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Program

Sunday, August 24th

16.30–18.30 Registration

17.30–18.30 Reception

18.40–18.50 Welcome – Gunnar Nyman

18.50–19.00 Welcome – Dean of Science, Elisabet Ahlberg

Chair: Dag Hanstorp

19.00–20.00 I1: Richard Zare, *Preparation of Molecular Hydrogen in a Controlled Superposition of $|vJM\rangle$ States*

20.00–21.00 I2: David Manolopoulos, *Photochemistry, semiclassical spin dynamics, and the avian navigation problem*

Monday, August 25th

Theory, Chair: Sture Nordholm

09.00 I3: Uwe Manthe, *State-resolved quantum dynamics of polyatomic reactions*

09.40 I4: Irene Burghardt, *Quantum dynamics of exciton migration and dissociation in functional organic polymer materials*

10.20 C1: Rita Prosimiti, *The role of large-amplitude motions in the IR spectra of H_5^+/D_5^+ cations*

10.40 Coffee

11.10 I5: Stuart C. Althorpe, *Is there a quantum transition-state theory?*

11.50 I6: Nandini Ananth, *Novel Path-Integral Based Dynamics for Photochemistry*

12.20 C2: Jeremy O. Richardson, *Nonadiabatic ring-polymer molecular dynamics rate theory*

12.40–14.00 Lunch

Experiments, Chair: Mats Larsson

14.00 I7: Kopin Liu, *Effects of reagent rotational excitation on $Cl + CH_4/CHD_3$ reactions*

14.40 I8: Ian Sims, *Radical reactivity at very low temperatures*

15.10 C3: Astrid Bergeat, *Crossed-beam inelastic scattering experiments at energies approaching the cold regime*

15.30 Coffee

16.00 I9: Gerard Meijer, *Taming beams of neutral molecules*

16.40 I10: Mark Brouard, *The stereodynamics of inelastic scattering of $NO(X)$ by the rare gases*

17.20 C4: Matthew Costen, *Probing the surface of ionic liquids through collisions with gas-phase atoms*

17.40 C5: Thomas Pino, *Intramolecular processes revealed using UV-Laser-Induced IR-Fluorescence of the first electronic transition of Benzene*

Monday evening – City of Gothenburg reception 19.00–20.30

Tuesday, August 26th

Astrochemistry/astrophysics, Chair: Stefan Andersson

09.00 I11: Eric Herbst, *Gas-Grain Chemical Simulations of Star-forming Regions*

09.40 I12: Liv Hornekær, *Polycyclic aromatic hydrocarbons as catalysts for interstellar chemical complexity*

10.10 C6: Victor Herrero, *Vibrational spectroscopy and kinetics of the astronomically relevant ArH^+ ion in Ar/H_2 cold plasmas*

10.30 Coffee

11.00 I13: Laurent Wiesenfeld, *Molecular collisions for Astrophysics: theory and experiments*

11.40 I14: Herma Cuppen, *Kinetic Monte Carlo simulations of interstellar grain surface chemistry*

12.10 C7: Nathalie de Ruette, *Merged beam studies for astrobiology*

12.30–14.00 Lunch

Theory, Chair: Magnus Gustafsson

- 14.00 I15: Donghui Zhang, *Differential Cross Sections for the H+CD₄ and H+SiH₄ reactions*
14.40 I16: Octavio Roncero, *State-to-state reactive collisions with H₂ of astrophysical interest*
15.10 C8: Judith Rommel, *Chemisorption on Metal Surfaces: The Role of Quantum Tunnelling*
15.30 Coffee
16.00 I17: Tamar Seideman, *Control of Transport and Mechanical Motions in Junctions with Coherent light*
16.40 I18: Terry Frankcombe, *New Gaussian basis set methods for quantum systems*
17.10 I19: Anthony Meijer, *Quantum dynamics studies of surface-catalysed H atom recombination*
17.40 C9: Jens Poulsen, *The Classical Wigner model and the ensemble conserving problem*
18.15–19.30 Dinner
19.30–21.30 Poster session (odd numbered posters)

Wednesday, August 27th

Experiments, Chair: Raimund Feifel

- 09.00 I20: Murthy Gudipati, *Chemical Reaction Dynamics in Cryogenic Ices in Our Galaxy*
09.40 I21: Henrik Cederquist, *Fragmentation of polycyclic aromatic hydrocarbons and their clusters and ion storage in DESIREE*
10.10 C10: Alexandre Perret, *Temperature dependence of dissolved CO₂ diffusion in Champagne wines: a theoretical and experimental investigation*
10.30 Coffee
11.00 I22: Lars H. Andersen, *Time-resolved action spectroscopy in ion storage rings*
11.40 I23: Vitali Zhaunerchyk, *Site-specific fragmentation of varying size molecules induced by resonant K-shell excitation*
12.10 C11: David Bonhommeau, *Structure and stability of multiply-charged clusters: Application to charged droplets produced by electropray ionisation*

Wednesday afternoon – boat excursion with lunch 13.30–16.30

17.00–19.00 Poster session (even numbered posters)

Thursday, August 28th

Atmospheric chemistry, Chair: Matthew Johnson

- 09.00 I24: Kristie A. Boering, *Reaction dynamics and kinetics of oxygen isotope exchange reactions: Insights into unusual isotope effects and their applications in earth and planetary science*
09.40 I25: Johan A. Schmidt, *On the origin of the high levels of Br radicals in tropical free troposphere*
10.10 I26: Theo Kurtén, *Exploring atmospheric autoxidation using quantum chemistry*
10.40 Coffee
11.10 C12: Ad van der Avoird, *In depth experimental and theoretical studies of molecular collisions*
11.30 C13: Morgane Vacher, *Coupled electron-nuclear dynamics following photoionisation of benzenes*
11.50 C14: Luís Viegas, *Exploring the influence of water in ozone depletion through the HO₂ + nH₂O + O₃ reaction: from a single water molecule to a water cage*
12.10 C15: Gábor Czakó, *Dynamics of polyatomic chemical reactions on ab initio potential energy surfaces*

12.30–14.00 Lunch

Control/Cold, Chair: Jens Poulsen

- 14.00 I27: Dmitry Shalashilin, *Multidimensional quantum mechanics with trajectory guided basis sets of Coherent States. From nonadiabatic photochemical reactions to dynamics of electrons in strong laser field.*
14.40 I28: Åsa Larson, *Molecular dynamics involving electronic resonant states of HeH*
15.10 C16: Adam Kirrander, *Theory and simulations for ultrafast x-ray scattering*
15.30 Coffee
16.00 I29: Olivier Dulieu, *Radiative formation of cold molecular ions in an ion/atom hybrid trap*
16.30 I30: Andreas Osterwalder, *Penning Ionization Reactions of Polyatomic Molecules at Low Temperature*

17.00 C17: Alberto García-Vela, *Resonant detection of the signature of control on a resonance state lifetime using a pumpprobe scheme*

18.00 Theater play: Lise Meitner

19.30 Conference dinner

Friday, August 28th – departure

I1**Preparation of Molecular Hydrogen in a Controlled Superposition of $|vJM\rangle$ States**

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The $H + H_2$ bimolecular exchange reaction and its isotopic variants continues to be a benchmark system for theoretical developments and to hold unexpected surprises.¹ Using stimulated Raman adiabatic passage (SARP) it is possible, in principle, to transfer all the population in a rovibrational level of an isolated diatomic molecule to an excited rovibrational level.²⁻⁴ Dr. Wenrui Dong, Dr. Nandini Mukherjee, and I have been applying SARP to a molecular beam of hydrogen molecules. We use an overlapping sequence of pump (532 nm) and dump (683 nm) single-mode laser pulses of unequal fluence. In the first series of experiments we were able to transfer more than half the population to an excited rovibrational level.⁵ Since then, we have achieved $97 \pm 7\%$ transfer of population from the H_2 ($v=0, J=0$) ground rovibrational level to the H_2 ($v=1, J=0$) excited rovibrational level.⁶ We have also prepared superpositions of different $|vjM\rangle$ states. We believe that this process is quite general. An explanation will be presented of the SARP process and how these results are obtained.

This work was supported by the U.S. Army Research Office under ARO Grant Nos. W911NF-10-1-01318 and W911NF-13-1-0126, a DURIP equipment Grant No. W911NF-11-1-0342, and a MURI Grant No. C13J225+(J00210).

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6. W. Dong, N. Mukherjee and R. N. Zare, *J. Chem. Phys.* **139**, 074204-1-6. (2013).

I2**Photochemistry, semiclassical spin dynamics, and the avian navigation problem**

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In this talk, I will review the semiclassical theory of photochemically-induced radical pair recombination reactions that we have developed during the past year [1,2], contrasting it with the exact quantum mechanical theory and an earlier approximate theory of Schulten and Wolynes [3]. I will then present an application of the semiclassical theory to a carotenoid-porphyrin-fullerene triad that has recently been used to establish a 'proof of principle' for the operation of a chemical compass [4], followed some by preliminary (as yet unpublished) results for a long-lived radical pair that is thought to act as the magnetic compass sensor in cryptochrome proteins in the avian retina [5]. One of the neatest aspects of the semiclassical theory is that it becomes more reliable as the number of nuclear spins in the radical pair increases and the environment of the electron spins becomes more complex, owing to the rapid quantum decoherence in complex systems. Both of the problems I shall consider (the carotenoid-porphyrin-fullerene triad and the cryptochrome radical pair) are in the regime where the semiclassical approximation is expected to be reliable and an exact quantum mechanical calculation would be completely unfeasible.

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- [2] A. M. Lewis, D. E. Manolopoulos and P. J. Hore, *J. Chem. Phys.* 141, 044111 (2014).
- [3] K. Schulten and P. G. Wolynes, *J. Chem. Phys.* 68, 3292 (1978).
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I3

State-resolved quantum dynamics of polyatomic reactions

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In the present talk, bimolecular reactions and intramolecular rearrangements in polyatomic systems are investigated on a fully quantum state-resolved level of theory. The $\text{H}+\text{CH}_4 \rightarrow \text{H}_2+\text{CH}_3$ reaction and the intramolecular quantum dynamics in the fluxional CH_5^+ cation are considered as examples. Combining intuitive theoretical concepts and the numerically efficient (multi-layer) multi-configurational time-dependent Hartree (MCTDH) approach, rigorous full-dimensional quantum dynamics calculations can investigate these six atom systems in detail.

The quantum transition state concept provides an accurate and intuitive description of reactions proceeding via a potential barrier. It is typically used to study reaction rates. The concept could recently be extended to the calculation of fully state-resolved reaction probabilities and cross-sections. In this approach, the reactive scattering is separated into two half-collisions starting from the transition state region and generalized flux correlation functions are used to rigorously compute fully state-resolved scattering matrix elements from the simulation data. In this talk, accurate results obtained for the $\text{H}+\text{CH}_4 \rightarrow \text{H}_2+\text{CH}_3$ reaction are presented. The ro-vibrational control of the chemical reactivity is discussed in the context of the Polanyi rules and the correlation between the quantum states of the reactants and products is analyzed.

The CH_5^+ cation is the prototypical example of a fluxional molecule. Its potential energy surface shows 120 minima separated by tiny potential barriers and its vibrational eigenfunctions are completely delocalized. Rigorous quantum dynamics calculations utilizing the multi-well structure of the system can compute eigenstates up to excitation energies of about 1600 cm^{-1} . Analyzing the numerical results, one finds that all computed vibrational levels can be assigned to local vibrational states. Tunneling splits these local states into the vibrational eigenstates of CH_5^+ . Thus, the level structure can be understood as the discrete analog of the typical vibrational band structures well known from solid state physics. Furthermore, it is found that the Pauli principle is of crucial importance in CH_5^+ . The majority of the vibrational levels which have been computed considering the hydrogen atoms as distinguishable are Pauli-forbidden due to nuclear spin statistics.

I4

Quantum dynamics of exciton migration and dissociation in functional organic polymer materials

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We present quantum dynamical studies of ultrafast photoinduced exciton migration and dissociation in functional organic materials, in view of understanding the key microscopic factors that lead to efficient charge generation in photovoltaics applications. As highlighted by recent experiments [1], these processes can be guided by quantum coherence, despite the presence of electron-phonon coupling and static and dynamic disorder. Our approach combines parametrized Hamiltonians, based on TDDFT and/or high-level electronic structure calculations, with accurate quantum dynamics simulations using the multi-configuration time-dependent Hartree (MCTDH) method [2] as well as non-Markovian reduced dynamics techniques [3]. This talk will specifically address (i) the dynamics of exciton migration in oligo-(p-phenylene vinylene) and oligothiophene fragments [4], and (ii) exciton dissociation in donor-acceptor materials, including models for P3HT-PCBM heterojunctions [5] as well as highly ordered thiophene-perylene diimide assemblies [6]. In line with experiment, our simulations show that the primary exciton breakup is an ultrafast (~ 50 – 100 fs) and coherent process. Furthermore, efficient free carrier generation from the interfacial charge transfer state is shown to be feasible, despite the Coulomb barrier that typically by far exceeds thermally available energy. This is due to two factors that can be shown to work together [5]: First, the effective lowering of the Coulomb barrier due to charge delocalization, and second, the vibronically hot nature of the primary charge transfer state.

