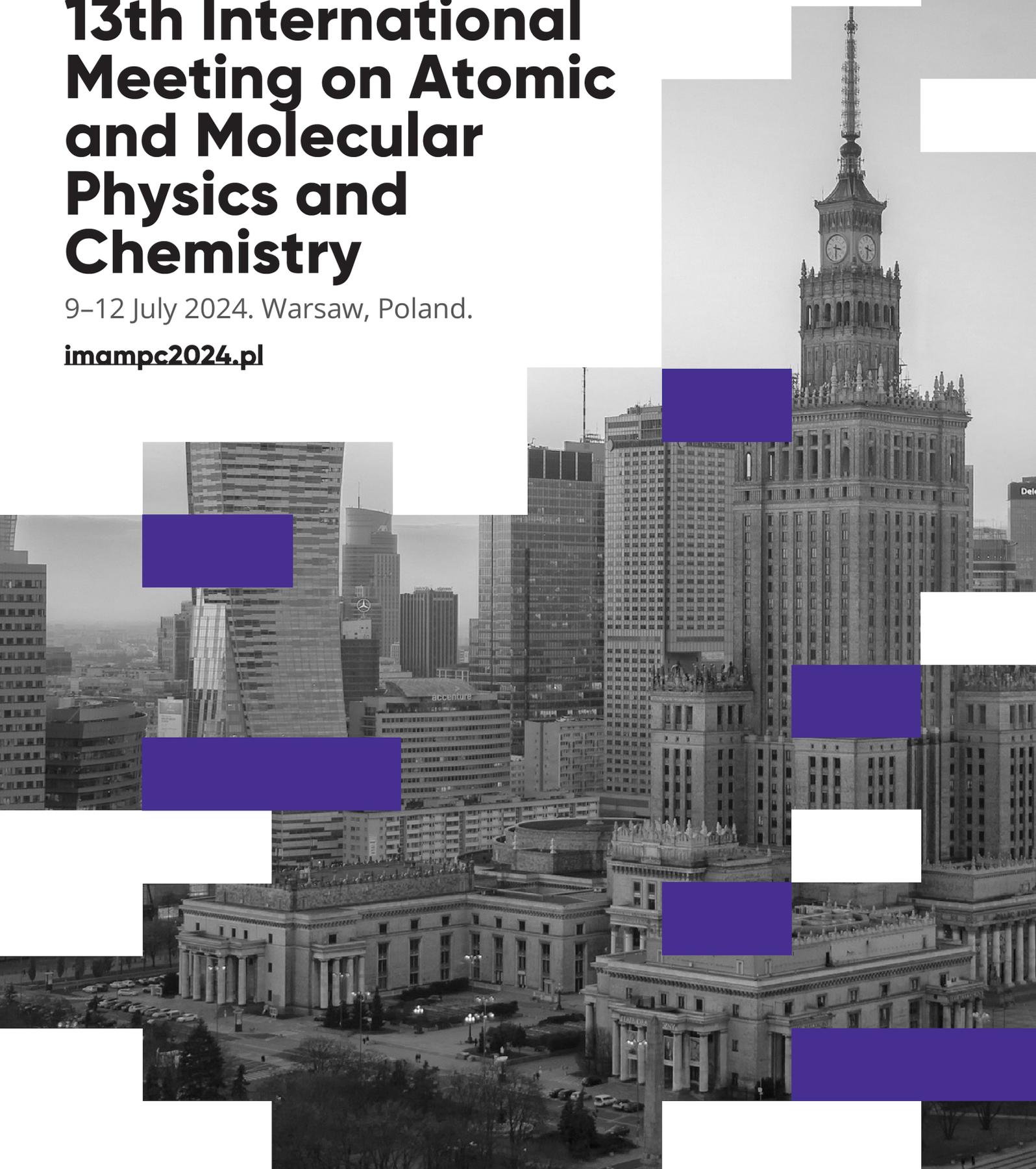


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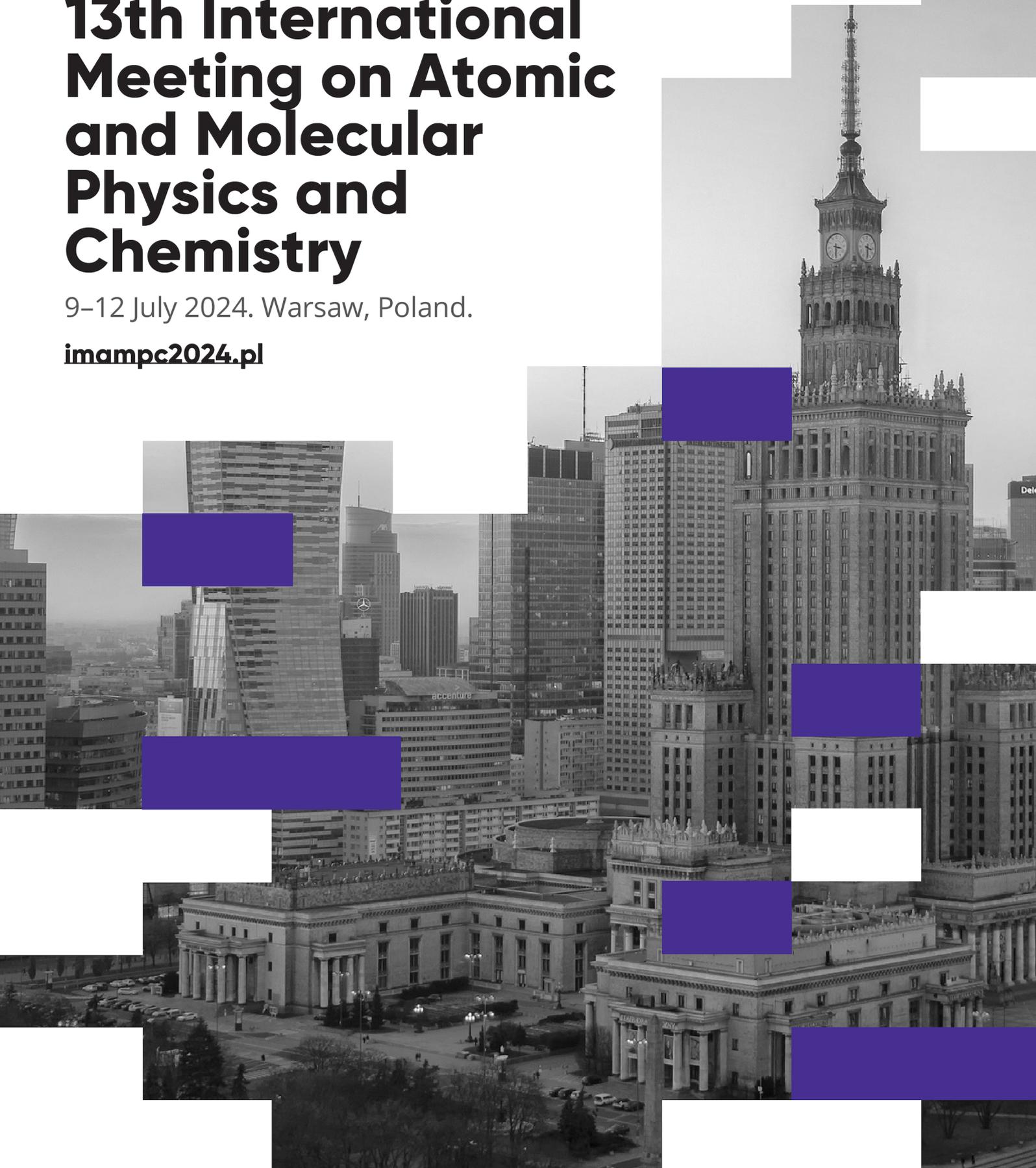


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Presentations

On chiral molecules and on laser cooling diatomic molecules

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Cold Molecules have been an important theme of the ongoing research in the Molecular Physics department at the Fritz Haber Institute (FHI) in Berlin. Up to 2012, our specific contributions to the field have been centred around the manipulation and control of molecular beams with electric fields [1]. In that year I left the FHI to serve a term as president of the Radboud University in Nijmegen, The Netherlands, my *alma mater*. Since my return to the FHI in 2017, we have started new research activities, and here I report on experiments that are currently being performed in our department to study and control chiral molecules and to laser cool and trap diatomic molecules.

In the study of chiral molecules, photo-electron circular dichroism (PECD) - a forward-backward asymmetry in the photoemission from a non-racemic sample induced by circularly polarized light - and microwave three wave mixing (M3WM) have emerged as powerful new techniques during the last decades. PECD has thus far almost exclusively been demonstrated on neutral chiral molecules in the gas phase, using VUV or X-ray ionization sources. We have demonstrated PECD on mass-selected anions with visible and near-UV laser light by recording energy resolved PECD signals for deprotonated 1-indanol anions, using velocity map imaging (VMI) of the photo-detached electrons [2]. The study on anions can elucidate the role of long-range interactions between the departing electron and the remaining core in the PECD process.

In most M3WM experiments that have been performed to date, the microwave signal itself, *i.e.*, the free induction decay, has been used for detection and characterization, and signal intensities have been limited by thermal population differences. We have performed experiments on a jet-cooled beam of 1-indanol, and first deplete selected rotational levels in the electronic and vibrational ground state via optical pumping. Further downstream, three consecutive microwave pulses with mutually perpendicular polarizations and with a well-defined duration and phase are then applied. The population in one of the originally depleted rotational levels is subsequently monitored via laser induced fluorescence detection. This implementation of enantiomer-specific state transfer (ESST) enables full quantum state control of chiral molecules [3].

In our search for "the most ideal molecule" for laser cooling and trapping, that is, yielding the highest densities of ultracold molecular samples, we have identified and focused in on aluminum monofluoride. The AlF molecule has a binding energy of almost 7 eV and vapour pressures of tens of mbar can be reached at temperatures around 1200-1350 °C. Therefore, a bright beam of AlF can be produced, either pulsed or cw. The photon scattering rate on the $A^1\Pi - X^1\Sigma^+$ band around 227 nm is very high, the Franck-Condon matrix is highly diagonal, all Q-lines of a $^1\Pi \leftarrow ^1\Sigma^+$ transition are rotationally closed and the hyperfine splitting in the $^1\Sigma^+$ state is within the natural linewidth of the optical transition. The distance needed for laser slowing a beam of AlF molecules to rest will therefore be only several centimeters and the capture velocity of a magneto-optical trap will be exceptionally large.

We have also started looking in more detail at some of the unusual spectroscopic properties of lanthanide containing diatomic species that are interesting for fundamental physics studies. In YbF we investigated a set of electronic states arising from the excitation of an inner-shell electron. These states can complicate the laser cooling process but offer at the same time new opportunities for fundamental physics studies themselves [4]. Several diatomic lanthanide oxides and fluorides have the peculiar property that their ionization potential is below the lowest dissociation limit. As demonstrated for the particular case of DyO, this feature can be exploited more generally to efficiently produce state-selected, cold molecular ions via auto-ionization.

A status update and a future outlook on the various studies mentioned above will be given.

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Toward quantum-controlled and trapped chiral molecular ions: searching for parity violation with CHDBrI⁺

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The weak force is predicted to break the parity symmetry between left and right-handed chiral molecules. So far searches for the phenomenon have been dominated by neutral molecule experiments. Recently, we began developing a trapped ion version of the search, leveraging the long coherence times. Our candidate molecule, CHDBrI⁺, [1] can be prepared via resonant ionization of CHDBrI to achieve internally cold temperatures that facilitate precision vibrational spectroscopy. Additionally, CHDBrI⁺ is predicted to exhibit a large parity violating (PV) shift of a few Hz for the C-H bend vibrational transition, where the transition's natural linewidth is narrower than the expected shift at ~0.2 Hz according to ab initio calculations [2]. Other transitions such as the C-H stretch are also predicted to have Hz scale PV shifts between enantiomers.

We plan to probe the PV signature in a racemic, mixed-handedness ensemble of trapped CHDBrI⁺, using vibrational Ramsey spectroscopy that is embedded within the 3-wave mixing framework [3]. Our scheme enables differential precision spectroscopy of the same vibrational transition in the two enantiomers by translating the transition frequency information into different two rotational state populations, which need to be detected simultaneously. We are currently developing an ion trap that is integrated with velocity map imaging detector to resolve our molecules' internal state populations by separating photo-fragment velocities.

We will discuss the current status of the experiment.

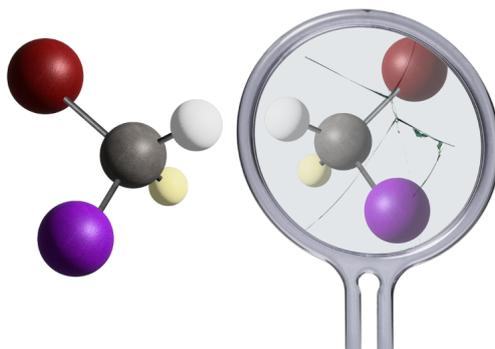


Figure 1: Are chiral molecules mirror images?

Acknowledgments

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Cold molecular hydrogen

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Due to its simplicity, H₂ constitutes a perfect tool for testing fundamental physics: testing quantum electrodynamics, determining fundamental constants, or searching for new physics beyond the Standard Model. H₂ has a huge advantage over the other simple calculable systems of having a set of a few hundred ultralong living rovibrational states, which implies the ultimate limit for testing fundamental physics with H₂ at a relative accuracy level of 10⁻²⁴. The present experiments are far from this limit. I will present our so far results and ongoing projects aimed at exploring this huge potential with cold H₂. I will present our recent H₂ spectra collected with high-finesse optical cavity cooled down to a deep cryogenic temperature (T = 5 K). I will present our new ongoing project aiming at trapping cold H₂.

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Fiber Lasers: Ultrafast Dynamics and Applications

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Ultrafast fiber lasers have remained a subject of ongoing research, continually drawing significant interest from the scientific community for both fundamental and applied purposes. Indeed, mode-locked fiber lasers offer a powerful platform for exploring nonlinear dynamics, resulting from the interplay of nonlinearity, dispersion, and dissipation. While fiber lasers have been known for many years, recent advancements in measurement techniques have enabled their ultrafast characterization [1,2]. These real-time methods have allowed to resolve and then directly observed the ultrafast dynamics of dissipative solitons, which so far have been accessible only through numerical simulations. This progress has deepened our understanding of fiber laser operation complexity.

On the practical side, fiber laser technology has advanced considerably in the last few decades and nowadays, ultrafast fiber lasers are commercially available superseding their solid-state counterparts due to their competitive performances. Their compactness, alignment-free operation, and cost-effectiveness make them highly appealing, especially for industrial applications. However, currently available fiber gain media limit the operation of high-performing fiber lasers mostly to specific spectral regions around 1.0 μm , 1.55 μm or 1.9 μm . There is a growing demand for fiber light sources offering widely tunable wavelengths beyond these regions, crucial for numerous applications like various techniques of nonlinear spectroscopy and microscopy. Despite recent progress in developing such multicolor fiber lasers based on nonlinear effects [3,4], continual research efforts are necessary to meet the evolving demands of advanced applications.

In this talk, we will address two main topics. Firstly, we will offer a concise summary of recent developments in fiber laser dynamics, highlighting various ultrafast nonlinear phenomena discovered experimentally in ultrafast fiber lasers. These include insights into the internal motions of soliton molecules and an exploration of the intricate dynamics of the laser system, illustrated with experimental evidence of double-Hopf-like bifurcation [5].

Secondly, we will present an overview of the latest advancements and discuss innovative concepts for building multicolor tunable light sources, which have been subsequently integrated into Coherent Raman microscopes. We will present some of our results, particularly focusing on widely tunable light sources based on the four-wave-mixing (FWM) nonlinear effect. We will discuss a new method for shifting FWM sidebands by utilizing self-phase-modulation (SPM) of chirped pulses [6].

Acknowledgments

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Ultracold molecules: how not to lose them – A step towards larger molecular quantum computers

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Ultracold molecules, like CaF, provide a powerful platform for quantum computing. These molecules are arranged in a grid and are held in place by an array of lasers, known as an optical tweezer array. To build this up, tweezers are loaded stochastically with 50% probability, which must be followed by rearrangement of these tweezers to create defect-free arrays. However, this can take too long compared to the lifetime of the molecules, which limits the scalability of such molecular quantum computers. Deterministic loading of tweezers with single molecules at 100% success rate is therefore desirable.

We propose a novel scheme to increase the efficiency [1]: repeatedly load laser-cooled molecules into optical tweezers, and transfer them to storage states that are rotationally excited by two additional quanta. We show using quantum scattering calculations that collisional loss of molecules in these storage states is suppressed [2], and a dipolar blockade prevents the accumulation of more than one molecule. This scheme greatly improves the efficiency to 80%, leading to the possibility of creating larger molecular quantum computers.

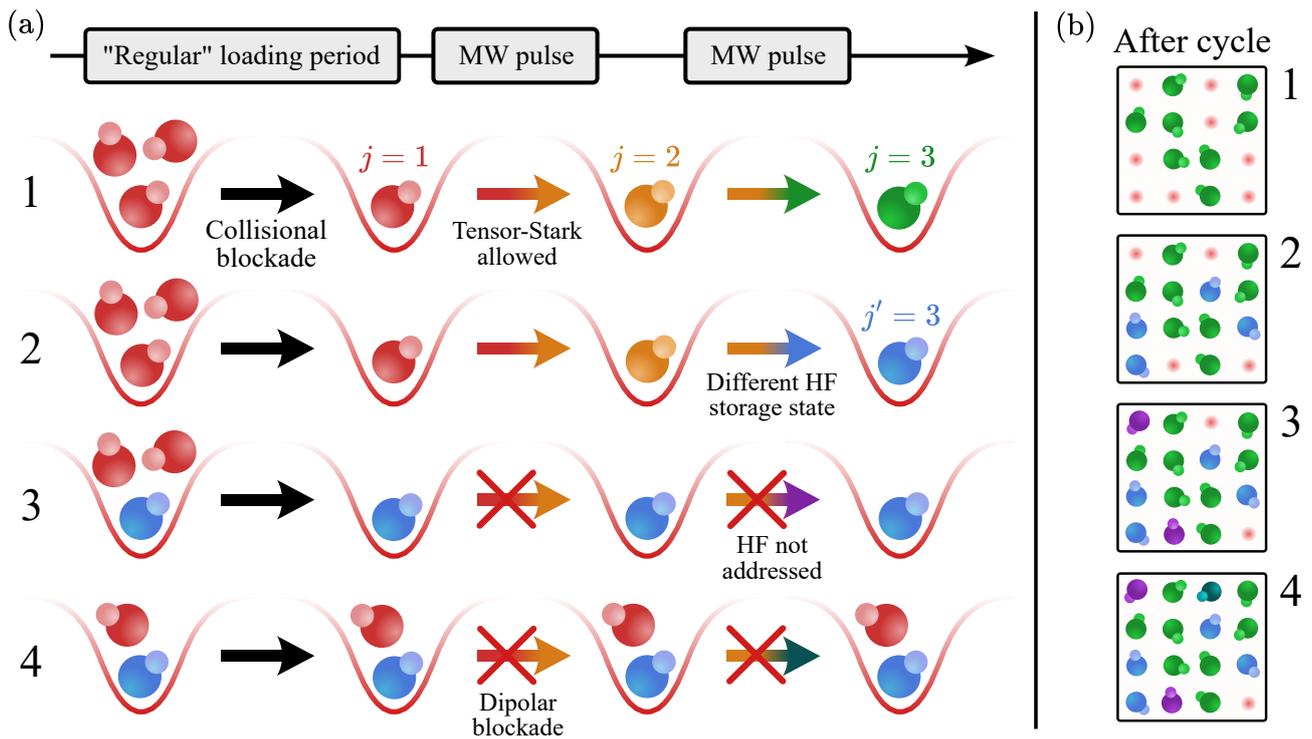


Figure 1: Proposed scheme for deterministic loading of laser-cooled molecules into optical tweezers.

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\mathcal{P}, \mathcal{T} -odd eEDM enhancement factors in Yb-containing diatomic molecules**I.A. Aucar^{1,2*}**¹Van Swinderen Institute for Particle Physics and Gravity, University of Groningen,
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The Standard Model of Particle Physics (SM) describes matter, radiation, and their interactions in terms of elementary particles. Although it provides very accurate predictions for many known physical phenomena, there are still open questions that this model cannot answer. Between them is the origin of the matter-antimatter imbalance and the nature of dark matter. This limitation is enough to think that new physics must exist beyond SM. One way to search for such physics is to investigate new sources of violation of the combined charge conjugation (C) and parity (\mathcal{P}) symmetries, as they are crucial to explain the matter-antimatter asymmetry [1, 2].

Permanent electric dipole moments (EDMs) induce interactions that violate the $C\mathcal{P}$ symmetry, and even though the SM predicts some contributions to them [3], they are not sufficient to explain the matter-antimatter asymmetry. According to the SM, paramagnetic diatomic molecules with spin-zero nuclei are expected to be especially sensitive to two sources of $C\mathcal{P}$ violation, i.e., interactions between electron EDMs (eEDMs) and electromagnetic fields, and parity and time-reversal (\mathcal{T}) violating electron-nucleus scalar-pseudoscalar (\mathcal{P}, \mathcal{T} -eN-SPS) interactions. Since their effects are far from experimental limits, a non-zero detection of $C\mathcal{P}$ violation would be evidence of new physics.

In this work, we present a study of SM-based $C\mathcal{P}$ -odd interactions on molecules. To investigate the eEDM and \mathcal{P}, \mathcal{T} -eN-SPS interactions through precision experiments on molecular systems, two \mathcal{P}, \mathcal{T} -odd enhancement factors (W_d and W_s) must be predicted using accurate *ab-initio* electronic structure computations, as they cannot be measured. Furthermore, choosing the right candidate system has a significant impact on the sensitivity of these effects, since the enhancement factors depend on the molecular electronic structure. We have predicted the values of W_d and W_s for three paramagnetic molecules, YbCu, YbAg and YbAu, with a significant level of theoretical precision. Although no experiments have been done with these molecules so far, very precise calculations of potential energy curves, quadrupole moments, and static electric dipole polarizabilities have recently been performed [4], paving the way to propose these molecules for the search for new physics. We provide recommended values of the enhancement factors, calculated using the four-component Dirac-Coulomb Hamiltonian to deal with relativistic effects and employing the Fock-space coupled-cluster method to include electron correlation effects with high precision. Furthermore, following an approach that has been validated in previous studies [5], we carried out a comprehensive uncertainty analysis in order to assign reliable error bars to the obtained results.

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Spectroscopy of trimers and polarons in ultracold mixtures

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Strongly interacting ultracold gases showcase a rich interplay between universal few-body physics and quantum many-body phenomena. Together with the experimental group of Martin Zwierlein at MIT, we study radiofrequency (rf) association spectra in an ultracold Na-K mixture close to an interspecies Feshbach resonance. In a dilute thermal gas, we do not only observe the formation of diatomic Na-K Feshbach molecules, but also a significant population of weakly bound Na₂K trimer states. When instead the rf-spectrum is taken in a Bose-Einstein condensate, polaron physics plays an important role. Indeed, the background condensate coherently couples the different particle number sectors, leading to the formation of dimer-trimer superpositions! In this talk, I will highlight simple theoretical models which allow us to understand the experimentally observed phenomena, both in the case of the bare trimers and the dimer-trimer superpositions.

