

# UV-induced photofragmentation of CF<sub>3</sub>C(O)Cl studied via VMI technique and ab initio simulations

## Content

Trifluoroacetyl chloride (CF<sub>3</sub>C(O)Cl) is produced during photooxidative degradation of various atmospheric halocarbon species, which were applied in the last decades as a replacement for strongly ozone-depleting freons. Therefore, the description of its own degradation pathway is important for atmospheric radical chemistry.[1,2] Two major radical forming reactions were reported for the UV-induced degradation channel with their mutual participation strongly dependent on the photon energy.[1] Whereas the photons with energy below  $< 4.8$  eV ( $> 260$  nm) induce preferentially two-body fragmentation with only Cl radical cleavage, the more energetic photons rather induce three-body fragmentation into Cl, CO, and CF<sub>3</sub> fragments.[1] Recently, we started to investigate the UV-photofragmentation channel between 193-280 nm by velocity map imaging (VMI) of Cl and CO fragments to get a detailed insight into the CF<sub>3</sub>C(O)Cl fragmentation dynamics.[2] The acquired VMI images of Cl fragments after excitation in the range of 235-280 nm demonstrate a single ring structure with an almost isotropic character. The fragments' kinetic energy ( $\approx 0.45$  eV) and  $\beta$ -parameter are increasing with photon energy due to shorter dwelling time in the shallow minimum of the excited state. [2] On the contrary, the CO signal shows a bimodal distribution of the ejected fragments between 235-280 nm with a broad central blob and narrow ring with anisotropy similar to Cl images. Whereas the origin of slow CO fragments was assigned to thermal decomposition of CF<sub>3</sub>CO\* fragment generated from two-body fragmentation, the fast CO fragments are generated from three-body fragmentation channel. This was confirmed by the VMI images of CO with a single narrow ring with profound anisotropy character at 193 nm. On the other hand, the size of the CO ring is not changed for more energetic photons at 193 nm contrary to VMI images of Cl fragments, where we observe a significant increase of kinetic energy to 0.65 eV and strong anisotropy character. This result indicates sequential three-body dissociation CF<sub>3</sub>C(O)Cl  $\rightarrow$  CF<sub>3</sub>C(O)\* + Cl  $\rightarrow$  CF<sub>3</sub> + CO + Cl. The experiment at 193 nm also reveals new components in the Cl signal coming from the possible involvement of higher excited states and significant differences between the ejected Cl radicals in the ground and excited states. These observations are currently investigated by our ab initio molecular dynamics simulations, which should help us to verify the origin of the new components and further explain the energy partitioning obtained from our VMI images.

Fig.1: VMI images of Cl fragments in the a) ground and b) excited states after photofragmentation at 193 nm.

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## Contribution Type:

# Studying rotational-state and conformational effects in chemi-ionisation reactions

## Content

Conformers are the dominant isomers of complex molecules. The conformation of a molecule can have pronounced effects on its chemical reactivity. However, because they often interconvert into one another under ambient conditions, individual molecular conformations are difficult to isolate. Consequently, only sparse experimental data exists on the chemical properties of distinct conformers [1]. Over the past years, we have developed experimental methods to study conformational effects in ion-molecule reactions under single-collision conditions [2,3]. Extending our methodology to neutral reactions, we have recently built a new crossed-molecular-beam setup. This setup is equipped with an electrostatic deflector which enables the spatial separation of different conformers or individual rotational states of molecules based on their effective dipole moments. The products of chemical reactions of the separated conformers are monitored by time-of-flight mass spectrometry (TOF-MS) and velocity-mapped ion imaging (VMI) [4].

As the first application of this new method, rotational-state and conformationally specific chemi-ionisation reactions of carbonyl sulfide (OCS) and hydroquinone with metastable neon atoms were investigated. Pronounced state- and conformation-specific effects on the product branching ratios of both reactions were observed. Our result suggests that OCS molecules in the rotational ground state  $J = 0$  are a factor of 2.5 more reactive for dissociative ionisation than Penning ionisation compared to the  $J = 1$  state [4,5]. Similarly, cis-hydroquinone shows a stronger propensity for dissociative ionization in comparison to Penning ionisation than trans-hydroquinone. Monte-Carlo trajectory simulations showed that the formation of the Penning ionised product depends on the initial conformational and rotational state of hydroquinone whereas the formation of the dissociative ionised product is independent of the initial conformational and rotational state. The disentanglement of conformational and rotational-state effects can be difficult to analyse due to the involvement of several rotational states [5]. However, choosing conformers that can be chemically separated and have high interconversion barriers could disentangle the conformational and rotational state dependencies. Therefore, we chose to study the chemi-ionisation reaction of 1,2-dibromoethylene (DBE), the conformers of which can be chemically separated [6,7]. Moreover, in a collaboration with the Korean Advanced Institute of Science and Technology (KAIST), we are also currently undertaking a comparative study of the photochemistry, photoionisation and chemi-ionisation of individual stereoisomers using 1,2-dibromoethylene (DBE) as a prototypical system [8]. These investigations aim at gaining a comprehensive understanding of the role of molecular conformations in unimolecular and bimolecular reactivity.

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# Comparative study of C60 impact interactions with low mass targets – experimentally motivated molecular dynamics calculations

## Content

Recently our group have reported the experimental observation of a novel process of velocity correlated cluster emission (VCCE effect) following impact of a C60- projectile on a metallic surface at the keV kinetic energies regime [1, 2]. In contrast to cluster emission induced by the impact of a heavy monoatomic ion, with a large polyatomic projectile such as C60 it was found that all clusters are emitted in a velocity correlated fashion, moving with nearly the same most probable velocity. The results were supported by modelling of the initial phase of the formation of the collisionally induced thermal spike and molecular dynamics (MD) simulations of the extremely fast (deep subpicosecond) thermalization of the collisional cascade nanovolume (see Fig.1) [2, 4]. It was shown that the VCCE effect is most pronounced for atomically heavy target (e.g., Au, Ag, Cu) and is getting weaker for lower mass targets (e.g., Al [3]). In order to gain a deeper microscopic insight into the underlying emission mechanism and its detailed dependence on physical properties of the specific targets we have carried out MD simulations (employing the LAMMPS [5] package) of the impact interaction of the C60 projectile with several low mass targets (Be, C, Al, Si), compared with that of the heavier (Cu, Ag, Au) targets. The simulations were focused on the sub-ps evolution of average kinetic energy (Fig.1a) and number density (Fig.1b) of the target atoms contained within the sub-surface impact excited zone and the sub-ps dynamics of the evolution of the impact crater at the nanoscale (Fig.2). One can clearly see the systematic difference in the dynamic physical properties of the heavy and low-mass bombarded targets, as well as the difference between the softer (Be, Al, Si) and harder (C, BN) low-mass targets. The trends observed comparing the different targets (experiment and simulation) explain the gradual weakening of the VCCE effect with decrease in target mass.

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# Effects of deuteration on the reaction dynamics of $F^-$ with $CH_3I$ .

## Content

Our group studies ion-molecule reactions using a crossed-beam setup with kinematically complete velocity map imaging (VMI). This has proven to be a powerful tool to obtain experimental insight into molecular reaction dynamics, as the obtained differential cross sections can be used to link and identify atomistic reaction mechanisms during the formation of reaction products.

In recent experiments we have investigated the reactive scattering of fully deuterated methyl iodide  $CD_3I$  with atomic fluorine anions in the energy range from 0.7 to 2.3 eV relative collision energy. The results are compared with the hydrogenated system  $F^- + CH_3I$  [1] as well as quasi-classical trajectory (QCT) simulations [2]. The two main reaction channels are nucleophilic substitution ( $S_N2$ ) and deuteron/proton transfer for both systems. The  $F^- + CH_3I$  reaction shows a significant large-impact parameter contribution in the  $S_N2$  channel, a feature that is absent for its deuterated counterpart. While the simulations can fully capture the  $S_N2$  dynamics in the reaction with  $CD_3I$ , large-impact parameter events from  $F^- + CH_3I$  cannot be reproduced. Such a discrepancy between experimental and theoretical work might hint towards a quantum effect that cannot be captured by QCT simulations.

We also present preliminary results on the reactive scattering of  $CH_3I$  with radical anions, more specifically with atomic oxygen anions  $O^-$ . We discuss energy-dependent differential cross sections and branching ratios for four observed, competing reaction pathways.

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# Temperature dependent reactions of atomic hydrogen with the astrochemically relevant anions $\text{CN}^-$ and $\text{C}_3\text{N}^-$

## Content

Currently about 270 molecules have been identified in the interstellar medium (ISM). This already hints at the ample chemistry that has to happen in the cold and diffuse regions of space. A driving source of the chemistry in space are reactions of neutrals with molecular ions, as the long-range interaction leads to significantly larger reaction rates. Although most of these ions are positively charged, six negative ions have been found among the molecules in space so far. All six of the detected anions are carbon containing species [1].

The most abundant elemental collision partner in the ISM is hydrogen. Previously our group showed that reaction rates of carbon chain anions with  $\text{H}_2$  are too small to contribute to the chemistry of these ions in the ISM [2]. However, we cannot assume the same for atomic hydrogen, since it is more reactive than its molecular counterpart.

Here we present reaction rate coefficient measurements of  $\text{CN}^-$  and  $\text{C}_3\text{N}^-$  with atomic hydrogen in a temperature variable 16-pole wire-ion-trap in the range from 300K to 7K [3]. The H atoms are created by thermal cracking in a commercially available H-Atom source. Subsequently, they are cooled by a Teflon coated copper block attached to the cold ion trap housing.

In this contribution we will present the H atom density calibration and discuss the temperature-dependent behavior of the measured reaction rate coefficients.

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# On the formation of C<sub>2</sub>H<sub>4</sub>O isomers on dust surfaces in the ISM

## Content

The most abundant elements in the ISM are H and He with small contribution of biogenic elements such as O, C, and N. The combination of these elements leads to the formation of small, large and complex organic molecules. Formation of CO, CH<sup>+</sup>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and other small organic molecules has been reported in the cold dense clouds.

Accumulations of these atoms and molecules may lead to the formation of species such as CH<sub>3</sub>OH, H<sub>2</sub>CCHOH, CH<sub>3</sub>CHO, and C<sub>2</sub>H<sub>4</sub> isomers by their reactions on dust surfaces. Detection of these species has attracted special attention because they play an important role in astrobiology. In particular, acetaldehyde and ethylene oxide are key raw materials for the formation of amino acids, which are key for life. However, the abundance of these molecules depends upon the physical and chemical environment of the ISM. Therefore, it is important to investigate how the environment affects their formation pathways. In the past, the formation pathways of three isomers of C<sub>2</sub>H<sub>4</sub>O from O(3P) and H<sub>2</sub>C=CH<sub>2</sub> (acetaldehyde CH<sub>3</sub>CHO, ethylene oxide (CH<sub>2</sub>OCH<sub>2</sub>), and vinyl alcohol CH<sub>2</sub>CHOH) in the gas phase have been reported.<sup>2-4</sup> However, the formation pathways of these isomers on dust surfaces is still unclear.