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C1

The role of large-amplitude motions in the IR spectra of $\text{H}_5^+/\text{D}_5^+$ cations

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The recent increased interest on research studies on the H_5^+ cation and its isotopologues, is due to the postulation for their presence, although still not detected, in the interstellar medium. The protonated hydrogen/deuterium dimer is the intermediate complex in the astrochemically important proton transfer reactions between H/D_3^+ and H/D_2 . These systems are prototypical examples of studying large amplitude motions; as they are highly delocalized, interconverting between equivalent minima through rotation and proton transfer motions requiring fully coupled anharmonic treatments. There is no doubt, particularly in the light of the recent laboratory observations [1], that their spectroscopic characterization is also a great challenge for the theorists. To this end, we report a full-dimensional converged quantum calculations using the MCTDH (multi-configuration time-dependent Hartree) method on their vibrational spectroscopy, providing important information in a rigorous manner [2]. The predominant features in the IR spectra are assigned to the excitations of the shared-proton stretching and to internal rotation of the H_3^+ with excitation in the $\text{H}_3^+ \dots \text{H}_2$ stretch mode. Such states include considerable excitation in the reaction coordinate, and are expected to play an important role in the low temperature deuterium fractionation reaction via external proton transfer (scrambling mechanism). Above dissociation the symmetric and antisymmetric stretch modes of the two H_2 , as well as the breathing mode of the H_3^+ are also involved in the spectral assignment. The computed IR spectra for $\text{H}_5^+/\text{D}_5^+$ cations are compared very well with recent experimental measurements (see Figure 1) [1].

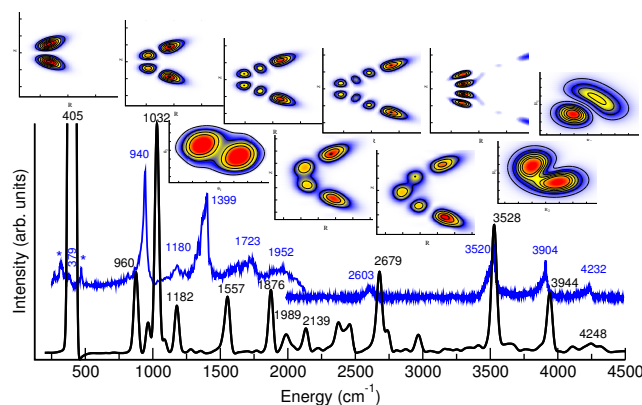


Figure 1: Simulated MCTDH spectrum of H_5^+ , and its comparison with experimental measurements. The assignment of some bands is also shown.

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I5

Is there a quantum transition-state theory?*

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Transition-state theory (TST) plays a central role in chemistry. It is a classical theory that states that the rate of a direct reaction can be approximated by the instantaneous flux through a dividing surface. This leads to the familiar picture of a reaction rate being dominated by a free-energy bottleneck which gives rise to an Arrhenius temperature-dependence. Various attempts have been made to incorporate quantum effects into TST, most famously the Wigner-Eyring expression (taught to generations of undergraduates). However, quantum rate-theory has seemed to show that a complete quantum generalization of transition-state theory is impossible.

In this talk we will show that a true quantum generalization of transition-state theory does exist, [1] that it appears to be unique, and that it is identical to a very practical rate-expression which was previously obtained heuristically, namely ring-polymer molecular dynamics (RPMD) TST. [2,3] This tells us that RPMD will give a good approximation to the exact quantum rate for reactions which are direct and not strongly influenced by real-time quantum coherence.

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*yes

I6**Novel Path-Integral Based Dynamics for Photochemistry**

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Addressing the challenge of designing efficient organic photovoltaics requires theoretical methods that accurately describe the coupling between electronic state transitions and nuclear dynamics, and that are computationally efficient for complex many-dimensional systems. In this talk, we introduce a recently developed path-integral based model dynamics, Mapping-Variable Ring Polymer Molecular Dynamics (MV-RPMD), that extends the applicability of the RPMD method from simulations of thermal, one-electron processes to multi-electron photochemical processes in the condensed phase. This is achieved by deriving an exact path-integral representation of the canonical partition function for an N -level system using Cartesian phase-space variables to represent both discrete electronic states and nuclear degrees of freedom [1,2]. We demonstrate the numerical accuracy of our method in simulations of model systems that exhibit dynamics in both the adiabatic and nonadiabatic limits. Further, we derive good electronic state population estimators that provide accurate, instantaneous state information necessary for the detailed mechanistic analysis of photochemical reactions [3].

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C2

Nonadiabatic ring-polymer molecular dynamics rate theory

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There is currently much work on the development of computationally practical methods for the simulation of nonadiabatic dynamics based on classical trajectories and path integrals such as ring-polymer molecular dynamics (RPMD) [1, 2, 3, 4]. An important goal for such methods is the accurate calculation of the rate constant over a wide range of electronic coupling strengths without the need to approximate the potential energy surfaces by harmonic oscillators, as is commonly the case for less general methods. It is often easy to ensure that the dynamics reduce to well-known results in the adiabatic strong-coupling limit but more difficult to simulate the correct behaviour in the weak-coupling golden-rule limit.

We derive a generalization of the nonadiabatic flux correlation function [5], from which the rate can, in principle, be computed exactly regardless of the coupling strength, but which unlike the usual version is not oscillatory. This new formalism thus provides a rigorous way for a wide variety of methods from trajectory- to wavefunction-based approaches to calculate the nonadiabatic rate more efficiently.

We show how nonadiabatic RPMD [1], based on the rigorous mapping approach [6, 7], performs significantly better than its classical limit. In particular, combination of this approach with the new flux correlation function formalism gives an accurate and efficient method for calculating nonadiabatic reaction rates in complex molecular systems.

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I7

20th MOLEC Conference, Gothenburg, Sweden, August 24-29, 2014

Effects of reagent rotational excitation on Cl + CH₄/CHD₃ reactions

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Effects of reactant rotation are of great importance in understanding and controlling the steric effects in chemical reactions. Here, we report the rotational quantum-state control of a late-barrier reaction of chlorine atom with CH₄ and CHD₃ in a crossed molecular beam experiment. Experimental results demonstrate that, in both reactions, the more detailed product state and angular distributions are essentially invariant for different rotational states of the vibrationally excited CH₄ and CHD₃ reactants. Yet, the integral cross sections show strong dependence on the reactant rotational excitation, suggesting that the differential reactivity arises from the anisotropic interactions en route to the reaction barrier. More detailed analysis indicates that the effects of reactant rotational excitation do not derive from the rotational-energy effects or long-range forces, rather originate from the short-range forces in the transition state region. Exactly how the transition-state properties, e.g., the barrier location and/or the tightness of the saddle point, influence the observed rotational-reactivity diversity, however, remains to be elucidated. Further investigations are on-going to gain deeper insights.

I8

Radical reactivity at very low temperatures

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The use of the CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme, or Reaction Kinetics in Uniform Supersonic Flow) technique coupled with pulsed laser photochemical kinetics methods¹ has enabled us to show that radical-radical, radical-unsaturated molecule and even radical-saturated molecule reactions may be rapid down to the temperatures of dense interstellar clouds (10–20 K), as well as proving an exacting test for theory.² Rate coefficients have been measured as low as 5.8 K for the reaction $S(^1D) + H_2$.³ The technique has also been applied to the formation of transient complexes of interest both in atmospheric chemistry⁴ and combustion.⁵

Results will be presented on the thermodynamics of the formation of the HO_3 radical,⁴ of potentially great importance in atmospheric chemistry, and the kinetics of reactions related to the formation of long chain cyanopolyne molecules $H(C_2)_nCN$,⁶ which may play an important role in the formation of the orange haze layer in Titan's atmosphere. Unlike most reactions of interest at low temperatures the $F + H_2 \rightarrow HF + H$ reaction does possess a substantial energetic barrier ($\cong 800$ K). It is nevertheless the only source of interstellar HF, recently detected in a wide variety of environments by the Herschel Space Observatory, many of which are very cold (10–100 K). In fact, this H-atom abstraction reaction does take place efficiently at low temperatures due entirely to quantum mechanical tunneling. I will report direct experimental measurements of the rate of this reaction down to a temperature of 11 K, in remarkable agreement with state-of-the-art quantum reactive scattering calculations by François Lique (Université du Havre) and Millard Alexander (University of Maryland).⁷

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C3

Crossed-beam inelastic scattering experiments at energies approaching the cold regime

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Theoretical calculations predict that rotational energy transfer to small molecules, such as CO or O₂, by collisions with H₂ or He are dominated by resonance phenomena, which can only be revealed at very low energies. Experiments conducted with a crossed, molecular beam apparatus with variable crossing angle allowed us to determine the integral cross sections as a function of the relative translational energy down to a few wavenumbers, *i.e.* below the thresholds of the $\{j = 0 - 1\}$ CO transition at 3.85 cm⁻¹ and the $\{(N = 1; j = 0) - (N = 1; j = 1)\}$ O₂ transition at 3.96 cm⁻¹. The experimental results, which exhibit behaviours characteristic of quantum resonances, are compared to QM scattering calculations. The results obtained for O₂ + H₂ show that this $\{(N = 1; j = 0) - (N = 1; j = 1)\}$ collision-induced transition occurs exclusively in a pure quantum regime via shape and Feshbach resonances arising from definite partial waves.¹ The close agreement between experimental and theoretical (QM scattering) integral cross sections allows for complete assignment of the resonances observed. Agreement with theory is shown to strongly depend on the characteristics of the potential energy surface (PES) used to perform the QM treatment. The ICS calculated with the new PES developed by P. Jankowski, A. R. W. McKellar and K. Szalewicz² for the CO(*j*=0) + *p*-H₂ → CO(*j*=1) + H₂ are in excellent agreement with our experimental data³ on CO + *p*-H₂ and this PES was also used for our recent studies of inelastic scattering of CO with *n*-H₂, *o*-D₂ and *n*-D₂.

This work is supported by the French National Research Agency (ANR- **HYDRIDES**, ANR-12-BS05-0011-01 contract), the Conseil Régional d'Aquitaine (contract 2007.122) and the PHC Van Gogh ("Cold Collisions", n°28484TH).

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I9

Taming beams of neutral molecules**Gerard Meijer**

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In this presentation, an overview will be given of the methods that have been developed to control the motion of neutral molecules with electric and magnetic fields [1]. These methods bear a lot of resemblance to the well-known methods used for the control of charged particles [2]. The neutral analogues of different types of linear accelerators, of a buncher, of a Paul trap, of a quadrupole mass-filter and of a synchrotron have all been demonstrated, and their operation principles will be described. An overview will be given of the possibilities that this molecular beam technology offers, ranging from ultrahigh-resolution spectroscopy and lifetime measurements to novel scattering experiments and the separation of structural isomers of (bio-)molecules. Time permitting, the progress towards the realization of a gas-phase molecular laboratory on a chip will be described [3,4].

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I10

The stereodynamics of inelastic scattering of NO(X) by the rare gases

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This talk will present new experimental results on the inelastic scattering of NO(X) by Ar, and other rare gases, in which the NO(X) molecule is fully quantum state-selected both before and after collision. State-to-state differential cross-sections (DCSs) and collision-induced angular momentum polarizations observed following the fully Λ -doublet resolved inelastic scattering of NO($X^2\Pi_{1/2}, v=0, j=1/2, f$) with the rare gases will be presented, and compared with the results state-of-the-art theoretical calculations.

The dependence of the DCSs and angular momentum polarization on rotational and Λ -doublet state will be discussed, with reference to simple classical and semi-classical models, as well as to exact quantum scattering calculations. A particular focus of the talk will be a discussion of the quantum mechanical origin of collision induced angular momentum orientation.

New experimental results will also be presented in which it has been possible to measure the DCSs and polarization of the inelastically scattered NO(X) products arising from collisions with oriented NO molecules. These results may be considered the first 'complete' experiment on the inelastic scattering of NO(X) by the rare gases.

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C4

Probing the surface of ionic liquids through collisions with gas-phase atoms

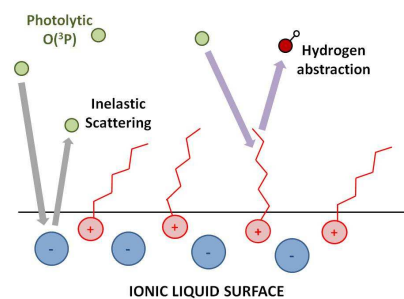
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The ionic-liquid(IL)/gas interface plays a crucial role in applications such as gas capture and multiphase catalysis. Understanding how the ionic-liquid chemical composition affects the surface structure would facilitate the efficient design of ILs for particular applications. We report a systematic study of surface composition of ionic liquids using a novel, spectroscopically based experimental technique illustrated schematically in the figure.[1] Gas-phase superthermal O(3P) atoms are generated by photolysis. They react selectively with alkyl chains in the interface, acting as an extremely surface-sensitive chemical probe for the presence of abstractable H atoms. The OH radicals produced in the reaction are detected by laser-induced fluorescence (LIF) in the gas phase, allowing us to quantify differences in surface coverage by alkyl chains. This approach has been employed to study the interfacial reactivity of a widely studied and exploited family of ILs containing the 1-alkyl-methylimidazolium cation with different chain lengths and with a series of representative anions. Our results, supported by complementary high-energy molecular beam scattering experiments, show that the alkyl chains on the cation preferentially occupy the outer surface layer, resulting in a composition that is substantially different from that of the bulk. This preference is strongly dependent on alkyl chain length. The alkyl surface enrichment has also been found to depend on the counteranion in a way that can be predicted from its steric bulk.