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Towards cavity-enhanced two-dimensional infrared spectroscopy of gas-phase molecules

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Time-resolved nonlinear spectroscopy techniques, such as transient absorption spectroscopy and 2D spectroscopy, are routinely used to study ultrafast dynamics [1]. Owing to the limited sensitivity of these techniques, they are most commonly applied to optically thick samples, such as solid and liquid solutions. Using frequency comb lasers and optical cavities one can perform ultrafast optical spectroscopy with high sensitivity, enabling work in dilute gas-phase molecules and clusters. In a recent example, cavity-enhanced transient absorption spectroscopy was used to explain excited-state intramolecular proton transfer in salicylideneaniline and to explain previously observed differences between solution-phase optical measurements and gas-phase photoelectron measurements of this system [2]. These results and advances in generation of high-power optical frequency combs in the mid infrared provide a way to perform cavity-enhanced 2D infrared (CE-2DIR) spectroscopy [3].

CE-2DIR spectroscopy with broadly tunable light sources and ultrabroadband cavities will enable tracking of the evolving couplings between molecular vibrational modes and intramolecular degrees of freedom, for example in hydrogen bond networks of small water clusters. On the other hand, 2DIR spectroscopy can be combined with the high resolution of multicombed spectroscopy [4] or Fourier-transform spectroscopy [5] to enable measurements of the shapes of individual resonances within a single vibrational mode. While collisional damping/dephasing and their correlations with translational motion are most commonly observed in linear spectroscopy, high-resolution 2DIR spectroscopy will shine a new light on the problem. 2DIR spectroscopy separates inhomogeneous from homogeneous broadening, which will allow us to decouple various line-shape effects and more directly probe the underlying physical mechanisms.

In 2DIR liquid-phase spectroscopy of coupled vibrational modes it is common to use sequences of pulse polarizations that eliminate parts of the molecular response and reveal weaker signals or use polarization dependence to constrain fit models. In general, these polarization conditions do not apply to the gas phase since the orientational dynamics in these two phases are vastly different. With the help of spherical tensor decomposition of rovibrational nonlinear response, new polarization conditions can be derived that enable precise control of 2D IR gas-phase spectra [6]. The effect of these conditions will be demonstrated on experimental 2DIR spectra of CO₂ ν_3 mode.

In this talk I will discuss the basic principles of cavity-enhanced ultrafast spectroscopy, our recent experimental and theoretical results, future plans and other potential applications.

Acknowledgments

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Chiral coherent control of electronic population transfer with femtosecond pulses: towards all-optical and highly enantioselective photochemistry

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Enantioselective photochemistry relies on the ability to induce different electronic transitions in left and right handed versions (opposite enantiomers) of a chiral molecule using light. This is challenging because opposite enantiomers share the same energy spectrum and excitation with circularly polarized light is very weakly enantioselective. Highly enantioselective photochemistry is very attractive because it could provide a laser-based alternative to the usual chemical methods for enantiomeric purification and enantioselective synthesis. These are tasks of immense importance in the chemical industry, where the objective is to produce samples with only one of the two enantiomers starting from 50:50 mixtures. Great progress has been achieved recently in the context of coherent control over rotational excitations [1]. Extending such techniques to electronic excitations and shorter time scales is challenging but holds great promise as it could enable enantio-selective control on the femtosecond time scale in the liquid phase. Here we discuss how to tailor the polarization and the spectrum of the light to induce highly enantioselective population transfer between electronic states using intense femtosecond pulses. Our results are supported by an analytical model and ab-initio simulations, and take into account the molecular orientation distribution and the variation of the field across the sample [2].

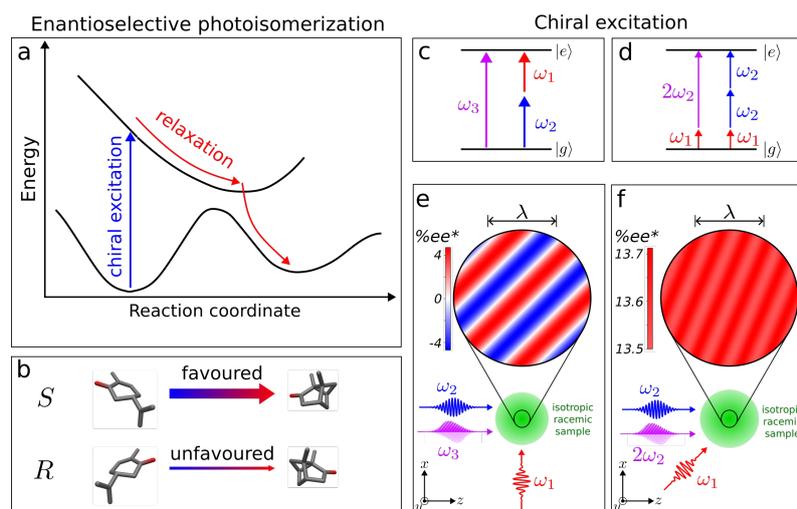


Figure 1: **a**. Photochemistry is triggered by electronic excitation, which often leads to chemical rearrangements (e.g. isomerization or dissociation). **b**. If the electronic excitation is driven by chiral light, the excitation becomes more likely in one of the two enantiomers. **c**. Enantioselective excitation can be achieved via coherent control. The ‘microwave approach’ [1] relies on 1-vs-2 photon interference. It leads to a subwavelength oscillation of the enantioselectivity across the interaction region (see **e**, red and blue describe regions where more S and R enantiomers are excited, respectively), hindering applications in the optical domain. **d**. Such oscillations can be avoided (see **f**, note that enantioselectivity is approximately constant) by careful design in a 2-vs-3 photon interference scheme.

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Parity violation in laser-coolable chiral molecules

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Laser cooling is an excellent method to control molecules for precision measurement, quantum information, many-body physics, and fundamental physics applications. However, asymmetric top molecules (ATMs), due to their complex internal structure, are challenging for experimental manipulation. Although potentially difficult to produce, ultracold ATMs offer many qualitatively unique features useful for a broad range of science [1]. Chiral molecules, from the definition, are classified as ATMs. Precise spectroscopy of such molecules can probe small shifts caused by parity violation effects (PV) in vibrational spectra of right- and left-handed enantiomers[2]. In this study, we investigate the possibility of laser cooling of chiral systems like M-OCHDT, where M is a heavy metal atom, e.g. ytterbium (Yb) [3]. For this purpose, we calculate Frank-Condon factors using quantum chemistry methods. Next, we analyse parity violating potential along selected normal modes with Dirac-Coulomb Hamiltonian. Finally, we estimated PV shifts for selected vibrational transitions by solving the vibrational Schrodinger equation. We found out that for chiral isotopologues of symmetric top molecules, one can keep high values of FCFs and perform effective laser-cooling. In that way, the measurement of PV shifts on ultracold chiral molecules seems to be performed soon by experimentalists.

Acknowledgments

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Ultrafast control over chiral sum-frequency generation

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Just like a chiral glove would either fit our left or right hand, but not both, the two non-superimposable mirror-reflected versions of a chiral molecule (enantiomers) can behave very differently when they interact with another chiral entity, e.g. another chiral molecule or chiral light. Since the majority of molecules supporting biological life are chiral, methods for detecting, quantifying and manipulating molecular chirality are of great importance and interest, particularly in biochemical and pharmaceutical contexts.

Traditional chiral spectroscopy relies on the helix that circularly polarized light draws in space. However, the pitch of this helix is orders of magnitude larger than the molecules, which leads to tiny enantiosensitivity (<0.1%). One can overcome this limitation by creating *synthetic* chiral light, which is *locally* chiral: the tip of the electric-field vector draws a chiral Lissajous figure in time within one optical cycle. The enantiosensitive response of chiral molecules is driven by purely electric-dipole interactions and thus orders of magnitude stronger [1,2]. Here we bring this giant enantiosensitivity (100%) to the perturbative regime by driving a nonlinear interference between sum-frequency generation (SFG) and third-harmonic generation (THG).

SFG [3] is a well-established technique that uses two laser beams with frequencies $\omega_1 \neq \omega_2$, wave vectors \mathbf{k}_1 and \mathbf{k}_2 , and polarizations $\hat{\mathbf{e}}_1$ and $\hat{\mathbf{e}}_2$, to drive a second-order response with frequency $\omega_3 = \omega_1 + \omega_2$ and polarization $\hat{\mathbf{e}}_3 = \hat{\mathbf{e}}_1 \times \hat{\mathbf{e}}_2$, leading to emission of light along $\mathbf{k}_3 = \mathbf{k}_1 + \mathbf{k}_2$. SFG in randomly oriented molecules is symmetry-allowed only if they are chiral, and driven by purely electric-dipole interactions. However, the intensity of SFG is not enantiosensitive – the molecular handedness remains hidden in its *phase* [3].

We have found that, by making the driving field locally chiral, we can achieve full control over the intensity of SFG in randomly oriented chiral molecules [4]. Our setup (Fig. 1a) leads to emission of SFG and THG radiation in the same direction (Fig. 1b), enabling a highly enantiosensitive interference. By controlling the two-color phase delay (Fig. 1a), we control the field's local chirality, and thus the enantiosensitive interference. As a result, we can maximize emission of light at 266nm in one molecular enantiomer while fully quenching it in its mirror twin (Fig. 1c).

Our approach enables ultrafast imaging of molecular chirality via low-order nonlinear processes, which require gentle laser intensities, thus creating exciting opportunities for efficient chiral recognition in the liquid phase, the natural medium of biological molecules, or in amorphous chiral solids.

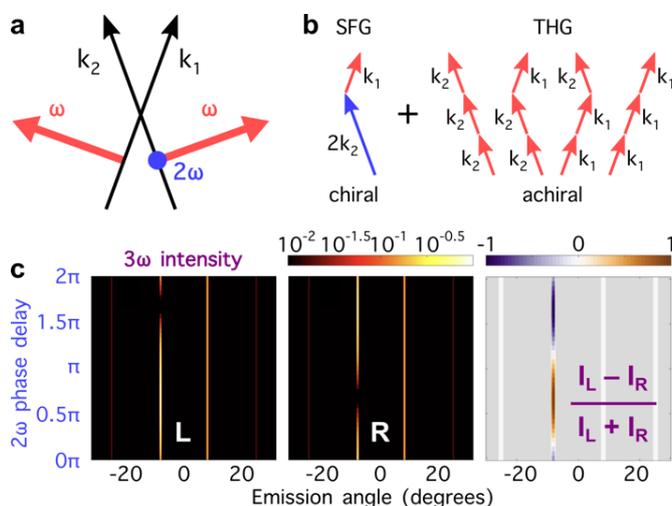


Fig. 1. a, Non-collinear setup combining linearly polarised ω and 2ω colors.

b, Multiphoton diagrams of momentum conservation in chiral SFG (left) and achiral THG (right). The induced polarization associated with SFG has the same amplitude and opposite phase in opposite enantiomers, $\mathbf{P}_{\text{SFG}}^{\text{L}} = -\mathbf{P}_{\text{SFG}}^{\text{R}}$, whereas $\mathbf{P}_{\text{THG}}^{\text{L}} = \mathbf{P}_{\text{THG}}^{\text{R}}$.

c, Intensity emitted from left/right propylene oxide at frequency 3ω (266nm). TDDFT results; laser parameters: $\omega = 0.057\text{au}$. (800nm), opening angle 25° , $I_\omega = 3 \cdot 10^{12}\text{Wcm}^{-2}$, $I_{2\omega} = 7 \cdot 10^{11}\text{Wcm}^{-2}$, $T = 7\text{fs}$; see [4] for additional details.

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Unexpected and delayed fragmentation dynamics of the organometallic ferrocene induced by ion-collision

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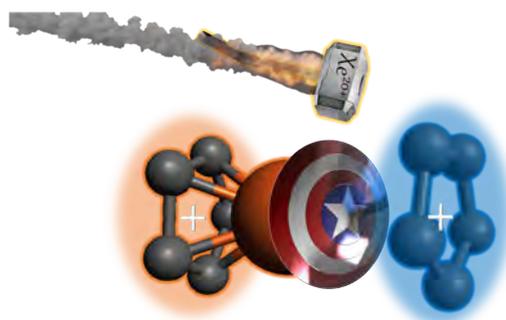
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Metal-ligand bonds are central in coordination chemistry involving a metallic cation bound to several molecular anions. Ferrocene $\text{Fe}(\text{C}_5\text{H}_5)_2$ is the prototype of organometallic complexes, and more specifically of metallocene compounds. Thus, it exhibits the typical stable sandwich structure with the Fe atom between the two C_5H_5 rings. In the ferrocene molecule, the iron atom which has an 18-electron configuration, exists in the +2 oxidation state. Both cyclopentadienyl rings satisfy Huckel's rule for aromatic compounds. Bonds are formed between a Fe^{2+} ion and two C_5H_5^- rings. These bonds are remarkably stable, so they rarely break under normal reaction conditions. Serving as a model system for iron containing organic molecules of biological relevance, ferrocene is also an important molecule for studying fundamental multi-electron processes in complex quantum systems. For instance, organometallic compounds containing ferrocene can enhance conversion efficiency in organic photovoltaic cells. In general, metallocene in general and ferrocene derivatives in particular play a prominent role in synthetic chemistry, nano-medicine and material science thanks to their ubiquitous applications.

Regarding astrochemistry, no ferrocene molecules or ions have been detected in space yet even though several organometallics are observed in the ISM, cosmic clouds and meteorites. Whereas the iron cation Fe^+ (most abundant metal in space) and cyclopentadienyl rings C_5H_5^- were detected and iron-aromatics compounds are suspected. Thus, one could easily imagine that signatures of the presence of ferrocene or larger related species will be evidenced in the future.

In the present study [1], we propose to investigate the dissociation dynamics of ferrocene cations induced by ion collisions, which relies on the transfer of charge and energy in the interaction. For this, we chose the combined experiment/theory approach using multicoincidence mass spectrometry and quantum chemistry calculations. We mainly focus on the fragmentation dynamics of doubly charged ferrocene and show that some fragmentation pathways involve a long-lived excited state leading to metastability of the dication and specific fragmentation dynamics.



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Modelling catalytic processes:

Structure and reactivity of metal clusters in superfluid helium nanodroplets

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Gas-phase metal clusters present a significant opportunity for probing catalytic processes at the molecular level. They afford precise control over the structure, charge, and composition of catalytically active sites, thereby enhancing activity compared to bulk metal due to their small size, high surface-to-volume ratio, and size-dependent physical and chemical properties.[1]

This study focuses on investigating the structure and reactivity of coinage metal clusters (Cu, Ag, Au) formed within multiply-charged superfluid helium nanodroplets to elucidate fundamental catalytic mechanisms. Given the strong influence of active site structure on catalytic activity, we examine the structures of positively and negatively charged metal clusters with sizes up to ten atoms. These clusters are meticulously solvated in helium, and the resulting complexes are analyzed using mass spectrometry. Computational analysis of the most stable complexes aids in estimating cluster structures.[2]

Furthermore, charged clusters are reacted with molecules of interest, such as CO₂ or acetylene, to unravel their size-dependent reactivity. IR photo detachment spectroscopy of helium-tagged complexes[3], play a crucial role in unravelling the intricate details of the cluster-molecule interactions providing direct insights into the structural arrangement and bonding nature of the molecules bound to the clusters.

Our comprehensive understanding of these properties not only advances fundamental knowledge of catalysis at the nanoscale but also provides insights into the rational design of efficient and selective catalysts for chemical transformations.

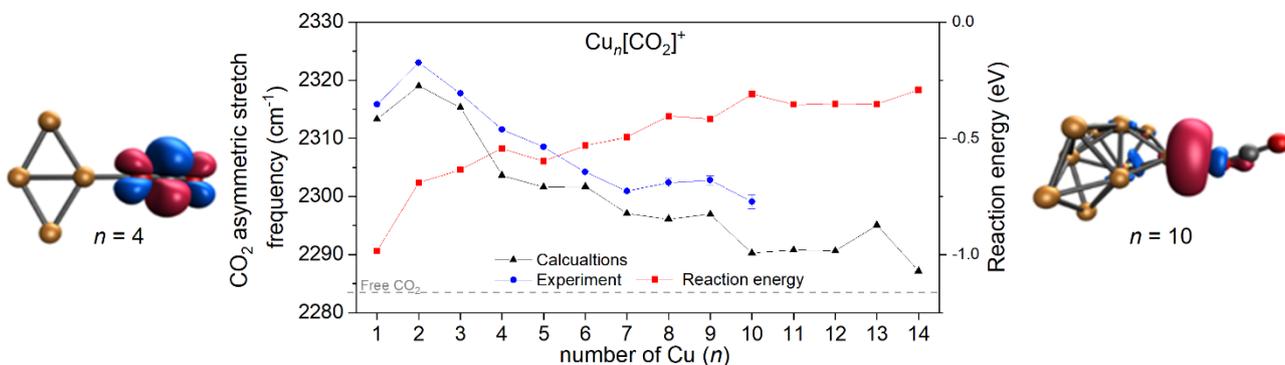


Figure 1: The frequency of the asymmetric stretch vibration of CO₂ bound to copper clusters of different sizes (n), obtained experimentally (blue circles) and computationally (black triangles). The dashed line represents the frequency for free CO₂. Additionally, the binding energy of CO₂ to each cluster is depicted with red squares. Geometric structures for selected configurations are also presented.

Acknowledgments

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Electron-induced fragmentation of MeCpPtMe₃ and implications for focused-beam nanofabrication

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This study aims to understand chemical reactions that are fundamental to the dissociative ionization of trimethyl(methylcyclopentadienyl)platinum(IV) (MeCpPtMe₃), a common precursor of platinum in nanofabrication using focused electron beam. Previous studies probing the electron-driven chemistry of this precursor with surface-science techniques [1, 2] revealed a surprising phenomenon: the primary product released upon electron irradiation is not the methyl radical but rather the methane molecule. The gas-phase study of Engman et al. [3] provided a large number of interesting data, however, it did not address this question.

In the present work, gas-phase MeCpPtMe₃ was irradiated with electrons of controlled energy, and the positive product ions were analyzed in a reflectron time-of-flight mass spectrometer (RTOF). By fitting complex isotope patterns, we identified the contributions of specific fragment ions to peaks in the mass spectrum. Additionally, the appearance energy for the parent molecule and selected groups of peaks corresponding to the loss of one and two methyl groups were determined. To support the experimental data, quantum calculations were performed using the B3LYP method with LANL2DZ basis and Empirical Dispersion correction GD3. The comparison of the experimental and calculated appearance energies suggests that methane and ethane are formed already in the binary collisions of the precursor with electrons at electron energies close to the ionization threshold.

Simulations of the irradiation-driven fragmentation process of MeCpPtMe₃ are also presented, performed using the advanced software package MBN Explorer [4] with a modified irradiation-driven MD methodology. This modification lies in expanding the reactive force field capability to form new bonds in run-time of simulations, resulting in more accurate estimations of the actual chemical processes. The results of the simulations are in good agreement with experimental data and support the hypothesis that rearrangement reactions occur at the ionization threshold.

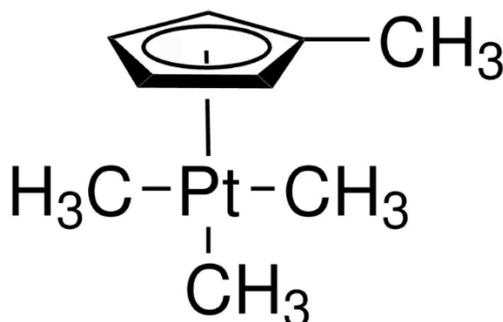


Figure 1: Trimethyl(methylcyclopentadienyl)platinum(IV) (MeCpPtMe₃)

Acknowledgments

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In silico investigation of the photoisomerization dynamics of a first-generation rotary motor

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Light-driven rotary motors are molecules capable of converting light energy into unidirectional intramolecular rotary motion [1]. These artificial molecular motors represent promising mechanical power sources for nanometer-sized devices, called molecular machines, performing specific tasks in a controlled manner. Among the most promising light-driven rotary motors are the chiral overcrowded alkenes introduced by the Nobel laureate Feringa and coworkers. In these molecular motors, the unidirectional rotary movement is achieved through a cycle consisting of four consecutive steps (Figure 1): two cis-trans photoisomerization reactions of the central double bond (which is the axle of rotation) and two thermal helix inversion steps. While the thermal steps of the rotation cycle are now rather well known, the photoisomerization reactions of overcrowded alkene-based motors are not yet fully understood. Here, we present a computational investigation of the photochemical behaviour of a prototypical first-generation molecular motor (Figure 1), recently studied by spectroscopic techniques [2, 3]. In particular, we performed quantum chemical calculations with the mixed-reference spin-flip TDDFT method [4] and nonadiabatic excited-state dynamics simulations, using the surface hopping methodology [5] and a reparametrized semiempirical electronic structure technique. In line with the spectroscopic findings [2, 3], our simulations show that the photoisomerization pathways in our investigated motor involve the crossing of potential energy barriers in the S_1 excited state. Moreover, our study indicates that the high yields of forward photoisomerization in this motor are mainly due to the favorable shape of the ground-state (S_0) potential energy surface in the region where the $S_1 \rightarrow S_0$ nonadiabatic transition takes place. These results allow to better understand the experimental observations for our investigated motor, as well as to contribute to the development of general rules connecting the chemical structure of a motor with its photochemical behaviour.

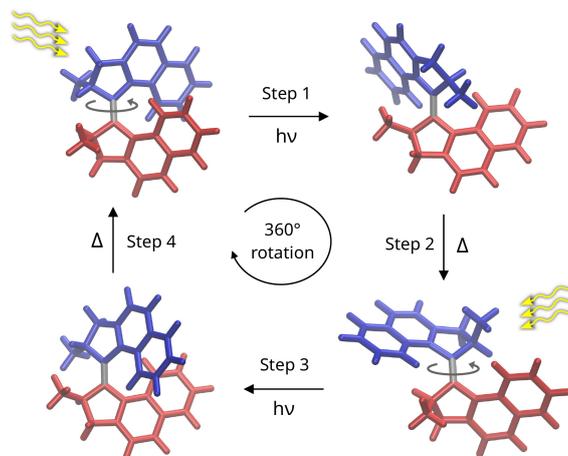


Figure 1: Photocycle of unidirectional rotation in a prototypical first-generation molecular motor.

Acknowledgments

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Interactions between electron-deficient systems. Interesting peculiarities

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The elements of the 2nd and 13th groups of the periodic table have a very peculiar chemistry in the gas phase, closely related to its electron deficient character. This character is reflected in their bonding capacity as Lewis acids. Although extensive information on beryllium-, magnesium- and triel-bonds is available, much less is known about the nature and characteristics of the bonding between electron-deficient compounds. In this lecture we will present a fairly systematic study of the clustering ability of alkaline-earth and triel derivatives with other electron-deficient compounds, including triel-alkaline-earth [1], triel-triel [2] and alkaline earth-alkaline earth [3] interactions. We will show, that even if triel and beryllium bonds are usually rather strong, dispersive effects may become dominant. Furthermore, in most cases the rehybridization of the triel and alkaline earth element, due to its high energetic cost, can dictate the relative stability of the cluster. Replacing the metalloid boron with the metallic aluminum, in the gas phase, leads to subtle differences in the stability trends of the *n*-mers, which are closely related to the ability of the triel atom to be pentacoordinated. Among the electrodeficient-electrodeficient complexes those stabilized by direct Be⋯B interactions are particularly interesting [4]. In these unusual bonds, the B derivative acts systematically as a Lewis base; but what is really amazing, is that the binding energies can reach values above 200 or 250 kJ·mol⁻¹. Finally, we will show that the interactions of electrodeficient-electrodeficient clusters with conventional Lewis bases, allow to modulate the intrinsic reactivity of the latter, to the point that they can behave as very strong proton donors.