Herein, we have performed Density functional theory (DFT) calculations to understand the formation of different isomers by the reaction of oxygen atom with ethylene in the gas phase as well as on a model dust surface (bi-layer graphite surface). The dust surface induced lower formation energy barrier and promoted the formation of C<sub>2</sub>H<sub>4</sub>O. In addition, some additional routes for the transformation of one isomer to other on the surface in comparison to the gas phase reactions will also be reported.

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# Disentangling sequential and concerted fragmentations of molecular polycations with covariant native frame analysis

## Content

The recent development of time-resolved Coulomb explosion imaging (CEI) as a method to probe ultrafast photochemistry [1,2] has increased interest in the fragmentation behaviour of polycations. In order to fully exploit CEI as a structural probe, a detailed understanding of many-body fragmentation dynamics of polycations is required.

We present results from an experimental ion imaging study into the fragmentation dynamics of 1- and 2-iodopropane (IP) following interaction with extreme ultraviolet intense femtosecond laser pulses. Using three-dimensional covariance imaging analysis, a range of fragmentation pathways of the resulting polycations can be isolated and interrogated in detail at high ion count rates. In our new data analysis approach, we incorporate the recently developed native frames method [3] into the covariance imaging procedure, enabling us to isolate contributions from concerted and sequential three-body Coulomb explosion pathways. The angular distributions of the fragment ions (Fig. 1) is much more complex than in previously reported studies for the three-body fragmentation of triatomic polycations, [3,4] and differs substantially between the two isomeric species.

To interpret the ion emission angular distributions, we use a classical model of the Coulomb explosion process. Despite the simplicity of the model, it offers valuable physical insights into the fragmentation dynamics of these polycations, including how the initial dissociation step in a sequential mechanism influences rovibrational dynamics in the metastable intermediate ion, and how signatures of this nuclear motion manifest in the extracted covariance signals.

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# High energy metal atoms as a probe of gas-liquid surface structure

## Content

The gas-liquid interface of ionic liquids (ILs) plays an important role in many applications including in supported IL phase catalysis. Methods to investigate surface structure in these systems will allow the performance to be improved in a systematic way. We use reactive-atom scattering (RAS) and molecular dynamics simulations to study the vacuum interface of mixtures partially fluorinated and alkyl ILs [1]. The underlying aim is to determine whether the fluorinated IL ions could be used as additives to modify the surface structure of one of the most commonly used families of ILs. Previous RAS studies[1-3] have used O atom projectiles which have sufficient energy to abstract Hydrogen atoms from alkyl chains and probe OH products in the gas phase as a method of determining the alkyl group surface coverage. In this work we extend this method by using high energy aluminium atoms as the probe, these atoms have sufficient energy to abstract a Fluorine atom from the fluoroalkyl chains. The reaction products are then probed in the gas-phase above the surface using laser-induced fluorescence.

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# Collisional excitation and dissociation of CO molecule by proton impact: application to astrophysics and astrochemistry

## Content

The CO molecule is one of the most abundant molecules in interstellar space [1] and proton is a major component of the stellar (solar) winds. Thus, the collisional excitation and collision-induced dissociation (CID) by proton impact are expected play important roles in the chemical evolution of interstellar molecules. A considerable amount of study has been performed to study this process in both experimentally and theoretically. [2-4]

We study the energy transfer and fragmentation of CO molecule by proton impact within the energy-range of 10 eV-1 keV. The classical trajectory (CT) calculation and the sudden-limit model [5,6] are applied. It is found that the sudden-limit model estimates the energy-transfer from the translational to the internal degrees of freedom with less efficiency.

Figure 1 represents calculated excitation spectra of CO molecule due to proton impact at the collision energy  $E=27$  eV in the center-of-mass frame. The spectra are obtained with the CT calculation as well as with the model. In both calculations, the spectral profile represents a triply peaks. One peak corresponds to the nearly elastic scattering and the others to the binary collision between projectile and atoms in the target. It is found that the probability of CID depends strongly on the orientation angle at the moment of the contact. The fragmentation takes place predominantly when a proton hits the molecule either perpendicular or parallel to the molecular axis. Otherwise, the energy transfer causes the rotational excitation of the target molecule which causes micro wave emission in molecular clouds.

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## Figure 1

The excitation spectrum of CO molecule in the backward scattering of H<sup>+</sup> + CO at the collision energy  $E = 27$  eV. The intensities  $f(\epsilon)$  as functions of the normalized excitation energy  $\epsilon = \Delta E / E$ ,

are shown. Solid and dashed curves indicate the spectra with the CT calculation and that with the sudden-limit model, respectively.

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# Formation of OH<sup>-</sup> in reaction of O<sup>-</sup> with CH<sub>4</sub> studied with 22-pole RF ion trap at low temperatures

## Content

According to models of the astrophysically relevant plasmas, the OH<sup>-</sup> anion should be abundant in many respective environments but has not yet been detected there. There are only a few ion-molecular reactions leading to the formation of OH<sup>-</sup> at low temperatures. We have already studied reaction O<sup>-</sup> + H<sub>2</sub> [1,2] and we want to explore the other possibilities.

The ion-molecular reaction of O<sup>-</sup> with methane was studied at 300 K by Bohme [3]  $1.0 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  and Parkes [4]  $1.1 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ . We used the 22-pole RF ion trap to measure the title reaction over the temperature range from 300 K down to 100 K. We observed the formation of anion OH<sup>-</sup> with indications of another channel. The formation of OH<sup>-</sup> represents approximately  $(70 \pm 15)$  % of the total reaction rate. The possible other channel is the formation of CH<sub>4</sub>O and electron detachment. The Langevin collision rate constant for the reaction of O<sup>-</sup> with methane is equal to  $1.3 \cdot 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ . Measurements show that the total reaction rate coefficient is at least an order of magnitude smaller than the collisional rate constant, with its preliminary values ranging from  $(9 \pm 3) \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  at 300 K to  $(2.0 \pm 0.6) \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  at 100 K.

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# Vibronic branching in VUV photodissociation of N<sub>2</sub> molecules probed by backward quantum dynamics

## Content

Non-adiabatic interaction has ubiquitous impact on various photochemical processes also in diatomic molecules [1]. High energy excited states are often involved in strong non-adiabatic coupling. Such terms induce population transfer between the coupled adiabatic electronic states and can open new channels for the dynamics.

In the present work we investigate the role of the non-adiabatic effects on the VUV photodissociation of N<sub>2</sub> into different atomic electronic states. The VUV photodissociation of the nitrogen molecule is known [2] to proceed through the triplet <sup>3</sup>Π<sub>u</sub> electronic states, reached via spin-orbit interaction from the optically accessible singlet <sup>1</sup>Σ<sub>u</sub><sup>+</sup> and <sup>1</sup>Π<sub>u</sub> states. High level ab initio quantum chemical calculations, e.g., [3], show that there are several regions of strong non-adiabatic interaction between the triplet states on the pathway towards dissociation. We here present a quantum dynamical approach that enables us to efficiently examine intricate paths of the electronic subsystem. We identify the particular vibronic states that are likely to dissociate into the specific atomic products by using the backward propagation technique: we begin the dynamics from the exit channel and study how it evolves back in time, see Fig. 1.

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# Probing molecular absorptions using cryogenic gas-phase action spectroscopy of helium-tagged ions

## Content

The absorptions of molecules in the solid state, in solution or in matrix are influenced by the respective environment. However, to be experimentally as close as possible to quantum chemical calculations, measurements in the gas-phase are essential. This is made possible by the newly built HeTag instrument for cryogenic gas-phase action spectroscopy. In addition to benchmarks for theory, this measurement method also offers the possibility to compare molecular absorptions in the laboratory with the light absorptions of the interstellar medium, the so-called Diffuse Interstellar Bands, in order to draw conclusions about the existence of ions in space. Campbell et al. have already been able to detect  $C_{60}^+$  in this way [1]. It also becomes possible to observe experimentally in detail the influence in the adaptation of ligands in a complex, to ultimately support synthesisists in the targeted preparation of complexes.

In the method used here, ions are first produced in an ESI or EI source, then mass-selected and stored. In the cryogenic quadrupole trap, the ions collide with helium, forming corresponding complexes ( $M..He_n^{+/-}$ ). By irradiating these ions through a tunable laser system, the extremely lightly bound helium complexes will dissociate if there is absorption at this wavelength. Following the irradiation, the ions are ejected from the trap and pass a second mass selection. Absorptions correspond to a reduction of the number of helium complexes.

As a tag, helium offers the advantage that it hardly affects the absorptions and is easy to remove. The hexapole pretrap specially introduced in this instrument allows ions with low intensity to be studied. Finally it is also possible to expose the generated ions to a gas such as carbon monoxide at room temperature to study possible reaction products.

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# The molecular depiction of acidic components and carbon dioxide in the biphasic hydrophilic/hydrophobic system

## Content

### Motivation and Objective

Understanding the hydrophobic oil/polar water interfacial phenomena dominates many important physical, chemical, and biological processes. Although a wide range of classical experiments has been conducted and reported, the phenomenological arguments have remained on the interactions in such a system.

### Methodology

To derive a molecular-level picture of this interface, recent interest has focused on fundamental simulations like molecular dynamics at the molecular/atomic level to solve the contradicted results in the classical experiments of the oil-water interface.

### Results

The well-organized structure of water molecules next to any hydrophobic surface due to the weak interactions between these hydrophilic and hydrophobic molecules has been established by researchers in terms of experimental and simulation studies. However, the natural environments are more complex than a simple hydrophobic/hydrophilic interface. Generally, the aqueous phase might have ions; gases like CO<sub>2</sub> and organic medium might include different acidic/basic components. Therefore, we need to investigate more complicated liquid/liquid interfaces to approach a real system. One of the complex biphasic hydrophobic/aqueous interfaces is related to the oil reservoirs. To extract more oil and simultaneously store carbon dioxide in the underground reservoirs, the carbonated water has been designed to inject into the oil pools. However, there is no concrete conclusion on which screening parameters should be considered to gain higher oil recovery and higher carbon footprint storage.