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C5

Intramolecular processes revealed using UV-Laser-Induced IR-Fluorescence of the first electronic transition of Benzene

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Radiative relaxation in the infrared (IR) is common following nonradiative electronic relaxation processes, but it is rarely measured. However it is observed in space throughout many lines of sight and gives rise to the so-called Aromatic Infrared Bands, at the origin of the PAH hypothesis in astrophysics [1]. At Orsay, we developed a spectrometer named FIREFLY (Fluorescence in the InfraRed from Excited FLYing molecules) [2] to tackle the IR emission of astrophysically relevant aromatic molecules. Thanks to this development, we have studied the ultraviolet laser-induced infrared fluorescence (UV-LIIRF) excitation spectroscopy and dispersed UV-LIIRF spectroscopy of gas phase benzene vibrationally excited in its first electronic excited state. We found that the vibrational IR fluorescence is observed through excitation of each the vibronic bands composing the first electronic transition in benzene, and the yield is clearly higher when benzene is excited above the onset of "channel 3" than when it is excited below. Significant changes in dispersed IR emission profiles resulting from excitations below and above the onset of channel 3 were also observed. These results suggest that isomerization of benzene toward fulvene occurs efficiently below the opening of channel 3 and confirm that channel 3 involves a photophysical relaxation pathway that efficiently competes with isomerization [3].

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I11

Gas-Grain Chemical Simulations of Star-forming Regions

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Stars and planets form from the collapse of portions of dense interstellar clouds, which are large assemblies of cold gas and dust (10 K) in the interstellar medium. The gas-phase is mainly molecular and contains many exotic species, including radicals, unusual isomers, and anions, most of which are organic in nature. Although hydrogen is the dominant element and H₂ the dominant gas-phase molecule, most organic molecules are very unsaturated and are labeled “carbon chains” by astronomers. The dust particles are covered with ices, mainly in the form of water, CO, and CO₂. During the collapse, the material evolves through a number of stages starting with an isothermal era, followed by a warm-up during which the gas-phase molecular inventory changes from an exotic one to one in which the organic molecules resemble standard laboratory solvents, albeit in the gas phase. Eventually a so-called protoplanetary disk is formed around the young star, and the disk can lead to the formation of planets via coagulation of the dust particles, with an initial molecular inventory at least partially determined by the chemistry that has already occurred.

Much of what we know about the physical conditions and lifetimes of the various stages of star formation derives from molecules, which, through spectroscopy and kinetic modeling, are excellent probes of sources where they exist.^{1,2} In this talk, I will discuss the types of gas-phase and solid-state processes that synthesize molecules in assorted regions of star formation, with an emphasis on exotic gas-phase reactions and the chemistry that occurs in ice mantles.

¹ E. Herbst, PCCP, **16**, 3344-3359 (2014)

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I12

Polycyclic aromatic hydrocarbons as catalysts for interstellar chemical complexity

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Even though Polycyclic Aromatic Hydrocarbons (PAHs) are ubiquitous in the interstellar medium, the role they play as catalysts for interstellar chemistry is still largely unexplored. However, existing experimental data [1-3] and theoretical calculations [4] indicate that PAHs may well play a very active role, in particular in connection with the formation of molecular hydrogen. These findings may explain observations of increased molecular hydrogen formation rates in Photodissociation regions with high PAH abundances. In my talk I will present temperature programmed desorption data demonstrating the formation of highly super-hydrogenated PAHs via hydrogen addition reactions and catalytic formation of molecular hydrogen via abstraction reactions at a wide range of H atom temperatures [1-3]. Approximate cross-sections for these reactions derived via model simulations will be presented [5]. The implications for the role played by PAHs in interstellar chemistry will be discussed.

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C6

Vibrational spectroscopy and kinetics of the astronomically relevant ArH⁺ ion in Ar/H₂ cold plasmas

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The recent detection by Barlow et al [1] of argonium (³⁶ArH⁺) in sub-millimeter emission spectra from the Crab Nebula has revived the interest in the spectroscopy and kinetics of this ion. It is the first noble gas compound observed hitherto in space. In the present work, we have studied the IR spectroscopy of the astronomically relevant ³⁶ArH⁺ and ³⁸ArH⁺ isotopologues, and the ion kinetics in Ar/H₂ hollow cathode discharges.

IR difference frequency laser spectroscopy was used for the accurate wavenumber determination of ³⁶ArH⁺ and ³⁸ArH⁺ rotation-vibration transitions of the $\nu = 1-0$ band in the range 4.1–3.7 μm (2450–2715 cm^{-1}). The wavenumbers of the $R(0)$ transitions of the $\nu = 1-0$ band are 2612.50135 ± 0.00033 and $2610.70177 \pm 0.00042 \text{ cm}^{-1} (\pm 3\sigma)$ for ³⁶ArH⁺ and ³⁸ArH⁺, respectively [2]. Opacity estimates indicate that significant absorption by the $R(0)$ line can be expected against bright mid-IR sources.

Mass spectrometry of neutrals and ions in combination with Langmuir probe measurements were used to investigate distributions of neutral and charged species in the Ar/H₂ plasmas. The range of mixture proportions leading to high relative abundances of ArH⁺ decreases appreciably with growing pressure. The simulation of the measured data with a kinetic model indicates that the relative concentrations of the major ions (Ar⁺, ArH⁺ and H₃⁺) depend markedly on the electron temperature and might also depend strongly on the internal excitation of H₃⁺. The results invite further dynamical studies on inelastic and reactive processes in these plasmas.

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I13

Molecular collisions for Astrophysics: theory and experiments

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In order to retrieve actual molecular abundances from astrophysical observations of molecular spectral lines, knowledge of the rotational levels excitation schemes is essential. Actual excitation results of a trade-off between photon excitation and collisional excitation by the main constituents of the interstellar gas, molecular hydrogen, and, to a lesser extent, atomic hydrogen and helium. These rates are almost always obtained from theoretical investigations, by computing classical or quantum dynamics of the interaction of molecules with these colliders.

Many types of molecules are observed and consequently, many collisions have been studied recently, like hydrides (1), water and its isotopomers (2), organic molecules (3).

In order to assess the quality of the computations, a systemic comparison with experiments is being undertaken. Observables are mainly integral or differential cross-sections (4), as well as pressure broadening cross sections (5).

All comparisons show an agreement between theory and experiments, thereby validating the quality of the Potential energy surfaces and the quantum scattering computations.

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I14**Kinetic Monte Carlo simulations of interstellar grain surface chemistry**

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At the moment, over 170 different molecules have been detected in the interstellar medium, including many saturated molecules like water, methanol, but also formic acid, and dimethyl ether. Gas phase mechanisms cannot account solely for the formation of these molecules, since they often require either high temperatures to be formed or three-body reactions along their formation routes, which are both not available in cold molecular clouds. Dust grains can act as a third body, facilitating surface reactions that lead to the formation of saturated molecules.

I will show how we can apply kinetic Monte Carlo simulations to learn more about this grain surface chemistry, since it can handle the long timescales necessary for interstellar conditions. I will present results of two different applications of this technique. A lattice-gas application which is applied to studied the build up of interstellar water ices through gas phase accretion of H, H₂ and O and the off-lattice adaptive Kinetic Monte Carlo implementation which allows us to simulate interstellar ice systems for a long period of time using realistic interaction potentials. I will focus on the diffusion of CO and CO₂ on different water ice substrates.

C7

Merged beam studies for astrobiology

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The chain of chemical reactions leading towards life is thought to begin in molecular clouds when atomic carbon and oxygen are "fixed" into molecules. Reactions of neutral atomic C with H_3^+ is one of the first steps in the gas phase chemistry leading to the formation of complex organic molecules within such clouds [1]. Water, believed to be essential for life, can form via a chain of gas-phase reactions that begin with neutral atomic O reacting with H_3^+ . Uncertainties in the thermal rate coefficient for each of these reactions hinder our ability to assess the validity of the present chemical network leading to the synthesis of complex organic molecules.

Theory and experiment have yet to converge in either the magnitude or temperature dependence for each of these reactions. Theory provides little insight as fully quantum mechanical calculations for reactions involving four or more atoms are too complex given current capabilities. On the other hand, measurements of cross sections and rate coefficients for reactions of atoms with molecular ions are extremely challenging. This is due to the difficulty in producing sufficiently intense and well characterized beams of neutral atoms. Ion trap studies of C on cold H_3^+ were performed at 1000 K, much hotter than molecular clouds [2]. For O on H_3^+ , two flowing afterglow results at 300 K exist, but with rather large uncertainties and no information on the temperature dependence [3,4].

We have developed a novel merged beam apparatus to study reactions of neutral atomic C and O with molecular ions at the low collision energies relevant for molecular cloud studies. Photodetachment of atomic anion beams, with an 808-nm (1.53-eV) laser beam, is used to produce beams of neutral atomic C and O, each in their ground term as occurs in molecular clouds. The neutral beam is then merged with a velocity matched, co-propagating H_3^+ beam.

The merged beams method allows us to use fast beams (keV in the lab frame), which are easy to handle and monitor, while being able to achieve relative collision energies down to ≈ 10 meV. Using the measured merged beams rate coefficient, we are able to extract cross sections which we can then convolve with a Maxwellian energy spread to generate a thermal rate coefficient for molecular cloud temperatures. Here we report recent results for reactions of C and O on H_3^+ . Our reaction studies will help to provide a better basis for astrochemical models and benchmarks for future theoretical development.

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I15**Differential Cross Sections for the H+CD₄ and H+SiH₄ reactions***Dong Hui Zhang**State Key Laboratory of Molecular Reaction Dynamics
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The success on the calculation of differential cross sections (DCS) for the HD+OH → H₂O+D reaction [Science **333**, 440 (2011)], in unprecedented agreement with experiment, declares the four-atom reactive scattering problem is largely solved. In this talk, I will present some of our recent work on calculating state-to-state DCSs for the H+CD₄ and H+SiH₄ reactions. Accurate potential energy surfaces for these systems have been constructed using neural network fitting method. Six dimensional quantum reactive scattering calculations were performed to obtain final state resolved integral and differential cross sections for the reactions. It is found that the DCS for the H+CD₄→HD+CD₃ reaction is largely independent on the rotational state of CD₃, while the DCS for the H+SiH₄→H₂+SiH₃ reaction is strongly dependent on the rotational state of SiH₃. Consequently, excellent agreement between theory and experiment on DCS is only obtained for the H+CD₄ reaction, but is much difficult for the H+SiH₄ reaction, due to lack of rotational information for the CD₃ and SiH₃ in the experiment.

I16

State-to-state reactive collisions with H₂ of astrophysical interest

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The state-to-state rate constants for exoergic O⁺+H₂ and endothermic C⁺ + H₂(v=0,1,2) reactive collisions [1] are studied using a wave packet method, and the effect of considering the vibrational excitation in PDR astrophysical models is analyzed.

The H₂ + H₃⁺ reactive collisions are studied using a combination of quasi-classical trajectory (QCT) and statistical methods to account for the nuclear spin statistics. The statistical approach of Park and Light[2] is improved by considering a full potential energy surface[3] to account for the shape of the charge distribution on H₃⁺. Also, the QCT reaction probabilities obtained for the identity/hop/exchange mechanisms are used to modify the so called scrambling matrix[4]. This allows to describe the transition between full scrambling statistical behavior, characteristic at low temperatures, and a more direct hop mechanism at higher temperatures. Comparison with recent experimental results[5] will be also discussed, and the rates for ortho/para transition presented.

Finally, some preliminary QCT results on the H₂ + H₂⁺ → H₃⁺ + H reaction will be presented based on a recently developed global potential energy surface[6], which describe very accurately the long range interactions.

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C8

Chemisorption on Metal Surfaces: The Role of Quantum Tunnelling

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Chemisorption plays an important role in a huge number of industrial processes such as for example the steam-reforming of methane during the Haber–Bosch process. The understanding of gas-surface reactions is key to improve the efficiency of catalysts involved. The chemisorption of methane on a single crystal metal surface, like Ni(100), is a prototypical system to study these processes. Experimental investigations gave clear evidence that transition state theory does not always offer an accurate description of gas-phase surface reactions [1]. Further studies hint that in CH₄ dissociative adsorption quantum effects such as tunnelling become important below a surface temperature of 200 K which is far above the theoretically predicted classical-quantum crossover temperature T_c . To understand the influence of quantum effects on these reactions we require a rate theory for multidimensional systems consistent over the full temperature range.

Instanton rate theory (also Imaginary Free Energy method), based on statistical Feynman path integrals, is increasingly used to investigate the role of tunnelling in chemical systems where often full quantum dynamical approaches are too expensive due to the size of the systems. The approach captures the essential physics of deep tunnelling, e.g. corner cutting, and allows to treat the dynamics classically. The instanton itself is the tunnelling path (ring polymer) with the highest statistical weight at a given temperature. Finding instanton paths by on-the-fly optimisations during rate calculations makes the method efficient for practical use in systems like enzymes [2,3,4]. However, the instanton method breaks down at temperatures near the crossover temperature T_c [5]. In many applications temperatures in that range are the most interesting ones.

Following up the discussions in [6] and by linking to approaches from field theory and the more mathematically oriented fields of differential geometry, oscillatory integrals, and dynamical systems theory, a deep understanding of the underlying theory was gained. The result is an improved methodology for predictions of the instanton rate at higher temperatures.