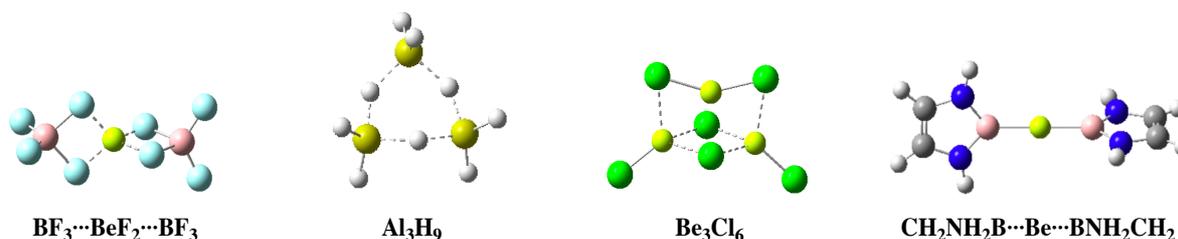


Figure 1: Examples of triel-alkaline-earth, triel-triel, alkaline earth-alkaline earth clusters and complexes stabilized by direct Be⋯B interactions.

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ATMOSPEC: Automated computational workflow for ab initio photoabsorption cross-sections

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A molecule's UV/Vis spectrum is a basic observable that determines its photophysical and photochemical properties. While conceptually simple, its accurate experimental determination for gas phase molecules is non-trivial, especially for short-lived intermediates. Accurate ab initio modelling of absorption cross-section is thus highly valuable.

We have recently shown that the Nuclear Ensemble Approach (NEA) offers a pragmatic route for UV spectra of Volatile Organic Compounds (VOCs).[1] Nevertheless, computing these spectra is a non-trivial exercise, requiring several steps, which hinders its adoption by non-experts. Here, I will present an initial version of ATMOSPEC[2], a user-friendly software package that implements a robust and automated protocol to determine absorption cross sections of molecules. The package utilizes automatic conformer sampling and ab initio calculations to generate the NEA spectrum on top of a harmonic Wigner distribution. The graphical interface is provided using the AiiDALab framework[5] as a web application. The ab initio calculations may utilize different levels of theory, such as TDDFT, ADC2 and EOM-CCSD, as implemented in the ORCA package[3] and are orchestrated by the AiiDA workflow manager.[4] I will also discuss future work aiming to massively improve performance by utilizing GPUs and machine learning techniques.



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Photoinduced quantum dynamics of the KRb multi-coupled electronic states

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Quantum dynamics is a growing discipline at the interface of chemistry, physics, and materials science [1, 2]. It allows us to study the behavior of objects in a way that emphasizes the quantum nature of their evolution in various time scales (from seconds to attoseconds). Quantum dynamics simulations are indispensable for investigating chemical reactions, field-atom and field-molecule interactions, cold physics, and cold chemistry, including cold collisions or even quantum computing areas. The particular emphasis is focused on exploring the photoinduced dynamics of breaking (dissociation) and creating (association) of the chemical bonds in the molecular systems.

In the present work, we focus on the theoretical time-dependent descriptions of the photoinduced processes in the system of 10 multi-coupled electronic states ($1-3^1\Sigma^+$, $1-3^3\Sigma^+$, $1-2^1\Pi$, and $1-2^3\Pi$) of the KRb molecule (Fig. 1A). We investigate the photoinduced processes based on the high accuracy rovibrational and electronic structure of the KRb molecule [3], appropriate permanent and transition dipole moment functions (Fig. 1B) [3], and various types of coupling matrix elements, like nonadiabatic couplings or spin-orbit couplings (Fig. 1C) [4]. In the quantum simulations, we use our newly developed quantum dynamics code [5] to study the nano- to femtoseconds time-scale dynamics of multiple coupled electronic states of KRb under the influence of an arbitrary time-dependent external field to investigate laser-driven processes like association and dissociation.

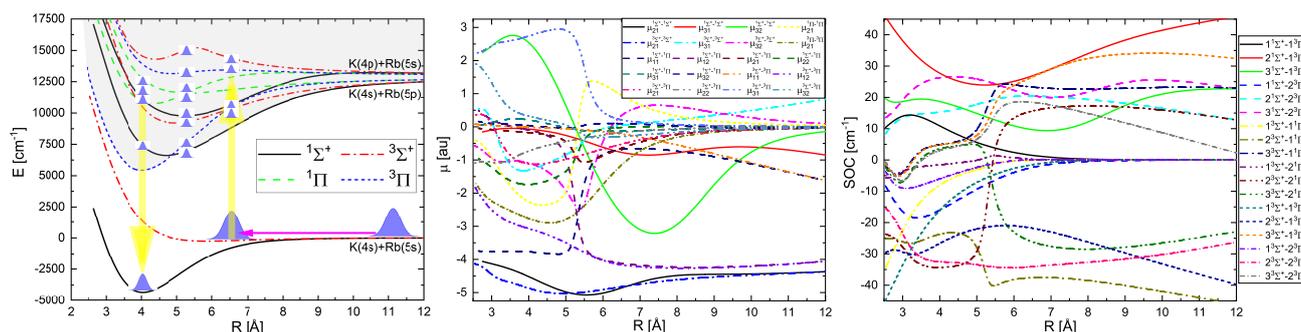


Figure 1: (A - left panel) The high-accuracy potential energy curves of the KRb molecule corresponding to the three lowest-lying atomic asymptotes. (B - middle panel) The electronic transition dipole moment functions μ . (C - right panel) The spin-orbit coupling matrix elements ξ .

Acknowledgments

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Processes of peptide bond formation and degradation in linear and cyclic dipeptides

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The investigation of peptide bond formation/disruption in small polypeptides can be very intriguing and it is relevant for different scientific and practical purposes, from the study of the origin of life to the development of self-assembled nanostructures. These processes can be triggered by activating agents or energetic processing, such as collision with heavy ions, and may have provided prebiotically plausible pathways for the survival and/or formation of polypeptides.

For these reasons in recent years we undertook the investigation of peptide bond formation and degradation in a series of cyclic and linear dipeptides, combining different experimental techniques with accurate theoretical simulations. In this work the main results from recent studies with synchrotron radiation and preliminary experiments with heavy ions will be presented.

We performed photoionization and photofragmentation studies in the gas-phase via Time-Of-Flight Mass Spectrometry (TOF-MS), Photoelectron Spectroscopy (PES) and Photoelectron-Photoion Coincidence (PEPICO) spectroscopy on cyclic dipeptides containing aromatic amino acids. Then, the comparison with accurate molecular dynamics simulations allowed us to investigate the state-selected fragmentation and electronic density distribution of these species [1]. Moreover, we found evidences of peculiar mechanisms triggered by a variation of the temperature and VUV photon irradiation in other linear and cyclic dipeptides. These mechanisms are the thermally-induced cyclization of a linear species in the condensed-phase [2] and the “smart” fragmentation of a cyclic dipeptide in the gas-phase which may lead to its reconstruction or trigger and support a polymerization process [3].

Finally, the preliminary results on recent studies “beyond the isolated molecule” will be presented. By the collaboration among different groups and institutions/facilities (CNR-ISM, Universidad Autónoma de Madrid, Stockholm University, Elettra, GANIL) we performed ion collisions experiments on films and clusters of a series of linear and cyclic dipeptides. The aims of these experiments are to investigate: i) the radioresistance and molecular reactivity in films of aminoacidic compounds and ii) the possible cyclization/polymerization processes in the gas-phase in case of molecular clusters.

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Chemically accurate free energies from hybrid QM:QM DFT-MD simulations

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I will present the recently developed MD-based theoretical methodology (DOS-P) to compute chemically accurate free energies [1] using the adsorption of ethanol in H-MFI zeolite as a test case. While sampling the free energy surface by Molecular Dynamics (MD) or Monte Carlo simulations requires respectively long simulations (50 ps up to 1ns) and/or millions of energy calculations, DOS-P allows obtaining well-converged enthalpies, entropies, and free energies of adsorption from vibrational partition functions based on the (anharmonic) VDOS signal using a set of short trajectories (maximum 3ps).

The reduced computational cost of DOS-P enables the use of QM:QM MD simulations in which an accurate high-level quantum mechanics description is used for the reactive sub-system, together with a low-level periodic quantum mechanics description for the rest (PBE+D2).

In the talk, I will critically compare the adsorption geometry, enthalpy, entropies, and free energy computed at the B3LYP+D2:PBE+D2 level of theory with the PBE+D2 data and the experimental values.

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Quantum-chemical studies of photoinduced electron transfer in nucleic acids

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Photoinduced electron transfer is a fundamental element of various processes involving nucleic acids, such as the formation of photodamage [1] and their self-repair [2]. Despite years of research, some aspects influencing this process are still poorly understood. One of these aspects is the role played by π - π stacking interactions between neighboring nitrogen bases in this process [3]. Another aspect is the influence of the neighbouring bases, adjacent to the pair in which the charge transfer takes place, on the stability of charge-transfer states. It is therefore important to investigate these aspects using theoretical methods. In this work, electron transfer properties within several tri- and tetranucleotides were examined. The sequences tested included AGG, GGA, AGGG, GGGA, AGAG, and GAGA oligonucleotides. The vertical excitation energies as well as the adiabatic excitation energies of charge transfer and locally excited S1 states were calculated using the time-dependent DFT methodology, with the CAM-B3LYP functional. Additionally, a novel geometry-based algorithm was developed and successfully implemented to calculate the "stacking score" between nucleobases. The results suggest that the π - π stacking between nucleotide bases and the subsequent geometry of the oligonucleotide can have a strong influence on the energies of the guanine-adenine charge transfer states, thereby influencing the ability of the oligonucleotide to undergo such processes as self-repair process, using the sequential electron transfer mechanism.

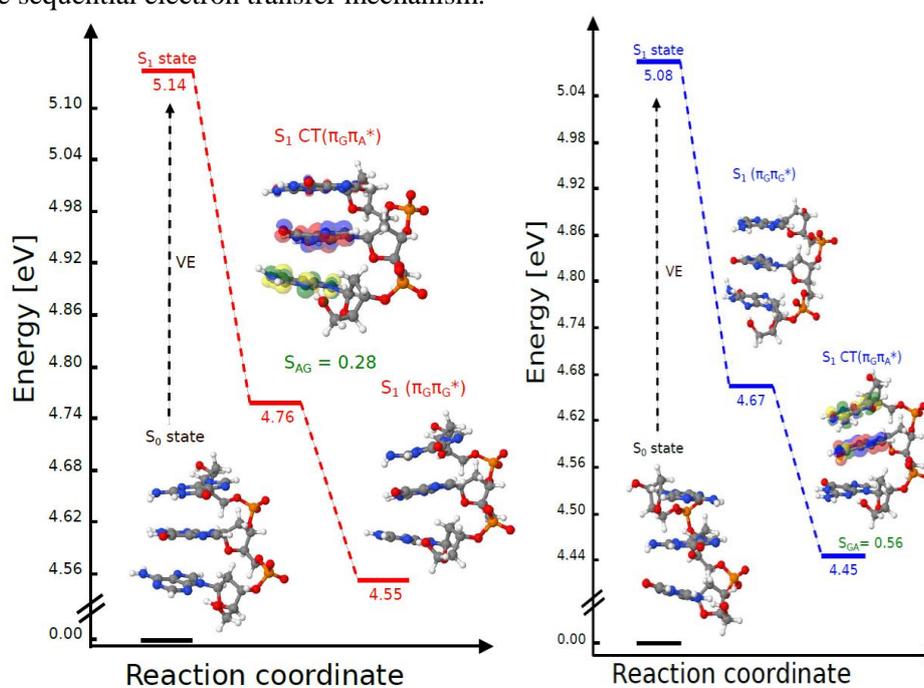


Figure 1: Possible relaxation pathways for AGG (left) and GGA (right) oligonucleotides. The stacking score value between G and A nucleobases (S_{AG}) is also shown.

Acknowledgments

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The results presented in this work were created using resources provided by Wrocław Centre for Networking and Supercomputing (WCSS).

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Joint experimental and theoretical study on electron scattering from propionaldehyde (C_2H_5CHO) molecule

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The desire to understand the processes incorporating simple organic molecules, basic building blocks of life, in extraterrestrial conditions in many cases requires comprehensive knowledge of the electron-molecule interaction. As one example, glycine, the simplest amino acid, was discovered to be a product of electron irradiation of ammonia and deuterated acetic acid molecules at extremely low temperatures [1]. Many others similar examples of such astrochemical studies can be found in the literature (see eg. [2], [3]).

Propionaldehyde, one of the simplest aliphatic aldehydes, is quite abundant in space, as it has been detected on the comet 67P/Churyumov-Gerasimenko, Murchison meteorite [4] and in interstellar molecular clouds [5]. Therefore, detailed data related to the interaction of electrons with this molecule may be very valuable.

In this study we measured the absolute *grand*-total cross section (TCS) for low-energy (0- 300 eV) electron scattering on propionaldehyde molecule using an electrostatic electron spectrometer [6] operating in the linear transmission mode [2]. Additionally, calculations of the elastic scattering cross section (ECS) were carried out using R-matrix method [7] with applied Born correction [8] within static-exchange (SE) and static-exchange with polarization (SEP) approximations. Figure 1 shows a comparison of experimental data and calculation results.

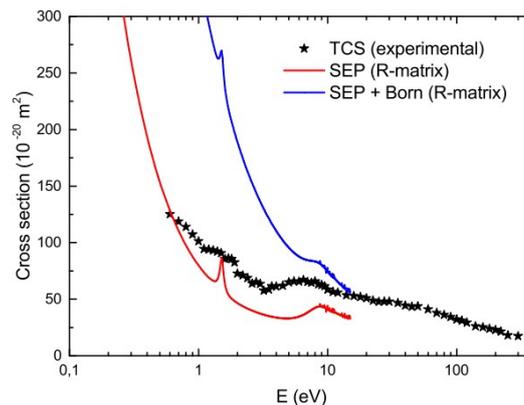


Figure 1: Comparison of measured total cross section with calculated elastic cross section.

Acknowledgments

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Sulfur reactivity on ice: a theoretical study

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Introduction: Astrochemistry is a multidisciplinary subject that allows us to investigate the formation and destruction routes of molecules found in extraterrestrial environments, such as planets and moons, comets or the interstellar medium (ISM) [1].

Many sulfur species (H_2S , OCS , SO , S_2 , SO_2 and CS_2) have been identified in the coma of the comet 67P/Churyumov-Grasimenko [2] and some have been proposed as the main carriers of S, such as H_2S and OCS , condensed in the icy mantles of interstellar dust grains.

In this contribution, we present a theoretical investigation of the reactions involving atomic sulphur, in its first electronically excited state ^1D , with water ice.

$\text{S}(^1\text{D})$ is produced by UV-induced photodissociation of precursor molecules, such as OCS [3] and CS_2 [4], which are relatively abundant in extraterrestrial environments.

As soon as $\text{S}(^1\text{D})$ is formed on the ice surface, it will be able to react with water. According to our calculations, the reaction proceeds either by $\text{S}(^1\text{D})$ addition to one of the lone pairs of O or via insertion into one of the two O-H bonds. Two different intermediates can be formed: H_2OS and HOSH .

Theoretical method: We first characterized the gas-phase potential energy surface (PES) of the reaction $\text{S}(^1\text{D}) + \text{H}_2\text{O}$. We used the GAUSSIAN09 program package [5] to optimize all stationary points of the PES at the DFT level of theory, using the ma-TZVP [6] basis set. Subsequently, we performed single-point calculations at the CCSD(T) level of theory [7] in order to refine the energy of each stationary point. We then optimized the geometry of an 18- H_2O cluster ice surface at DFT level of theory. After each DFT geometry optimization, we employed the Orca software [8] to refine all energies of the 18- $\text{H}_2\text{O} + \text{S}(^1\text{D})$ structures by using the DLPNO-CCSD(T) method [9].

Results: We computed the PES of the reaction $\text{S}(^1\text{D}) + \text{H}_2\text{O}$ in gas phase and subsequently compared the results with the same reaction taking place on an 18- H_2O cluster ice surface model. The energetic profile of the same reaction on ice proves how water molecules act as catalysts by actively participating in the H transfer process (which is the one responsible, for example, of the conversion of H_2OS to HSOH), lowering the energy barriers compared to the analogous gas phase steps. According to our results, when $\text{S}(^1\text{D})$ is formed by the dissociation of its precursors on the surface of water ice, it is immediately converted into H_2OS , H_2SO and HOSH . The chemistry of this excited species closely resembles that of $\text{O}(^1\text{D})$, recently investigated in interstellar ice analogues [10].

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Near-IR absorption and radiative cooling of naphthalene dimer $(C_{10}H_8)_2^+$ in electrostatic ion beam storage rings

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Polycyclic Aromatic Hydrocarbons (PAHs) are a class of organic molecules based on two or more fused hexagonal aromatic carbon rings with hydrogen atoms attached at their outer rims. They are found and formed in a wide variety of environments. PAHs are thought to play a significant role in the physics and chemistry of the interstellar medium. In addition, they are believed to be responsible for the IR emission features that characterize the spectra of numerous galactic and extragalactic sources [1]. Ionized dimers of PAHs have also been shown to be attractive candidates to carry other spectral features such as the extended red emission [2]. Since ionized PAH clusters of larger sizes often have a dimer or trimer core, the present study is a step towards a better understanding of elementary processes in PAH cluster fragmentation via excited states. The survival of PAH clusters is governed by the competition between dissociation and radiative cooling [3]. In contrast to several previously investigated PAH-monomers, which undergo fast radiative cooling via recurrent fluorescence [4][5], we measured much slower cooling rates of naphthalene dimer cation which is in line with a cooling mechanism primarily driven by IR vibrational emission. The radiative cooling of $(C_{10}H_8)_2^+$ was studied experimentally using action spectroscopy in two different electrostatic ion-beam storage rings - DESIREE in Stockholm and Mini-Ring in Lyon. We simulated the absorption spectra and determined the relation between the charged resonance (CR) band position and the ion temperature. By combining these results with the statistical model for the radiative cooling, we demonstrate how the observed blue shift of the CR band as a function of the storage time can be used to monitor the cooling rate [6].

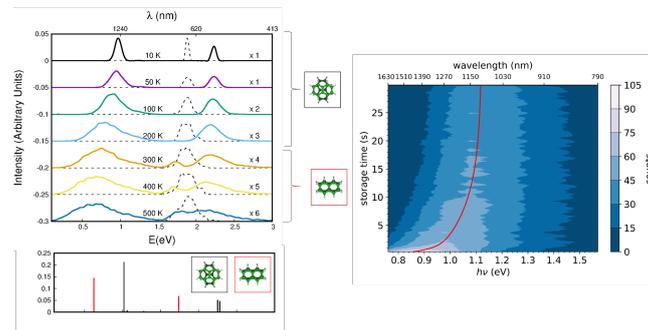


Figure 1: Left: Theoretical absorption spectra for $(C_{10}H_8)_2^+$ (colored) and monomer (dashed) as a function of the temperature. The bottom panel displays energies of the vertical absorption bands for parallel-twisted (black) and parallel-superposed (red) geometries. Right: Action spectra of laser-induced naphthalene-dimer dissociation. The intensity, varying with storage time before laser firing and laser photon energy, is represented by the color scale on the right. The red line depicts an exponential fit of the CR band position at maximum intensity, illustrating the shift of the CR band position over storage time.

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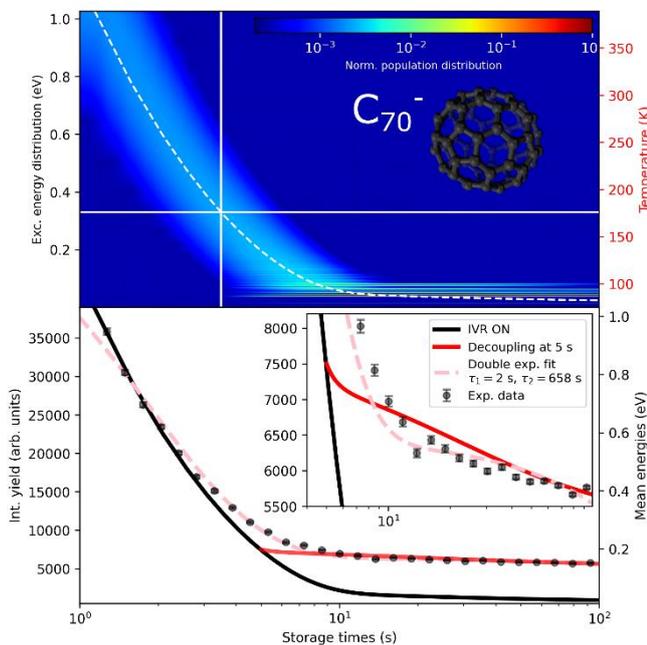
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Ultraslow cooling dynamics of C_{70}^-

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Astronomical observations and gas phase spectroscopic studies have unambiguously shown that fullerenes exist throughout the interstellar medium (ISM) [1]. To advance in the understanding of their survival and abundances in space, it is necessary to study the competition between different relaxation processes and how they depend on the initial internal energy distribution (IED) and time. On longer time scales exceeding milliseconds, the cooling dynamics is dominated by infrared vibrational emission [2]. This ultra-slow dynamic can now be studied with the development of cryogenic ion-beam storage devices. One interesting phenomenon occurring on these time scales is the intricate flow of internal energy over accessible vibrational degrees of freedom. This so-called Intramolecular Vibrational Redistribution (IVR) has been extensively studied both theoretically [3,4] and experimentally [5,6]. Understanding how this energy redistributes could shed insights into the cooling dynamics in later stages of cooling. Here, we have studied the cooling dynamics of internally



hot C_{70}^- on timescales up to hundreds of seconds in the cryogenic ion beam storage ring (DESIREE). By using Laser Photodetachment Threshold Spectroscopy (LPTS), we monitored how the vibrational IR-emission fades away, giving a constant contribution after 16 seconds. Master equation simulations within the harmonic cascade approximation describe well the fullerene ion's cooling behavior, while showing a clear deviation after ~ 3 s. This suggests that IVR in this system is not efficient on timescales exceeding this time, and thus, that the ions will need an indefinite time to cool in isolation. The decoupling of the internal energy, with a cut-off at 5 s, is performed (by following the treatment developed in [7]) showing a good agreement at longer times. This model suggests that after 5 s, there is no more redistribution among the vibrational degrees of freedom of the molecule and that the internal energy is *frozen* in long lived excited vibrational states.

Figure 1: Upper – Simulation of the IED as a function of time. The mean internal energy is indicated by the dashed white line. The micro canonical temperature is shown to the right. Lower – Integrated LPTS signal as a function of the ion storage time. The mean internal energy from simulations assuming that IVR is efficient at all times is shown in solid black. Decoupling of the internal energy at $t = 5$ s, (turning OFF of IVR) is simulated and shown in solid red. Inset shows a zoom in the yield which reveals that ions are still cooling down after 100 s. A double exponential fit shows a shorter ($\tau = 2$ s) and longer ($\tau = 658$ s) characteristic times.

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Vibrational signatures in astrochemical environments: from the Mid Infrared (MIR) to the Vacuum Ultraviolet (VUV) range

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Recent increased importance of vibrational spectroscopies in the astrochemistry context can be highlighted by the James Webb Space Telescope ISM observations, or Mars robotic missions, such as Perseverance rover. These new missions employ instruments based on vibrational spectroscopies, such as MidInfrared Instrument (MIRI), infrared spectrometers operating in the NIR region or Raman instruments. However, the vibrational features determine also the spectra related to the electronic transitions, in a broad energy ranges from the visible to the higher excitation regions. Moreover, depending on the type of study the spontaneous emission or absorption spectra can be of interest.