Herein, we investigated the effect of the most abundant polar acidic components (Benzoic acid, Decanoic acid, and phenol) in the hydrophilic phase on the interfacial phenomena of hydrophilic phase (Decane) and carbonated water. Hence, molecular dynamics simulation was used to analyze these systems. The structure, mass and charge density, hydrogen bonds, and Interfacial Tension (IFT) have been analyzed for different scenarios. To the authors' best knowledge, the effect of combining acidic components and carbon dioxide in the hydrophilic/hydrophobic interface has been investigated for the first time.

The results indicated that carbon dioxide molecules tend to accumulate at the interface of decane/water and then diffuse to the oleic phase. When the polar molecules are introduced to the hydrophobic phase, there is a competition between carbon dioxide and acidic components to accumulate at the interface. Since there is the electrostatic interaction between polar water molecules and polar acidic components compared to non-polar carbon dioxide molecules, the carbon dioxide molecules diffuse more evenly into the oleic phase and fill the voids in the oleic phase existing due to the entanglement of the alkane chains. Therefore, the acidic components replace the carbon dioxide at the interface and serve as a bridge between the hydrophobic and hydrophilic phases. Indeed, the predominant interaction corresponds to the water and polar molecules. The density peaks of polar molecules occur at the interface where the hydrophilic part of the polar component penetrates to the aqueous phase, and the lipophilic part of polar molecules is in the oleic phase, which is a surfactant-like action. The anchoring effect of acidic components at the water/decane

interface decreases the IFT between decane and water. Although there is a significant reduction in the IFT of systems involving acidic components compared to the simple decane/carbonated water system, there is no significant difference between these three types of acids in decreasing the IFT in the presence of carbon dioxide in the biphasic system. The charge distribution of water molecules in the systems involving polar components changes. In the simple decane/water case, water molecules show a recognized charge distribution at the interface with two well-ordered H-bonds networks. While in the biphasic systems, including polar molecules, the well-organized charge distribution at the interface (two water surface layers structures) changes, and the aqueous phase is disturbed inside itself. This is proof of destroying the shield of the well-organized water layer at the interface to the non-aqueous phase, which leads to IFT reduction as the surface forces between the two phases reach zero.

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# Inelastic collision dynamics of oriented NO(X) molecules

## Content

Examining the scattering dynamics of oriented NO molecules with a combined experimental and theoretical approach allows one to benchmark how well theory reflects reality. By orienting the NO molecule before collisions different regions of the potential energy surface and their associated collision pathways can be examined, such as side-on or end-on collisions [1-3]. An examination of simple collision partners, such as rare gasses, allows for an excellent starting point to examine the foundations of quasi-classical and quantum mechanical theory techniques, and how such techniques hold up in unique environments, such as “cold” collisions (NO + He) [4]. Expanding the scope to larger collision partners, such as ND<sub>3</sub> or CH<sub>3</sub>I, pushes these foundations of molecular dynamics, introducing new considerations such as the orientation and energy levels of the collision partner, and truly assesses the accuracy and applicability of the theory.

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# State-selective recombination of H<sub>3</sub><sup>+</sup> ions at low temperature: kinetic modeling and experimental study on plasma de-excitation

## Content

### Introduction

The H<sub>3</sub><sup>+</sup> ion is among the most produced ions in space and, also, a proton donor, which makes it an especially important ion in space. [1] Therefore, the dissociative recombination (DR) rate of H<sub>3</sub><sup>+</sup> with an electron is also of particular interest for plasma physics: H<sub>3</sub><sup>+</sup> + e<sup>-</sup> → H<sub>2</sub> + H or 3H. The ortho- and para-H<sub>3</sub><sup>+</sup> recombine with different rates. [4,5] The recent study confirmed that only the ortho-to-para ratio of H<sub>3</sub><sup>+</sup> ions decides the rotational distribution at 30 K. [6] In a planned study, we will measure the state-selective DR rate of H<sub>3</sub><sup>+</sup> at 50 K by changing its ortho-to-para ratio. This study focuses on preliminary studies connected with future experiments on state selective recombination of H<sub>3</sub><sup>+</sup> ions with electrons such as: determination of the feasibility of the experiment and of the Penning ionization of Ar by 2 1S and 2 3S states of He atoms (Hem.)

### Experiment

The ion-electron recombination is one of the fundamental processes in plasma. In particular, the dissociative recombination can be the dominant loss process in the cold plasmas containing molecular ions. The Stationary afterglow apparatus at Charles University [7] was used to ignite the plasma. The time evolution of the number densities of H<sub>3</sub><sup>+</sup> ions and electrons were monitored with a continuous wavelength Cavity Ring-Down Spectrometer and the microwave diagnostics, respectively.

### Result and discussion

First, chemical kinetics modelling was performed at 50 K to determine the best gas composition for experiments. The results are shown in the poster. In the helium-buffered stationary afterglow plasma, Hem are created in the discharge, heat up the electrons by superelastic collisions with ~20 eV, and delay their thermalization. [8] By adding some Ar to the gas, they can be eliminated from afterglow plasma by Penning ionization of Ar: Hem + Ar → Ar<sup>+</sup> + e<sup>-</sup> + He. Therefore, under the assumption that the loss processes of electrons are independent of time, the rate equation for electrons and Hem during the plasma decay are given, which establishes the electron number density as a function of time n<sub>e</sub>(t): Eq(1). Measured are the time evolution of electron number densities in different gas mixtures, which are fitted by Eq. (1). From this fitting, the Penning ionization of Ar by Hem is calculated as 2<sub>-</sub>(-1.5)<sup>-2</sup> × 10<sup>-10</sup> cm<sup>3</sup>/s, depending on the range of the fitting and the gas composition. The loss of the electrons is considered time-independent in Eq. (1) and, hence, the measured value is not reliable on the order of magnitude. In fact, one merged beam experiment reported k<sub>m</sub> = 2.5 × 10<sup>-11</sup> cm<sup>3</sup>s<sup>-1</sup> at collision energy of 5 meV. [9] We plan to directly monitor the Hem number density to obtain the ionization rate with better precision at low temperatures.

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# Ultrafast dynamics of the norbornadiene photoisomerization to quadricyclane induced by ultrashort deep-UV and IR pulses

## Content

We report on the early time quantum dynamics of the pericyclic photoisomerization of norbornadiene (NBD) to quadricyclane (QC) induced by short 1-2 fs UV and IR pulses, Figure 1A. The dynamics have been carried out as described in Ref. [1] for 8 coupled electronic states and three nuclear coordinates describing the main features of the four-carbon ring-closure reaction (Figure 1B). The coupling to the exciting pulse is explicitly included. Using a short, linearly polarized, weak, realistic 5 eV deep-UV pulse as published in Ref. [2], Figure 1C, we show that we can implement control of the populations in the lowest excited states via the direction of the linear polarization for oriented molecules. A X polarized pulse accesses selectively the S1 state while a Z polarized one accesses the S2 one (Figure 1D). In NBD, the onset of excitation is at  $\approx 5.7 - 6$  eV in the Franck-Condon region. The UV photoexcitation is via a one photon process, through the blue edge of the short pulse, wide energy bandwidth. The relative yield in QC at short times is larger for the Z polarized pulse than for the X polarized one (Figure 1E) as obtained in ref [1] with longer and stronger fs pulses. Using strong 720 nm IR pulses, we control multi photon processes to access excited states by changing the carrier envelope phase (CEP) to initiate different initial transient dynamics. Preliminary results from semiclassical surface hopping (SH) dynamics in full nuclear dimensionality, starting in different excited states, are presented (Figure 1G,H).

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# Predicting the x-ray diffraction images of ultrafast gas phase molecular dynamics

## Content

Time-dependent x-ray diffractive imaging of molecular dynamics in the gas phase promises a deep understanding of fundamental processes in nature. In that respect, the x-rays generated from XFELs with an ultrafast temporal resolution and sub-picometer wavelength have the potential to study the atomic scale structural dynamics of gaseous molecules on the ultrafast timescale. Here, we present CMIdiffract, an in-house python package developed to predict diffraction patterns of the controlled molecular ensemble. The package can predict the static as well as time-dependent diffraction images incorporating various aspects of the experiment such as the angular distribution of the aligned molecular sample the background signals from residual gases and photons, and the statistical noise. [1],[2],[3]

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# Probing Structural Dynamics of Molecules and Clusters Using Intense X-ray Pulses: The Case of Indole-water

## Content

The development of x-ray free-electron-lasers and third generation synchrotron radiation facilities allowed for the study of molecular dynamics on the (sub)picosecond timescale. Here we present results on the photo-physics of indole-water<sub>1</sub> clusters [1], using a UV-pump x-ray-probe scheme, at the Linac Coherent Light Source (LCLS).

Indole (C<sub>8</sub>H<sub>7</sub>N) [2] is the chromophore of the amino acid tryptophan and a key component in the UV radiation damage and protection of proteins, as it is the strongest near UV absorber. Upon x-ray ionization of the cluster, the different ionic fragments were collected using a velocity map imaging spectrometer. The yield of several observed fragments was studied as a function of the delay between the pump and the probe pulses. The transfer of a H atom from the indole moiety to water was observed through the detection of H<sub>3</sub>O<sup>+</sup> fragments, as was the case for the indole-ammonia cluster [3,4]. A detailed picture of the dynamics taking place will be presented on the poster. Finally, additional results showing the photoelectron spectra of gas phase indole and indole in the aqueous phase will also be presented [5].

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# An ultracompact vacuum-ultraviolet source for the investigation of time-resolved molecular dynamics

## Content

The generation of efficient and tunable vacuum-ultraviolet light (VUV, 100-200 nm, 6-12 eV) is relevant for multiple disciplines of basic science and technology [1]. In the field of molecular physics, VUV excitation is optimal for the study of Rydberg state dynamics as well as the temporal evolution of low valence electronic states in a large range of molecular targets [2].

However, not many techniques are currently available to efficiently generate VUV light. High-harmonic generation (HHG) for example, is more suitable for the production of higher photon energies, typically in the XUV and soft-x spectral region, while free-electron lasers hardly reach photon energies below 15 eV. Instead, several implementations of four-wave mixing (FWM) have been proposed and developed to generate light in the VUV range [3]. In particular, due to the extended guidance range in the VUV region and the confinement of the light over long distances, ultrafast FWM in capillaries offers an attractive route to generate VUV light with high conversion efficiencies [4].

In this presentation, we show the preliminary results of an ultracompact optical setup for the efficient and tunable generation of VUV light. The schematic principle is shown in Fig. 1. We employ an Ytterbium-based laser system for the generation of harmonics over two crystal-based frequency doubling stages and re-combine this pump beam with the fundamental seed beam in the hollow capillary, exploiting the advantages of both methods, i.e. nonlinear conversion in crystals and up-conversion in capillaries.

With our approach, we demonstrate to generate 150-nm light with unprecedented efficiency on a large range of temporal durations, from the fs to ps time scales.