Ultimately, the extended instanton rate theory will increase the understanding of the mechanism of chemisorption in the complete temperature range and will lead to the design of new optimised catalysts.

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I17

Control of Transport and Mechanical Motions in Junctions with Coherent light

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The optical response of nanoscale molecular junctions has been the topic of growing experimental and theoretical interest in recent years, fueled by the fascinating physics involved, the rapid advance of the experimental technology and the promise for long range applications. The ultimate goal of controlling electric transport with coherent light, however, has proven challenging to realize in the laboratory. Here we propose an approach to coherent control of electric transport and vibrational dynamics in molecular junctions, which bypasses several of the hurdles to experimental realization of optically manipulated nanoelectronics noted in the previous literature. Essential to our approach is the application of semiconductor contacts and optical frequencies below the semiconductor bandgap. Our theory combines very simple, analytical models to study the qualitative transport properties of semiconductor-based molecular junctions with an analytical density matrix theory and numerical quantum dynamics simulation to explore control opportunities. In the talk I will first discuss recent results for quantum control of the electronic dynamics via frozen molecular wires, where the vibrational modes of the molecular moiety of the junction play no role. Next I will introduce a unidirectional, coherently driven molecular motor, where solely the vibrational modes are optically controlled. Finally I will combine control of the vibrational and electronic dynamics to introduce an ultrafast, nanoscale switch for electrons. Before concluding I will outline a few of our favorite dreams in this area.

I18

New Gaussian basis set methods for quantum systems

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We have recently developed a new Gaussian basis set based method incorporating several key innovations. The Basis Expansion Leap multiconfigurational Gaussian (BEL-MCG) method uses Gaussian functions simply as a flexible, redundant basis set. Basis function motion is completely removed from the physics of the system, dramatically reducing the number of equations of motion required. This method allows accurate propagation of the quantum wave packet describing molecular nuclei, giving accurate reaction probabilities on any reasonable molecular potential energy surface. The Schrödinger equation is solved to a pre-specified level of accuracy, meaning all quantum effects are reproduced. This methodology can be used to calculate the rovibrational ground state wave function of a system, allowing the rapid calculation of zero point energies without reference to presumed functional forms or harmonic/anharmonic character. In this talk the BEL-MCG approach shall be described and demonstrated with simple and multi-dimensional examples.

Quantum dynamics studies of surface-catalysed H atom recombination

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Molecular hydrogen, H₂, is one of the fundamental constituents of the universe, acting as the molecular feedstock for much of the chemistry occurring within the interstellar medium.[1] Although gas phase models of the chemistry of interstellar clouds have been successful in explaining the abundances of some gas phase molecules, it has long been established that they cannot account for the large abundance of molecular hydrogen. The general consensus of the astronomical community is that carbonaceous interstellar dust grains assume a catalytic role in the formation of H₂ molecules within interstellar clouds.[2]

First-principles calculations using the VASP (Vienna ab initio simulation package) software package have been performed in order to scrutinise the hydrogen-dust grain interaction. In particular, this potential explicitly includes degrees-of-motion associated with motion of the surface.

Furthermore, the collinearly-dominated Eley-Rideal H₂ formation pathway has been studied using quantum dynamics. Our 3D, 4D, and 5D calculations were performed using the Multi Configuration Time Dependent Hartree (MCTDH) algorithm on this novel potential energy surface.[3] In contrast to early calculations[4] our PES accounts (given its construction) for energy transfer from the nascent H₂ bond to the dust grain surface, highlighting the importance of surface relaxation in the Eley-Rideal mechanism.[5,6]

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C9

The Classical Wigner model and the ensemble conserving problem

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The Classical Wigner method is a way of including quantum effects into molecular simulations. It works by sampling initial conditions from a Wigner distribution and trajectories are then propagated classically. Perhaps the largest problem of this approach is the non-conservation of the canonical ensemble Wigner distribution, which is a direct result of using fully classical trajectories to propagate the initial Wigner distribution. We demonstrate how this problem can be solved by using modified classical trajectories, which are specific to the so-called Feynman-Kleinert Linearized Path Integral implementation of the Classical Wigner model.

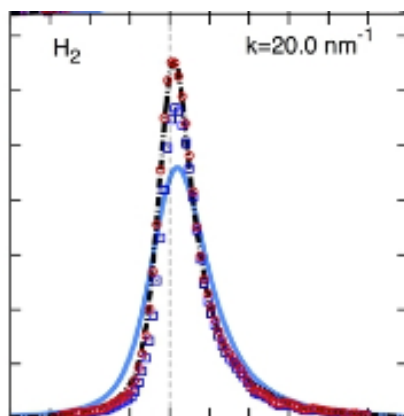


Fig. 1. Dynamical structure factor for liquid H₂.

Red dots – experimental results.
Black dash-dotted line – new method.
Blue line – classical time evolution.

The results of the new method are in excellent agreement with the experimental results.

I20

Chemical Reaction Dynamics in Cryogenic Ices in Our Galaxy

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Interstellar medium, where new stars form, solar systems evolve, and eventually die, is the coldest place in our galaxy and perhaps other galaxies¹⁻². Water and other molecular ices form in this medium, which occasionally get bombarded by photons from nearby stars, cosmic rays, and local electrons that are generated from cosmic ray ionization of hydrogen. These ice grains evolve into circumstellar ices (of a protostar), and eventually into Kuiper Belt Objects (KBOs) and Oort Cloud (of an evolved solar system like ours), which are the reservoirs of comets. Both the comets and asteroids were proposed to have impacted early Earth during the late heavy bombardment³, soon after which the life on Earth was formed⁴⁻⁵. Thus, the connectivity of comets/asteroids that could have triggered origin of life on Earth is traced back to the evolution interstellar ice grains and their subsequent journey through an evolving solar system.

Many spectroscopic techniques that have been used to understand the evolution of the water-rich icy analogs in the laboratory are limited by their ability to distinguish weaker organic impurity signals from very strong water-ice matrix signals themselves⁶.

We developed a two-step resonant laser ablation and laser ionization mass spectrometry (2S-LAIMS)⁷⁻⁹ to circumvent some of the disadvantages of conventional spectroscopy mentioned above and at the same time complementing them to enhance our understanding of the evolution of ices and organics in the Universe eventually leading to the origin of life on Earth. With this method, we scoop up a tiny fraction of cryogenic ice that is subjected to appropriate temperature and radiation processing through laser ablation (using an infrared 2.94 μm laser, resonant with H_2O vibrations). Plumes that are ejected during this laser ablation are then interrogated with a time-correlated ultraviolet laser (266 nm or 355 nm) that generates ions in the plume via a resonant enhanced multiphoton ionization (REMPI) process. These ions are accelerated into a time-of-flight (TOF) mass spectrometer and analyzed for the chemical composition of cryogenic ice.

Our studies show that (a) the lasers themselves do not have any observable effect on the chemical changes in the ice/plume, and (b) UV radiation and electron bombardment causes hydrogenation and oxygenation of organics even at 5 K - the lowest temperature of any solid expected in the interstellar medium. Our new studies for the first time show that even the coldest and perhaps the darkest places in the Universe may be actively involved in the chemical evolution of complex organics that eventually end up in triggering life on planets like Earth.

Acknowledgments: This research was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration. This research was enabled through partial funding from JPL's DRDF and R&TD funding for infrastructure of the "Ice Spectroscopy Laboratory" at JPL, NASA Spitzer Science Center, NASA funding through Planetary Atmospheres and Cassini Data Analysis Programs.

C10

Temperature dependence of dissolved CO₂ diffusion in Champagne wines : a theoretical and experimental investigation

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Champagne, the world-renowned French sparkling wine, is a multicomponent hydroalcoholic system mainly composed of water, ethanol and dissolved carbon dioxide. In champagne and sparkling wine tasting, the presence of dissolved CO₂ in the liquid phase is a key parameter impacting several sensory properties, such as the frequency of bubble formation, and the bubble size in the glass. Molecular diffusion of CO₂ molecules is indeed the mechanism behind the bubble nucleation and growth [1]. Therefore, evaluating the CO₂ diffusion coefficient by both experimental and theoretical techniques is of considerable importance to study the role of each type of molecules in the diffusion process.

Since Champagne wines can be considered in first approximation as hydroalcoholic solutions (12,5 % vol/vol) holding about 12 g/L of dissolved CO₂, classical force field molecular dynamics simulations of CO₂ in water/ethanol mixtures were performed, at different temperatures, respecting Champagne wine proportions. Therefore, the molecular system used in the simulation was composed of 50 CO₂ molecules, 440 ethanol molecules and 10⁴ water molecules. Five different temperatures were investigated, from 277 K to 293 K. Replica exchange molecular dynamics simulations were used to equilibrate the molecular systems at those temperatures. Temperature and pressure were controlled and maintained at their reference values to ensure that simulations comply as best as possible with experimental conditions.

CO₂ diffusion coefficients determined from simulations were found in remarkable agreement with experimental data on Champagne wines from the literature and ethanol was found to be the main component responsible for the value of the CO₂ diffusion coefficient in these beverages [2,3]. Moreover, CO₂ diffusion coefficients were also experimentally determined through diffusion-ordered ¹³C NMR experiments at different temperatures, and indirectly approached by measuring growth rates of ascending CO₂ bubbles in a flute filled with champagne. The results from these experiments were found in good agreement with each other and theoretical simulations [4].

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I22

Time-resolved action spectroscopy in ion storage rings

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The photo absorption of isolated chromophore molecules in vacuum may readily be measured by some detectable ‘action’, for example photo fragments, by particle detectors with high efficiency. In this talk, I will discuss how the action-absorption technique may be applied to study photo-physical properties of chromophores of biologically relevant proteins like visual opsins, the Green Fluorescent Protein (GFP) [1], and others. By using ion-storage devices like the electrostatic ion storage ring (ELISA) [2], the molecular response (action) may be recorded time-resolved in the sense that it may be registered at different times after the initial photo excitation of the chromophore [3]. The photo-excited chromophore ion is simply kept stored after the laser excitation, until it responds to the absorption by dissociation or electron emission. The ability to register both prompt and delayed action allows us to distinguish between fast (prompt) electronic and slow (delayed) nuclear photo response. For the chromophores in question, with extended π orbitals, the first electronically excited state corresponds to a $\pi - \pi^*$ transition in the visible or near UV region of the spectrum, which is easily studied by tunable OPA lasers.

It is shown that specific vibrational modes in the GFP chromophore can facilitate fast energy exchange between nuclei and electrons on the (sub) picosecond timescale. Pairs of coupling modes, in-plane breathing and out-of-plane twisting, enables energy-borrowing mechanisms resulting in either vibrationally-mediated electron ejection, or electronic de-excitation (internal conversion) through conical intersections [4]. The mechanisms are recognized from wavelength-dependent branching ratios into the prompt and delayed action channels since the specific vibrational modes are excited directly upon photo absorption.

Recent measurements in the deep blue spectral regime reveal rich spectroscopic structures associated with highly excited electronic states of the GFP chromophore anion [5]. These states serve as doorway for electron emission to the continuum, and play a role for the isolated chromophore as well as for the photo physics of GFP proteins, where electron acceptors may be present.

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I23

Site-specific fragmentation of varying size molecules induced by resonant *K*-shell excitation

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X-ray excitation of inner-shell electrons to unoccupied molecular orbitals is the heart of synchrotron radiation based near-edge X-ray absorption fine-structure (NEXAFS) spectroscopy. Fast Auger decay, typically occurring on the femtosecond time scale, usually follows such excitations and leaves the molecule with various other internal degrees of excitation which can eventually be stabilized through fragmentation. Because of the high X-ray photon energy resolving power, modern synchrotron light sources enable selective inner-shell electron excitation of a certain atom located on a specific site of a molecule, *i.e.* enable controlling with a high precision an initial step of excitation. Therefore, site-specific molecular fragmentation followed by resonant *K*-shell excitation can be expected.

In this presentation I will give an overview of our recent NEXAFS studies carried out at the Elettra synchrotron facility in Trieste, Italy, on nitrosyl chloride (ClNO), *N*-methylacetamide (CH₃CONHCH₃) and *N*-methyltrifluoroacetamide (CF₃CONHCH₃) putting an emphasis on site-specific molecular fragmentation. For nitrosyl chloride I will present some tentative theoretical assignments of the experimentally observed NEXAFS features. I will also briefly discuss a method of covariance mapping analysis enabling elimination of accidental coincidences which we plan in the future to implement for the experimental data obtained by us.

