that some C–F bonds are more susceptible for reactions than the others. There are many factors that influence C–F bond characteristics. Firstly, a greater deformation of graphene plane caused by chemisorption of fluorine atom weakens the C–F bond. Secondly, those C–F bonds that violate the π-conjugation of graphene are more susceptible to dissociation. Graphene is a material in which a change on one carbon atom may induce changes in the whole material. By various degrees of fluorination, we can obtain materials with different characteristics. For further applications of fluorinated graphenes it is, therefore, necessary to elucidate their reactivity and its dependence on fluorination pattern.

The isotopic substitution in reactions of ultracold molecules

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Ultracold molecules have been extensively studied in recent years because of wide range of potential applications in quantum information theory, simulations of quantum gases or high-precision spectroscopy [1, 2]. Using statistical assumptions we have obtained theoretical predictions for possibilities of cooling polar molecules by their collisions with atoms. For this purposes, we have studied low-energy reactive collisions corresponding to reactions of the isotopic substitution in ultracold NaK molecules. We have collected spectroscopic, long-range interactions, and nuclear constants; we have calculated exothermictity; we have used the full, effective Hamiltonian to predict the energy levels of the monomers in the electric fields, which are subject to Stark effect. Cross sections were computed used WKB-Langevin model. Our research include statistical distributions of products which may be helpful in explaining the results of the ongoing experiments: so far, only states of reactants were measured.

References

[1] Maykel L. González-Martínez, et al., *Phys. Rev. A*, **90**, 052716 (2014).

[2] Sebastian A. Will, et al., *Phys. Rev. Lett.*, **116**, 225306 (2016).

Water droplets and icicles in condensed phase: molecular dynamics simulations of reverse micelles

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Water droplets and icicles were studied in a system of acetyl trimethylammonium bromide (CTAB). Reverse micelles in chloroform formed above the critical micellar concentration at above- and subzero temperatures.

With an effort to clarify the experimental results, molecular dynamics simulations were used to model the structure of CTAB/water/chloroform reverse micelles of different size. The experiments [1] showed that supercooled micellar water pool becomes unstable upon cooling to relatively high temperatures (253 K), and smaller micelles are formed. Upon freezing to lower temperatures (233 K), micelles become completely frozen and remain intact in the solution. It was estimated that the water pool contains approximately 50 water molecules, which is well below the onset of ice crystal formation, thus the frozen water should be in an amorphous form.

The main aim of this investigation is to explain formation of ice inside of reverse micelles from liquid water in a finite size. Is it really ice or is it supercooled liquid? Why are we loosing a signal for the water in NMR spectra? Is it caused by structural changes or is the micelle unstable?

References

[1] L. Klíčová, E. Muchová, P. Šebej, P. Slavíček, P. Klán, *Langmuir*, **31**, 8284–8293 (2015).

Timetable of the COST Training School

WED, Aug 30 17:00–20:00	Registration after 5:00 PM	

THU, Aug 31 9:00–11:00	Martin Quack (Zürich) Laurent Wiesenfeld (Grenoble) Sonja Grubišić (Belgrade) Stanka Jerosimić (Belgrade)	General Introduction
11:00–11:30	Coffee break	
THU, Aug 31 11:30–13:30	Martin Quack (Zürich)	Standard Model of Atoms and Molecules
13:30–15:00	Lunch break	
THU, Aug 31 15:00–17:00	Ingo Waldmann (London)	Atmosphere
17:00–17:15	Coffee break	
17:15–18:15	Practice	

FRI, Sep 1 9:00–10:00	Ingo Waldmann (contd.)	
10:00–10:30	Coffee break	
FRI, Sep 1 10:30–13:30	Edit Matyus (Budapest)	Pre-Born-Oppenheimer Molecular Structure Theory
13:30–15:00	Lunch break	
FRI, Sep 1 15:00–16:00	Pierre Hily-Blant (Grenoble)	Astrophysical Observations
16:00–16:15	Coffee break	
16:15–17:15	Practice	
18:00–	Poster session, from 6:00 PM	

SAT, Sep 2 9:00–10:00	Pierre Hily-Blant (contd.)	
10:00–10:30	Coffee break	
SAT, Sep 2 10:30–12:30	Helen Fraser (Milton Keynes)	Solid-state Spectroscopy
13:30–15:00	Lunch break	
SAT, Sep 2 15:00–17:00	Gerrit Groenenboom (Nijmegen)	Atomic and Molecular Collisions
17:00–17:15	Coffee break	
17:15–18:15	Practice	
20:00–	Social dinner, at 8:00 PM	
SUN, Sep 3	Sightseeing, Guided tours, etc.	

MON, Sep 4 9:00–11:00	Sergey Yurchenko (London)	Symmetry in Computational Molecular Physics
11:00–11:30	Coffee break	
MON, Sep 4 11:30–13:30	Walther Caminati (Bologna)	Spectroscopy of Weakly Bound Systems
13:30–15:00	Lunch break	
MON, Sep 4 15:00–17:00	Jürgen Troe (Göttingen)	Reactivity
17:00–17:15	Coffee break	
17:15–18:15	Practice	

TUE, Sep 5 9:00–10:00	Jürgen Troe (contd.)	
TUE, Sep 5 10:00–11:30	Albert Rimola (Barcelona)	Solid-state Reactivity
11:30–12:00	Coffee break	
12:00–13:30	Albert Rimola (contd.)	
13:30–15:00	Lunch break	
15:00–16:00	Practice	
16:00–16:15	Coffee break	
TUE, Sep 5 16:15–17:15	Isabelle Kleiner (Paris)	High Resolution Molecular Spectroscopy

WED, Sep 6 9:00–10:00	Isabelle Kleiner (contd.)	
WED, Sep 6 10:00–12:00	Majdi Hochlaf (Paris)	Ions in Astrophysical Media
12:00–12:30	Coffee break	
WED, Sep 6 12:30–13:30	Inga Kamp (Groningen)	Astrophysical Modelling
13:30–15:00	Lunch break	
15:00–16:00	Inga Kamp (contd.)	
16:00–16:15	Coffee break	
16:15–17:15	Practice	
WED, Sep 6 17:15–17:45	Attila Császár (Budapest)	What brings together *Molecules in motion* and *Our Astrochemical History* in this COST Training School
WED, Sep 6 18:00–18:30	Closing Addresses	

Timetable of the
COST Training School
Belgrade, 2017