In this context computational spectroscopy provides a valuable support for all these experimental data [1] aiming at the identification and characterization of the composition of the interstellar medium, planetary atmospheres or the exoplanets soil through vibrational signatures. I will present few suitable examples focusing on the complex organic molecules, including semi-rigid [2] and flexible prebiotic molecules [3,4], and the spectra range from the MIR (20 μm) up to the VUV (100 nm).

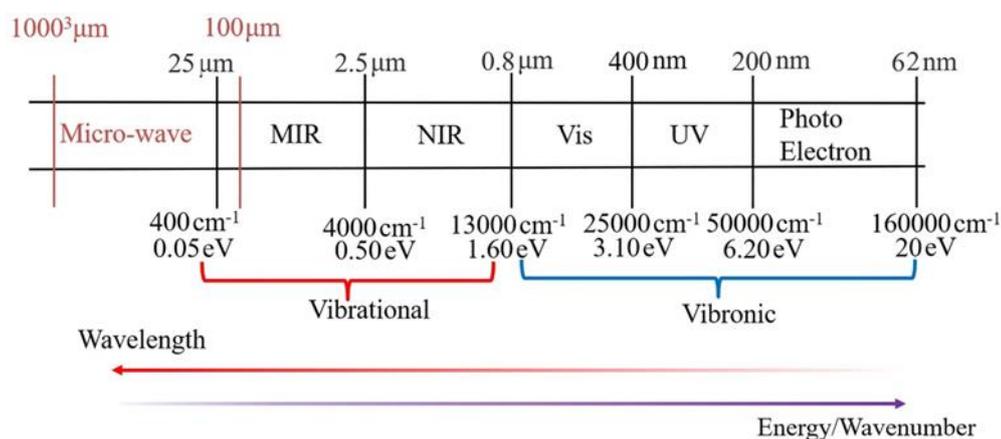


Figure 1: The spectra ranges corresponding to vibrational and vibronic computations

Acknowledgments

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Three-body collisions in ultracold hybrid ion-atom systems

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Hybrid ion-atom ultracold gases are particularly interesting in the context of three-body recombination and other collisional processes involving molecular ions. At ultracold temperatures, three-body recombination becomes the dominant inelastic process generating atomic losses in ion-atom samples. We apply quantum scattering theory to model the inelastic collisions in this regime, where classical descriptions fail to properly describe the outcomes of experiments. Absent in neutral ultracold matter, long-range interactions ion-atom systems give the prospect for a qualitatively new and interesting induction-dominated dynamics. We focus on describing the three-body processes in a sample comprised of trapped barium [1] or ytterbium [2] ions immersed in the ultracold lithium gas, where recently Feshbach resonances between an ion and neutral atoms were observed. We calculate the recombination rates into both neutral and ionic diatomic molecules across a series of ion-atom scattering lengths. We observe a novel type of interference phenomena possibly indicating a unique feature of recombination in ion-atom-atom systems. In order to characterize such interference phenomena, we study the nonadiabatic couplings driving the transitions along the relevant pathways. Additionally, we identify the appearance of weakly bound ionic triatomic molecules and predict their lifetimes.

Acknowledgments

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Chemical reactions of ultracold alkaline-earth-metal diatomic molecules

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We study the energetics of chemical reactions between ultracold, ground state alkali-metal and alkaline-earth-metal diatomic molecules. We show that the atom-exchange reactions forming homonuclear dimers are energetically allowed for all heteronuclear alkaline-earth-metal combinations. We perform high-level electronic structure calculations on the potential energy surfaces of all possible homo- and heteronuclear alkaline-earth-metal trimers and show that trimer formation is also energetically possible in collisions of all considered dimers. Interactions between alkaline-earth-metal diatomic molecules lead to the formation of deeply bound reaction complexes stabilized by large non-additive interactions. We check that there are no barriers to the studied chemical reactions. This means that all alkaline-earth-metal diatomic molecules are chemically unstable at ultralow temperatures. Optical lattice or shielding schemes may be necessary to segregate the molecules and suppress losses.

Acknowledgments

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Ab initio calculations of molecular double Auger-Meitner decay rates

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Two-electron relaxation processes following inner-shell ionisation of matter, such as the Auger-Meitner effect or interatomic Coulombic decay (ICD), are known to play an essential role in biological damage inflicted by radiation. Relevant mechanisms comprise the acceleration of photodissociation or the production of reactive secondary particles. Recent experiments suggest that even higher-order relaxation processes involving multi-electron transitions might reach surprisingly high intensities in molecules and weakly bound clusters [1, 2]. Thus, these little-studied mechanisms also significantly affect the response of matter to radiation.

Among the fundamental characteristics of a metastable state is the decay width, which is directly related to its lifetime. One of the most successful approaches to computing *ab initio* intra- and interatomic electronic decay widths, which has been used in many important studies of ICD or collective decay processes involving more than two electrons [3, 4], is the Fano-ADC method [5]. It is based on the Fano theory of resonances and algebraic diagrammatic construction (ADC) to describe the many-electron wave function. Previously, all implementations of the method were based on the extended second-order ADC scheme [ADC(2)x], which involves only the lowest two excitation classes (i.e., one hole [1*h*] and two-holes-one particle [2*h*1*p*] with respect to the neutral ground state) in the wave function expansion. At this level, the 2*h*1*p*-like states (shake-up ionisation satellites or dicationic decay channels with an electron in the continuum) are seriously under-correlated compared to the 1*h*-like main ionic states, which can affect the accuracy of the calculated decay widths. Furthermore, decay processes in which 3*h*1*p*-like shake-up dicationic channels play an important role or multielectron effects, such as double Auger-Meitner decay, are not included.

To remedy these issues, we have developed the ADC(2,2) scheme [5] in which both the main and shake-up states are treated through the second-order perturbation theory. This unprecedented consistency is particularly valuable for the study of the inner valence ionisation of molecules in spectral regions where the 1*h* and 2*h*1*p* characters of states are usually strongly mixed due to the so-called molecular orbital picture breakdown [6]. The resulting Fano-ADC(2,2) method then represents a versatile and highly accurate tool for studying electronic decay in molecules and clusters, providing both the lifetimes and decay spectra. Through the 3*h*2*p* excitation class, the method also provides access to second-order decay processes with two electrons in the continuum.

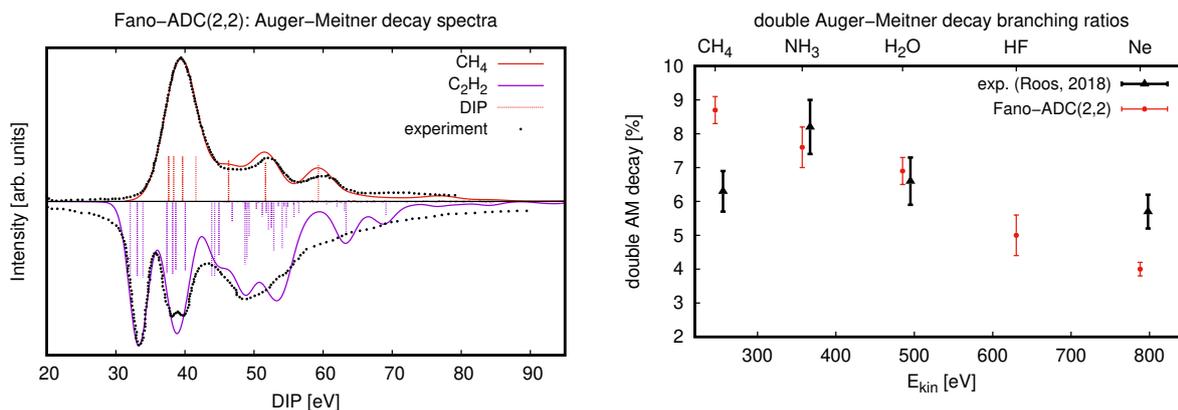


Figure 1: Left: Computed Auger-Meitner spectra of methane and ethyne (full lines) compared to experiment (Kivimäki 1996,1997). Right: Double Auger-Meitner decay branching ratios.

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A non-adiabatic molecular dynamics method for every photoactivated system

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In my upcoming presentation, I will tackle three nuclear propagation methods for nuclear dynamics and apply them to non-adiabatic processes in photoactivated systems. The methods are Multiconfiguration Time Dependent Hartree (MCTDH)[1], a grid-based wavepacket method; Direct Dynamics Variational Multiconfigurational Gaussian (DD-vMCG)[2], a quantum dynamics method using multidimensional Gaussians; and Trajectory Surface Hopping (TSH)[3], where nuclei follow Newton's equations of motion independently and stochastic hops occur among surfaces.

Many researchers adhere to the methodologies already known within their respective research environment rather than exploring alternative methods. I will present the three nuclear dynamics methods in detail, focusing on photoexcited systems that we studied in our group and the rationale behind the selection of the method chosen for their time evolution. I will also present the QUANTICS program package[4], which allows the user to test every method presented here on the same potential energy surfaces. Additionally, I will stretch the necessity of standardized benchmarks in non-adiabatic dynamics to facilitate methodological evaluation and further developments.

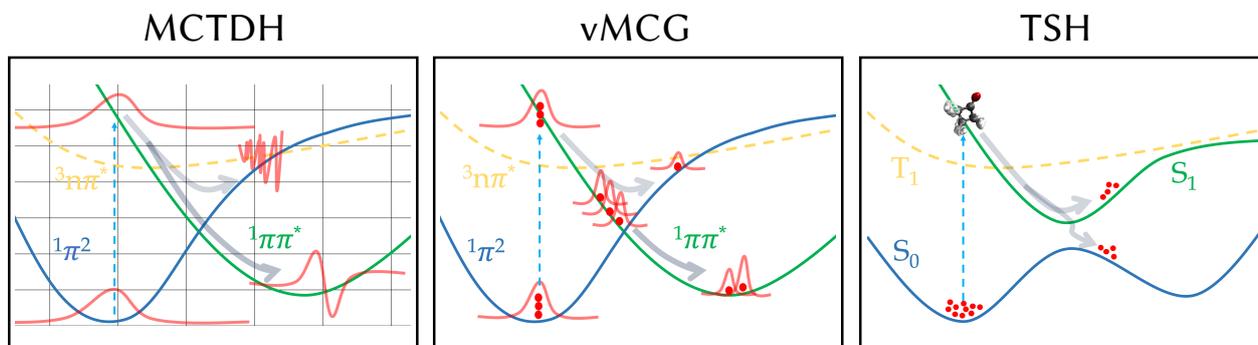


Figure 1: A schematic depiction of three of the most used non-adiabatic molecular dynamics methods to study photoinitiated systems.

Acknowledgments

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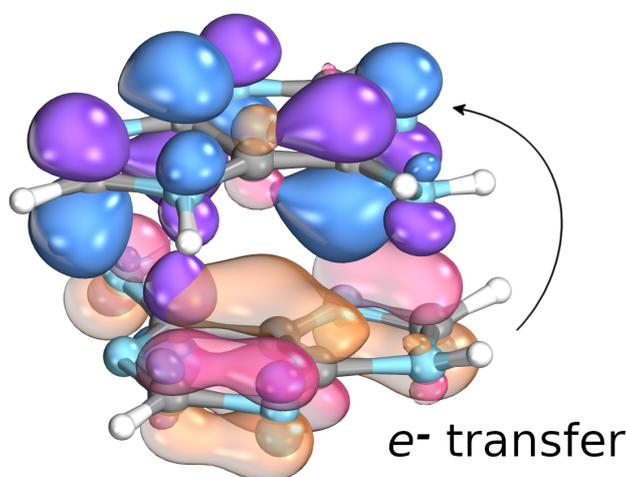
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Quantifying rates of photoinduced electron transfer in biomolecular systems

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Electron transfer is one of the most fundamental processes that sustain the key functions of living organisms. It drives essential metabolic redox reactions, photoinduced CO₂ fixation, signalling between proteins and DNA repair processes. Several approaches were proposed for the evaluation of equilibrium electron transfer processes, including the ever-present Marcus Theory for electron transfer. However, computational description of non-equilibrium (*e.g.* photoinduced) electron transfer is still a notorious challenge. In this talk, I will discuss the key aspects controlling photoinduced electron transfer in DNA and related systems[1, 2, 3]. In particular, I will show how different components of electron transfer rate equations are affected by molecular structure, including base stacking. I will also show how to quantify rates and/or time-scales of nonequilibrium electron transfer processes with surface hopping excited-state dynamics and our new tool which employs the advantages of nonadiabatic transition state theory.



Rysunek 1: Molecular orbitals associated with the excited state that is responsible for photoinduced electron transfer between two stacked adenine nucleobases.

Acknowledgments

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Machine Learning IR spectroscopy: Tradeoff Between the Quality and the Cost of Production

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The infrared (IR) spectrum of a molecule serves as its molecular fingerprint and is thus widely used in chemistry as a mean of molecules' identification. Furthermore, the ability to compute good quality spectra is crucial for comparison with experiments. This is an active research area and there exist different theoretical approaches. The so-called static methods,^[1-3] provide discrete spectra that need to be smoothed out. An alternative to these methods is the production of IR spectra through the Fourier Transform of the dipole auto-correlation function (DACF) computed during *ab initio* Molecular Dynamics (AIMD) simulations.

As opposed to the static methods, AIMD dynamic method allows for the exploration of different conformations of a molecule -or molecular system, e.g. in the presence of solvent- and for the adjustment of the temperature. While advantageous, AIMD has a significant computational cost since at each time step of a given trajectory, *ab initio* forces need to be calculated. This cost increases with the level of theory and the system size. The requirement of small-time steps and long simulation times to achieve converged spectra contribute to increase even more the computational cost. To overcome these limitations, forces can be alternatively calculated by means of Machine Learning (ML).

In this work, we interfaced Q-Chem^[5] software with sGDML^[4] model to allow for the calculation of ML-IR spectra. We evaluate the influence of training data on the ML-IR spectra and, in addition, we study the time evolution of the accuracy of the ML approach.

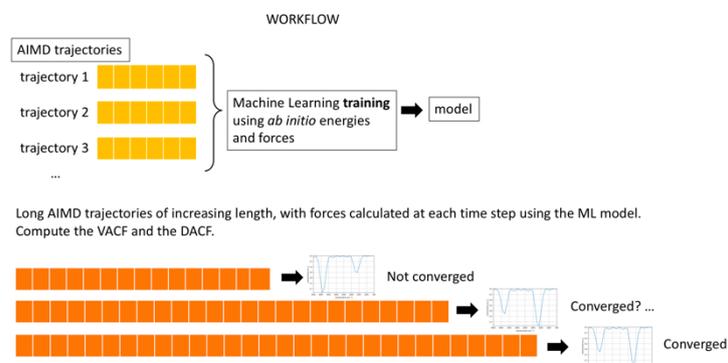


Figure 1: Workflow to calculate IR spectra from dipole autocorrelation function from AIMD with ML forces.

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Improving the precision of quantum chemical calculations by novel embedding scheme including Friedel oscillations

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Abstract

Hereby we present a first known accurate analytical description of the 3D half-infinite conductive half-space (modelling the metal surface) response to the charged perturbations (modelling the molecules). [1] The response is constructed out of the quasi-3D expansion of the 1D Kronig-Penney metal together with the Tamm's surface states and a multipole molecule. The model proven its correspondence to the reality by two significantly accurate points. Firstly, it does agree with the DFT results for CO adsorption on a relatively large slab of Pt(111). The image of the molecule inside the metal depicts the change of the hybridization and shows that it can be treated as an impurity itself. The location of the *image* corresponds well to the analytical theory and equals the spacing between the initial CO molecule and the first metallic layer. Secondly, the model is perfectly scaled by the comparison to the CO-CO interacting on the Pt(111) surface potential from the literature. Finally, the model allows to find the solution at ~ 1000 times reduced computational costs.

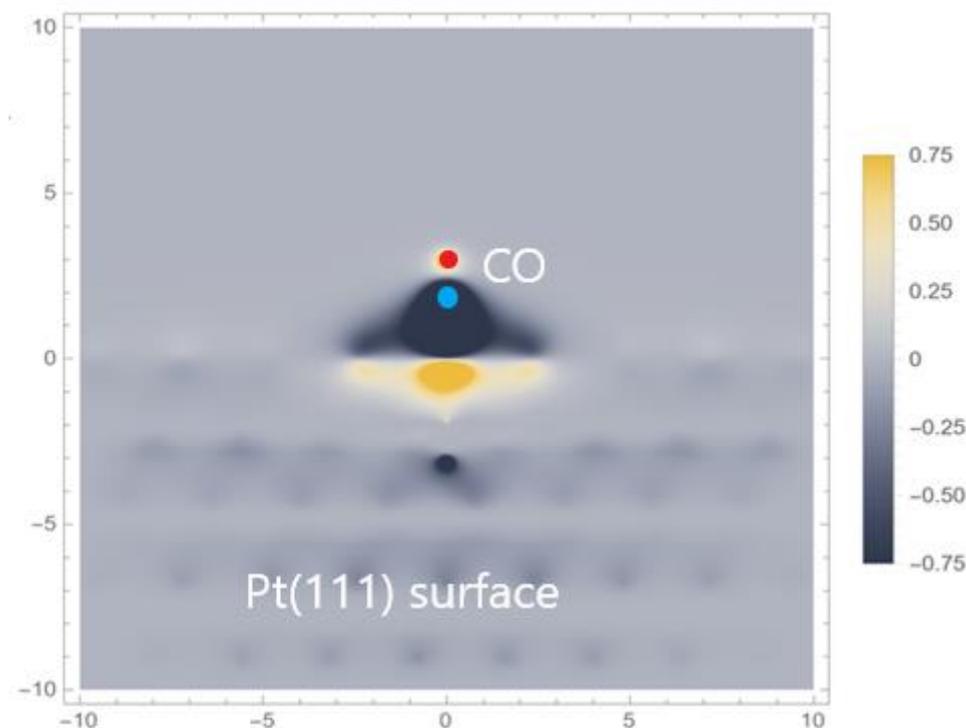


Figure 1: Analytical model results: a CO particle approaching the Pt (111) surface. [1]

Acknowledgments

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Ultrafast molecular chirality: a topological connection

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An object is said to be chiral if it cannot be superimposed on its mirror image by any rotation. The two mirror images of the same chiral molecule are called enantiomers and are often referred to as “left”- and “right”-handed. While the physical properties of the two enantiomers of the same chiral molecule are nearly identical, the geometric property of chirality leads to vastly different chemical properties of the two enantiomers. The well-known thalidomide disaster of the second half of the XX-th century is but one among the many examples of how dramatic the change of the enantiomer can be for functions in live matter. The need for rigorous selection of a specific enantiomer, a now standard requirement in drug design, is one of the many reasons behind the ever-greater need for improving sensitivity of chiral sensing.

Yet, standard optical methods of chiral detection still use the same principles as the method discovered by Louis Pasteur in the XIX century: the linear interaction between chiral molecules and light, which becomes chiral-sensitive due to the magnetic field component of the light wave.

Ultrafast non-linear spectroscopies promise to increase the enantio-sensitive signal by three orders of magnitude [1] by removing the need to rely on the interaction with the magnetic field component of light. The second important feature of non-linear light-matter interactions is the opportunity to imprint topological properties of light on matter, presenting an opportunity to achieve *topologically robust* enantio-sensitive observables.

The connection between topology and chirality in electronic or optical response of gas phase chiral molecules to light is an emergent topic [2,3,4]. The topological aspects of the *electronic* response have so far been mainly harvested in condensed matter systems and have yet to find their room in the gas and liquid phases. Since topology has an attractive property of robustness to external perturbations and noise, one may be able to create efficient and robust new enantio-sensitive observables by combining chirality and topology in the ultrafast electronic and optical response of chiral gases and liquids. The efficiency comes from driving an ultrafast non-linear response which enables chiral detection via *electric-dipole interactions* [1], whereas the robustness comes from the *topological* concepts.

I will describe our very recent results [5,6] on marrying chiral and topological properties in ultrafast electronic response of chiral molecules in the gas phase which implement the program outlined above, enabling highly efficient and robust chiral observables. I will present two vignettes where topological connection appears in optical or electronic chiral response:

- (i) **Chiral topological light:** a new concept enabling chiral-sensitive and topologically robust properties of high harmonic emission, generated by such light in chiral molecular gases
- (ii) **Enantio-sensitive exceptional points:** chiral topology in non-Hermitian chiral systems

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Mixed quantum-classical and quantum approaches to nonadiabatic dynamics: Speaking the same language

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Nonadiabatic dynamics simulations beyond the Born-Oppenheimer approximation are a necessary tool for understanding reactions involving electronically excited states of molecules. The two dominant approaches to these simulations are mixed quantum-classical approaches, most commonly trajectory surface hopping (TSH) methods, and fully quantum approaches, such as multi-configuration time-dependent Hartree (MCTDH). The approximation of treating the nuclei as classical particles in mixed quantum-classical approaches greatly simplifies calculations of this type and allows the treatment of systems with many degrees of freedom, limited only by the cost of evaluating the potential energy surfaces. Apart from the computational cost, simulations of this type are simpler because they can be run "on-the-fly", without pregenerating diabatic potential energy surfaces. However, results obtained from TSH simulations in terms of adiabatic states contain (without further processing) significantly less information on the changes in the electronic excited states compared to analogous results obtained in terms of diabatic states.

When studying the photochemistry of a molecule with a mixed quantum-classical approach, results are usually presented in terms of adiabatic populations, final products and averaged motions along the trajectories. On the other hand, another study looking at the same molecule using a fully quantum approach on a model potential would present results in terms of diabatic populations and relevance of particular vibrational modes, making any comparisons between the two studies difficult. Here, I will present recent attempts to create a set of tools for analysis of TSH simulations with the goal of obtaining approximate diabatic populations and similar properties without the need to generate global diabatic potentials [1]. These tools allow for easier assignment of spectra based on TSH simulations [2, 3], but also simplify comparisons between TSH and fully quantum approaches [4, 5].

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Preventing Zero-Point Energy Leakage in Classical Trajectories

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The problem associated with the zero-point energy (ZPE) “leakage” in classical trajectory calculations are well known. Since ZPE is a manifestation of the quantum uncertainty principle, there are no restrictions on energy during the classical propagation of nuclei, causing energy leakage. Methods based on classical dynamics of the nuclei may present artefacts due to this erroneous ZPE leakage. This phenomenon can lead to unphysical results, such as forming products without the ZPE in the internal vibrational degrees of freedom (DOFs). It may also permit reactions below the quantum threshold for the reaction.

In this talk, a new Hessian-free method [1] will be presented to prevent energy leakage below a threshold in the internal vibrational DOFs. The idea is to pump the leaked energy to the corresponding internal DOF, taken from the other internal DOFs. Thus, the energy is redistributed over the DOFs conserving the total energy of the system. We have applied the new correction protocol on the ab-initio ground-state molecular dynamics simulation of the water dimer, which dissociates due to unphysical ZPE spilling from high-frequency OH modes. The LP-ZPE method has been able to prevent the ZPE spilling of the OH stretching modes by pumping back the leaked energy into the corresponding modes, while this energy is taken from the other modes of the dimer itself, keeping the system as a microcanonical ensemble.