C11

Structure and stability of multiply-charged clusters : Application to charged droplets produced by electrospray ionisation

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Electrospray ionisation (ESI) is a widespread technique to produce multicomponent charged droplets for studying heterogenous processes in atmospheric physics and macromolecular assemblies in proteomics. The life cycle of such droplets, from their birth at the tip of the ESI source to their fragmentation and the subsequent detection of ejected analytes in mass spectrometers, raises several questions about their structure, conditions of stability, and fragmentation mechanisms. In the present work, we investigate these questions by classical Monte Carlo and molecular dynamics simulations performed with in-house programs [1-3] that model droplets as charged clusters in a coarse-grained representation. We briefly discuss possible definitions of the Rayleigh charge, the charge above which droplets become unstable, and demonstrate on relatively small charged clusters ($N \leq 1169$) that the excess droplet charge can be located on the cluster surface while most of charged particles remain inside the cluster which enables to moderate the common assumption that charged entities should be located on the droplet surface in ESI experiments [4]. The fragmentation mechanisms of small charged clusters ($N \leq 309$) are then characterized by studying cluster distortion parameters and theoretical mass spectra as a function of time for clusters with different numbers of charged particles and different particle charge values. Preliminary results obtained on much larger clusters ($N \approx 10000$) will also be presented. All these results are related to fragmentation mechanisms postulated in ESI experiments, namely successive fissions by the Charged Residue Model (CRM) and ionic desorption by the Ionic Evaporation Model (IEM). Beside questions on electrospray ionization, we also discuss how simple Monte Carlo simulations performed on charged clusters can be helpful to investigate some deformations of atomic nuclei. Distortions of small charged clusters ($208 \leq N \leq 234$) are compared to the expected shapes of the corresponding atomic nuclei [5], namely heavy atoms from ^{208}Pb to ^{234}U , and the limitations of this approach are highlighted.

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I24

Reaction dynamics and kinetics of oxygen isotope exchange reactions: Insights into unusual isotope effects and their applications in earth and planetary science

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The chemical physics of the unusual quantum symmetry-driven kinetic isotope effects in the ozone formation reaction remain unexplained and, in turn, whether or not similar isotope effects may occur in other chemical systems important in atmospheric and combustion chemistry and earth history. I will give an overview of crossed beam results for the oxygen isotope exchange reactions for $O+O_2$, $O+CO_2$, $O+CO$, and $O+NO_2$, performed in collaboration with Professors Jim Lin and Y.T. Lee at the Institute for Atomic and Molecular Science, Academia Sinica, Taiwan, as well as results from recent bulk photochemical kinetics experiments for O_3 and CO_2 . The dynamics and kinetics explored for these reactions provide new insights into the "non-mass-dependent" isotope effects in ozone formation, their relationship to the "non-mass-dependent" oxygen isotope compositions of other species such as CO_2 , CO , and NO and NO_2 , and possible analogies to the isotopic compositions of species made up of other elements besides oxygen with multiple stable isotopes, such as sulfur. These non-mass-dependent isotopic compositions have diverse biogeochemical and paleoclimate applications, and a better understanding of their chemical physics will provide a sounder foundation for their use as tracers in the environment.

I25

On the origin of the high levels of Br radicals in tropical free troposphere

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Gas phase halogen (Cl, Br and I) chemistry can drive destruction of ozone, NO_x deposition and removal of atmospheric elemental Hg [1]. Halogens (Cl and Br in-particular) are known to have a strong impact on ozone in the stratosphere [2] and polar troposphere [3]. However, it is still not clear if halogens impact tropospheric chemistry on a global scale. Recent aircraft based spectroscopic observations reveal significant levels of bromine radicals in the Free Troposphere (FT) over the Eastern Pacific [4]. We compare observations to bromine simulations using the GEOS-Chem chemical transport model [5] and find that the observed levels of BrO are too high to be explained by the known sources (emissions from sea salt aerosol and photo-chemical degradation of organo bromine) and gas phase photo-chemistry alone. We show that activation and recycling of bromide in cloud droplets and other aerosols by heterogeneous chemistry greatly enhance the levels of BrO in the FT, and that the resulting high levels of bromine significantly lowers tropospheric ozone.

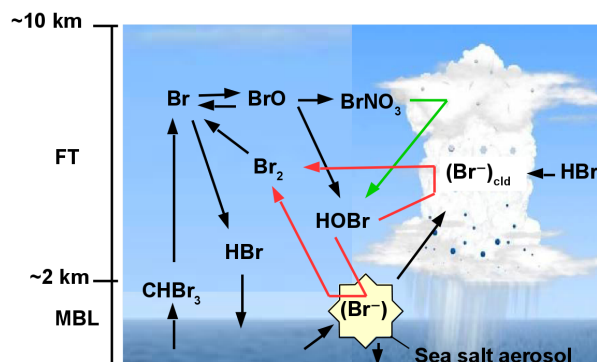


Figure: Main reaction paths for inorganic bromine the troposphere. Heterogeneous activation of Br⁻ and hydrolysis are shown in red and green respectively.

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I26

Exploring atmospheric autoxidation using quantum chemistryTheo Kurtén^{1*}, Henrik G. Kjaergaard², Solvejg Jørgensen², Matti Rissanen³¹University of Helsinki, Department of Chemistry²University of Copenhagen, Department of Chemistry³University of Helsinki, Department of Physics

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Quantum chemical calculations are becoming an increasingly important part of atmospheric chemistry research. This is due to both improvements in algorithms (e.g. more accurate density functionals, explicitly correlated methods and localization approaches), and to the continuing growth in computing power. Recently, quantum chemistry has been used to answer fundamental questions concerning, for example, the vapors responsible for the formation of aerosol particles, and the chemical mechanisms of atmospheric oxidation reactions. As the size of systems treatable by quantum chemical methods increases, configurational sampling - finding all relevant arrangements of reacting molecules - becomes more and more challenging. For molecular clusters with reasonably rigid constituent molecules, sampling methods based on randomly generated trial structures combined with semiempirical initial optimizations have proven useful [1]. For larger, chemically complex molecules with multiple torsional angles, sampling methods developed e.g. for drug design may be useful also for atmospheric chemists.

We have developed and tested a configurational sampling approach for studying hydrogen shift reactions in peroxyradicals relevant to atmospheric autoxidation [2], and applied it to the cyclohexene ozonolysis system. Force-field methods are first used to explore all possible combinations of torsional angles, yielding a set of up to thousands of distinct trial structures for each reactant, transition state or product. This set is narrowed down by subsequent density functional theory calculations of increasing sophistication. The energy of the lowest-lying conformers are then finally evaluated using the explicitly correlated coupled cluster method CCSD(T)-F12 in order to accurately assess the reaction energy barriers.

In agreement with recent experiments [2,3,4], our calculations predict the surprisingly rapid (timescale of seconds) formation of products with O:C ratios above one from cyclohexene ozonolysis. The formation mechanism is based on peroxy radical ($\bullet\text{RO}_2$) isomerizations through almost thermoneutral intramolecular hydrogen shifts, followed by strongly exothermal sequential O_2 additions. Other endocyclic alkenes, such as biogenic monoterpenes, are likely to undergo similar autoxidation reactions. This leads to the formation of extremely low volatility organic compounds (ELVOCs), which are not included in present-day atmospheric chemistry models. Nevertheless, ELVOCs are probably responsible for a large part of the growth of nanometer-sized atmospheric aerosol particles to climate-relevant sizes.

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C12**In depth experimental and theoretical studies of molecular collisions**

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In a joint experimental and theoretical study of molecular collisions the interactions between molecules are probed with unprecedented detail. Angularly resolved state-to-state scattering cross sections are measured in a crossed molecular beam setup, with the use of a Stark decelerated beam and combined with velocity map imaging [1]. Theoretical results calculated on different intermolecular potential energy surfaces were useful in the analysis of the measured data and comparisons with these data provide a very sensitive test of the accuracy of the potentials. New challenges for experiment —the study of scattering resonances predicted by theory— and for theory —the study of radical-radical collisions with the complete inclusion of nonadiabatic coupling effects— will be discussed.

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C13

Coupled electron-nuclear dynamics following photoionisation of benzenes

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Photoionisation can create a coherent superposition of electronic states and therefore initiates electronic dynamics in atoms and molecules. Observing and controlling this experimentally is a target of attosecond spectroscopy.

Theoretical studies of pure electron dynamics at a fixed nuclear geometry have demonstrated oscillatory charge migration [1-2]. Using a CASSCF implementation of the Ehrenfest method, we can study the evolution of a non-stationary electronic wavefunction for fixed atomic nuclei, and where the nuclei are allowed to move, to investigate the differences for the first time [3]. The method has been used to investigate both charge migration and charge transfer upon ionisation of small organic molecules, focusing on benzene cation and its substituted derivatives. We choose benzene cation as a prototype because ionising the neutral species leads to a Jahn-Teller degeneracy between ground and first excited states of the cation.

In all of our calculations, the initial geometry is the equilibrium geometry of the neutral species. The simulations were initially started with equal populations of ground and first excited states, with no deliberate relative phase between them. With nuclei fixed, there is no electron dynamics in this case. However, if we add substituents that break symmetry but do not radically alter the electronic structure, we see charge migration: oscillations in the spin density that we can correlate with particular localised electronic structures, with a period depending on the gap between the states initially populated.

We systematically investigated the effect of changing the relative amplitudes and phases in the initial superposition of electronic states, including using a complex phase. By controlling the initial electronic conditions in this way, we can control the subsequent initial nuclear motion [4]. For example, relative real phase allows us to predict which minimum on the ground state potential energy surface we decay towards; complex phase can be chosen such that the system remains with the degenerate intersection space for at least 5 fs.

Our calculations have explicitly shown how changing the initial electronic wavefunction can control nuclear dynamics for an ionised molecule where multiple electronic states are close in energy. For benzene cation we have also been able to show how chemical substitution affects the outcome of the electronic dynamics.

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C14

Exploring the influence of water in ozone depletion through the $\text{HO}_2 + n\text{H}_2\text{O} + \text{O}_3$ reaction: from a single water molecule to a water cage

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The reaction of hydroperoxyl radical with ozone is the rate limiting step in the natural cycle of ozone depletion, believed to be responsible for approximately half of the global ozone loss in the lower stratosphere [1]. This reaction is challenging to the state of the art ab initio methods and its mechanism still remains unclear to both experimentalists and theoreticians. The importance of studying the influence of water molecules has two sources. One is related to the fact that there is no conclusive evidence from the publications that the experiments on the $\text{HO}_2 + \text{O}_3$ reaction do not have the presence of water. Secondly, and besides knowing that water vapour is present in the atmosphere, it is well known that approximately 30% of HO_2 can be in the form of the $\text{HO}_2\cdot\text{H}_2\text{O}$ complex. It is therefore evident that theoretical investigations of the title reaction might be extremely useful. In this work we present our detailed electronic structure calculation results on the $\text{HO}_2 + \text{O}_3$ [2-4] and $\text{HO}_2 + \text{H}_2\text{O} + \text{O}_3$ reactions [5-8], investigating the effect of one ($n=1$) water molecule on the barrier heights and mechanistic details of this reactive cluster. Emphasis will be put on multireference calculations (CASSCF and MRPT2) [3,7] and on the KS-DFT methodology, where we first: 1) test different functionals belonging to different rungs of the so called “Jacob’s ladder” of density functional approximations to the exchange-correlation energy; 2) build [4] and use [4-6] density functionals from the fourth and fifth rungs of the “Jacob’s ladder”, particularly the ones designed for the accurate calculation of barrier heights, since saddle points are normally affected by the well known self-interaction error. We will also critically analyse the widely used coupled-cluster//KS-DFT model chemistry by presenting two problematic cases in the context of our studies [8]. Finally, we will briefly present exploratory calculations for $n=2,3,4,20$ where we discuss the appearance of a hydrogen transfer mechanism along water wires ($n=3,4$) and the possibility of having the $\text{HO}_2 + \text{O}_3$ reaction inside a $(\text{H}_2\text{O})_{20}$ water cage.

The results show that water molecules have a strong influence in the barrier heights and pathways of the oxygen- and hydrogen-abstraction mechanisms and therefore the title reaction should not be discarded from dynamics and atmospheric modelling studies of ozone depletion.

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C15

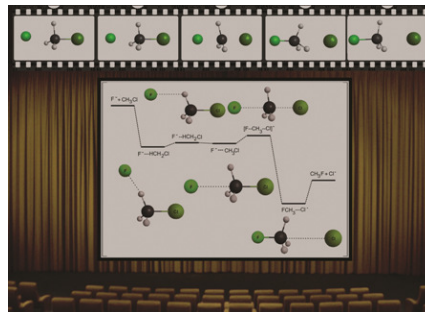
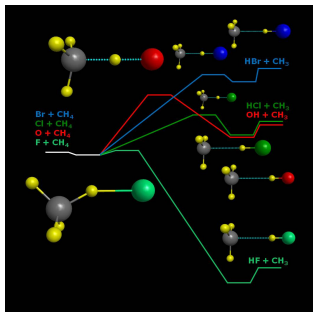
Dynamics of polyatomic chemical reactions on *ab initio* potential energy surfaces

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Experimental and theoretical studies on $X + \text{methane}$ abstraction and $X^- + \text{CH}_3\text{Y}$ substitution reactions extended and modified our fundamental knowledge on chemical reactivity. In order to study the dynamics of these reactions theoretically, we develop chemically accurate *ab initio* potential energy surfaces (PESs) and perform quasiclassical trajectory (QCT) and/or (reduced-dimensional) quantum dynamics computations using these PESs. Our goal is to achieve chemical accuracy (< 1 kcal/mol) for the PESs of polyatomic systems, which requires the computation of high-quality *ab initio* energy points [1] and the accurate mathematical representation of these points. We can calculate mode-specific vibrational distributions of the polyatomic products obtained from QCTs using the novel 1GB binning method [2, 3]. We apply these methods for several polyatomic chemical reactions, such as $X + \text{CH}_4 \rightarrow \text{HX} + \text{CH}_3$ ($X = \text{F}, \text{Cl}, \text{Br}, \text{O}(^3\text{P})$) [4–7], $\text{Cl} + \text{CH}_4 \rightarrow \text{H} + \text{CH}_3\text{Cl}$ [3], $\text{F}^- + \text{CH}_3\text{Cl} \rightarrow \text{Cl}^- + \text{CH}_3\text{F}$ [8], and $(\text{H}_2\text{O})_2 \rightarrow 2\text{H}_2\text{O}$ [9].