Among other applications, we aim at employing this source to study and manipulate highly excited neutral states and low-valence ionic states in atoms and molecules.

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# Probing nanoscale surface charge redistribution on laser-ionized dielectric nanoparticles

## Content

Based on the recently developed reaction nanoscopy technique [1], it has been shown that the surface ion emission permits in-situ discrimination for nanoparticle morphology [2], and allows spatially resolving and controlling the nanoparticle reaction yield landscape with nanoscopic resolution [3]. The emission of charged molecular ions from the nanoparticle surfaces, for instance, the protons, which are the most abundantly produced ionic species, serves as a sensitive probe for the local dynamical surface, including the surface charge density and reaction yields. Most of the observations so far, have been focusing on the near-field mapping based on the electrostatic interaction between surface charges and proton emission. However, the visualization of dynamical behavior of the laser-induced surface charges on isolated nanoparticles has not been experimentally realized yet. Here, we have examined the charge diffusion process via time-resolved two-color pump-probe measurements using reaction nanoscopy. We used  $2\ \mu\text{m}$ ,  $\sim 25\ \text{fs}$  laser pulses as a pump to induce surface charges on isolated spherical  $\text{SiO}_2$  nanoparticles, and used the second-harmonic centered at  $1\ \mu\text{m}$  to generate surface ion emission. The time-resolved proton emission was observed for the first time which can give insight into the associated charge dynamics on the nanoparticle surfaces.

Figure 1 (a) The kinetic energy (KE) distribution of protons as a function of the time-delay between the pump and probe pulses. (b) The change in proton angular distribution as a function of the proton KE, as integrated over time delay-dependent signal between the red curves in (a). It appears to commence from a dipolar distribution and converge into a more uniform distribution as the kinetic energy decreases. We attribute this decrease in energy to the redistribution of surface charges.

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# A beamline for studying ultrafast UV-induced molecular dynamics

## Content

Different techniques have been recently applied to generate few-femtosecond (fs) laser pulses in the ultraviolet (UV) spectral region such as frequency up-conversion of few-cycle near-infrared (NIR) pulses [1,2] and resonant dispersive-wave emission in hollow capillary fibres [3]. Time-resolved spectroscopy methods utilizing ultrashort UV pulses can be applied to studying the ultrafast dynamics of various photoinduced reactions.

In our work, broadband UV pulses are produced via third harmonic generation driven by sub-5-fs NIR pulses in a high-pressure gas cell. We present a novel cell design that incorporates a miniaturized differential pumping system, providing not only an ultra-compact setup but also results in better confinement of the gas distribution, therefore allowing for better phase matching and optimal vacuum conditions to be achieved. The temporal characterization of ultrashort UV pulses is challenging and requires special methods, such as dispersion-free, Fringe-Resolved Interferometric Autocorrelation (FRIAC) [4]. With this method, we measured UV pulses with a temporal duration of 3.4 fs. The FRIAC setup can be easily integrated into an all-vacuum beamline, allowing for reliable in-situ pulse measurements.

Combining these ultrashort UV pulses with few-fs NIR pulses in a pump-probe scheme, we tracked ultrafast UV-induced dynamics of iodomethane (CH<sub>3</sub>I) and acetone (C<sub>3</sub>H<sub>6</sub>O) with unprecedented time resolution. In iodomethane, we measured the 5.5 fs decay of the parent ion and observed a prominent increase in the iodine fragment yield with a delay of 27 fs. These findings allow for mapping the motion of the molecular wavepacket on the energy surfaces. In acetone, the photoelectron signal appeared to be modulated with a period of 3.2 fs which could be assigned to the temporal evolution of electronic coherences.

The advanced source of UV pulses is the most suitable tool for studying the photodissociation of bio-relevant molecules as nucleobases of DNA due to their strong absorption bands in that spectral region. Our beamline provides the possibility of combining few-fs UV pulses with attosecond XUV pulses, allowing us to reveal the earlier inaccessible dynamic response of the molecules under investigation.

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# UV and mid-IR photo-induced dissociation dynamics of solvated (bio)molecular complexes

## Content

We present the ultrafast imaging of UV- and thermal-energy-induced chemical dynamics of micro-solvated (bio)molecular complexes probed with strong-field techniques [1]. The interaction between (bio)molecules and their solvent are model systems for the interactions between proteins and their solvent environment, and these interaction affect the folding mechanism and therefore directly the function of proteins [2]. To investigate this, we study the elementary processes in great details on small model system, that's why we wanted to use hydrogen-bonded indole-water system. Indole is the chromophore of tryptophan, a strongest (near) UV-absorber found in proteins.

A pure sample of the indole-water in the gas phase was produced by using a combination of a molecular beam and an electrostatic deflector [3]. To study the photo-induced dissociation dynamics, we set up a UV-IR pump-probe experiment, in which a 267 nm laser was used to excite the system. Ionization is provided by a 1.3  $\mu\text{m}$  laser. We observe a dissociation of the indole-water system and, determined the time-dependent appearance of the different reaction products, and disentangled which ultrafast processes occur. The next step is to use a mid-IR pump to excite a single vibrational mode, which induces a dynamics between the indole and water.

Furthermore, we will report on laser-induced electron diffraction (LIED) [4,5] to probe the thermally-excited molecular system in order to obtain structural information about the system with atomic resolution. LIED is a rapidly evolving technique to study the structural changes of molecular systems on the attosecond to the few-femtosecond timescale. The diffraction patterns produced in LIED experiments can be resolved using the ideas from "classical electron diffraction to retrieve the structure of the molecule of interest. To an extensive degree, our group has already started working on LIED thereby imaging (bio)molecular complexes. In the future, we will perform time-resolved studies of thermally-excited molecular systems.

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# Recent advances in the first principle simulation of attosecond XUV pump - XUV probe ionization spectra

## Content

Tunable sub-fs soft X-Ray (SXR) pulses has become available at the LCLS X-Ray free electron laser (XFEL) at intensities that exceed those of current SXR high harmonic generation (HHG) sources by several orders of magnitude [1]. This overcomes the current intensity restriction of HHG based attosecond XUV pump-probe experiments to using XUV or SXR pulses as either the pump or the probe fields and thus paves the way for attosecond nonlinear X-Ray spectroscopic experiments. From the theoretical side, the description of the process still entitles a formidable challenge for each step: i) accurate evaluation of ionization amplitudes, i.e. electronic wave packet created by the sub-fs SXR pump [2], (ii) description of the ensuing coupled electron-nuclear dynamics [3], and (iii) extracting the measurable observables upon the interaction with the sub-fs SXR probe. A reliable description of each step, in a single study, severely limits the tractable system size, in particular if the transient probe photoionization spectrum is sought after, which mandates an additional, more involved, ionization calculation for the probe step.

We here report an approach that marks a trade-off between computational cost and accuracy to facilitate the complete treatment (i)-(iii) in simulating sub-fs pump-probe photoionization spectra from XUV to SXR photon energies for small organic molecules. To this end, we employ complete active space wave functions with perturbative correlation energy correction (CASPT2) to describe the molecular bound states of the neutral, cationic and dicationic species, respectively. Further, the pump and probe ionization amplitudes are evaluated by a Dyson orbital approach, where the continuum states of the outgoing electron are obtained with the static exchange B-spline DFT method based on respective CASPT2 densities. Finally, the coupled electron-nuclear dynamics between the pump and probe interactions is modeled with the fewest switches trajectory surface hopping method, where an ensemble of trajectories represents the nuclear zero point energy spread. The performance of the outlined protocol will be scrutinized for different molecules and various spectroscopic setups. Facilitating sub-fs XUV and SXR pulses, the dynamics induced by the pump ionization of valence orbitals are interrogated by probing either valence ionization, or core ionization, respectively. In addition to that we are going to study the performance of further simplifications to the outlined protocol, such as neglecting the motion of the nuclei and disregarding the explicit evaluation of the continuum states for the probe ionization step, i.e., the sudden approximation.

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# Cold and controlled beams of nanoparticles and bio-macromolecules

## Content

\*Please see the formal version of this abstract in attachment

Unravelling the elementary steps of biological processes and chemical reactions has been a long-time goal. By using x-ray single-particle diffractive imaging (SPI), we can investigate the three-dimensional molecular structure of individual nanoparticles at atomic resolution through reconstructing a series of two-dimensional diffraction patterns[1].

The major challenge of SPI is the generation and preparation of high-density particle beams. Here, we present the generation of room-temperature high-density particle beams consisting of down to 25 nm polystyrene spheres, as well as cryogenically cooled particle beams for large particles (>88 nm) with the buffer-gas cell (BGC) cooling technique. Additionally, we demonstrate an approach for increasing the particle-beam density using an aerodynamic lens stack (ALS) compared to the previous experiments[2].

Furthermore, the cooling and control techniques we developed for SPI can be extended to experiments to study the electron dynamics in complex biomolecules on the few-femtosecond timescale, such as charge and energy transfer following electronic excitation, where the details have not been revealed so far[3]. We present an approach towards investigating the time-resolved ultrafast dynamics in protein with UV/VIS ultrashort-pulse lasers. The photoexcitation-induced energy transfer, for instance, can be studied by photofragmentation of cryogenically-cooled proteins with time-of-flight mass spectrometry.

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# Time-resolved Photodynamics of Nitrobenzene and Methylated Derivatives in Solution

## Content

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# Arbitrary image reinflation: A deep learning technique for recovering 3D photoproduct distributions from a single 2D projection

## Content

Many charged particle imaging measurements rely on the inverse Abel transform (or related methods) to reconstruct three-dimensional (3D) photoproduct distributions from a single two-dimensional (2D) projection image. This technique allows for both energy- and angle-resolved information to be recorded in a relatively inexpensive experimental setup, and its use is now widespread within the field of photochemical dynamics. There are restrictions, however, as cylindrical symmetry constraints on the overall form of the distribution mean that it can only be used with a limited range of laser polarization geometries. The more general problem of reconstructing arbitrary 3D distributions from a single 2D projection remains open. Here, we demonstrate how artificial neural networks can be used as a replacement for the inverse Abel transform and—more importantly—how they can be used to directly “reinflate” 2D projections into their original 3D distributions, even in cases where no cylindrical symmetry is present. This is subject to the simulation of appropriate training data based on known analytical expressions describing the general functional form of the overall anisotropy. Using both simulated and real experimental data, we show how our arbitrary image reinflation (AIR) neural network can be utilized for a range of different examples, potentially offering a simple and flexible alternative to more expensive and complicated 3D imaging techniques.

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# C-C bond formation reactions promoted by counterion components

## Content

Making C-C bonds is at the very heart of chemistry, and represents a key path of simple-to-complex molecular system evolution. Here we present a high-level ab initio modelling of formation of such bonds between small halocarbon molecules with attached alkali-metal atoms.