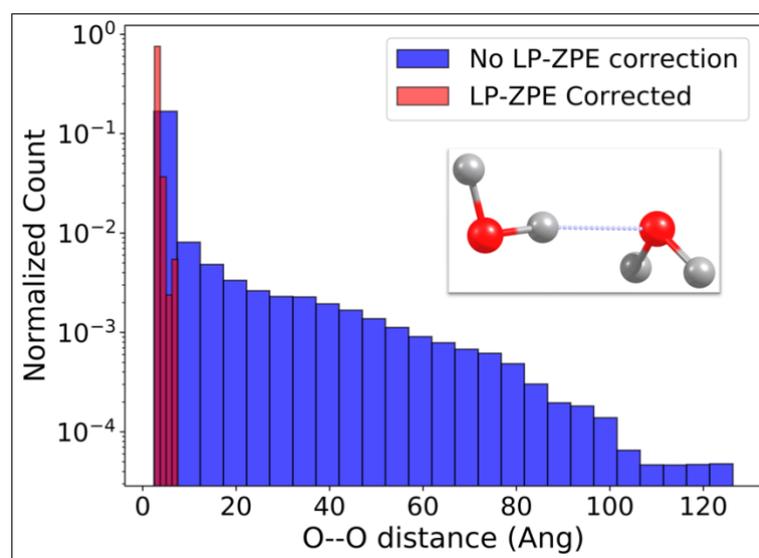


Figure 1: The radial distribution functions of the two oxygen atoms in water dimer are obtained from classical BOMD trajectories with (red) and without (blue) the LP-ZPE correction. The LP-ZPE correction protocol ceases the artificial dissociation of the water dimer.

Acknowledgments

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Computational investigation of cage-opening and fragmentation of adamantane dications

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Adamantane (C₁₀H₁₆) is the simplest molecule belonging to the family of diamondoids, carbon cage structures formed by C(sp³)-C(sp³)-hybridized bonds and fully terminated by hydrogen atoms. Due to their high thermal stability and well-defined structure they attract increasing interest for applications as nanomaterials in e.g. nano- and optoelectronics, biotechnology and medicine [1]. Moreover, it has been shown that these carbon-bearing molecules are expected to be abundant in the interstellar medium [2] making it crucial to understand their response to the ionizing radiation.

In this work, we performed calculations based on the DFT approach as well as statistical mechanics in order to explore the initial energy redistribution process after an ionizing event. The theoretical approach applied in this work follows our previous strategy [3], which relies on studying the energetic structure, time propagation and entropy maximization. Firstly, we explored the potential energy surface of fragmenting adamantane dication at the B3LYP/6-31G(d) level of theory. Secondly, we carried out the molecular dynamics (MD) simulations with the Atom Centered Density Matrix Propagation (ADMP) method. Finally, the Microcanonical Metropolis Monte Carlo method, in its recent implementation in the M₃C code [4], was applied to obtain the fragmentation breakdown curves. Our theoretical results have been compared with the PIPICO experimental measurements obtained at the ELETTRA facility.

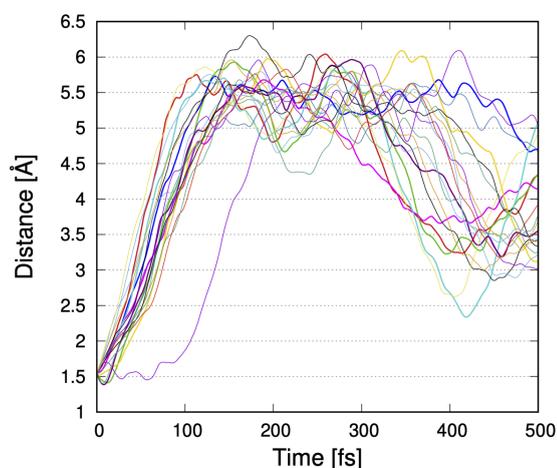


Figure 1: Progression of C-C bond length in 20 MD trajectories with only one bond cleavage

From the obtained results we can see that the cage opening is accompanied by hydrogen migration and takes place quickly, on average within 60 fs. In the energy range studied with the molecular dynamics, the cage of the adamantane dication remains for the most part open and we observe little fragmentation before the end of the simulation (500 fs). The most abundant fragmentation channel produced ions C₃H₅⁺ and C₇H₁₁⁺. In order to study processes taking place on a longer time scale we applied the statistical M₃C theory. M₃C results show a much richer fragmentation pattern than MD. The M₃C calculations for this system have been performed recently [5], however, in this work we wanted to expand the fragments database, which previously was limited to the fragments observed in the experiment. In doing so our goal is to obtain fragmentation branching ratios by combining experimental PIPICO results with M₃C breakdown curves.

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X-ray induced charge transfer in conjugated polymers by Auger spectroscopy

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Charge transfer (CT) involving electron and nuclear dynamics is of paramount importance not only in chemistry, but also in biology and materials science. When CT involves complex systems where nuclear and electron dynamics become relevant, X-ray sources, which allow for element-specific core-shell excitation, are essential. In this regard, X-ray spectroscopy enables us to glimpse at ultrafast dynamics processes taking place in molecular ensembles. The core-hole clock spectroscopy (CHCS) method relies on high resolution, monochromatic X-ray radiation to provide an insight into processes with a span shorter than the core-hole lifetime [1]. Core-excitation and decay processes, in which an X-ray photon or an Auger electron are emitted, occur within the lifetime of a core-excited state, and serve as a probe for dynamics occurring in the molecule on the same timescale. Inducing site-specific electron dynamics through absorption of an X-ray photon and emission of a resonant Auger electron enables us in turn to investigate electron delocalization in macro-molecules and extended systems in the solid-state. Using the HAXPES end-station at the GALAXIES beamline of the SOLEIL French synchrotron facility, we measured high resolution resonant *SKLL* Auger spectra below the sulfur 1s threshold of the π -conjugated polymers 1) polythiophene (PT), in powder form (where delocalization is possible *only along* the polymer chain), and 2) P3HT, as a thin-film (where delocalization is possible *both along and between* chains). An earlier investigation on PT in powder form using resonant Auger spectroscopy (RAS), found no evidence of CT [2]. While a following study of PT as a thin-film showed the presence of electron delocalization in resonant Auger spectra in the low femtosecond regime [3]. The prevailing interpretation of the observed dynamics was ascribed to an interaction between polymer chains. Our results using RAS exhibit hallmark features of CT in *both* PT and P3HT (white dashed line region in Fig. 1), indicating a predominant delocalization mechanism along the chain. Our work is in good agreement with theory based on real-time time-dependent DFT methods.

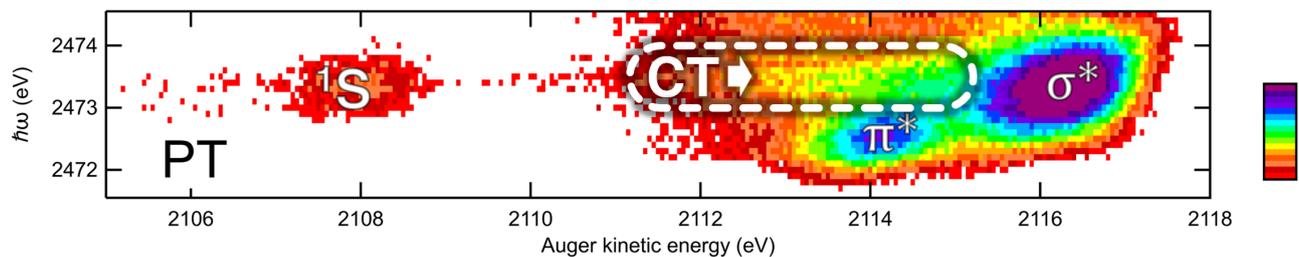


Figure 1: 2D map of S $KL_{2,3}L_{2,3}$ Auger spectra of PT. White dashed line stadium-shape highlights CT region.

Acknowledgments

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Ultrafast electron dynamics in hybrid organic-metal interfaces

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Electronic excited states offer a powerful means of modulating chemical reactivity. However, when molecules interact with surfaces, the presence of the substrate alters properties of these states, such as their energies and lifetimes. This phenomenon is particularly pronounced on metal surfaces, where the substantial polarization of the substrate facilitates charge-transfer effects. Consequently, the molecular electronic structure undergoes an important modification, leading to changes in the strengths of the chemical bonds. Moreover, the interaction between the molecule and the metal continuum generates diverse pathways for the (non-radiative) decay of excited electrons, which affects the lifetime of the excited states, affecting induced reactivity. Consequently, accurately elucidating the intricacies of processes occurring at metal-molecule hybrid interfaces is a significant challenge.

In this communication, we present a methodology that combines Density Functional Theory (DFT) calculations for investigating adsorption and to describe of the electronic structure of the system, with Wave Packet Propagation (WPP) for analyzing electron dynamics. The advantage of our WPP implementation is the ability to explicitly consider the atomic structure of the system, providing a more accurate representation of the behavior of the active electron [1]. We also provide some examples of possible applications of WPP, including the study of the lifetime of excited states of molecules adsorbed on surfaces and the quenching of signal in STM-induced fluorescence [2]. With the help of WPP calculations, we offer a detailed explanation of these experimental observations and we understand the role of the electronic structure of the surface on the mechanism of the electronic decay [3], as well as the control in the photoemitted electrons under the effect of (ultrafast) laser pulses.

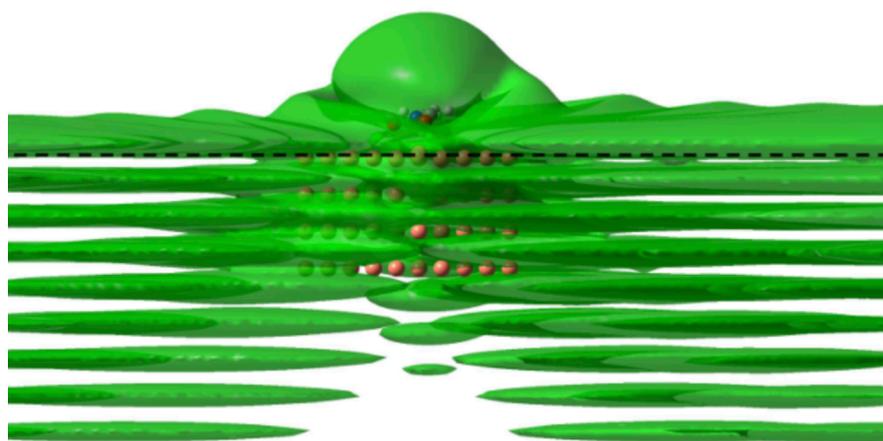


Figure 1: Resonant wave function of the anionic state of nitroethylene adsorbed on a Cu surface.

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Properties and reactivity of few-atom complexes in the ultracold collisions

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We investigate the properties of intermediate few-atom complexes formed during nonreactive collisions, crucial for understanding experiments involving ultracold alkali-metal molecules. We analyze three representative systems: KRb ($X^1\Sigma^+$) + Rb (2S), NaLi ($a^3\Sigma^+$) + Na (2S), and NaK ($X^1\Sigma^+$) + NaK ($X^1\Sigma^+$) using *ab initio* electronic structure quantum-chemical methods.

For the KRb ($X^1\Sigma^+$) + Rb (2S) system, we explore the potential energy surface and dynamics. We identify a conical intersection between the ground and first excited doublet electronic states. The electron spin-rotation coupling is significantly enhanced near this intersection, potentially increasing the lifetime of the collisional complex. Utilizing an analytical representation of the ground-state X^2A' potential energy surface, we perform classical molecular dynamics calculations. Our results reveal substantial rubidium atom substitution inside KRb, indicating the necessity to move beyond rigid rotator approximations in describing the quantum-scattering dynamics.

In the NaLi ($^3\Sigma^+$) + Na (2S) system, a substantial nonadditive three-body potential alters the shape of the potential energy surface [1]. The combination of electron spin-spin and electron spin-rotation interactions with the potential anisotropy increases loss rate [2].

We propose [3] that unexpectedly large loss rates observed in closed-shell molecules, such as NaK ($^1\Sigma^+$) + NaK ($^1\Sigma^+$) collisions, may be explained by variations in nuclear spin-spin and quadrupole couplings. Electronic structure calculations demonstrate that at small inter-monomer separations, these couplings are sufficiently strong to couple different rotational manifolds, necessitating their inclusion in estimating complex lifetimes.

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Density-based basis-set correction within local domain approximations

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In electronic structure calculations, the coupled-cluster singles and doubles with perturbative triples [CCSD(T)] approach stands as the “gold standard” for weakly correlated systems, providing reliable results. However, the computational cost scales steeply with system size, primarily due to the slow convergence of energies and properties with the size of the one-electron basis set. To address this, a possible solution was recently proposed by Toulouse *et al.* [1] The main objective of their density-based basis-set correction (DBBSC) is to account for the missing part of short-range correlation effects, arising due to the incompleteness of the one-electron basis set. Consequently, this energy correction is approximated using a short-range density functional that complements a long-range interaction properly described by wave function theory, resulting in a range-separation function that automatically adapts to the spatial inhomogeneity of the basis-set incompleteness.

First, an efficient implementation of DBBSC is presented utilizing the density-fitting (DF) approximation, resulting in a fourth-power scaling correction. Using the infrastructure obtained, a thorough comparison is carried out for explicitly correlated and DBBSC-CCSD(T) approaches. It is demonstrated that DBBSC, together with complementary auxiliary basis set (CABS)-corrected Hartree-Fock energies, is highly robust and effectively reduces the error of CCSD(T) for atomization, reaction, and noncovalent interaction energies [2].

Thereafter, to aim for large-scale applications, the implementation of DBBSC within our highly efficient linear-scaling local natural orbital (LNO)-CCSD(T) framework [3] is presented. In this approach, the local nature of the electron-electron interaction is exploited. That is, a domain is formed around each localized occupied orbital, which contains only the strongly interacting orbitals. The contributions to the range-separation function are expressed as sums over these compact domains, significantly decreasing the wall-clock times. In addition, further methodological developments are also presented, such as the local DF approximation for the time-consuming step of the CABS correction. This effective framework allows us to evaluate near basis-set limit LNO-CCSD(T) energies for systems of up to 1000 atoms (see Figure 1) even using double- ζ basis sets.

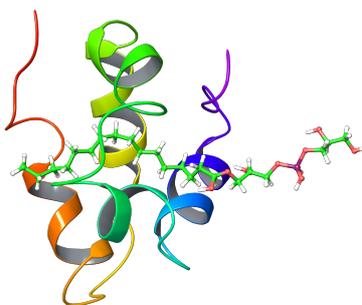


Figure 1: Lipid transfer protein containing 1023 atoms, including its ligand of 79 atoms.

Acknowledgments

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Quantum dynamics of the spin-forbidden peroxidation catalyzed by the DpgC enzyme

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Reactions between molecular oxygen and closed-shell organic molecules leading to the formation of stable (closed-shell) adducts involve the change of the spin state of the system, and accordingly should be slow at room temperatures. Nevertheless, enzymes are able to catalyze these reactions, even in the absence of cofactors that may promote the intersystem crossing.[1]

One of these reactions is the addition of O₂ to S-methyl-but-3-enethionate that occurs in the active site of the DpgC enzyme. Previous electronic structure calculations showed that this process involves two electron transfer steps, the first of them concomitant with the intersystem crossing.[2] To analyze the importance of the quantum dynamical effects that could be present on this system, here we report quantum scattering calculations on seven MRCI 2D PESs (six singlets and the triplet state), including the spin-orbit coupling between the triplet and the singlet PESs. The MCTDH[3] method as implemented in QUANTICS[4] package, is used for the quantum dynamics calculations.

Quantum integral cross-sections and thermal rate constants are presented, shedding light on the dynamics of the spin-forbidden process.

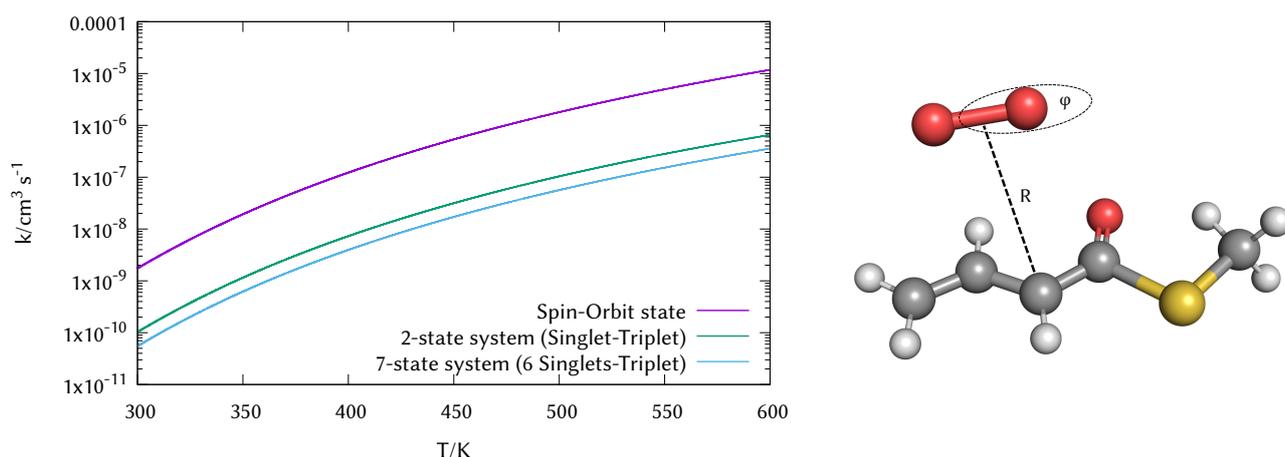


Figure 1: Left panel: Thermal rate constant over the range $T=300-600\text{K}$ for the spin-orbit state, the singlet-triplet system and the seven electronic states. Right panel: Representation of S-methyl-but-3-enethionate - O₂ system

Acknowledgments

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Abiotic molecular oxygen production – ionic pathway from SO₂

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Molecular oxygen, O₂, is vital to life on Earth and possibly also on exoplanets. Although the biogenic processes leading to its accumulation in the Earth's atmosphere are well understood, its abiotic origin is still not fully established. Recently [1], we investigated SO₂ experimentally by multi-particle coincidence detection using our established TOF-PEPEPICO technique where the target species were irradiated by 40.81 eV photons (HeII α) from a pulsed helium discharge lamp, mimicking an intense component of the solar spectrum and of many stellar spectra. In addition, ion-ion coincidence measurements on SO₂ were carried out at the synchrotron radiation facility BESSY-II where photon energies of several more solar X-ray lines were available to us. We find experimental evidence for electronic-state-selective production of O₂ from SO₂, a chemical constituent of many planetary atmospheres and one which played an important part on Earth in the Great Oxidation Event. Our finding is supported by advanced ab initio computations, leading to the following model: The O₂ production involves isomerization of SO₂ by a roaming mechanism (cf. Fig. 1) leading to efficient formation of the O₂⁺ species in form of dissociative double ionisation of SO₂, which can be converted to abiotic O₂, for instance by electron neutralisation. This formation process may contribute significantly to the abundance of O₂ and related ions in planetary atmospheres, such as the Jovian moons Io, Europa and Ganymede. It represents an alternative to and may compete with the well-established abiotic O₂ production pathways via the photodissociation of water vapor by extreme ultraviolet light or the near ultraviolet photochemistry of titanium-(IV)-oxide (titania). We suggest that this sort of ionic pathway for the formation of abiotic O₂ involving multiply-charged molecular ion decomposition may also exist for other atmospheric and planetary molecules.

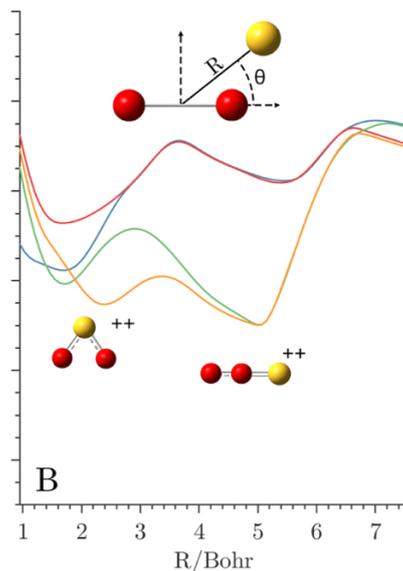


Figure 1: Partial minimal energy path of SO₂, showing the roaming mechanism leading to abiotic production of O₂ [1].

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Excited-State Odyssey: Charting Maps with Data-Driven Strategies

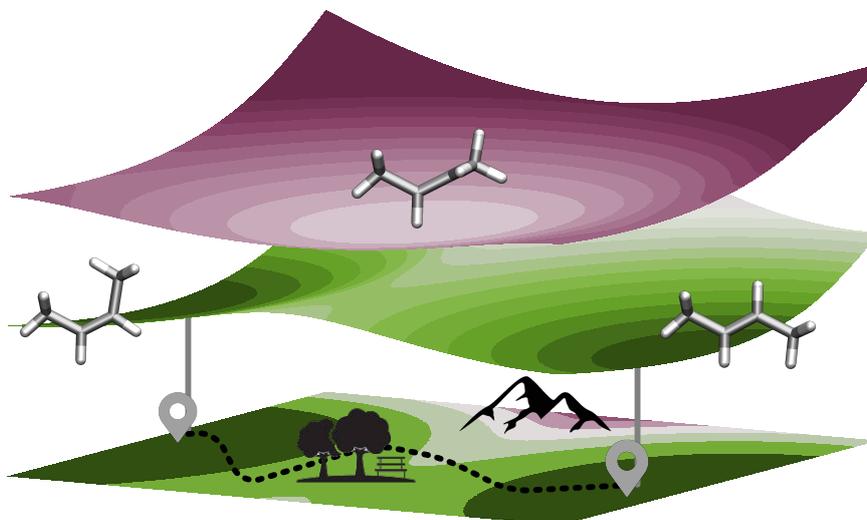
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Photochemistry offers a promising route to sustainable chemical processes. However, to exploit its full potential, it is necessary to explore the potential energy landscapes of different excited states. This exploration resembles an odyssey, because in the absence of design principles and detailed structural information for excited states, detailed maps for these surfaces are lacking.

Quantum chemical simulations provide glimpses on these landscapes, yet their accuracy is hampered by computational costs associated with quantum chemical methods, restricting their use to small systems (*e.g.*, ≤ 100 atoms) and short timeframes (ranging from femto- to picoseconds). Here, data- and science-driven strategies emerge as a guiding force. For example, by leveraging existing quantum chemical data across various molecular configurations and excited states, machine learning approaches can accelerate photodynamics simulations to navigate the excited state manifold or drive static approaches to localize critical points on various excited-state surfaces.

This presentation provides an overview of how machine learning can streamline the charting of maps for the landscape of photochemical reactions involving various excited states. Introducing the machine learning method, SPAINN [1], and its companion database, SHNITSEL [2,3], we delve into a promising duo driving the exploration and prediction of excited-state landscapes. SHNITSEL serves as a comprehensive repository housing computational data for various photochemical reactions, meticulously crafted as the **S**urface **H**opping **N**ewly **I**nvented **T**raining **S**et for **E**xcited-state **L**earning. Specialized in training and predicting excited state properties, SPAINN will be showcased using examples from the SHNITSEL database, marking the commencement of an Excited-State Odyssey, charting maps with data-driven strategies.



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Ab Initio Calculation of Atomic and Molecular Properties for Precision Metrology

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In this talk we outline recent advances in *ab initio* prediction of various properties of atomic and molecular gases. The focus is on quantities which are important from the point of view of precision metrology and experimental techniques such as dielectric constant gas thermometry [1] or refractive index gas thermometry [2]. The progress in theoretical determination of atomic and collision-induced static and dynamic polarizabilities, magnetic susceptibilities, and interaction potentials is summarized. Next, we discuss how these quantities are used to compute macroscopic properties of a gas such as density or dielectric virial coefficients, shear viscosity or thermal conductivity, which are experimentally relevant, see Fig. 1 for example results. We outline how the development of the current primary pressure standard established in 2020 [3] has been enabled by an interplay of theory and experiment and would not be possible otherwise. Finally, we discuss the ongoing efforts in development of, e.g. a secondary pressure standard based on molecular gases such as dinitrogen.