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I27**Multidimensional quantum mechanics with trajectory guided basis sets of Coherent States. From nonadiabatic photochemical reactions to dynamics of electrons in strong laser field.**

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Three formally exact approaches to quantum dynamics, i.e. Coupled Coherent States, Multiconfigurational Ehrenfest method and Fermionic Coupled Coherent States, which are based on trajectory guided grids of Gaussian Coherent States, will be presented. The methods are capable of treating quantum systems with many degrees freedom and the application range from nuclear wavepackets describing nonadiabatic photochemical reactions to electron dynamics in strong laser field. Recently first principle direct dynamics version of Multiconfigurational Ehrenfest approach has been developed and applied to description of ultrafast photodynamics.

I28

Molecular dynamics involving electronic resonant states of HeHÅsa Larson^{1*}, Sifiso Nkambule¹, Ann E. Orel²¹Department of Physics, Stockholm University, SE-106 91 Stockholm, Sweden²Department of Chemical Engineering and Materials Science, University of California, Davis, USA**E-mail: aasal@fysik.su.se*

HeH is a molecular system with only two nuclei and three electrons, which allows for accurate structure calculations. Processes involving electronic resonant states of HeH are studied. These states have potential energy curves embedded in the ionization continuum. We combine quantum chemistry calculations with electron scattering calculations to compute molecular potential energy curves, non-adiabatic interactions and autoionization widths. The goal is to obtain a rigorous and consistent set of molecular data and then use it to study a number of reactions. The processes we intend to study include mutual neutralization, dissociative recombination, ion-pair formation, penning ionization, vibrational- and dissociative excitation. The molecular dynamics will here be studied quantum mechanically. We want to examine how accurate we can describe these processes *ab initio* and quantum mechanically for a molecular system as simple as HeH.

C16

Theory and simulations for ultrafast x-ray scattering

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New x-ray free-electron lasers, such as the LCLS [1] and the XFEL [2], provide ultra-short bursts of intense x-rays that can be used to study processes in matter with temporal and spatial resolution. One important goal is to follow the motion of atoms during photochemical reactions. As a benchmark reaction, we simulate the ring-opening of 1,3-cyclohexadiene (CHD) initiated by an optical pump laser [3] using the *ab initio* multiconfigurational Ehrenfest method [4]. Importantly, the simulations do not rely on reduced dimensionality models, and the potential energies, forces and non-adiabatic couplings are calculated *on-the-fly* using the Molpro package [5].

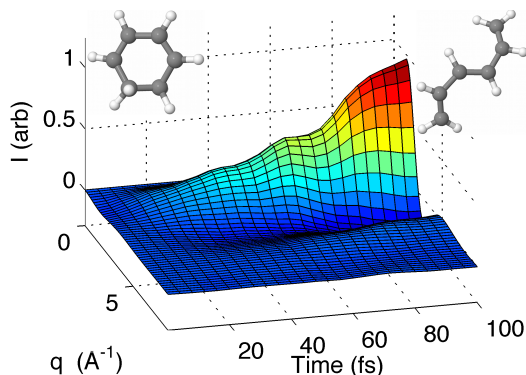


Figure 1: The differential intensity (laser on - laser off) for the ring-opening reaction of CHD as a function of time (fs) and momentum transfer q (\AA^{-1}) for 9 keV x-ray photons.

A key question is the level of theory required to adequately reproduce the signal likely to be observed in future experiments, and to what degree inelastic effects must be accounted for [6]. As recently discussed [7], it is conceivable that not only the dynamics of atoms, but also electron dynamics may be observed in time-resolved x-ray scattering experiments. However, in the case of nonstationary electronic states the issue of an adequate level of theory becomes critical, and it is likely that a treatment based on full quantum electrodynamics is necessary to account for the interaction between electrons and ultrashort x-ray pulses.

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I29

Radiative formation of cold molecular ions in an ion/atom hybrid trap

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Collisions between laser-cooled ions and alkali-metal atoms are studied in several experimental groups represented at the conference. Several processes have been demonstrated like radiative and non-radiative charge exchange, and molecular ion formation. The dynamics seems to be very sensitive to the couple of atomic/ionic species, as well as on the experimental arrangement.

In this talk I will present a comparative theoretical study of the Rb-(Ca⁺, Sr⁺, Ba⁺, Yb⁺) pairs. High-level quantum-chemical calculations of the electronic structure of the associated molecular ions will be presented together with quantum-scattering calculations for the radiative channels [2, 3]. Reaction rate constants are determined in the collision energy range $E_{coll}/k_B = 20$ mK-20 K. It is shown that the energy dependence of the reaction rates is governed by long-range interactions, while its magnitude is determined by short-range non-adiabatic and radiative couplings which induce a chemical change. The quantum character of the collisions is predicted to manifest itself in the occurrence of narrow shape resonances at well-defined collision energies. Destruction mechanisms of the produced cold molecular ions will be also discussed. Thus the present results highlight both universal and system-specific phenomena in cold ion-neutral reactive collisions.

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I30

Penning Ionization Reactions of Polyatomic Molecules at Low Temperature

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We have developed an experiment to study gas-phase reactions between polar molecules and paramagnetic particles in a temperature range 0.1 K-200 K. For this we bend two supersonic molecular beams, one in an electrostatic guide and one in a magnetic guide, such that in the end they are overlapped and move in parallel. By adjusting the conditions of the supersonic expansions we can set the two beam velocities to be equal, resulting in very low relative velocities of particles from the two beams.

This experiment has been used to study different Penning ionization reactions between metastable He or Ne atoms and polyatomic molecules. Product molecular ions in these reactions can be produced in different electronic states, some of which are dissociative. By independently monitoring each of the fragment yields as a function of collision energy we not only obtain information about the overall collision dynamics and the governing forces, but in particular also about possible stereodynamical effects.

C17

Resonant detection of the signature of control on a resonance state lifetime using a pump-probe schemeA. García-Vela^{1*}¹Instituto de Física Fundamental, Consejo Superior de Investigaciones Científicas,
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Quantum coherent control of the lifetime of a specific target resonance state has been recently achieved by creating a coherent superposition of resonances overlapping with the target resonance [1-3]. Such a superposition is prepared by using one [1], two [2,3], or even three [3] pump laser pulses. The control scheme is based on exploiting the interference effects that occur between overlapping resonances that are excited simultaneously [1]. Performance of the control schemes is illustrated by three-dimensional wave packet simulations of resonance decay in the Br₂(B)-Ne complex. More specifically, in the simplest case of preparing a superposition of only two overlapping resonances by exciting each resonance with a different pump pulse, enhancement of the lifetime of the target resonance by a factor of three is achieved when the amplitude ratio and the time delay between the two pulses is varied [2]. A most relevant aspect of the above control schemes is its experimental realization, and this point has been investigated by carrying out simulations applying an experimentally realistic and feasible time-resolved pump-probe scheme [4]. Such simulations show that indeed experimental detection of the signature and effects of control on the survival probability of the target resonance is possible by selective resonant excitation with the probe laser pulse.

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P1

Three-Dimensional Slice Imaging of OCS and CH₃CH₂I at 230 and 245 nm, respectively, using the Pixel Imaging Mass Spectrometry (PIImMS) camera

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The Pixel Imaging Mass Spectrometry (PIImMS) camera [1] is used in a proof-of-principle three-dimensional (3D) slice imaging experiment on the photodissociation of OCS and EtI at 230 and 245 nm, respectively. Coupling the PIImMS camera with Velocity Map Imaging (VMI) [2,3], the 3D Newton sphere of fragment ions can be directly obtained since the PIImMS1 sensor records the two-dimensional impact position of charged particles and their time-of-flight with 12.5 ns resolution. Time slices through the 3D Newton sphere of CO⁺ ion fragments are presented in Figure 1.

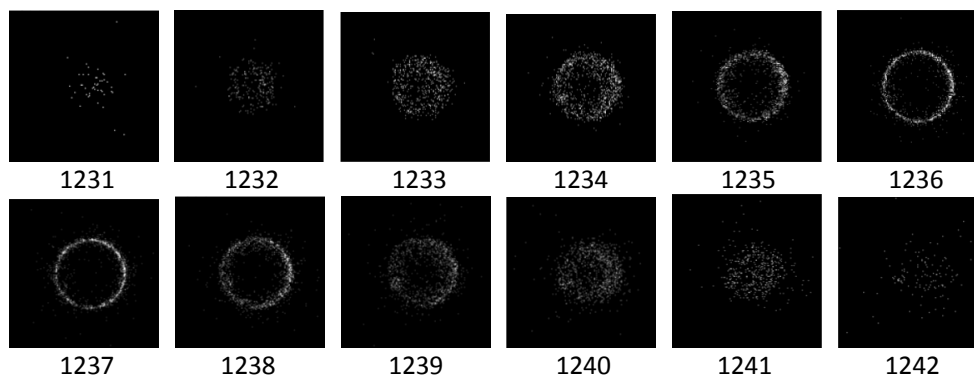


Figure 1 – A series of time slices through the CO⁺ ($J = 48$) Newton sphere using the PIImMS camera. Each number indicates the time bin of the slice image with each time bin spanning 12.5 ns. This dataset was centroided and cluster thresholded between 5-8 pixel clusters, producing images of 144 by 144 pixels.

The central slice and therefore velocity and angular information can be directly obtained avoiding the need to use indirect methods and the constraint of cylindrical symmetry. A relative velocity resolution of $\Delta v/v = 0.06$ was observed in the experiment which is limited by the experimental setup rather than by the PIImMS camera. Four digital registers within each pixel guarantee the detection of multiple events within the same pixel in the same experimental cycle.

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P2**Quantum chemistry, kinetics and computational fluid dynamics studies of silicon dioxide production in exhaust gas from silicon furnaces**

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Silicon is produced on an industrial scale by heating quartz with coal, coke, or wood in a furnace. The gas released from the process consists of large amounts of CO, with smaller amounts of H₂O, SiO and other species. This gas is burnt in the furnace hood where it meets an inflow of air. The resulting exhaust gas consists of, e.g., CO₂, SiO₂ particles (silica dust), and NO_x. Emissions of the latter two species have been found to be strongly correlated. Numerical modeling of the combustion process, including gas flow and chemistry, is an attractive way of understanding this correlation and to design measures to reduce emissions of NO_x. Reactions of SiO to form SiO₂ are also of importance in the combustion of other silicon-bearing species, in the ablation of meteorites in the upper atmosphere, as well as in reactions in interstellar and circumstellar space.

Unfortunately, there is a lack of reliable experimental rate data on the formation of SiO₂, i.e., reactions of SiO with O₂, OH, and other oxygen-bearing species. To rectify this, we have aimed to obtain estimates of the rate constants in the relevant temperature range of the most important SiO₂ forming reactions. To this end we have used DFT and CCSD(T) calculations together with Transition State Theory or quasiclassical trajectory studies. Potential energy surface To assess the quality of the calculated rate constants, we have also studied the analogous reactions of CO leading to CO₂. Agreement with available experiments is good. The calculated rate constants are included in kinetics modeling with tabulated rate constants for other important reactions.

Computational Fluid Dynamics, CFD, is used to model the combustion process, i.e., flow, heat transfer, and thermochemistry in 3D space. The results indicate that the formation of NO_x and SiO₂ particles cannot be treated separately. Rather, the reactions responsible for SiO₂ formation also drive the NO_x formation. This is the first time the correlation between NO_x and SiO₂ dust formation is quantified using simulations

P3

Quantum chemical investigation of sodium diffusion through graphite

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Considerable costs are associated with the repair and replacement of carbon materials used as cell linings in primary aluminium production. An important factor in the deterioration of these cathode materials is the penetration and diffusion of sodium through the cell lining [1]. Sodium diffusion has been investigated experimentally and the diffusivity has been determined for a variety of different graphitic materials under various conditions [2]. The mechanisms behind penetration and diffusion are still unclear. This has motivated an atom-scale investigation of the interactions between sodium and graphite-like materials. In order to investigate model systems that are large enough to model bulk graphite, a computationally affordable method is needed. DFT is a computationally cheap and commonly used method that can provide reasonably accurate results for a broad range of applications.

The accuracy of DFT for a given application crucially depends on the exchange-correlation (XC) functional. Typically, density functionals can show quite different accuracy in the description of different properties of varying types of molecular and condensed-phase systems. For instance, most commonly used XC functionals today have been shown to be unable to correctly predict dispersion interactions. At the same time, DFT is the most accurate electronic-structure method that is viable for our applications. The objective was therefore to find a functional that gives sufficient accuracy for sodium-graphite systems. The accuracy of many of the most commonly used XC functionals in literature has been evaluated through comparison with potential energy curves from highly accurate *ab initio* calculations [3].

The equilibrium intermolecular distances can be well reproduced by the functionals PBE and PBE0, which among the tested functionals are the only two that predict correct bonding of all six complexes studied in this work.