A specific feature is related to metal-halide counterions produced along the way. Their mutual attraction facilitates bonding of reactants via, in effect, externally “pressing” them into one another as well as generating intra-system electric field, and thus altering the associated potential energy barrier. In particular, some uncommon species are involved, including a “counterintuitive” isomer of metal-atom attached halocarbon and an intermediate insertion complex with the product molecule trapped between the counterions, analogous to those in earlier studies [1]. In addition, in some cases still another intermediate species appears, exhibiting an unusual hyper-coordination of carbon, similar to that reported previously [2]. The overall reactions are predicted to proceed via “umbrella” inversions of carbon-halogen bonds and intersections of potential energy surfaces for different systems [3].

Furthermore, the processes are “tracked” spectroscopically by predicting characteristic IR spectra at all stages, from reactants to intermediates and up to products. This is anticipated to enable experimental verification of the relevant species formation, their differentiation, and monitoring of the system evolution as well.

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# Imaging the Photoelectron Circular Dichroism in the Photodetachment of Deprotonated 1-Indanol Anion

## Content

Photoelectron Circular Dichroism (PECD) is a method of chiral discrimination, which can aid in our fundamental understanding of electron dynamics and holds promise for future analytical techniques of chiral compounds. This technique has significant advantages over other optical CD methods as sensitivity to the molecular chirality manifests within the electric-dipole approximation, bypassing the need for observation of weak interactions with a molecule's magnetic moment. Combining the PECD phenomenon with anion photodetachment would enable mass-selectivity and eliminate the need for X-ray based ionization sources, thus leading to a potentially robust analytical tool for chiral discrimination of dilute multicomponent gas-phase samples. In addition, the study of PECD of anions could provide more information regarding the short range interactions involved in a PECD effect. The field of PECD in the photoionization of neutral chiral species has flourished over the past two decades, evident by the many theoretical and experimental works now available.<sup>1</sup> In contrast, PECD of anions has historically not seen the same success, leading some to doubt its feasibility. However, recently PECD in anions has been observed in an experiment for the first time.<sup>2</sup> Although this is a great step forward, this first experiment could not provide the necessary spectroscopic information to further understand the PECD phenomenon in anion photodetachment. We have built upon this initial success by coupling the PECD technique with pre-photodetachment mass selection and velocity-map imaging to provide an energy-resolved PECD signal for the isolated deprotonated 1-indanol anion. We have measured the eKE-dependence of the PECD signal for numerous detachment channels, and identified a maximum PECD signal of approximately 10%. This result is similar to what has been seen for neutral 1-indanol.<sup>3</sup>

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# Capturing ultrafast synergistic spin transition in a multifunctional hybrid spin crossover system by ultrafast optical spectroscopy and electron diffraction

## Content

Spin crossover (SCO) is a phenomenon observed in some transition metal complexes whereby is triggered through changes in pressure, temperature, magnetic fields, or light irradiation<sup>1</sup>. The design of multifunctional SCO photoswitches which combine a SCO cation and an anion with functional electronic properties (conductivity, magnetism, and dielectrics) has been an active research field<sup>2</sup>. The goal is to use the photoinduced SCO to gain control over various electronic properties of anions by a coupling between SCO and changes in functional moieties. A prototypical halogen-bonded hybrid system,  $[\text{Fe}(\text{Iqsal})_2][\text{Ni}(\text{dmit})_2] \cdot \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$  (SCO-dmit) (Iqsal = 5-iodo-N-(8'-quinolyl)-salicylaldimine, dmit = 4,5-dithiolato-1,3-dithiole-2-thione) exhibits synergistic spin transition between the SCO in cation and dimerization in anion<sup>3</sup>. Here, we exploited ultrafast electron diffraction (UED) to reveal a detailed picture of ultrafast electronic and structural dynamics of upon photoexcitation (Fig. 1b). These results indicate a transition intermediate state (TIS) after initial photoexcitation, and it has different structure to the ground state and the HT-like excited state. The fast dynamics has two time constants (600 fs, (limited by the 450-fs instrument response time), and 1.1 ps) which match the timescales of intersystem crossing (ISC) and intermolecular vibrational energy redistribution (IVR)<sup>1</sup>. To investigate the slow dynamics observed in the UED data and gain insight into the molecular motions, we use a structural refinement algorithm based on a parameterized molecular model<sup>4</sup>. The results show in the short and long time-delay, the motion of the Fe–ligand expansion in the cation and the rearrangement between the  $\text{Ni}(\text{dmit})_2$  anions have different behaviors in the fast and slow dynamics. Optical excitation drives the formation of the TIS through initial SCO in the cation, and the  $\text{Ni}(\text{dmit})_2$  anion stays unchanged during the short timescale. The slow dynamics provide an ensemble-averaged picture of the molecular rearrangement of the  $\text{Ni}(\text{dmit})_2$  anions which is a relaxation process stabilizing the final HT-like structure. Further data analysis of is still in progress.

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# Simulating and Screening Photophysics of Transition-Metal Complexes

## Content

The study of excited-state dynamics of transition-metal complexes is challenging due to their large number of vibrational degrees of freedom and many close-lying electronic states.[1] When quantum dynamics is used to simulate transition-metal complexes, this imposes the use of truncated models with typically only few degrees of freedom and electronic states, where the electronic potentials are often described in parameterized vibronic coupling models. An alternative to quantum dynamics that can include all degrees of freedom and large number of electronic states is given by on-the-fly surface hopping (SH) methods. However, the repeating cost of the underlying electronic structure calculations restricts the range of possible simulation times for molecules the size of transition-metal complexes severely.

By using SH on vibronic-coupling potentials, we can now lift the simulation-time restriction in SH and enable full-dimensional nonadiabatic dynamics simulations of transition-metal complexes on picosecond time scales.[2,3] This is first demonstrated for a near-infrared emitting vanadium(III) complex with an open-shell triplet ground state.[4] Using multi-reference CASSCF-derived linear vibronic-coupling (LVC) potentials, we can unravel the relaxation mechanism populating the phosphorescent singlet state.[5] Based on the mechanistic insights, several derivatives of the complex are proposed to improve luminescence and their excited-state dynamics are simulated as well, an effort only possible due to the efficiency of the SH/LVC approach.

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# Charge transfer reactions of neutral polar molecules and noble gas ions

## Content

Ca<sup>+</sup> Coulomb crystals are utilised as an environment to study the reactions of thermal neutral polar molecules (NH<sub>3</sub>, ND<sub>3</sub>, H<sub>2</sub>O or D<sub>2</sub>O) with sympathetically cooled rare gas ions (Xe<sup>+</sup>, Kr<sup>+</sup> or Ar<sup>+</sup>) [1-3]. Reaction rate coefficients, their relative magnitudes, and *ab initio* calculations will be discussed, with reference to capture theory models. Capture theory predictions are in mixed agreement with experimental data: water reaction rate coefficients are in good agreement, whereas ammonia reactions are not. In addition, inverse kinetic isotope effects are observed with ammonia and not with water reactions.

Current work will be detailed, using a supersonic beam of ammonia neutrals (low rotational state distribution and variable velocity) and reacting this molecular beam with sympathetically cooled noble gas ions. This allows further investigation into the mechanism of charge transfer reactions and the presence of kinetic isotope effects.

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# Vibrational excitation of CO<sub>2</sub> by slow electrons: Multidimensional nonlocal calculations of the vibronic dynamics

## Content

The  $e + \text{CO}_2$  system has been extensively studied but yet some observations [1, 2], especially the shape of the electron energy-loss spectrum, either lack an interpretation or the suggested ones have not been supported by dynamical calculations. We present results of our nonlocal calculations for vibrational excitation of CO<sub>2</sub> that take into account the  $^2\Sigma_g^+$  virtual state and  $^2\Pi_u$  shape resonance doublet of the molecular anion CO<sub>2</sub><sup>-</sup> in combination with all vibrational modes [3]. The  $^2\Pi_u$  doublet splits into  $^2A_1$  and  $^2B_1$  states due to the Renner-Teller effect upon bending of the molecule, and furthermore, the virtual state mixes with the  $^2A_1$  component. These electronic states are described by discrete states that interact directly with each other but also indirectly through an energy-dependent coupling to the electron continuum, which consists of the  $s$  and  $p$  (all components) partial waves. We obtained model parameters from *ab initio*  $R$ -matrix fixed-nuclei eigenphase sums for hundreds of geometries using a fitting procedure that utilizes the high symmetry of the system.

The geometry-dependent coupling to the electron continuum allows excitation of nontotally symmetric vibrational states of CO<sub>2</sub> and the explicit inclusion of the electron  $s$ -wave describes the peculiar behavior of the  $^2A_1$  Renner-Teller component. Our primary result is the full two-dimensional (2D) electron energy-loss spectrum of CO<sub>2</sub> for energies up to 5 eV, which is in qualitative agreement with previous experimental observations and the new 2D experimental spectrum [4]. We found that not only the totally symmetric ( $\Sigma_g^+$ ) vibrational states but also states of the  $\Pi_u$  symmetry are significantly excited, which explains the shape of the energy-loss spectra. The  $\Pi_u$  vibrational states dominate in the highly-inelastic region because the resonant  $p$ -wave electron that attaches to the resonance preferentially leaves as an  $s$ -wave which forces the molecule to change its angular momentum. Such a phenomenon is important in polyatomic systems but actual dynamical calculations are rare.

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# Dynamics of UV-excited neutral molecules studied with 5 fs resolution and electron–ion covariance spectrometry

## Content

We trace ultrafast dissociation with few-femtosecond resolution, experimentally and theoretically, and demonstrate electron–ion covariance spectrometry to distinguish photoreaction paths.

Many pump–probe experiments use an attosecond pulse in the extreme ultraviolet (XUV) and a near-infrared (NIR) pulse. We have recently developed an attosecond beamline with the key ability to also generate ultraviolet (UV) 4–6 eV pulses with record-breaking durations of a few femtoseconds [1]. By exciting in the ultraviolet we can study photochemically relevant dynamics in neutral molecules. Strong UV absorption bands are found in many aromatic molecules (e.g. the nucleobases of DNA) and a clean example of ultrafast UV-induced dynamics is the photodissociation of iodomethane (methyl iodide). Due to a steep potential energy surface, this excited molecule rapidly elongates and breaks the CH<sub>3</sub>–I bond. It is known that a conical intersection is reached within a few tens of femtoseconds but only recently has this time scale become available, with 20 fs UV-pulses as state-of-the-art[2]. We report on a combined experimental and theoretical study of the UV-induced photodissociation of iodomethane. The experiment, probing with near-infrared (1.7 eV) multi-photon ionization, achieves an unprecedented time resolution of 5 fs (cross-correlation FWHM) and we clearly resolve a delayed second increase in the yield of I<sup>+</sup> fragment ions. Parent ions are mainly seen at temporal overlap, when the short pulses ensure that ionization takes place before the dissociation starts. The fact that the impulsive excitation ends before the conical intersection is reached, allows for an accurate comparison with theory, where new surface-hopping trajectory calculations are benchmarked against the experimental results and aid the interpretation.