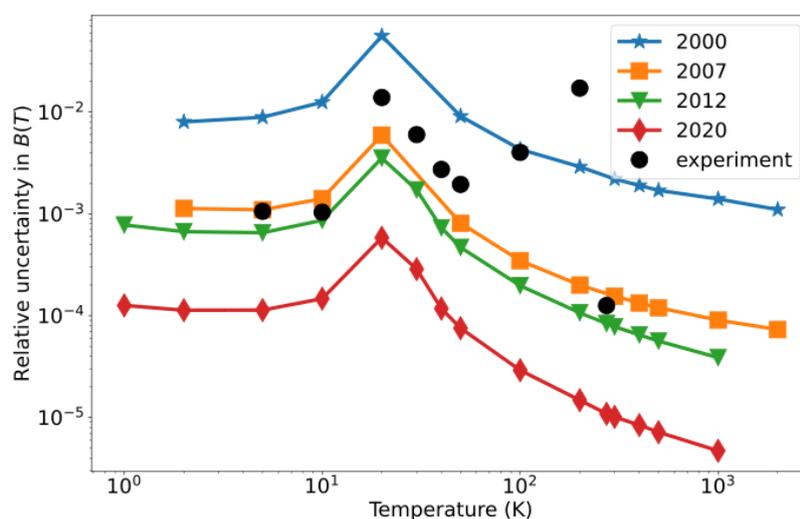


Figure 1: Relative uncertainty in the values of the second density virial coefficient, $B(T)$, for ^4He . The colored curves represent the best theoretical data available in a given year, while the black dots are the most accurate experimental results available at the moment. Note the logarithmic scale of the plot. Reproduced from Ref. [4] based on the data from Ref. [5].

Acknowledgments

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Lighting-up nanocarbons through hybridization: Optoelectronic properties and perspectives

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In recent years, a plethora of material systems have been designed and prepared to increase the performance of light harvesting and light-emitting technologies, and to develop new and attractive applications. Limitations of state-of-the-art devices based on organics (both conjugated polymers or small molecules/oligomers) derive largely from material stability issues after prolonged operation. This challenge could be tackled by leveraging the enhanced stability of carbon nanostructures (CNSs, including carbon nanotubes and the large family of graphene based materials) in carefully designed nano-hybrid or nano-composite architectures to be integrated within photo-active layers, paving the way to the exploitation of these materials in contexts in which their potential has not been yet fully revealed [1]. In this talk, I will discuss the theoretical background behind CNSs hybridization with other materials such as graphene with donor-acceptor molecules [2], for the establishment of novel optoelectronic properties and provide an overview of new optoelectronic and transfer properties of twisted graphene nanoribbons with controlled peripheral size [3-5] that allow to forecast interesting future perspectives for use in real devices. and molecular physics and chemistry, opening up new research directions and opportunities for collaboration. We believe that the conference in Warsaw will create a pleasant environment for fruitful discussions and inspiration.

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Cross-relaxation near zero magnetic field in nitrogen-vacancy centers in nanodiamonds

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The negatively charged nitrogen-vacancy (NV-) center in diamond has interesting optical and spin properties, making it useful for developing sensors for magnetic and electric fields, temperature, and pressure. NV-center-containing nanodiamonds are non-toxic and photostable and can be easily functionalized so that they can be used as fluorescent markers and sensors in biological materials.

In this work, we examine how the size of the diamond (which can range from 30 nm to 3000 nm) and the strength of a bias magnetic field applied transversely to the scanning field affect the zero-field resonance (ZFR) width and contrast. Furthermore, we estimate the net strain splitting of the zero-field ODMR resonance across different nanodiamond sizes using optically detected magnetic resonance (ODMR). Next, we compare these results with the ZFR features' breadth and contrast for both bulk samples and nanodiamonds. Our findings offer strong evidence of cross-relaxation effects at zero magnetic fields in the NV system [1,2].

We show that the ZFR method has potential applications in real-world, microwave-free magnetometry. We map magnetic fields above micrometer-sized current-carrying structures with drop-casted NV nanodiamonds, and we also perform similar experiments in an endoscopic configuration with a high-numerical-aperture imaging fiber bundle, opening the door to the development of NV-diamond borescopes and endoscopes.

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Ab-initio Green's functions methods for molecules and solids

What accuracy can we reach?

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I will address the current theoretical challenges encountered in the study of solid-state materials and highlight the contributions made by my research group towards the advancement of post-density functional theory (DFT) methods.

In the initial segment of my presentation, I will introduce a formulation of relativistic self-consistent GW for solids. This formulation is based on the exact two-component formalism with a one-electron approximation (X2C1e) and incorporates non-relativistic Coulomb interactions. Our theory enables the investigation of scalar relativistic effects, spin-orbit coupling, and the intricate interplay between relativistic effects and electron correlation, all without the need for adjustable parameters.

In the subsequent part, I will focus on the treatment of strongly correlated electrons localized in d- and f-orbitals within crystalline structures containing transition metals. I will analyze correlation effects observed in compounds such as SrMnO₃ and BiVO₃, alongside exploring Neel temperatures in compounds like NiO, MnO, and CoO. Finally, I will outline potential future directions for research in this domain.

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Acceleration of Chemical Reactions by Mechanical Distortion

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The organic solvents employed in the great majority of organic reactions carried out in industry account for >60% of all chemical manufacturing waste. Because of the energy demand of so-called solvothermal syntheses, where solvent and heat drive reactions, the chemical industry consumes 37% of the total energy used in manufacturing. Replacing solvothermal with mechanically-activated organic chemistry – where force, rather than heat and solvent, drives the making and breaking of covalent bonds – can solve the waste and energy challenges of organic synthesis. Poor understanding of the effect of the force on reaction rates and resulting reaction kinetics, however, limits more wide-spread use of mechanochemistry.[1]

Herein, I discuss how to reliably determine how force alters reactions between simple organic compounds, and how this force affects reaction barriers and, in turn, reaction rates.[2] The experimentally measured force needed to achieve this acceleration, which we define as uniaxial force, is three orders of magnitude smaller than those applied under hydrostatic pressure. DFT calculations reveal that the acceleration occurs due to a force distorting the system along a specific reaction coordinate which results in a decrease of the transition state energy. This phenomenon suggests that mechanochemical reactivity is more widespread than previously anticipated.

Acknowledgments

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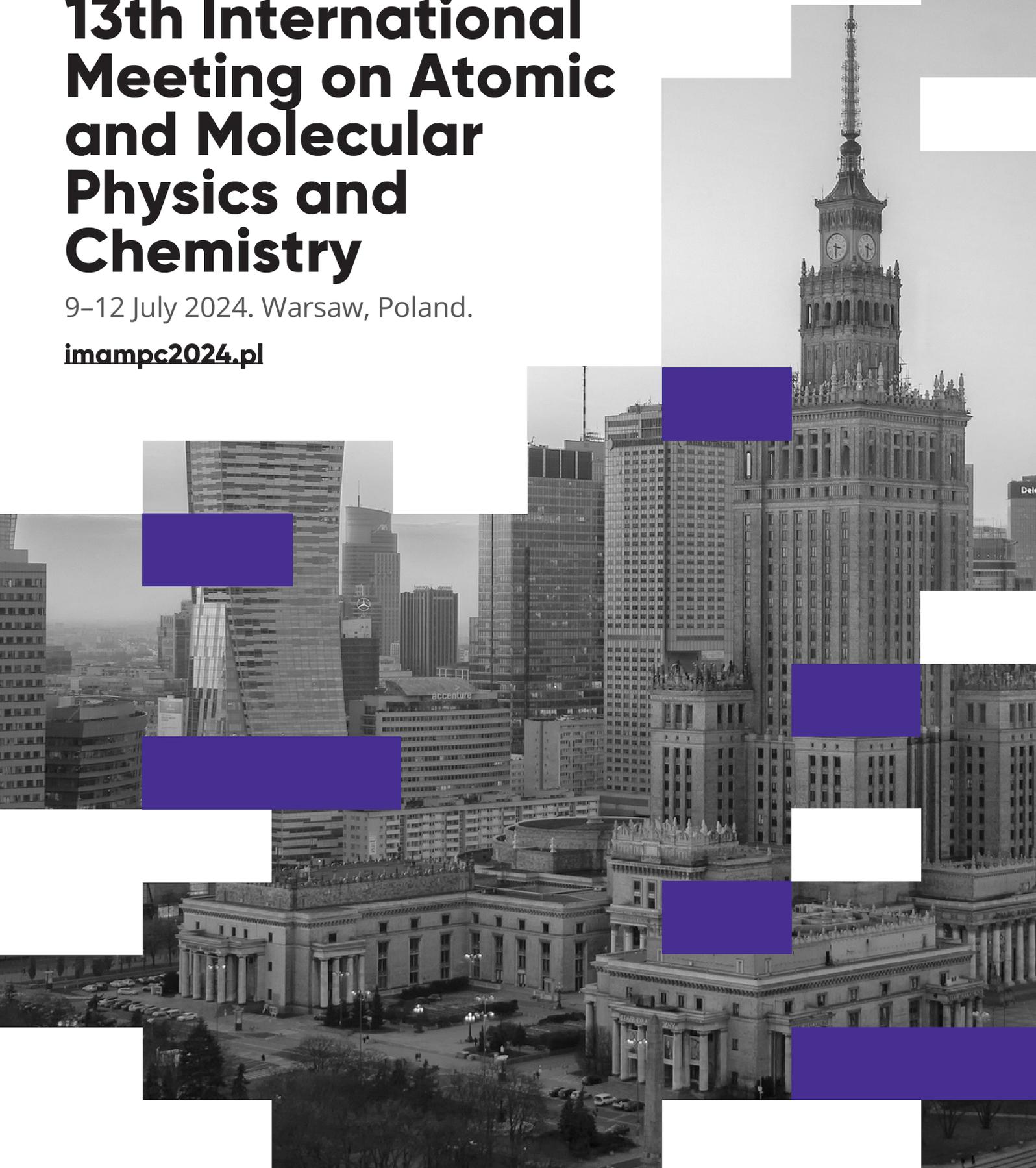
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Posters

Exploring the Spectroscopic Properties of Low-Charge Atomic Ions

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A novel apparatus has been developed to facilitate the spectroscopic study of low charge atomic ions using synchrotron and Free Electron Laser (FEL) photoabsorption in the soft X-ray spectrum (0.1-2 KeV) at Elettra (Trieste, Italy). This experimental apparatus enables high-resolution measurements of the energies and cross-sections of the main photoabsorption features of various atomic ions, which will greatly benefit a variety of upcoming astrophysical observations [1-3].

The setup comprises a customized commercial quadrupole mass analyzer (Balzers, model QMA 125), followed by a specifically designed electrostatic lens system to produce mass-selected ions of relevant atomic species and bring them into an octupolar ion guide, which is used as a scattering cell against a counter-propagating photon beam. Finally, a second quadrupole mass analyzer (Extrel, 150-QC) positioned after a 90-degree electrostatic quadrupole deflector stage reveals photon-ion scattering products. Preliminary results obtained on rare gas ions have been collected for the characterization of the instrument and will be presented.

Acknowledgments

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The Transition Dipole Moments from the Linear Response pCCD-based Methods

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Pair Coupled Cluster Doubles (pCCD) type methods offer valuable tools for electronic structure calculations, particularly in strongly correlated systems [1]. Extensions to excited states are possible within the Equation of Motion formalism. The EOM-pCCD-based models have advantages over standard methods in modeling large molecular polymer structures, often present in organic photovoltaic (OPV) devices and dye-sensitized solar cells (DSSC) [2]. However, we also need the transition dipole moments (TDMs) to be able to compare with experimental spectra. These are computationally expensive within the EOM formalism as we need both left and right eigenvectors. An additional disadvantage of EOM-CC-based TDMs is the lack of size intensivity [3,4]. That limits the possibility of studying large-polymer chains of different lengths. That motivated us to develop a linear response theory on top of the pCCD-reference wave function [5]. Specifically, we focus on the LR-pCCD and LR-pCCD+S models, their derivations, and their implementation in the PyBEST software package [5,6]. This work presents preliminary results for TDMs computed with the LR-pCCD+S method and their comparison to the reference data [7].



Figure1 : pip install pybest

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Cold CaF+Rb Interactions in Ground and Excited States

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Ultracold paramagnetic molecules, such as Calcium monofluoride (CaF), have emerged as a promising candidate for their potential application in precise measurements [1], quantum simulations [2], and ultracold chemistry experiments. Recently inelastic and reactive molecular collisions between two laser-cooled CaF molecules were studied in optical tweezers [3], sparking further interest in investigating collisions involving cold rubidium (Rb) atoms and CaF molecules.

The ground state of the atom-molecule system Rb-CaF, asymptotically goes $\text{CaF}(^2\Sigma^+) + \text{Rb}(^2S)$, corresponds to states $^1A'$ and $^3A'$. However, the excited state asymptote supports both A' and A'' states with singlet and triplet characteristics. The combination of singlet and triplet states in the ground state asymptote enables the formation of weakly bound Feshbach molecules. This weakly bound molecule can be transferred into specific ro-vibrational levels of the $^1A'$ potential using coherent Stimulated Raman Adiabatic processes (STIRAP) facilitated by two counterintuitive lasers.

To accomplish this idea of state transfer process by STIRAP, it is important to study the complete interaction potential for atom-molecule system Rb-CaF not only in the ground state but also in excited states, including the transition dipole moment. Here, we analyze the interaction potential for Rb-CaF by *ab initio* methods within the Born-Oppenheimer approximation, considering CaF as a rigid-rotor.

To analyze these states, we use Hartree-Fock (HF) followed by coupled-cluster (CC) methods, encompassing single, double, and perturbative triple excitations, to investigate the single-determinant states $^3A'$ and $^3A''$. For other ground and excited states, we employ a multi-reference configuration interaction (MRCI) approach, considering a suitable active space (AS). In Fig.1 and Fig.2, we show complete 2D-potential surfaces for the states $^3A'$ and $^1A'$ correspond to the ground state asymptote $\text{CaF}(^2\Sigma^+) + \text{Rb}(^2S)$.

We expect that our results is significant for the investigation of molecule formation in its ground ro-vibrational state through coherent or incoherent Raman processes.

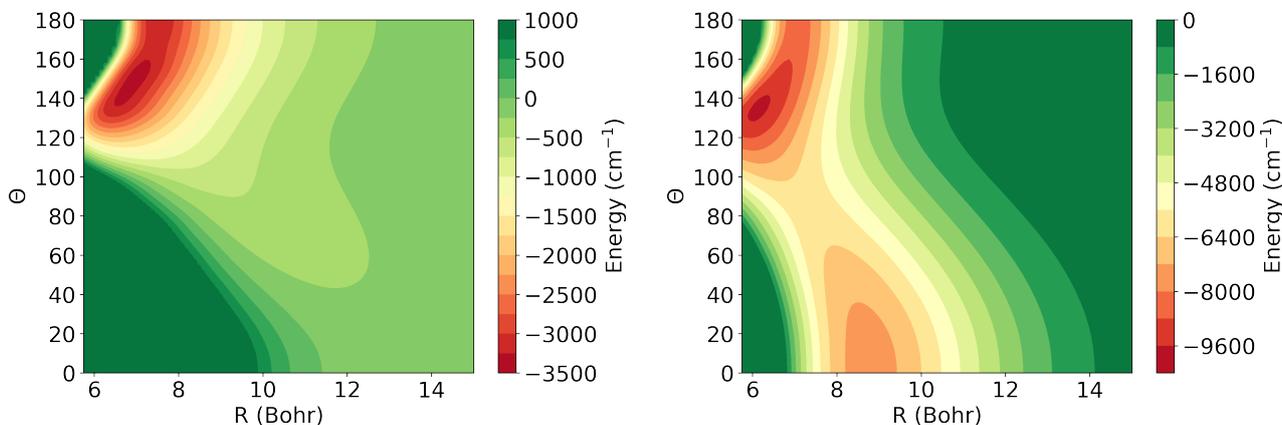


Figure 1: 2D-potential energy surface of the state $^3A'$. Figure 2: 2D-potential energy surface of the state $^1A'$

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Calculations of dipole polarizabilities of singly charged aluminium monohalides using KRCI method

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The field of cold and ultracold physics using diatomic molecules is growing very fast owing to the recent advancements in experimental techniques. The knowledge of components of static dipole polarizabilities (DPs) has crucial applications in the field of ultracold physics [1, 2]. Recently, it has been studied theoretically that the lowest members, AlF⁺ and AlCl⁺, of singly charged aluminium monohalide series are laser coolable [3] which could open new avenues for using these molecular systems for various applications. A few theoretical calculations on these molecules have been reported in the literature [4, 5, 6, 7, 8, 9, 10]. However, we could not find the DP results for these molecules in the literature. In this work, we have performed the relativistic calculations for the DPs of AlX⁺ (X: F, Cl, Br, I, At, Ts) ions using Kramers-restricted configuration interaction method together with the quadruple zeta quality basis sets. The relativistic and electron correlation trends are studied in detail.

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Carbonaceous Nanoparticles as Catalysts in the Interstellar Medium

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The gigantic interstellar medium (ISM) is full of molecular clouds, cosmic rays and dust particles that subserves the formation of diverse molecular species through catalytic processes, strongly affecting the interstellar chemistry. The major catalytic activities usually take place on the interstellar icy dust grains surfaces, being one of the main mechanisms for the formation of complex organic molecules (COMs); from small organic molecules and polycyclic aromatic hydrocarbons (PAHs) to big carbonaceous nanoparticles (CNPs) [1, 2]. Also, with the astronomical observation of CNPs such as C₆₀ and C₇₀ in various astrophysical environments, it is expected that other CNPs like carbon quantum dots (CQDs) could be present in space, especially in very cold environments. These entirely carbon core-shell particles have shown great facilities in absorbing and emitting lights of different wavelengths, making them suitable candidate as photocatalysts. The absorbed cosmic lights of different wavelengths by CQDs could thus potentially alter the molecular structure on the CQD surface [3]. Additionally, the presence of carboxylic acid and hydroxyl functional groups on the CQD surface may lead to organocatalytic activities [4]. These issues can be examined and studied by computational chemistry, and its detailed investigation can improve our understanding of Astrobiology and original life on earth.

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Laser Spectroscopic Investigation of Supersonic Jet Cooled Hydrogen-Bonded Solvent Clusters of 2,7-Diazaindole Isolated in the Gas Phase

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We have done the first extensive gas phase investigation of 2,7-diazaindole (27DAI) molecule which may serve as an efficient prototype for understanding excited state hydrogen/proton transfer reactions. We performed single vibronic level fluorescence spectroscopy (SVLF) to determine the ground state vibrational bands of the molecule and a large Franck–Condon activity was observed till 2600 cm⁻¹. Laser-induced fluorescence (LIF) and two-color resonant two-photon ionization spectroscopy (2C-R2PI) were performed to determine the excited state structure of the molecule. The band origin for S₁←S₀ transition was positioned at 33910 cm⁻¹ which was largely red shifted by 718 cm⁻¹ and 1322 cm⁻¹ compared to its parent molecules, 7-azaindole and indole, respectively. The excitation spectrum spreads till the 1600 cm⁻¹ region. The IR-UV hole burning experiment confirmed the presence of only one isomer in the molecular beam. The ionization energy (IE) of the molecule was measured to be 8.921±0.001 eV, recorded using photoionization efficiency spectroscopy. The above value was much higher compared to the other indole derivatives, which suggests the higher photostability of the molecule due to N(2) substitution. We performed fluorescence-dip infrared spectroscopy (FDIR) and resonant ion-dip infrared spectroscopy (IDIR) to determine the ν_{NH} values in the molecule. The values are 3523 and 3467 cm⁻¹ in the ground and excited state respectively. The lower value of ν_{NH} in the excited state is due to the increased photo acidity of the N(1)-H group. Then, we investigated 1:1 and 1:2 complexes of 27DAI with water in the gas phase. The origin band for the S₁←S₀ electronic transition of 27DAI-H₂O complex was obtained at 33074 cm⁻¹ which was highly red shifted by 836 cm⁻¹ on comparison with the bare 27DAI. In the 2C-R2PI spectrum, the modes observed at 141 (ν'_{Tx}), 169 (ν'_{Ty}) and 194 (ν'_{Ry}) cm⁻¹ were identified as the internal motions of H₂O molecule in the complex. These modes were detected at 115 (ν''_{Tx}), 152 (ν''_{Ty}) and 190 (ν''_{Ry}) cm⁻¹ in the ground state. The higher values in the excited state suggest a stronger hydrogen bonding interaction in the photo-excited state. The structural determination was achieved by the detection of ν_{NH} and ν_{OH} values in the ground and excited state of the water complex. The ν_{NH} at 3414 cm⁻¹ and ν_{OH} bands at 3447 cm⁻¹ in 27DAI-H₂O have shown a good agreement with the most stable structure with N(1)-H···O and OH···N(7) hydrogen bonded bridging water molecule in the ground state. In the electronic excited state, the corresponding bands were detected at 3210 (ν_{NH}) and 3265 cm⁻¹ (ν_{OH}). The IR-UV hole burning spectroscopy confirmed the absence of any other isomer in the beam. The ionization energy (IE) of the 27DAI-H₂O complex was measured as 8.789±0.001 eV, which was lower than the bare 27DAI. The strongest transition for 1:2 complex, i.e., 27DAI-(H₂O)₂ was observed at 32565 cm⁻¹, red shifted by 1345 cm⁻¹ compared to the monomer. In the FDIR spectrum, three bands at 3207, 3261 and 3385 cm⁻¹ are assigned as the hydrogen bonded ν_{NH} of 27DAI and two ν_{OH} vibrations from solvent chain connecting N(1)H and N(7) groups. The obtained structures have shown the formation of cyclic one- and two-solvent bridges incorporating N(1)-H···O and O-H···N(7) hydrogen bonds upon micro solvation. To understand the role of solvent polarity, we have investigated the hydrogen bonded 2,7-diazaindole-ammonia complex. The band origin for the S₁←S₀ electronic transition was positioned at 33045 cm⁻¹, exhibiting a large red shift of 865 cm⁻¹ relative to the band origin of monomer. However, the band origin is marginally red shifted by 29 cm⁻¹ compared to 27DAI-H₂O complex. The band detected at 183 cm⁻¹ (ν'_{Ty}) is assigned to the internal motion of the NH₃ molecule along y-axis with respect to 27DAI. The above mode is detected at 169 cm⁻¹ in the ground state of the complex. Only one isomer of 27DAI-NH₃ was detected in the range of 33020-34500 cm⁻¹. The ground state structure of 27DAI-NH₃ is assigned by recording the FDIR spectrum in the range 3100-3500 cm⁻¹, which depicted four bands at 3240, 3304, 3403 and 3433 cm⁻¹. The values have shown good agreement with the vibrational frequencies simulated for the most stable isomer, i.e., 27DAI-NH₃ (I₁) at 3253, 3302, 3418 and 3253 cm⁻¹. The study highlights the potential to desirably tune the excitation wavelengths and alter the photostability of the aromatic prototypes via additional N-insertion. The role of N(2) substitution in governing the feasibility of excited state hydrogen/proton transfer processes has been vastly explored through gas phase experiments aided by ab-initio calculations

Acknowledgments

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Modelling the Absorption Spectra of Luciferin Derivatives

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Abstract

When paired with luciferase, D-oxyluciferin is responsible for the bioluminescence of insects. This photoreaction has been harnessed for ATP assays and *in vivo* imaging. However, the use of D-luciferin for imaging living subjects is limited by the current range of emission wavelengths, 558 nm to 610 nm, which are unable to be detected from deep within tissues.^[1] Thus, novel luciferins, like oxy-infraluciferin, have been designed for bioluminescence in the near-infrared region.^[2] Little is known about the relaxation pathways of oxy-infraluciferin on a quantum level and so computational studies attempt to elucidate this.