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P4

Dynamically consistent method for mixed quantum-classical simulations: a semiclassical approach

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We present a novel semiclassical approach to molecular dynamics simulations [1], which is based on combination of the modified Filinov transformation [2] and the Double Herman–Kluk Initial Value Representation (DHK-IVR) method [3].

The key feature of the presented formulation is the ability to control the net action of pairs of trajectories incorporated in describing the dynamics of a given degree of freedom by varying the corresponding Filinov parameter. It can be shown analytically that the presented approach can continuously tune between full semiclassical and classical limits of Initial Value Representation. Thus, the described methodology allows to use different levels of theory for different modes of a complex system without introducing approximations at the quantum-classical boundary and provides a uniform framework for mixed quantum-classical molecular dynamics simulations. A detailed description of the methodology and application to some model systems are presented.

Acknowledgments: This work is supported by the Army Research Office (grant W911NF-13-1-0102) and the Cornell Start-Up Grant.

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P5

The role of molecular quadrupole transitions in the depopulation of metastable helium

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Depopulation of metastable He(2^3S) and He(2^1S) by radiative association with helium ions resulting in the formation of the He $_2^+$ molecular ions is investigated [1]. Rate coefficients for spontaneous radiative association of the He $_2^+$ molecular ion on the spin-doublet manifold are presented as functions of temperature up to 500 000 K considering the association to rotational-vibrational bound states of the lowest doublet electronic states $X^2\Sigma_u^+$ and $A^2\Sigma_g^+$ from the continuum states of the excited doublet electronic states $B^2\Sigma_u^+$ and $D^2\Sigma_u^+$. The dipole-driven processes $B \rightarrow A$ and $D \rightarrow A$ are compared to the quadrupole-driven processes $B \rightarrow X$ and $D \rightarrow X$. For all considered temperatures the dipole-driven process $D \rightarrow A$ dominates over the other processes. The rate coefficient for the quadrupole-driven process $B \rightarrow X$ is at least three orders of magnitude larger than the rate coefficient of the dipole-driven process $B \rightarrow A$.

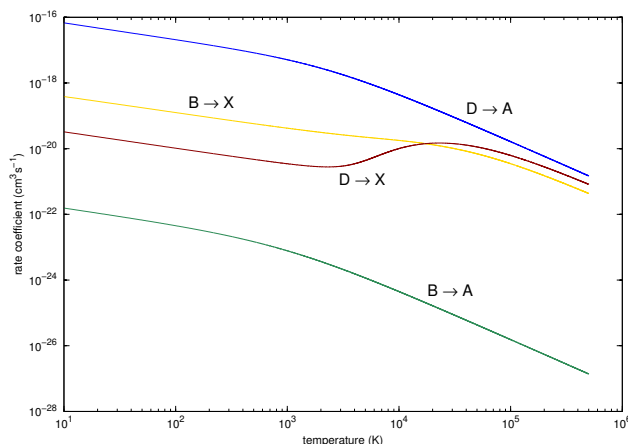


Figure 1: Rate coefficients for spontaneous radiative association of He $_2^+$.

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P6

Potential Energy Surface for $H_2 \cdots HX$ and $H_2 \cdots X_2$ system, with $X=H, F, Cl, Br$

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In this work we report the explicit representation of the potential energy surfaces for the $H_2 \cdots HX$ and $H_2 \cdots X_2$ systems, with $X = H, F, Cl$ or Br , via a harmonic expansion functional form for rigid diatom-diatom interactions^{1,2}. The framework of the supermolecular approach was used, as well as the counterpoise-corrected interaction energies at CCSD(T)/aug-cc-pVQZ levels. The energies were calculated in nine or six leading configurations according to the orientation of the dimers and type, depending on a radial coordinate R between centers-of-mass of the two molecules, and the polar and dihedral angles $(\theta_1, \theta_2, \phi)$. The analytical form of the potential energy surfaces, for each of the leading configurations, is constructed by fitting the energies to a fifth degree generalized Rydberg function. Comparing the fitted energies with the CCSD(T)/aug-cc-pVQZ one for the $H_2 \cdots HX$ and $H_2 \cdots X_2$ systems, with $X=H, F, Cl$ or Br we found a maximum rms error of 21.1 cm^{-1} for Lb configuration of $H_2 \cdots HBr$ and a minimum rms error of 1.13 cm^{-1} for H configuration of $H_2 \cdots H_2$. This study predicts the T-shaped structures to be the most stable configurations for the above dimers, but with different orientation. For $H_2 \cdots HF$ and $H_2 \cdots HBr$ it is the T_a configuration $(\pi/2, 0, 0)$, with energy of 361.3 and 170.1 cm^{-1} , respectively, while the T_c configuration $(0, \pi/2, 0)$ is the most stable for the $H_2 \cdots HCl$, with energy of 202.4 cm^{-1} . For the $H_2 \cdots H_2$ the T-shape has a minimum with energy of 33.3 cm^{-1} , while for the $H_2 \cdots F_2$ and $H_2 \cdots Cl_2$ it is the T_b configuration $(0, \pi/2, 0)$, with energy of 99.783 and 193.673 cm^{-1} , respectively, and the T_a configuration $(\pi/2, 0, 0)$ is the most stable for the $H_2 \cdots Br_2$, with energy of 228.321 cm^{-1} .

Comparison of the isotropic term for $H_2 \cdots HX$ and $H_2 \cdots X_2$ systems, with $X=H, F, Cl$ and Br .

	This Work		Reference	
	Energy [cm^{-1}]	Distance [\AA]	Energy [cm^{-1}]	Distance [\AA]
$H_2 \cdots H_2$	22.0409	3.4735	25.12421 ^a , 24.11682 ^b	3.43401 ^a , 3.482 ^b
$H_2 \cdots F_2$	45.4734	3.6569	40.89634 ^c	3.48284 ^c
$H_2 \cdots Cl_2$	46.2139	4.4268	53.22654 ³	3.99374 ³
$H_2 \cdots Br_2$	47.9948	4.6244	56.08254 ³	3.87534 ³
$H_2 \cdots HF$	52.9978	3.2959	40.0567 ³	3.3421 ³
$H_2 \cdots HCl$	53.1073	3.8105	45 \pm 2 ^c	3.99 ^c
$H_2 \cdots HBr$	50.0583	3.9796	56.0825 ³	3.8753 ³

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The authors are grateful to the FAPESP and CAPES for the support.

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P7

Microscope-mode linear time-of-flight mass spectrometry with the PImMS camera

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Two-dimensional imaging mass spectrometry is a robust method for exploring the chemical dynamics of state-selected ions. With optical modifications, a time-of-flight mass spectrometer (ToF-MS) may also be converted to a “microscope” spatial imaging instrument where a defocused laser is rastered across a sample surface to establish a molecular map. Here we present modifications to a linear ToF-MS that enabled the surfaces of four dye samples (auramine, crystal violet, exalite 384, and exalite 404) to be imaged. Notable changes include: defocusing the laser spot to a diameter of 400 μm ; tuning the ion optics to conserve spatial information of the ablated ions; and exchanging the ToF detector with a multichannel plate/scintillator unit coupled to the Pixel Imaging Mass Spectrometry (PImMS) camera. PImMS is a triggered device that records the positional and temporal coordinate of each ionization event, enabling spatial and mass information of multiple fragments to be obtained simultaneously.

P8

Simulation Of The Photoisomerization In Self Assembled Monolayers Of Azobenzene Derivatives

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Molecular rods containing the azobenzene moiety (4'-{[1-1'-biphenyl]-4-yl}diazanyl)-(1-1'-biphenyl)-4-thiol, 2DA-thiol from now on) supported on a gold surface were found to be able to perform mechanical work upon isomerization from *cis* to *trans* isomer [1]. A Self Assembled Monolayer (SAM) made by molecules of the most stable 2DA-thiol isomer, i.e. the *trans* one, when irradiated can be partially isomerized to form islands of the "pure" *cis* isomer [2]. The explanation of this phenomenon has been related to the presence of a cooperative behavior.

Classical molecular dynamics combined with the time evolution of the electronic wavefunction constitutes the best computational compromise to study photochemical and thermal phenomena in large systems. In particular, the effect of the monolayer on the photoisomerization process of a single molecule can be investigated using a QM/MM approach: the molecular mechanics description of the whole SAM based on an *ad hoc* parametrization is combined with a quantum mechanical description (at semiempirical level) of the light-excited molecule. In this way, through surface hopping non-adiabatic dynamics, we observed that the photoisomerization quantum yield of a compact SAM of all *trans*-2DA-thiol molecules is practically zero, in agreement with experiments. [3,4] Our interpretation for this phenomenon is that for a tight hindered environment such as that of a SAM made by all *trans* molecules, the photoisomerization is not possible in the bulk but only at the boundary of the sample (including the boundary between an all-*trans* island and an all-*cis* one) or in the presence of defects of the surface or of the SAM itself.

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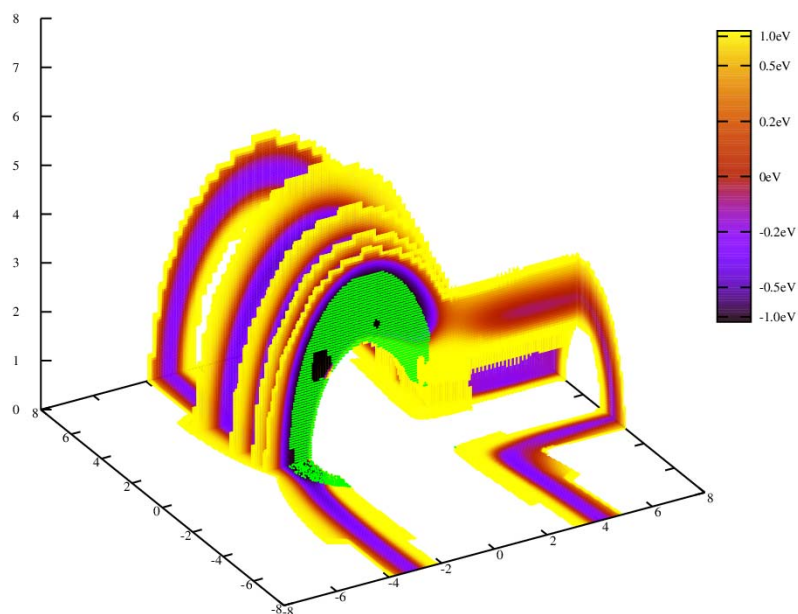
P9

Low-energy reactive collisions in $O^- + H_2$

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We present preliminary results for theoretical calculation of reactive scattering of O^- ion with hydrogen molecule. The three lowest potential energy surfaces for the anion coupled through conical intersection are calculated for large number of geometries. Auto-detachment regions are located (green area in figure), where one electron can freely leave the system. Preliminary analysis of the dynamics using classical trajectories is also presented. To understand the recent low-energy experiments [1] we also analyze the capture cross section quantum mechanically. Following figure shows the potential energy for lowest electronic state in symmetric coordinates. Zero corresponds to $O^- + H_2$ asymptote, which is located in right hand side of figure. $OH^- + H$ asymptotes go in forward and backward direction. Plane $z=0$ corresponds to linear geometries.



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P10

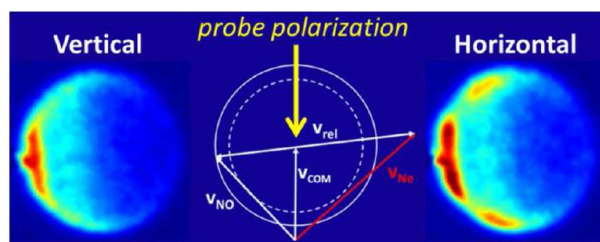
Direct Measurements of the Scattering-Angle Resolved Dynamics of Rotational Energy Transfer in $\text{NO}(\text{A}^2\Sigma^+)$

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There have been very few previous studies of the vector dynamics of collisions of *electronically excited* molecules. We have demonstrated that the stereodynamics of state-to-state rotational energy transfer in $\text{NO}(\text{A})+\text{Rg}$ collisions may be investigated through excitation within the crossing region of a crossed-molecular-beam velocity-map-imaging (CMB-VMI) apparatus.^[1] These experiments also demonstrate that a substantial advantage arises over ground-state CMB-VMI experiments from the preparation of the $\text{NO}(\text{A})$ collider at a well-defined point in time, which removes the flux-density transform required to analyse conventional CMB experiments.



Differential cross sections and the scattering-angle dependent rotational alignment of $\text{NO}(\text{A})+\text{Rg}$ collisions have been measured, and are compared to both a classical kinematic-apse

(KA) model, and quantum scattering (QS) calculations using the most recent *ab initio* potential energy surfaces. The alignment moments show large oscillations as a function of scattering angle, which are well reproduced by the QS calculations, but not by the KA model. This is in marked contrast to the behaviour of $\text{NO}(\text{X})+\text{Rg}$ scattering, where previous experiments have demonstrated good agreement of the measured alignment with the predictions of a KA model. The differences observed between the two electronic states with identical collision kinematics are a particularly sensitive probe of the differences in the potential energy surfaces.

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P11

Same abstract as C15.