High temporal resolution generally leads to broad spectra, many excited states and many open dissociation paths. It is therefore useful to record not just the average spectra but single-shot data and analyse the correlations between photoelectrons and fragment ions, conceptually filtering the electron spectrum based on the mass spectrum or vice versa. For this purpose, we have also developed a covariance spectrometer[3] combining a 2D velocity map imaging electron spectrometer with a reflectron time-of-flight mass spectrometer. We present results from acetone where different parts of the electron spectrum correlate with different fragmentation outcomes, thereby providing additional information to identify the underlying mechanisms and transient states.

Combining high mass resolution with the information about energy and angle of the correlated electron opens many possibilities for studying more complex molecules with better-than-vibrational time-resolution. As an outlook, the beamline will allow even better temporal resolution by using an isolated attosecond pulse in the XUV (15–40 eV, typically 300 as) as probe after UV-excitation.

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# Carbonic acid is more stable and a potent protonation agent in non-aqueous media

## Content

Carbonic acid (CA) is a key component in many naturally occurring systems varying from the human body to extraterrestrial ices. However, its fast decomposition to H<sub>2</sub>O and CO<sub>2</sub> has hampered for many years the studies of CA properties and reaction mechanisms. Recently, stopped-flow and ultrafast pulsed laser techniques [1,2] have opened the door for investigating this exceedingly important but elusive molecule. Advanced molecular dynamical calculations allowed to rationalize the long standing observations placing water and the proton as the main catalyzes for intact CA being unstable in presence of water and acids [3,4]. With this in mind, it has made sense to suggest that CA would be much more stable when present in non-aqueous media.

Herein, we use an advanced stopped-flow set-up for investigating the kinetics of intact CA in methanol solutions. We find that CA acid is much more stable in methanol than in water. Two different processes, dissociation and proton transfer from carbonic acid to a base were studied in methanol. The pK<sub>a</sub> of CA as a function of the temperature, its isotope H/D substitution effect and the lifetime of CA in methanol solutions have been determined. We successfully modelled the protonation reaction of Brønsted bases by CA in methanol. Efficient protonation of the investigated mild bases were observed and was driven by the much increased stability of CA in methanol. Our experimental data was reproduced numerically by solving a set of coupled reactions for the bimolecular CA-base proton transfer reaction assuming second-order, bimolecular encounters between intact CA and the base.

The prospect of further investigations of CA in non-aqueous medium is promising to result with finding experimental conditions where CA is long-lived in solutions. We discuss the possibility of directly measuring CA spectroscopic properties and studying its chemistry in solution using steady-state techniques where CA lifetime will be measured in minutes rather than in milliseconds.

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# Photodetachment and decarboxylation dynamics of the Fluorescein dianion

## Content

The electron loss and decarboxylation dynamics of the fluorescein dianion,  $\text{Fl}^{2-}$ , have been investigated using frequency-resolved photoelectron imaging and fragment action spectroscopy. Electron loss is observed via resonant tunnelling through two distinct repulsive Coulomb barriers ( $\text{RCB}_1$  and  $\text{RCB}_2$ ), which link different excited dianion ( $S_1$  and  $S_2$ ) and anions states ( $D_0$  and  $D_1$ ), as well as direct photodetachment. This is the first experimental observation of resonant tunnelling mediated via a highly excited electronic state ( $\geq S_2$ ). Anti-Kasha rule behaviour is observed, in contrast to other dianions, due to the similar timescales of internal conversion from  $S_2$  to  $S_1$  and tunnelling through  $\text{RCB}_2$  in  $\text{Fl}^{2-}$ .

Fragment action spectroscopy is performed on  $\text{Fl}^{2-}$ , via a newly implemented reflectron secondary mass spectrometer, in order to study  $\text{CO}_2$  loss. The  $\text{Fl}^-$  and  $\text{Fl-CO}_2^-$  action spectra indicate that at higher photon energies, one-photon dissociative photodetachment i.e. simultaneous decarboxylation and electron loss, competes with photodetachment. At lower photon energies decarboxylation of  $\text{Fl}^{2-}$  only occurs via a multiple photon process, which allows the absorption spectrum of the doubly deprotonated radical anion,  $\text{Fl}^-$ , to be extracted. In effect, decarboxylation only occurs when an anion with sufficient vibrational excitation is formed, either directly following electron loss from a highly internally excited dianion or via the absorption of a second photon.

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# Crossed-beams and theoretical studies of the O(3P) + acrylonitrile reaction dynamics

## Content

The difficulties in rationalizing the behavior of complex systems, such as combustion and extraterrestrial environments, are mainly due to the great number of chemical reactions that are involved. The best way to shed light on these complex mechanisms is to study each single elementary reaction using a synergistic experimental and theoretical approach that allows to unveil the reaction micro-mechanism, the primary products, and their branching fractions (BFs). Inspired by these general motivations, we have investigated the O(3P)+CH<sub>2</sub>CHCN (acrylonitrile) reaction, given its numerous implications in many fields. In fact, acrylonitrile is widespread in textile and plastics industries, with thermal combustion and selective catalytic combustion being the most useful methods to convert it into non-toxic species, and it was also detected in various interstellar environments. Being atomic oxygen an important component of flames and of the Interstellar Medium (ISM), a detailed knowledge of the O(3P)+CH<sub>2</sub>CHCN reaction dynamics might contribute to improve both combustion and astrochemical models.

In this work, we have used a well-established strategy, already used for many systems involving O(3P) and aliphatic[1] and aromatic[2] hydrocarbons, based on the coupling between experiments and theoretical computations. In particular, we have exploited the crossed molecular beams (CMB) technique with mass spectrometric detection and time-of-flight analysis to identify the primary products of the title reaction and their BFs. The experiments were assisted by theoretical calculations of the relevant triplet/singlet Potential Energy Surfaces (PESs) and by kinetic studies (RRKM/Master Equation) on the two individual PESs to derive the product channel BFs. It was found that, after the initial barrierless attack of O(3P) to the C=C double bond of acrylonitrile, the system can essentially evolve towards two main different pathways: (i) the initial triplet intermediate can unimolecularly dissociate to H+HCOCHCN products adiabatically on the triplet PES, or (ii) undergo a nonadiabatic transition (intersystem crossing, ISC) from the entrance triplet PES to the underlying singlet PES, leading to the formation of CO+CH<sub>2</sub>CNH (ketenimine). The latter is found to be the main product channel (BF=0.90), while the H-displacement channel is minor (BF=0.10). Therefore, in the title reaction, ISC guides the reactive flux and the finding that ketenimine formation is dominant might represent an important new step forward in the discovery of new formation pathways of biologically relevant molecules in the ISM.

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# High spectro-temporal resolution soft X-ray spectroscopy in gas phase media

## Content

The binding energy of inner-shell electrons, accessible by X-ray photons, is a sensitive parameter characteristic of the parent atomic species. Moreover, changes in the local chemical environment of these atoms generate shifts in their corresponding core binding energies [1]. This property is particularly useful for time-resolved spectroscopy, allowing to monitor changes in the nuclear and electronic structure after photo-excitation or -ionization. Despite great advances in the development of laser-based X-ray sources, such as high-harmonic generation, only X-ray free-electron lasers (FEL) have so far demonstrated high flux X-ray pulses with femtosecond durations and broadly tunable narrow-band spectra. However, due to the size of these large-scale facilities, femtosecond synchronization of an optical laser with the FEL beam has been a formidable challenge, ultimately limiting the resolution of pump/probe experiments.

At the European XFEL, we have overcome this challenge through a combination of an optical synchronization system [2], both short X-ray and optical pulse durations, and non-invasive electron arrival-time correction [3]. This has led to a sub-20 fs temporal resolution (FWHM) for pump/probe experiments, without the additional use of photon arrival-time monitors [4]. This achievement was combined with the use of a monochromatic beam of sub-eV bandwidth [5], leading to high spectral and temporal resolution.

In the presentation we will discuss how this capability enables exciting prospects for the investigation of photoinduced molecular dynamics. The high spectral and temporal resolution allows to directly track the time evolution of the changes in the chemical environment at specific sites within a molecule. As a first novel example, we show how ionization dynamics can be captured in simple halogenated molecules after strong-field interaction, allowing unambiguous identification of the different populated states. Additionally, we present recent steps towards the investigation of single-photon excitation processes in molecules through the combination of ultrafast pump sources in the ultraviolet spectral region together with the soft X-ray pulses. Finally, we will discuss further improvements towards higher temporal stability, in the context of recent developments towards X-ray pulses in the attosecond regime.

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# Control of electron wave packets close to the continuum threshold using near-single-cycle THz waveforms

## Content

The light-based control of electrons forms the foundation of ultrafast science and enables the observation of quantum dynamics on its inherent time and length scale. Various effects such as high-harmonic generation, light-induced electron diffraction, or photoelectron holography have been successfully exploited to steer and probe electron dynamics. At their heart are recollisions of light-driven electron wave packets created by strong-field ionization. A major obstacle in controlling electron wave packets with a single pulse is that both the creation of the wave packet and its further motion are governed by the same field. In our combined experimental and theoretical work, we use two distinct light fields such that each field is responsible for only one of the two steps. Multiphoton ionization of atoms by a short femtosecond IR-laser pulse is used to create a wave packet at the continuum edge, i.e., extending across weakly-bound and continuum states. Afterwards the motion of the wave packet is governed by a carrier-envelope-phase-stable near-single-cycle THz pulse (A).

This scheme is reminiscent of the attosecond streak camera [1,2], but in our case, the combination of fields enables us to control the dynamics of electrons right at the boundary between bound Rydberg states and low-energy continuum states. In the investigated energy range, the interplay between the dynamics caused by the electron-core interaction and by the THz field is usually of major importance. However, we demonstrate that the high degree of temporal localization of the wave packet creation on the scale of an optical cycle of the THz field provides the opportunity to deliberately switch electron-ion collisions on and off and adjust their properties depending on the pulse delay. By recording the photoelectron momentum distributions as a function of the time delay, we observe signatures of various regimes of dynamics, ranging from weak Coulomb focusing of the outgoing wave packet over pronounced collision dynamics such as large-angle scattering and appearance of caustics to chaotic ionization of Rydberg states. The measurements are confirmed by three-dimensional time-dependent Schrödinger equation simulations. A classical model is used to understand the physical processes in detail. In the future, these controlling and imaging capabilities could be exploited, e.g., to study the trapping in Rydberg states after strong-field ionization or to transfer well-known techniques from attosecond physics to explore the motion of low-energy electrons in molecules or involving multiple electrons.