Due to the expense of studying oxy-infraluciferin with current non-adiabatic dynamic simulations, a smaller fragment of this system was studied, thiazole. A vibronic coupling model and the Multiconfigurational Time-Dependent Hartree (MCTDH) algorithm were applied to thiazole in the gas phase, using the Quantics software package^[3], with LT-DF-ADC(2)/6-311++G(3df) as the electronic structure method. The absorption spectra was consequently simulated.

The resulting absorption spectra, Figure 1, was close in shape and energy to that provided by experiment in literature sources.^[4] Although the experimental data lacks resolution, it can be said that LT-DF-ADC(2) sufficiently described the absorption spectra and so should be reliable for simulating the dynamics of oxy-infraluciferin, as a whole system. Photoisomerism occurs in alike five-membered ring molecules, oxazole, and so the next step will be to run direct dynamics with the variational Multi-Configurational Gaussian (DD-vMCG) algorithm, where trajectories of the photoreaction may be observed.^[5] The overall future goal is to model the relaxation pathways of the whole oxy-infraluciferin molecule in both the gas phase and in solution.

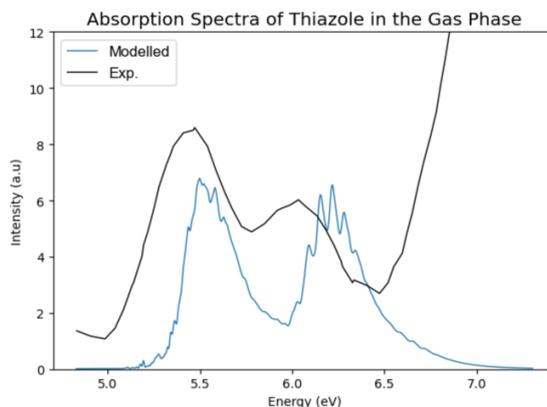


Figure 1: Experimental^[4] (black) and modelled (blue) absorption spectra of thiazole in the gas phase. Unpublished work.

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An intermediate phase between jammed and unjammed amorphous solids

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The phenomena of athermal amorphous solids jamming due to an increase in the volume fraction of their tiny constituents has received a great deal of interest in recent years. At a critical value of the volume fraction, pressure shoots up from zero to finite values with a host of critical exponents discovered and discussed. In this work, we present evidence for the existence of a second transition between two regimes of distinct mechanical responses within the jammed state of two-dimensional granular systems. Specifically, systems that are densely packed display quasielastic behaviour with quadrupole screening, while systems that are less densely packed display anomalous mechanics with dipole screening. A distinct shift between these two regimes is demonstrated, which is evocative of the middle hexatic phase of crystal melting in two-dimensional crystals. Theoretical estimates of the screening parameters and the pressure where transition takes place are provided.

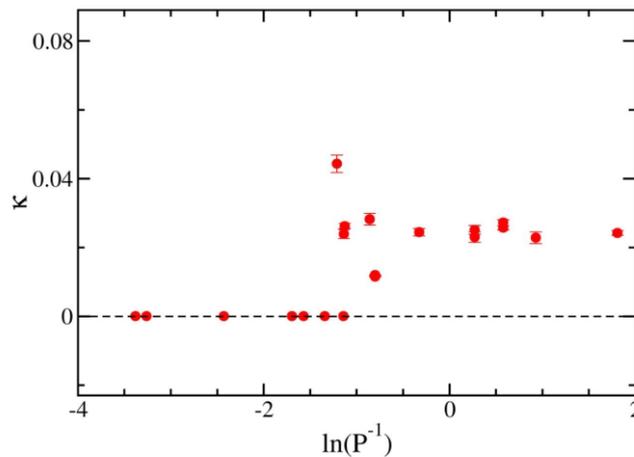


Figure 1: The screening parameter κ as a function of the logarithm of the inverse pressure. A transition between material phases with quasi-elastic response and with anomalous response is clearly observed

Acknowledgments

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Interaction induced dipole surfaces for H₂ - X (X = He, Ne, Ar) molecules for high temperatures

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When gas molecules interact through the Van der Waals force, minute rearrangements of their normal charge distribution occur, resulting in interaction-induced dipole moment. These interaction-induced dipole surfaces (IDS) are important in the calculation of collision induced absorption (CIA) spectra [1]. In this study, IDS for H₂ - X (X = He, Ne, Ar) systems are evaluated numerically in MOLPRO 2015 using the finite field approach, on a dense 3D grid. The vibrational average of the induced dipole components is also obtained. These results make it possible to calculate transition probabilities for molecules in excited vibrational states and overtones up to 26000 K. The convergence of the calculations at the CCSD(T) method using different basis functions, aug-cc-pVNZ (N = T, Q 5) is comparatively studied. Also, the effects of collisional partners such as X = He, Ne, Ar in the resulting dipole moment surfaces of H₂-X are analyzed. Furthermore, the dipole components at certain geometries are compared using Symmetry Adapted Perturbation Theory (SAPT) [2] and larger basis set such as aug-cc-pV6Z.

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Non-Orthogonal Pauli-Blockade: Towards Accurate Definition of Induction in Intermolecular Interaction

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Induction energy has significant contribution to intermolecular interaction, specially for strongly bonded systems. In present Symmetry-Adapted Perturbation Theory (SAPT) [1] for intermolecular interaction, the compensation for the higher-order induction [4] terms by delta-Hartree Fock term has several drawbacks. To have a complete and consistent induction with other interaction counterparts, it needs an alternative treatment in theory. Pauli-Blockade (PB) [2] [3] poses a variational approach with mutually polarized monomers. Apart from including infinite-order induction, PB method stands out as a potentially dispersion-less, many-body theory. In our present study, we work on a modified theory, Non-Orthogonal Pauli-Blockade (NO-PB) with strong symmetry forcing for inter-monomer interaction. This avoids the mixing of orbitals of monomers as previously in Pauli-Blockade (PB) method. Here we present the methods developed in second quantisation and implemented using Psi4numpy[5], a python interface of computational chemistry software (Psi4). We report the agreement between interaction energy calculated with our method and supermolecular energy at Hartree-Fock level, which essentially captures the infinite-order induction.

Acknowledgments

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Environmental Influence on Quantum Tunneling in Porphycenes Embedded in Polymer Matrices

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The recent surge of interest in quantum technologies has driven the search for objects that can serve as carriers or processors of quantum information as well as sensors and actuators in quantum devices. It has already been demonstrated that molecules can be candidates for such objects [1,2]. Although exploiting the quantum properties of molecules can be challenging due to their many internal degrees of freedom and coupling to the environment, they offer great flexibility in terms of combining into large structures and controlling via electromagnetic waves from various parts of the spectrum.

Over the last decade, it has been shown that porphycene and its derivatives constitute a class of molecules that exhibit an easily accessible quantum effect, namely the tunneling of internal hydrogen atoms (Fig. 1) [3,4]. These atoms are efficiently protected from the environment, allowing their quantum properties to be observed even in condensed matter at room temperature, with tunneling remaining the dominant channel of hydrogen transfer under these conditions [5]. Experiments conducted with single molecules on metal surfaces have shown that the position of the hydrogen atoms can be controlled by electric current [6,7] and is affected by the presence of other molecules and atoms in the vicinity of the molecule [8]. Thus, the construction of quantum networks made of multiple porphycene molecules is conceivable.

Applications of porphycenes in quantum devices require a full understanding of the coupling of the internal hydrogen atoms to nuclear degrees of freedom and to the environment. In this work, we studied the hydrogen transfer process in porphycene embedded in polymer matrices at both room and cryogenic temperatures. The results confirmed that the process is strongly coupled to a particular vibrational mode, but also demonstrated that it is affected by intermolecular vibrations localized in separate regions of the polymer [9].

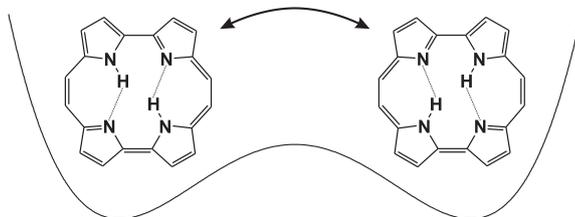


Figure 1: Double hydrogen transfer in a porphycene molecule

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Dissecting the electronic spectrum of ytterbium compounds. A relativistic 4-component analysis.

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Cold and ultracold chemistry can bridge theory and experiment in uncovering the fundamental properties of matter within the quantum realm. Providing reliable and accurate theoretical data for cold molecules is of paramount importance. The ytterbium atom has emerged as a highly valuable element in the field of cold chemistry due to its closed f-shell and the $4f^{14}6s^2$ ground-state electronic configuration, which renders its electronic structure similar to that of group II atoms. However, ytterbium, with its 70 electrons, is classified as a heavy element, posing significant challenges for state-of-the-art quantum chemistry due to non-negligible spin-orbit coupling (SOC) effects and the extensive electron correlation required.

Despite these challenges, SOC effects are often neglected in quantum chemistry investigations of ytterbium compounds due to the increased computational cost. In this project, we investigate the influence of relativistic effects on the low-lying excited states of diatomic ytterbium compounds using the Equation of Motion Coupled Cluster with Single and Double excitations (EOM-CCSD) methods. All presented calculations were performed with a relativistic four-component Hamiltonian implemented in the DIRAC quantum chemistry software.

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Femtosecond transient absorption study of the ground and excited state relaxation and tautomerization processes in 9-fluoroporphycenes

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We constructed new pump-probe transient absorption laser system, which can measure transient spectra and time-resolved profiles from sub-ps to few ns time range with very wide range of excitation wavelengths and good s/n ratio. This setup will be used to investigate relaxation processes and tautomerism in halogen-atoms substituted porphycenes in solutions and in cryogenic conditions [1].

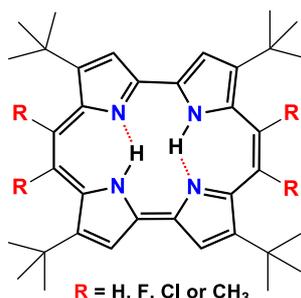


Figure1. Tetra-t-butyl-porphycene and its derivatives.

Porphycene and its derivatives are excellent model systems for studying a proton transfer reaction, one of the most basic chemical processes. They exhibit double proton-transfer within the cavity formed by four nitrogen atoms. The process may occur in the ground and excited electronic states and leads to isomeric structures (tautomers) having different arrangements of inner hydrogens. In the case of asymmetric substitution, these tautomers have slightly different energies of the electronic transitions. Here, we take advantage of this property to monitor tautomeric populations in spectral and time domains.

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INTERACTION ENERGY COMPONENTS FOR MOLECULES IN EXCITED STATE

A comparison of induction energy from finite-field and SAPT

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The induction energy is one of the component of interaction energy, which is tremendously difficult to calculate for molecules in their excited state (ES). When considering the interaction between an ES of one system and the ground state (GS) of another system, the multipole moments of the ES charge distribution can be different from those of the GS. [1] A purely multipolar description of the inductive effects encounters serious problems because of the divergent nature of the multipole expansion, while the bipolar expansion of the induction energy converges slowly. [2] For many years there was no methodology to use Symmetry-Adapted Perturbation Theory (SAPT) [3] for calculating induction energy of molecules in ES. Recently, such possibility became available due to work from research group of Michał Hapka from University of Warsaw and Katarzyna Pernal from Lodz University of Technology called SAPT(MC). [4][5] which can calculate induction energy in ES. However, there is possibility to calculate induction energies in ES using numerical derivatives of Energies (Finite Field Approach) given that one can obtain ES energies of a given monomer in presence of other monomer, which is the difficult part. This method allows using energies from various theories ranging from cheaper-faster to expensive-accurate theories.

We have calculated induction energies from second derivative of ES energies in presence of field from other monomer. While for the SAPT calculation we have selected SAPT(UHF) [6] with the Maximum Overlap Method (MOM), [7] and SAPT(MC). SAPT(UHF) for the ES leverages non-aufbau orbitals derived from MOM, allowing it to effectively handle cases of broken spin symmetry. Remarkably, SAPT(UHF) shows a high level of agreement with SAPT(MC), demonstrating its robustness in accurately predicting interaction energies even in cases of ES. Our study will attempt to benchmark the Induction energy of molecules in ES using Finite Field Approach to determine the best suitable method for describing the ES property, ultimately contributing to the development of method under the formalism of SAPT for ES.

Acknowledgments

We would like to thank Nicolaus Copernicus University for providing the computational resources. The extension of thanks is expressed for the funding of this work to the Center of Excellence and National Science Center NCN Sonata Bis9 2019/34/E/ST4/00407.

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Shaking Up ICEC: Exploring Nuclear Dynamics in Inter-Particle Coulombic Electron Capture

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Inter-particle Coulombic electron capture (ICEC) is a recently proposed electron capture process facilitated by the presence of an environment. Observations of related mechanisms [4] suggest that nuclear dynamics may significantly influence efficiency and/or final states. We develop analytical approaches to gain insights into nuclear dynamics in ICEC and aid in the interpretation of numerical simulations.

Since its introduction in 2009 [1], ICEC has been predicted in various systems, including van der Waals and hydrogen-bonded systems as well as quantum dot arrays [3]. During the ICEC process, a free electron attaches to a system (atom, molecule, or quantum dot), transferring excess electron attachment energy to a neighbouring system, which simultaneously undergoes ionization to release the excess energy [1, 2, 3], as illustrated in Fig. 1.

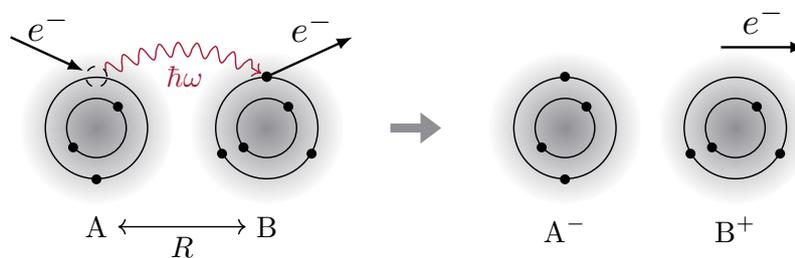


Figure 1: In ICEC, the excess energy from the electron capture by unit A is transferred to a neighbouring unit B, leading to its ionization [5].

While existing theoretical approaches for ICEC range from analytical models to ab initio calculations of electronic structure and dynamics, they have traditionally assumed static atomic nuclei [3]. Our approach, however, incorporates nuclear dynamics into the asymptotic description of ICEC. We will present promising systems and their nuclear dynamics, demonstrating their dominance over simple radiative recombination in our models, with the aim of informing future experiments.

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Combining the Hückel and PPP-Model Hamiltonians with pCCD-based methods in PyBEST

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In quantum chemistry, theoretical models are crucial for understanding electronic structures and molecular behaviour. The Hückel model, introduced by Erich Hückel in 1931 [1], offers a simplified method to estimate molecular orbital energies by focusing on π -electrons in conjugated systems. The Pariser-Parr-Pople (PPP) model, developed in the early 1950s [1], extends this concept by incorporating electron-electron interactions for a more comprehensive understanding of molecular electronic structures [2].

This study provides a detailed analysis of both model Hamiltonians, utilising advanced software tools and modern quantum chemistry methods to study the electronic structure and properties of large conjugated systems available in the PyBEST software package [3,4]. Specifically, we focus on pCCD-based methods for modeling prototypical organic molecules. [5,6].



Figure : PyBEST Logo

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Plasmons in bi-metallic particles: multiresonant structures able to strongly couple with multiple molecules

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Photoabsorption spectra of metallic nanostructures can be skilfully manipulated by changing their geometry and material composition. In principle, it should be possible to create nanoparticles showing more than one plasmonic resonance that can be utilised to enhance activation of excitons in molecules or non-organic nanostructures and possibly act as catalysts for some specific reactions.

We utilise Density Functional Theory (DFT) and Time Dependent DFT (TDDFT) to study plasmon formation in bi-metallic core-shell nanoparticles and its interaction with molecular excitons. As a case of study we chose Na and Mg as material domains in core-shell nanoparticles and benzene derivatives as molecules. We analyse excited electronic states landscape and contributions to the photoabsorption spectrum coming from electronic transitions between particular nanoparticle material domains and molecules.

In agreement with our expectations plasmon resonance position and shape of photoabsorption spectra is affected by specific order and thickness of core and shell layers (see 1 A). We show, on the example of $Mg_{147}@Na_{162}$ core-shell nanoparticle, that indeed it is possible to achieve nanoparticles with two intense separated resonances that can be strongly coupled to two different molecular excitons (see 1 B,C). Analysis of electronic transitions present in the system reveals a high hybridisation of electronic states and electron delocalisation resulting in the electrons being shared by Mg and Na atoms, effectively transferring some of them from Mg to Na. Interestingly, the set of transitions constituting a plasmon excitation is the same for both resonances indicating that the exact position of the resonance is given by the active single particle resonant transitions, which screen the plasmon oscillations (see 1 C).

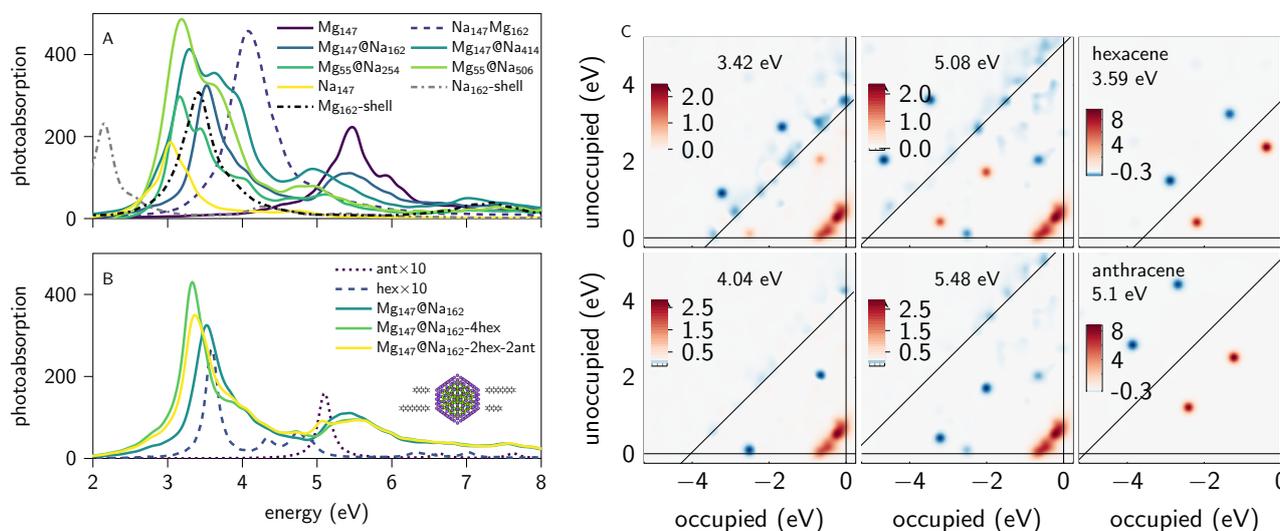


Figure 1: (A) Photoabsorption spectra of Na/Mg nanoparticles with various arrangement and size of Na/Mg domains. (B) Photoabsorption spectra of $Mg_{147}@Na_{162}$ nanoparticle coupled with hexacene and anthracene molecules. (C) Transition contribution maps for subsequent resonant frequencies in $Mg_{147}@Na_{162}$ nanoparticle coupled to hexacene and anthracene.

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Optical Potentials for the He* + Ar Penning Ionization Through Complex Basis Functions Method

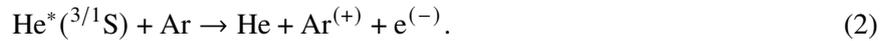
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Penning ionization[1] (PI) of neutral atom or molecule B through collisions with metastable species A is described by the reaction:



This is a two-electron process in which a valence electron from the reactant B fills the vacant valence orbital of A* causing the simultaneous ejection of the excited A* electron into the continuum. This phenomenon is referred as autoionization, driven by the coupling between bound and continuum electronic states[2]. Consequently, methods based on non-Hermitian quantum mechanics (NHQM) are necessary to properly take into account the coupling with the continuum within the Born-Oppenheimer approximation. From the NHQM methods the entrance channel of the reaction is treated as an electronic resonance with complex energy, $E_{\text{res}} = E_R - i\frac{\Gamma}{2}$, where E_R denotes the position of the resonance and Γ is the decay width (related to the lifetime of the resonance state). Here we explore the NHQM-based Complex Basis Functions (CBFs) method[3] to calculate optical potentials E_{res} for Penning ionization systems. As an example we consider collisions between metastable He atom (in its singlet or triplet excited state) with Ar atom:



For both singlet and triplet states, the short-range part of the interaction potential is calculated using the excitation energy variant of the equation-of-motion coupled-cluster (EOM-EE-CCSD) method combined with CBF approach. We demonstrate that the CBF method accurately predicts the exponential dependence of the width Γ on the interatomic distance. Furthermore, our calculations indicate that Γ reaches saturation when the interatomic distance becomes less than 4 Bohr, aligning with experimentally fitted optical potentials[4]. Additionally, we examine the orbital basis-set requirements for the PI width calculations using the CBF method for the two molecular systems under study.

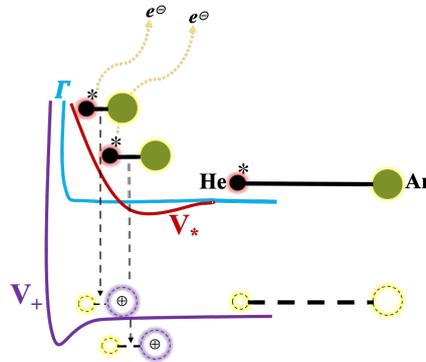


Figure 1: Penning ionization of He*+Ar .

Acknowledgments

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Mass Spectrometry Platform as Sample Delivery System for Gas-phase Small-angle X-ray scattering (SAXS) and Ion Spectroscopy Experiments

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The Mass Spectrometry for Single Particle Imaging of Dipole Oriented Complexes (MS SPIDOC) consortium has designed and constructed a MS platform for single particle imaging and related experiments at X-ray light sources [1].

MS and other well-developed gas-phase techniques are beneficial for sample delivery in X-ray structural biology experiments. Major advantages include the reduction of background scattering in the solvent-free environment, and separation and isolation of analytes by their masses and conformations. The MS SPIDOC instrument prototype is a MS platform that exploits these advantages. An additional instrument component provides the capability of dipole orientation of the particles, which enable structural reconstruction from much smaller scattering datasets.

The benefits of MS and the MS SPIDOC prototype have been explored in two X-ray experiments, gas-phase small-angle X-ray scattering (SAXS) and X-ray ion spectroscopy. Both experiments were performed at the PETRA III X-ray source, with scattering at the EMBL BioSAXS Beamline and spectroscopy at the P04 beamline. In the gas-phase SAXS experiment using our prototype, the first instance of scattering signal above noise has been detected. In the ion spectroscopy experiment, the ion mobility module was demonstrated to be capable of separating ions by their mobility for subsequent X-ray fragmentation.

With further experiments at different light sources, the MS SPIDOC platform promises to be a valuable sample delivery system for X-ray enabled experiments.