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# Harvesting electronic coherences in disordered room temperature CdSe quantum dot dimeric assemblies

## Content

Several distinct photoinduced electronic coherences are unambiguously characterized in ensembles of quasi-homodimers that were assembled with sub-nm ligands from disordered small (2.5-3nm) colloidal CdSe quantum dots (QDs)[1]. These electronic coherences, with periods ranging from 40 to 300 fs, are measured in solution and solid state dimer samples by 2-dimensional electronic spectroscopy (2DES), and are shown to be robust with respect to dephasing. A theoretical model[2] of the dimer states, which includes size dispersion, interdot electronic coupling, spin orbit interactions and crystal field splitting, is used to characterize these coherences. It is shown that one can tune the number of electronic coherences observable by 2DES, as well as their delocalization and optical activity, by controlling the mean diameter (2.5-3nm) and the size dispersion (5-10%) of the QDs. The measurement in size dispersed ensembles, in both the solid-state and in solution, of such a variety of coherences, together with their unambiguous characterizability and tunability, presents great opportunities for their exploitation in quantum technological applications.

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# Electron Scattering in Water Clusters

## Content

A detailed understanding of electron scattering properties in water is crucial to modeling and controlling many processes occurring in nature, ranging from atmospheric chemistry to radiation biology. For example, low-energy electrons (with kinetic energies below 100 eV) have been shown to play a central role in DNA damage [1]. Yet, the details of low energy scattering are still debated. Except in the sub-excitation region [3, 4, 5], electron scattering cross sections in water for such low energy electrons were so far only reported for amorphous ice [2]. Only recently, it was shown that liquid water cross sections in the 10-100 eV range are the same as those of amorphous ice [3].

Recently, electron scattering in neutral water clusters  $(\text{H}_2\text{O})_n$  was investigated experimentally and compared with detailed scattering models based on gas and condensed-phase scattering cross sections [6, 7]. Scattering in clusters for electron kinetic energies up to 15 eV could not be reproduced by models based on gas or condensed phase cross sections, but turned out to be rather an intermediate case. It was found that the cluster scattering cross sections are higher than those in the condensed phase, likely due to reduced dielectric screening in clusters. Scattering simulations employing intermediate scattering cross sections were shown to capture the observed evolution of electron scattering as a function of mean cluster size.

In this contribution, we present results on the evolution of scattering cross sections in neutral water clusters of various sizes for electron kinetic energies up to 60 eV. By performing cluster size and kinetic energy dependent studies, we can answer questions, such as, how does electron scattering in water evolve between the gas and condensed phases? Experimentally, electron scattering is probed by ionizing the clusters with high harmonic radiation and collecting angle-resolved photoelectron spectra. Photoemission anisotropy is a sensitive observable of said scattering and is used to compare experiment with simulations. Both simulated and as experimentally obtained values for transport scattering in clusters are examined and used to extend previous studies [6, 7].

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# Effect Assessment of HBD-2 and HD-5 on SARS-CoV-2 Membrane model, A Molecular Dynamics Simulation Study

## Content

### Abstract:

Anti-microbial peptides (AMPs) are a class of small peptides and part of the host-defense system of many organisms, and promising candidates for becoming a new class of therapeutics. Defensins are cationic and amphipathic AMPs with three pairs of disulfide-bond-forming cysteines, where membrane disruption is one of their direct irreversible effects on target organisms. Recent studies have also elucidated antiviral effects of human defensins, on both enveloped and non-enveloped viruses. [1]

Human beta defensin 2 (HBD-2), a positively charged 41-aminoacid peptide, is expressed mainly in the epithelial cells, mucous, skin, and also throughout the respiratory epithelium, from mouth to the lungs. On the other hand, human alpha defensin 5 (HD-5) consists of 32 residues and is mainly expressed by specialized Paneth cells of the small intestine. [2] Although Sars-Cov-2 is a respiratory virus and infects the respiratory tract, it can also enter into all human cells through using a certain cell receptor, called angiotensin converting enzyme 2 (ACE2), which is expressed on cells throughout the human body. It is known that cationic AMPs interact with negatively charged bacterial membrane and increase its permeability, which leads to the leakage of cell content and finally the cell death. Considering the reported antiviral activities of defensins, this study aims to assess the effect of two AMPs, HBD-2, and HD-5, on severe acute respiratory syndrome coronavirus 2 (Sars-CoV-2) membrane model, employing the all-atom molecular dynamics simulation (MD) approach.

CHARMM-GUI membrane builder was utilized to construct the liquid-ordered viral membrane model, according to the mixed lipid ratio reported in Ref. [3], while initial structures of both HD-5 and HBD-2 peptides were taken from the protein data bank. After adding enough water molecules and counter-ions to the simulation boxes, the membrane-only, and the two AMP-only systems were simulated for 250 ns and 100 ns, respectively. The CHARMM36 force field was used to simulate the lipid and peptide molecules, while the TIP3P model was selected for the water molecules. Finally, each of the two merged membrane-HBD-2 and membrane-HD-5 systems, were simulated for 50 ns. All classical NPT MD simulations were conducted under 1 atm pressure and 310 K temperature, with the 2.0 fs time step for the numerical integration of the Newtonian equations of motion. All simulations were carried out employing the GPU-accelerated NAMD simulation package.

In order to assess the effect of studied AMPs on the SARS-CoV-2 membrane model, different structural properties of lipid bilayers were analyzed for the two membrane-AMP systems, and compared with the corresponding properties of the membrane-only system. These structural properties include the area per lipid, bilayer thickness and deuterium order parameter (Scd). Overall results showed that addition of both HBD-2 and HD-5 molecules to the Sars-CoV-2 membrane model, leads to the increase in area per lipid, and simultaneous decrease in the bilayer thickness and deuterium order parameters of both SN-1 and SN-2 lipid chains. It is clear that these structural changes result in an increased membrane permeability, which in turn disrupts the lipid bilayer, and hopefully destroys or destabilizes the virus. In this respect, HBD-2 and HD-5 AMPs are suggested as potent inhibitors of SARS-CoV-2, while clinical trials are required to support this claim.

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# Efficient simulation of X-ray scattering signals

## Content

The advent of x-ray free electron lasers with high peak brilliance and subfemtosecond pulse durations has allowed the study of gas-phase molecules with an unprecedented accuracy [1]. The high repetition rates achieved by these light sources have increased the signal-to-noise ratio of the measured x-ray scattering cross-sections showing subtle electronic signatures [2,3]. Effects like electron correlation, closely related to the multiconfigurational and multireference character of the molecular wavefunction, need to be considered to describe the experimental observables. From a theoretical perspective, simulating these accurate x-ray cross sections has become challenging and new methods, such as the one that will be presented here, are required. We will introduce a novel method to obtain total x-ray scattering cross-sections using the Fourier transform of an efficiently precomputed molecular two-particle density matrix [4]. We will evaluate different levels of electronic structure theory and unravel the effects of those in the different components of the x-ray signal. With the example of ozone, known to have strong multireference character and constituting a challenge for conventional electronic structure methods, we demonstrate how state-of-the-art stochastic multireference methods, with a special attention to Monte Carlo Configuration Interaction (MCCI), constitute an affordable alternative to Full Configuration Interaction, how wavefunctions with multiple Slater determinants can be treated to efficiently calculate two-electron densities, and which procedures can we use to analytically Fourier transform them. Based on our simulations, it will be also shown how strongly electron correlation can affect the observable signal [6,7].

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# Near-Ambient Pressure Velocity Map Imaging

## Content

We present a new instrument that allows Velocity Map Imaging (VMI) of ions from a sample region at Near-Ambient Pressure (NAP) and demonstrate its performance.

The instrument has been developed to help close the 'pressure gap' between surface science and applications of catalysis, by measuring the dynamics and kinetics of reactions on meta-stable surfaces formed in the presence of reactive gases. NAP-VMI may also be useful for experiments with liquid jets, e.g. molecular beam scattering or photoelectron spectroscopy, where elevated pressures cannot be avoided.

NAP-VMI is achieved by using two sets of ion optics and a small aperture that separates the sample region from the detector, allowing differential pumping of the two regions and protecting the microchannel plate detector.

The first set of ion optics accelerate ions created in the sample region and bring them to a hard focus at the aperture. The second set of optics then provide additional acceleration and focusing to velocity map the ions at the 2D detector. The two-stage acceleration, combined with pulsed detection, has a DC-slicing effect, removing the need for an inverse Abel transform of the image. We have tested the performance the instrument by imaging the photodissociation products of  $\text{N}_2\text{O}$ , and molecular beam scattering of  $\text{N}_2$  from a Pd(110) surface at pressures up to  $1 \times 10^{-3}$  mbar [1].

With the new instrument we can extend Velocity Resolved Kinetics into the NAP regime to measure surface reaction kinetics on metastable surfaces. VRK is a pump-probe technique that uses a short-pulsed molecular beam to start a surface process, with pulsed laser ionization and imaging detection as the probe [2]. Here, we use NAP-VRK to study trapping-desorption of CO on Pd(110) with ca. 20  $\mu\text{s}$  time resolution in elevated pressures of  $\text{H}_2$  and CO.

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# Tunable isolated attosecond pulse generation by sub-cycle synthesized waveforms

## Content

The future development of attosecond science will largely depend on the availability of better attosecond pulse sources. In particular, the current generation of laser-based attosecond sources suffers from a low photon-flux, especially in the soft X-ray region, and a limited tunability of attosecond pulse parameters, such as its central energy, bandwidth and consequently pulse duration, from a single source. The latter is of particular interest in order to selectively excite electronic transitions and to concentrate the photon flux in the spectral region of interest. Moreover, the possibility of controlling the pulse duration can elucidate its impact on the decoherence mechanisms that follow ionization[1].

In our group we use tailored IR waveforms, obtained via coherent synthesis of the output pulses from different OPA sources, to drive the generation of attosecond pulses via HHG. Due to the optical bandwidth of almost 2 octaves, these IR waveforms can have FWHM durations down to a fraction of the central optical cycle, allowing to directly generate isolated attosecond pulses (IAPs) without additional gating[2]. Moreover by controlling two synthesis parameters, the relative phase among the two combined pulses and the overall CEP, we demonstrated the possibility to tune the central energy and the bandwidth of the IAPs as well as their duration, in the XUV spectral region[3]. Recently we started investigating the generation of IAPs in the soft X-ray region. Preliminary observations, shown in Fig.1, suggests the possibility to obtain IAPs with photon energies up to ~450 eV. At present, measurements to explore the possibility of increasing IAP generation efficiency in the soft X-ray region by means of non-sinusoidal optical waveforms are underway. We believe that the possibility of tuning the IAP parameters over a wide range offered by waveform synthesis could be a great stimulus for the development of increasingly sophisticated attosecond experiments.

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# Probing ultrafast structural dynamics through covariance imaging of laser-induced Coulomb explosions

**Status:** ACCEPTED**Content**Submitted by **LAM, Chow-shing** on **Wednesday, 15 June 2022**

Recording the real-time nuclear positions in molecules during structural transformations, has been a long-standing dream in the study of molecular dynamics. Filming a ‘molecular movie’ to visualize the photo-induced structural change of molecules is of fundamental interest in understanding the essence of photochemistry, but the required timescale naturally poses formidable challenges [1]. The advent of ultrafast techniques has been trailblazing to elucidate transient evolution of electronic structure accompanied with changing molecular geometry yet limited to provide definitive pictures anticipated.

Coulomb explosion imaging (CEI) with coincidence detection have been ranked as the most promising movie-making approach by accumulating snapshots of the photochemical process. Through the correlated measurement of multiple charged fragments, which are unambiguously assigned to a single origin, unparalleled structural details in the molecular frame can be deduced. However, this methodology is restricted to low-count rate regime (<1 per laser shot) to avoid false coincidences. Instead, covariance imaging circumvents this constraint by measurement of the joint variability of velocity distributions from two fragments in each laser shot to determine the correlations at high count rate, immensely expedites data acquisition [2].

In this work, nitrobenzene and its methyl- substituted derivatives have been selected to demonstrate the multitude of promising aspects of time-resolved covariance CEI technique. They permit prototypical study for nitro-aromatic compounds, a class which sees wide applications in the field of photoswitches, photolabile protecting groups and NO-donors in vasodilators [3]. Pump-probe covariance CEI studies identify cofragment pairs, for examples, the NO-loss pathway which still has its dynamics under debate [4]. In particular, the observed delay-dependence of the covariance of (C<sub>4</sub>H<sub>3</sub><sup>+</sup>, NO<sup>+</sup>) reveals that the UV-excitation dynamics in the kinetic energy release for this channel extends well into the range of picoseconds. The torsional-dynamic effect of the nitro group on the NO-loss channel, which is a nonadiabatic process complicated by intramolecular rearrangement can be evaluated and conclusive remarks can be made by comparisons with results from time-resolved photoelectron imaging from ref. [4].

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# The molecular depiction of acidic components and carbon dioxide in the biphasic hydrophilic/hydrophobic system

## Content

Understanding the hydrophobic oil/polar water interfacial phenomena dominates many important physical, chemical, and biological processes, including oil extraction, interfacial polymerization, surfactant implications, ion transport across the membrane, protein folding, chemical separation, and nanoparticle formation. Although a wide range of classical experiments has been conducted and reported, the phenomenological arguments have remained on the interactions in such a system. To derive a molecular-level picture of this interface, recent interest has focused on fundamental simulations like molecular dynamics at the molecular/atomic level to solve the contradicted results in the classical experiments of the oil-water interface.

The well-organized structure of water molecules next to any hydrophobic surface due to the weak interactions between these hydrophilic and hydrophobic molecules has been established by researchers in terms of experimental and simulation studies. However, the natural environments are more complex than a simple hydrophobic/hydrophilic interface. Generally, the aqueous phase might have ions; gases like CO<sub>2</sub> and organic medium might include different acidic/basic components. Therefore, we need to investigate more complicated liquid/liquid interfaces to approach a real system. One of the complex biphasic hydrophobic/aqueous interfaces is related to the oil reservoirs. To extract more oil and simultaneously store carbon dioxide in the underground reservoirs, the carbonated water has been designed to inject into the oil pools. However, there is no concrete conclusion on which screening parameters should be considered to gain higher oil recovery and higher carbon footprint storage.

Herein, we investigated the effect of the most abundant polar acidic components (Benzoic acid, Decanoic acid, and phenol) in the hydrophilic phase on the interfacial phenomena of hydrophilic phase (Decane) and carbonated water. Hence, molecular dynamics simulation was used to analyze these systems. The structure, mass and charge density, hydrogen bonds, and Interfacial Tension (IFT) have been analyzed for different scenarios. To the authors' best knowledge, the effect of combining acidic components and carbon dioxide in the hydrophilic/hydrophobic interface has been investigated for the first time.

The results indicated that carbon dioxide molecules tend to accumulate at the interface of decane/water and then diffuse to the oleic phase. When the polar molecules are introduced to the hydrophobic phase, there is a competition between carbon dioxide and acidic components to accumulate at the interface. Since there is a Columbic interaction between polar water molecules and polar acidic components compared to non-polar carbon dioxide molecules, the carbon dioxide molecules diffuse more evenly into the oleic phase and fill the voids in the oleic phase existing due to the entanglement of the alkane chains. Therefore, the acidic components replace the carbon dioxide at the interface and serve as a bridge between the hydrophobic and hydrophilic phases. Indeed, the predominant interaction corresponds to the water and polar molecules. The density peaks of polar molecules occur at the interface where the hydrophilic part of the polar component penetrates to the aqueous phase, and the lipophilic part of polar molecules is in the oleic phase, which is a surfactant-like action. The anchoring effect of acidic components at the water/decane interface decreases the IFT between decane and water. Although there is a significant reduction in the IFT of systems involving acidic components compared to the simple decane/carbonated

water system, there is no significant difference between these three types of acids in decreasing the IFT in the presence of carbon dioxide in the biphasic system. The charge distribution of water molecules in the systems involving polar components changes. In the simple decane/water case, water molecules show a recognized charge distribution at the interface with two well-order H-bonds networks. While in the biphasic systems, including polar molecules, the well-organized charge distribution at the interface (two water surface layer structure) change, and the aqueous phase is disturbed inside itself. This is proof of destroying the shield of the well-organized water layer at the interface to the non-aqueous phase, which leads to IFT reduction as the surface forces between the two phases reach zero.

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# Laser-induced alignment of nanoparticles and macromolecules: modeling and realization

## Content

X-ray free-electron lasers (XFELs) promise the diffractive imaging of single molecules and nanoparticles. It relies on recording a series of two-dimensional (2D) diffraction images from randomly oriented isolated particles, which can then be assembled in silico to a three-dimensional (3D) diffraction volume and the structure reconstructed[1]. In this approach, the orientational uncertainty is solved by using advanced algorithms. However, this can be very challenging at times and assumed to be one major bottleneck in achieving atomic spatial resolution [2]. Laser-induced alignment of nanoparticles has the potential to improve the achievable resolution by reducing complexity of the diffraction volume search space and push it toward the atomic scale [3, 4].

We set up a project to implement strong laser alignment of nanoparticles and large biomolecules in a way that is applicable to XFEL experiments. Here, we will present quantitative computational modeling of nanoparticle alignment using classical mechanics and electrodynamics. Firstly, we developed methods to accurately predict the polarizability tensors of nanoparticles and biomolecules[5]. Then we predict the laser-induced rotational dynamics and the alignment of these particles, which demonstrate that the laser-induced alignment of nanorods and biological macromolecules is possible. Furthermore, the relation between geometrical properties of nanorods and the adequate alignment laser pulse is investigated for improvement of the alignment.

Last but not least, we will present first experimental demonstration of the laser-induced alignment of gold nanorods.

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# Time-Resolved Measurement of Interparticle Coulombic Decay Processes

## Content

Interparticle Coulombic Decay (ICD) processes are electronic decay processes of weakly interacting systems, which are initiated by inner-valence excitation ionized ionization. These weakly interacting systems include solvents, biomolecules and quantum dots in semiconductors, that interact via electron correlation. We report about a new theory for the time-resolved description of the spectator resonant ICD processes initiated by and measured with short laser pulses. We propose to excite the system with an XUV laser pulse, measure the absorption spectrum of the system and to quench the decay process with a strong IR laser pulse at different time delays. The quenching results in the initiation of an ICD process, whose ICD electron signal can then be measured without interference effects.

Additionally, the lifetime regime of the ICD processes allow for the observation of oscillations of the time- and energy-differential ionization probability close to the peak energy of the RICD electron signal. The here derived formulas show that commonly used fitting schemes used in the analysis of experimental data yield lower or upper boundaries to the real lifetime instead of the true value.

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## Alternative approach to construction of nonlocal resonance models

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### Content

Submitted by ALT, Václav on Friday, 22 July 2022

We are interested mainly in the nuclear dynamics of diatomic molecules in resonant collisions with electrons. In our work the nuclear dynamics is usually solved within the discrete-state-in-continuum theory which is built on the Feshbach projection operator approach [1].

The electron projectile is assumed to get trapped in a single, discrete state  $|\phi_d\rangle$  and the collisional dynamics is then governed by the following quantities: the potential energy of the neutral molecule  $V_0(R)$ , the discrete state potential  $V_d(R)$  and the coupling between the discrete state and the electron continuum  $V_{d\varepsilon}(R)$ . These three quantities constitute a nonlocal resonance model (NRM).

Apart from  $V_0(R)$ , these quantities often remain unknown and to construct a nonlocal resonant model, one has to estimate the functional form of  $V_d(R)$  and  $V_{d\varepsilon}(R)$  and fit it to other known quantities, such as the fixed-nuclei scattering phaseshifts. The discrete state potential and the coupling are assumed to take one of few commonly used functional forms. This fitting procedure is rather limiting and can become quite tedious.

We present a method of solving the nuclear dynamics without the need of any fitting. The main idea lies in choosing a discrete state  $|\phi_d\rangle$  and calculating  $V_d(R)$  directly together with a fixed-nuclei, complex level-shift operator

$$F(\varepsilon, R) = \varepsilon - V_d(R) - \langle \phi_d | \hat{G}(\varepsilon) | \phi_d \rangle^{-1},$$

which is related to the discrete-state-continuum coupling

$$|V_{d\varepsilon}(R)| = \sqrt{2\Im(F(\varepsilon, R))}.$$

This method is demonstrated on vibrational excitation for three molecules described by a simple two-dimensional model [2] (N<sub>2</sub>-, NO- and O<sub>2</sub>-like models). For this model we can compare the exact cross sections for vibrational excitation with results obtained through coupling calculated from  $F(\varepsilon, R)$ . It is shown that the choice of the discrete state  $|\phi_d\rangle$  is not too important while the cross sections remain unchanged. The method can be applied to real molecules as well.

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