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Controlling collisional loss of ultracold polar molecules with external fields

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Ultracold molecules have many potential applications, ranging from quantum simulation and quantum computing to the creation of novel quantum phases [1]. There is particular interest in polar molecules, which can have long-range anisotropic interactions resulting from their permanent dipoles. A variety of such molecules have been produced at micro to nanokelvin temperatures by association of pairs of atoms, or by direct laser cooling. Many applications of ultracold molecules need high phase-space densities. For atoms, this is usually achieved by evaporative or sympathetic cooling. However, high-density samples of ultracold molecules usually undergo collisional loss, due to a variety of short-range mechanisms including inelastic or reactive collisions or photoinduced loss. Over the last decade, there has been tremendous efforts in understanding these loss mechanisms and how we can suppress such losses with *shielding* methods. Shielding can be achieved by various methods, most notably with static electric [2] and microwave fields [3]. Shielding has enabled the achievement of a new regime, a molecular gas dominated by elastic interactions, which can then be cooled to quantum degeneracy to study complex dipolar systems [4].

In my poster, I will present shielding mechanisms to control collisional loss of ultracold molecules using external static electric fields [5]. The external fields *engineer* repulsive interactions between two molecules based on their dipole-dipole interaction. Using such a methodology, we show that rates of two-body loss processes can be reduced by more than 10 orders of magnitude compared to the elastic collision rate [6]. This opens up new doors to cool and stabilize ultracold molecules to quantum degeneracy like recently achieved molecular Bose Einstein condensate [7].

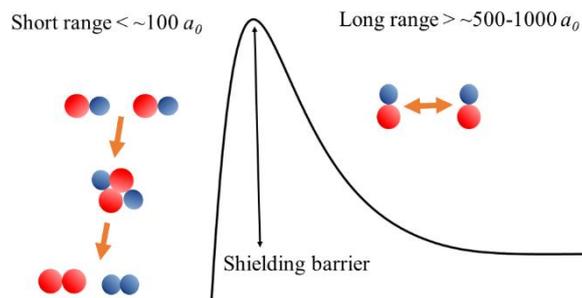


Figure 1: Schematic showing the shielding mechanism

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Fragmentation patterns of singly, doubly positively, and singly negatively charged triazole derivatives

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This study investigates the fragmentation patterns of triazole derivatives: 3-bromo-1H-1,2,4-triazole (1HBrT), 3-bromo-4H-1,2,4-triazole (4HBrT), and 3-benzyl-4H-1,2,3-triazole-5-methanol (OGM-1) in different charge states. These molecules might be relevant as potential radiosensitizers, as such compounds typically exhibit high electron affinity, a critical property for effective radiosensitization [1].

The quantum chemical calculations were conducted using Gaussian16, focusing on the potential energy surfaces study on cationic and dication as well as negative charge states. OGM-1 was modeled using density functional theory (DFT): functionals B3LYP and M06-2X with 6-311++G(d,p) basis set, while 1HBrT and 4HBrT were modeled using B3LYP-GD3BJ with def2-SVP and aug-cc-pVTZ basis sets. Additionally, for 1HBrT and 4HBrT we performed DFT-based molecular dynamics simulations to obtain the statistical distribution between various fragmentation channels, i.e., theoretical mass spectra. Our computational studies provided detailed insights into the energetic and dynamical mechanisms of the fragmentations. Our preliminary theoretical findings reveal ring openings and H-migration processes for singly negatively charged 4HBrT, as well as for doubly positively charged OGM-1 target.

Complementary experimental work involving the fragmentation of our targets induced by XUV and low energy electrons, were conducted in our experimental colleagues' laboratories (L. Carlini, CNR, Italy and J. Kocisek, Heyrovsky Institute, Czech Republic), highlighting a complete picture of reactivity and the generation of reactive intermediates. The OGM-1 sample was synthesized by O. García Mancheño (WWU, Münster).

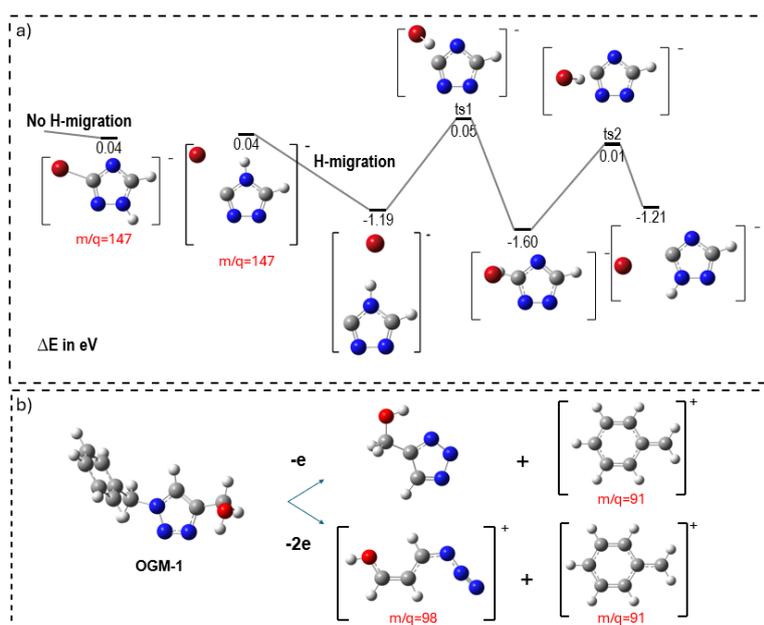


Figure 1: Schematic representation of the fragmentation patterns of triazole derivatives: a) singly negatively charged 1HBrT and 4HBrT, b) singly and doubly positively charged OGM-1.

Acknowledgments

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The effects of Ramsauer-Townsend minimum on the thermalization of electrons

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In this work, we develop a Monte Carlo (MC) simulation and apply it to investigate the effects of the Ramsauer-Townsend minimum (RTM) in the elastic cross section during the thermalization of low-energy electrons immersed in a background gas. The MC simulation can be summarized in a few steps:

1. An ensemble of electrons is created at the origin with a given energy.
2. The time between collisions is chosen according with the collision rate.
3. The velocity of the colliding partner is sampled from a distribution obtained by combining the collision probability with the Maxwell distribution of the background gas particles [1].
4. The momentum transfer between the colliding pair is calculated using Newtonian mechanics.

To perform the investigation, we choose the Beryllium atom as the background gas, as this system presents a deep RTM in its elastic cross section at an incident electron energy of ≈ 0.0029 eV [2]. It is expected that the presence of a RTM in the cross section will play an important role in the thermalization time by decreasing the collision rate and, consequently, considerably increasing the average time between collisions.

We find that, under the right circumstances, the motion of the background gas impacts the collision rate by attenuating the RTM. Using a simple model, we show that the correction to the collision rate grows linearly with the temperature. Fig. 1 illustrates the effects of this correction on the average collision time for $T = 3000K$. The uncorrected model (solid line) does not account for the background gas motion in the collision rate, while the corrected model (dashed line) accounts for it. By simulating 10^5 electrons with initial speed of $0.8v_m$ ($v_m \approx 0.0154$ a.u. is the RTM position), we find that it takes, on average, ≈ 500 ns for the electrons to reach speeds $\geq 1.2v_m$ in the uncorrected model, and ≈ 433 ns in the corrected one.

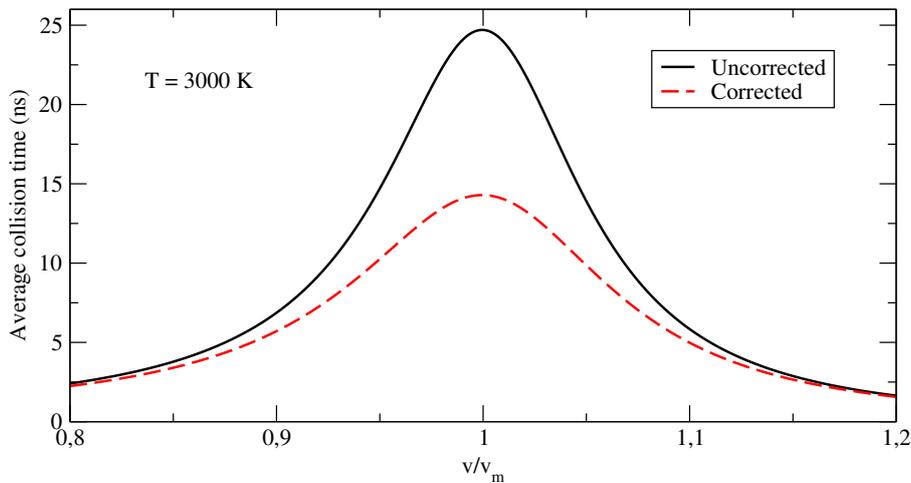


Figure 1: Average time between collisions for electrons immersed in a Beryllium gas at a temperature of $3000K$ as a function of the electron speed. $v_m \approx 0.0154$ a.u. is the RTM position. The solid line shows the result without the background gas motion correction, while the dashed line accounts for the correction.

Acknowledgments

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Unraveling Photoluminescence in a Gold Nanoparticles–Aryl Iodides System

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The search for and analysis of the photophysical properties of new materials are crucial because of the diverse applications of photoactive systems. Complex materials with long photoluminescence lifetimes and greater photostability than purely organic systems are particularly valuable. Beyond the intrinsic value of researching emission properties, these materials play a decisive role in advancing various branches of technology and medical science. However, in the course of the search for novel materials, all possible processes in the system must be considered in depth.

In the work of Maity *et al.*, an experiment on metal-enhanced luminescence was described [1]. It was found that this phenomenon occurs during the chemisorption of aryl iodides on gold nanoparticles (AuNPs), with the probable mechanism involving excimer formation. To investigate these promising literature reports, we conducted stationary fluorescence measurements of individual samples and analyzed excited state lifetimes using the time-correlated single photon counting (TCSPC) technique. The results revealed an even more remarkable reality than previously anticipated.

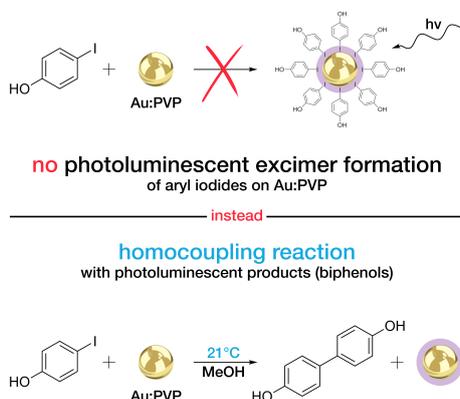


Figure 1: A diagram summarizing the previous assumptions and the results of our study – that is, the observation of a gold-mediated homocoupling reaction.

Through in-depth optical analysis, we have demonstrated that mixing aryl iodides with gold nanoparticles results in a homocoupling reaction (Fig. 1). The observed luminescence originates from the resulting products, whose emission spectra were mistakenly attributed in the literature to the formation of aryl iodide excimers on AuNPs. Moreover, this reaction occurs under exceptionally mild conditions, contrary to its typically known demanding nature. Therefore, this discovery not only clarifies the true source of the observed luminescence but also represents a significant advancement in improving the Ullmann homocoupling reaction, opening a new chapter in this field. [2].

Acknowledgments

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Computing Resonance Widths of Autoionizing Rydberg States via Feshbach-Fano Approach and EOM-CCSD Method

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Rydberg excited states with energies above the lowest ionization threshold can decay through autoionization (Figure 1), appearing as sharp features near higher ionization thresholds in photoionization spectra. Electronically, such states are embedded in the ionization continuum and are examples of Feshbach resonances. Here we consider autoionizing Rydberg states formed by exciting an electron from an inner-valence orbital of a neutral closed-shell. We start from the neutral system, where the initial state is an inner-valence excited state. Since the standard equation-of-motion coupled-cluster EOM-EE-CCSD method only allows excitation from the valence orbitals, we added a projector to the standard EOM-EE operator and applied it to the neutral system to obtain the inner valence excited states. The final state is a valence ionized state, which is computed by the standard EOM-IP-CCSD method. The free electron is modeled as a Coulomb wave where the charge of the wave is the effective charge of the ionized core. The resonance phenomena modeled here are based on the Feshbach-Fano approach² where the resonance width is obtained through coupling between the initial (quasi-bound) state and the final (continuum, ionized) states. The correlation-consistent Dunning basis sets aug-cc-PVXZ (X=Q, 5, and 6) with further augmentation by the Kaufmann functions³ are used as the basis set. We applied our technique to two systems: Ne atom and N₂ molecule. We focus on 3s, 3p, 3d, 4s and 4p Rydberg states for neon and 3s_g, 4s_g, 3d_g, 4d_g, and 3dπ_g Rydberg states for the N₂ molecule. Our methodology provides results consistent with those obtained from other computational techniques such as complex scaling and complex basis function technique⁴. Additionally, it is possible to apply to larger systems.

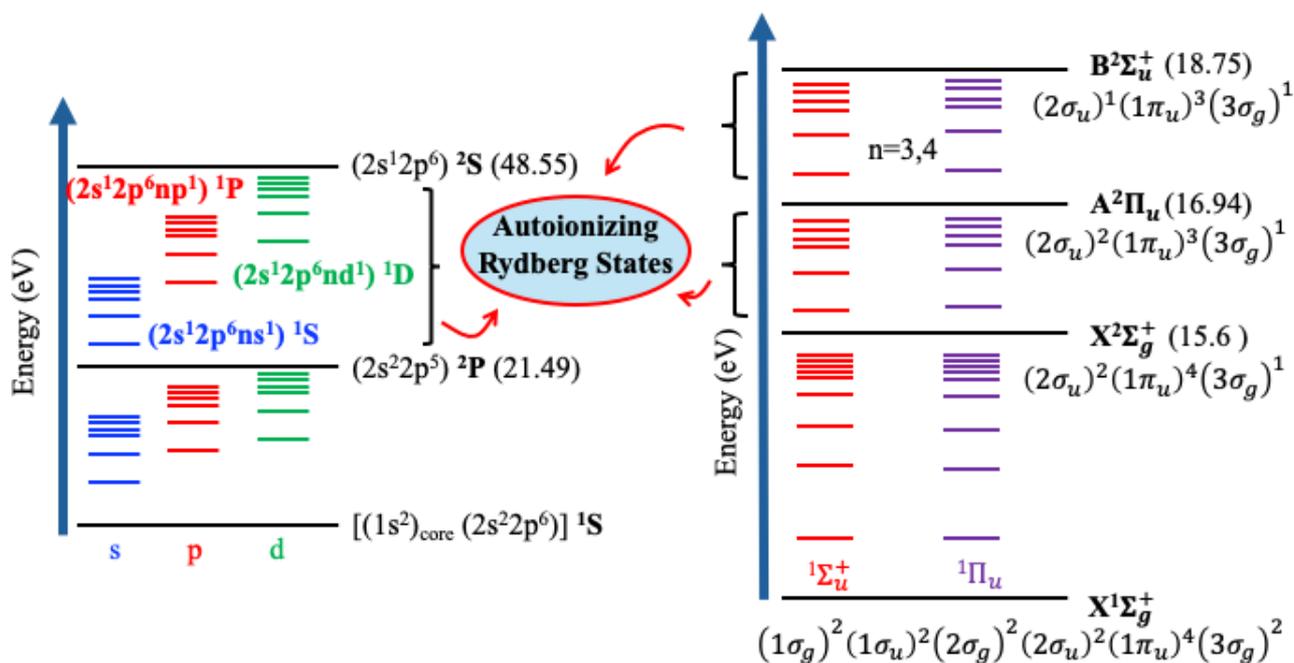


Figure 1: Energy level diagrams of Rydberg series in Ne atom (Left) and N₂ molecule (Right).

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Investigating reaction dynamics of acetone using photoion photoion coincidence spectroscopy

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Acetone is the simplest and smallest ketone with two methyl groups attached to the carbonyl group, studied as a model system for understanding the hydrophobic-hydrophilic balance in solute-solvent [1]. Although a few studies have investigated its gas-phase X-ray fragmentation [2,3], many details on the kinematics of the reaction, as well as the role of hydrogen motion, are lacking but may be of fundamental importance for understanding the interaction of this polar molecule with the solvating environment. Here, we present a study of the fragmentation of acetone molecules using PhotoElectron-PhotoIon-PhotoIon coincidence (PEPIPICO) technique using 3D momentum imaging spectroscopy.

The experiment was carried out with our spectrometer [4] at the I411 soft X-ray beamline of the MAX-IV laboratory. The acetone molecular beam intersects the soft X-ray radiation at the center of the spectrometer, allowing the time of flight of multiple ions and their momentum to be recorded, once a (photo)electron triggers the acquisition. We investigate coincidence events with two ions, knowing that at the photon energy used 240-320 eV most species are doubly charged.

In figure 1, we present a PEPIPICO plot revealing several distinct dissociation channels. We categorized these channels based on the presence and absence of hydrogen migration during the fragmentation process. An analysis of yields shows that the C-C bond breakings are dominant fragmentation pathways, but 10-20 % of channels contain hydroxyl group (or hydroxyl radical) related to hydrogen migration. Figure 2 illustrates the momentum sharing between the ion pairs in the primary fragmentation channel ($\text{CH}_3\text{CO}^+/\text{CH}_3^+$) formed by a two-body coulomb explosion. The correlation between momenta of fragments from other channels highlights a complex dynamic, suggesting rearrangement at different time scales.

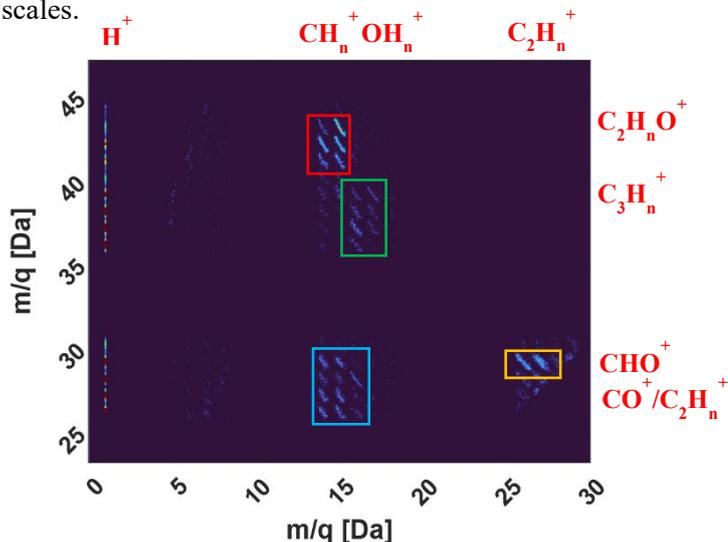


Figure 1: PEPIPICO plot showing two-dimensional time of flight coincidence map of fragment ion pairs formed by core ionization of acetone at photon energy of 320 eV. Time of flight has been converted to mass to charge ratio to simplify the ion identification. Different colors are used to distinguish between various fragmentation pathways.

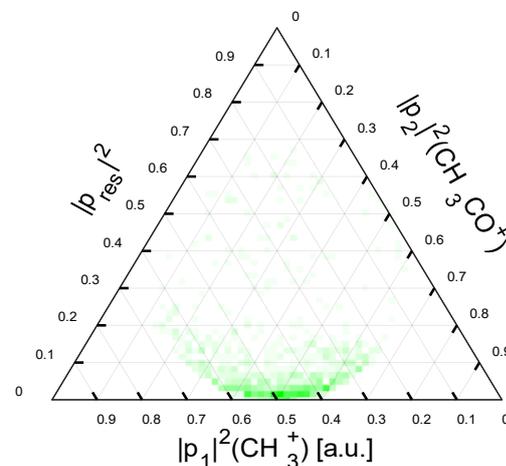


Figure 2: Dalitz plot representing the momentum correlation between the $\text{CH}_3\text{CO}^+/\text{CH}_3^+$ ion pair in coincidence events resulting from a two body break up with no missing fragments.

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Third-order exchange-induction-dispersion energy without single-exchange approximation in symmetry-adapted perturbation theory

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In symmetry-adapted perturbation theory (SAPT), the exchange terms are often calculated utilizing the so-called *single-exchange* approximation, i.e. by approximating the antisymmetrizer of the whole system by permutations of a single pair of electrons between non-covalently interacting subsystems. The error introduced in this approximation is typically tolerable. However, it has been proven to be the reason for qualitatively wrong results of S^2 SAPT corrections for some ionic systems. [1, 2]

This work presents the third-order exchange-induction-dispersion correction ($E_{\text{exch-ind-disp}}^{(30)}$) of SAPT derived without the *single-exchange* approximation in the second-quantization formalism. In order to obtain the explicit orbital expression for the $E_{\text{exch-ind-disp}}^{(30)}$ energy, the approach of Ref. [3] was extended to the third order of SAPT. The quality of the S^2 approximation of exchange corrections (including the unapproximated $E_{\text{exch-ind-disp}}^{(30)}$ energy) has been studied on a selection of benchmark databases for non-covalent interactions, including some ionic datasets.

Acknowledgments

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Time-independent vs. time-dependent treatment of excited states; dynamics of an ultracold dipolar gas in an external field

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In the context of electronic structure and cold quantum gases the concept of dynamics is closely related to that of the excited states. Standard wavefunction methods of quantum chemistry (e.g. MBPT, EOM-CC)[1] address excited states by transforming single reference ground state amplitudes to find low-lying stationary solution without use of explicit time dependence. Alternatively, the reference state can be "kicked" out of the equilibrium, followed by a real-time propagation to evolve it into an excited state, as in field-based methods (Sine-Gordon, eGPE)[2] or by applying linear-response formalism on top of a ground state as in TD-DFT[3]. Since the advent of dipolar molecular condensates, the inter-molecular interactions have been made tunable by microwave shielding at very short time-scales[4]. Such dynamics would best be described by an explicitly time dependent method that would allow for fast switching of the external field, yet with high accuracy to capture correct optical and scattering properties of dipolar species. This contribution aims to spark up the discussion, and show preliminary findings that contrast the treatment of excited states by time independent Coupled Cluster formalism, with the dynamics of quenched dipolar BEC obtained by split-step TD-eGPE.

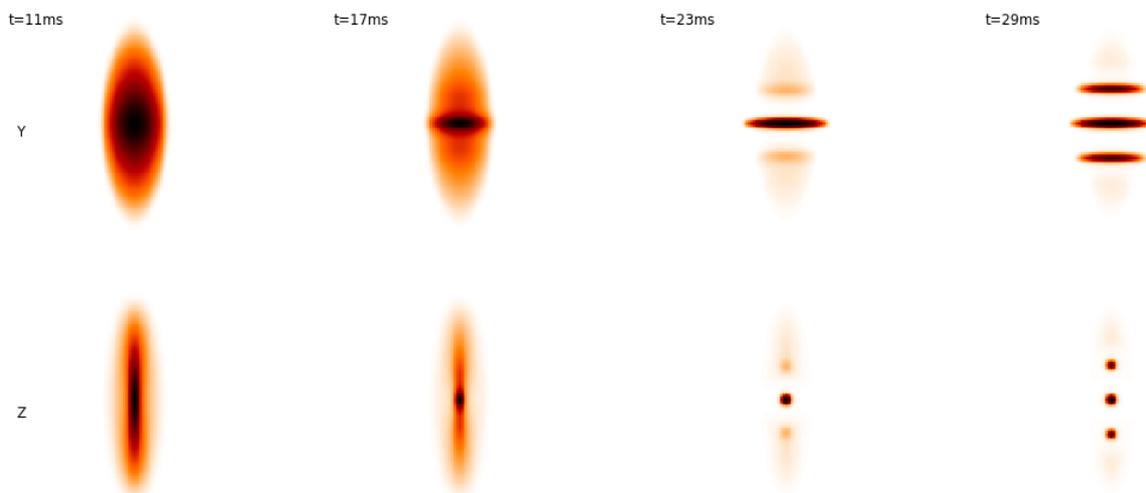


Figure 1: Dynamics of dipolar BEC in a harmonic trap, magnetically polarized in \hat{z} , including S-wave and dipole-dipole scattering as well as Lee-Huang-Yang quantum fluctuations; shown are the density projections onto \hat{y} and \hat{z} axis as a function of the propagation time.

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