P12**Dynamics of the O(³P) + CH₄ hydrogen abstraction reaction
at hyperthermal collision energies**

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Ground-state oxygen atoms are the most abundant species in low Earth orbit (LEO, ≈200-700 Km altitude), and their reaction with methane has been used to understand the erosion mechanisms of polymeric materials in the hyperthermal conditions of the LEO. Recently Minton et al.¹ reported experimental studies on this reaction using two crossed-molecular-beams techniques at hyperthermal collision energies (64 kcal mol⁻¹). They found that the dynamics of the reaction of the O(³P) atom with CH₄ shows forward-scattered distributions associated with a direct abstraction mechanism at large impact parameters. Therefore, it is interesting to survey how theory can complement experiment in the understanding of materials erosion due to high-energy oxygen atom collisions.

Based on an analytical PES recently developed in our group,² using exclusively high-level ab initio calculations at the CCSD(T)=FULL/aug-cc-pVTZ level, for the O(³P) + CH₄(v) → HO + CH₃ gas-phase reaction, quasi-classical trajectory (QCT) calculations were performed at collision energy of 64 kcal mol⁻¹. Our results reproduce the experimental evidence: most of the available energy appears as translational energy (80%) and scattering distribution is forward, suggesting a stripping mechanism associated with high impact parameters. Of special interest is the triple (angle-velocity) differential cross section (combination of translational and scattering distributions) which shows the same structure associated with the products.

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This work was partially supported by the Gobierno de Extremadura, Spain, and Fondo Social Europeo, Proj. n°. IB10001.

P13**Spectroscopy and dynamics of ethene clathrate hydrates:
a tight-binding/molecular mechanics approach**C. Falvo^{1*}, P. Parneix¹, E. Dartois², F. Calvo³¹Institut des Sciences Moléculaires d'Orsay, CNRS, Université Paris-Sud, Bât. 210, 91405 Orsay, France²Institut d'Astrophysique Spatiale, CNRS, Université Paris-Sud, Bât. 120, 91405 Orsay, France³Laboratoire Interdisciplinaire de Physique, CNRS, Université Joseph Fourier, 140 Avenue de la Physique, 38402 Saint Martin d'Hères, France**E-mail: cyril.falvo@u-psud.fr*

Clathrate hydrates are ice-like nanoporous structures in which water molecules form cages that encapsulate guest molecules. Depending on the guest molecule, clathrate hydrates are most commonly found in three structures referred to as I, II, and H [1]. Clathrate hydrates incorporating small molecules such as methane have received a lot of attention owing to their known presence in the earth permafrost as well as potential uses as an energy source [2]. The presence of clathrate hydrates in many Solar system objects including Saturn's satellite Titan has been proposed in order to explain the observed gas abundances [3]. The present work takes advantage of recent IR spectroscopy measurements that have been performed to characterize the spectral signature of gas hydrates other than methane, including small alkane and alkene guest molecules. These spectroscopic data require theoretical analyses to characterize quantitatively the interactions between the host and guest molecules and as a function of external conditions such as temperature and pressure. In this work, we present molecular dynamics simulations of ethene clathrate hydrates using a tight-binding model to describe the intramolecular dynamics of ethene combined with a parametrized force field to describe the interactions between the water molecules and the hydrocarbons.

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P14**Effect of the intermolecular excitation in the vibrational predissociation dynamics of van der Waals complexes and the implications for control**A. García-Vela^{1*}¹Instituto de Física Fundamental, Consejo Superior de Investigaciones Científicas,
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The effect of intermolecular excitation on the vibrational predissociation lifetime is investigated systematically for the first time for four different vdW complexes $Rg-X_2(B,v')$ ($Rg=He, Ne, X=Cl_2, Br_2, I_2$) by means of wave packet simulations. The lifetime as a function of intermolecular excitation displays a pattern of maxima and minima, with a similar shape for the different $Rg-X_2(B,v')$ complexes [1]. The pattern is consistent with previous experimental findings involving lifetimes of intermolecular excitations in similar systems [2,3]. The structure of the lifetime pattern is found to be determined by the shape of the resonance wave functions in the two van der Waals degrees of freedom, and more specifically by the magnitude of the overlap between the wave function and the coupling responsible for predissociation. Lifetime maxima and minima are associated with minima and maxima of this overlap, respectively. Implications for control of the complex lifetime are discussed.

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P15

Scattering of Molecular Oxygen with State Selected NO(X)

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Inelastic scattering of NO(X) with rare gases is the paradigm for the investigation of atom diatom molecular interactions[1,2,3]. NO(X) is highly desirable as it has a rich electronic structure and beautifully complex interactions with a scattering partner. Theory is now sufficiently advanced that effectively exact *ab initio* potential energy surfaces are available to describe the interactions between the NO(X)-Rg systems[4]. Thanks to recent advances in imaging[5] and electronics, we are able to envisage an experiment that can take these measurements to a new frontier.

By adding a diatomic collision partner, many new experimental complexities arise (see *fig. 1*)[1]. We have developed technology and procedures to optimize the imaging stack. These simple modifications overcome many of the new complexities and allow the extraction of differential and polarisation dependent differential cross sections for the NO(X)+O₂ system. We envisage guiding theory by careful measurement of the balance of attractive and repulsive forces that our apparatus can provide.

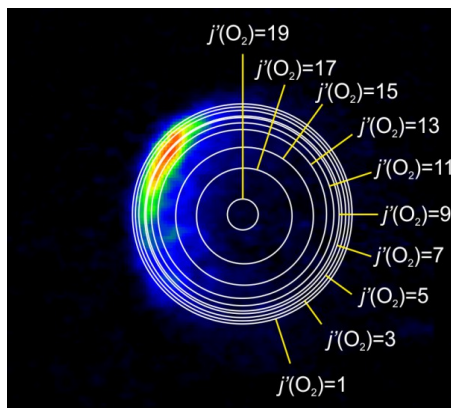


Fig. 1 A velocity mapped image of the scattered NO(X) in the $j'=5.5e$ state. The white rings on the image represent pairwise correlations from oxygen in various final rotational states that lead to the same NO product state. Blurring from overlapping Newton Spheres is clearly visible; our new apparatus can significantly reduce this blurring.

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P16

The Origin of The Intense Forward Scattered Peak in Molecular Scattering

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The forward scattered region of a differential cross section (DCS) contains a set of intricate structures called diffraction oscillations[1]. The diffraction oscillations are associated with the diffraction of the molecular matter waves through one another as the targets approach resulting in low angle scattering. Recent advances in experimental resolution[2,3] have allowed the diffraction oscillations to be analysed in exacting detail.

One peak in the diffraction oscillations stands out above the others. We present a joint experimental and theoretical study of the origin of this peak and reveal that according to diffraction theory[4,5], it should be present for every collision system, regardless of size or shape.

Further, by analysis of the magnetically resolved contributions to the peak as described by the Fraunhofer diffraction model, we reveal that the measurement the experiment is in fact making over the forward scattered region, constitutes measurement of the m - m' resolved DCSs - A truly fully quantum state selected measurement.

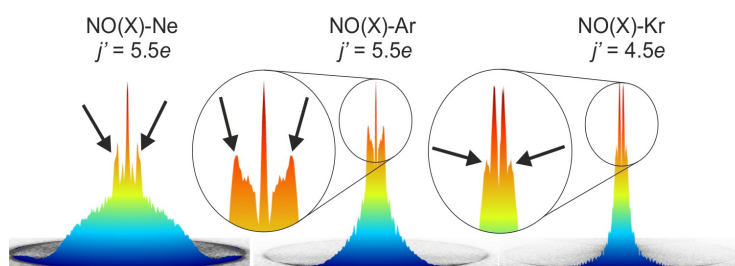


Fig. 1 Diffraction oscillations imaged for a number of different collision systems. The prominent peak is present in almost all DCSs for almost all states. The experiment is in essence recovering an m - m' resolved DCS in the forward scattered direction.

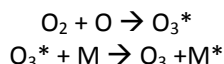
References

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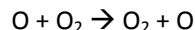
P17

Full quantum reaction rates for the O + O₂ exchange processG. Guillon^{1*}, T. Rajagopala Rao¹, P. Honvault^{1*}, B. Bussery-Honvault¹¹Lab. Interdisciplinaire Carnot de Bourgogne, UMR CNRS 6303, Univ. Bourgogne, 21078 Dijon Cedex, France[*gregoire.guillon@u-bourgogne.fr](mailto:gregoire.guillon@u-bourgogne.fr), pascal.honvault@u-bourgogne.fr

Certainly one of the most relevant processes occurring in Earth's atmosphere is the recombination reaction forming the ozone molecule, from atomic and molecular oxygen. In the presence of an energy-absorbing third body M, the overall reaction follows the sequence:



The metastable ozone O₃* is a transient intermediate complex of the exchange reaction



which is then a prerequisite for the formation of ozone in the atmosphere.

It has been shown experimentally [1] and confirmed by theoretical studies [2] that this reaction presents a highly non-statistical character, suggesting a short-lived metastable ozone osculating complex preventing complete energy randomization and uniform availability of open exit channels, and thus excluding a SQM-type statistical treatment [2,3].

So far, previous studies of this reaction have made use of classical (QCT) and time-dependent quantum methods, or a mix of both techniques. Moreover, a completely new potential energy surface has been developed since then in R. Dawes' group [4], presenting important features (most-notably no reef in the transition region) that were absent in former potentials used for all previous dynamical studies.

We will present preliminary results for the reaction rates of this exchange process, obtained from a time-independent full quantum scattering treatment and supported by Dawes' group new potential. We will start with the process involving only the ¹⁶O isotope. Lifetimes associated with osculating resonances will be analyzed to understand the efficiency of their impact for ozone formation.

In a second step, we will consider the effect of ¹⁸O isotopic substitutions on the reactive dynamics, hopefully shedding light on the difference in rate formation of symmetric and asymmetric isotopomers of ozone.

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P18

Cold ion-molecule reactions with Coulomb crystalsB. R. Heazlewood^{1*}, N. Deb¹, T. P. Softley¹¹Department of Chemistry, University of Oxford, Chemistry Research Laboratory,
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Reactive collisions between selected ions and molecules are examined within a Ca^+ Coulomb crystal. An ion trap is loaded with calcium ions, which upon laser cooling adopt a Coulomb crystal phase. Xenon molecules leaked into the reaction chamber are subsequently photoionised, enabling Xe^+ to be sympathetically cooled into the crystal. The incorporation of Xe^+ ions into the crystal is monitored through spatial changes in the fluorescence emitted by the trapped Ca^+ ions, indicated by a flattening of the observed crystal shape. To investigate the charge-exchange reaction between cold, trapped xenon ions and internally cold neutral molecules, ND_3 is introduced to the reaction chamber. ND_3^+ ions (formed following charge-exchange with Xe^+) are sympathetically cooled into the centre of the Coulomb crystal.

Changes in the spatial location of the fluorescing Ca^+ ions enable the charge exchange process to be examined and the rate of reaction calculated. Examination of this reaction with Stark decelerated ND_3 is discussed, in addition to the incorporation of polyatomic ionic reactants (such as C_2H_2^+) [1] in place of Xe^+ . Finally, the development of a destructive mass spectrometric ejection technique is examined, for the unambiguous assignment of ion identities and numbers. These experiments represent an important step towards the ultimate goal: complete control over the reaction through full quantum state selection of reactants, tunable reaction energy and sensitive product ion detection.

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P19

Dynamics of the asymmetric D + MuH reaction.F. J. Aoiz¹, J. Aldegunde², V. J. Herrero^{3*}, and V. Sáez-Rábanos⁴¹ Departamento de Química Física, Facultad de Química, Universidad Complutense de Madrid (Unidad Asociada CSIC), 28040 Madrid, Spain² Departamento de Química Física, Facultad de Química, Universidad de Salamanca, 37008 Salamanca, Spain³ Instituto de Estructura de la Materia (IEM-CSIC), Serrano 123, 28006 Madrid, Spain⁴ Departamento de Química y Bioquímica, ETS Ingenieros de Montes, Universidad Politécnica de Madrid, 28040 Madrid, Spain.**E-mail: v.herrero@csic.es*

The dynamics of the asymmetric D + MuH (Mu = Muonium) reaction leading to Mu exchange, DMu + H, and H abstraction, DH + Mu, channels has been investigated using time-independent quantum mechanical (QM) calculations. Quasiclassical trajectory (QCT) calculations were also performed in order to check the reliability of the method for this reaction and to discern genuine quantum effects [1]. Overall, the Mu exchange channel exhibits more structured reaction probabilities and cross sections, with much larger rate coefficients, $k(T)$, than its H abstraction counterpart. Over the 100–1000 K temperature interval considered, the QM $k(T)$ for Mu exchange vary between $\approx 5 \times 10^{-15}$ and $2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and those for the generation of DH + Mu between 2×10^{-18} and $3.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. In common with the rest of the isotopologues of the H + H₂ system, the height of the respective barriers in the collinear (symmetric stretch) vibrationally adiabatic potential energy curves matches the classical total energy threshold very accurately. The preponderance of the DMu + H channel is determined by its lower and narrower vibrationally adiabatic collinear barrier as compared with that for DH + Mu formation. Comparison of QM and QCT results shows that tunneling accounts for the reactivity at energies below the height of these barriers and that its effect on $k(T)$ becomes appreciable below 300 K. As expected, with growing temperature the contribution of tunneling to the global reactivity decreases markedly, but the rate coefficients are still much higher for the Mu exchange channel due to the effect of MuH rotational excitation that boosts the formation of DMu while diminishing the H abstraction channel that leads to the production DH. The analysis of the thermal cumulative reaction probabilities of the two channels indicates that at the lowest energies/temperatures the reaction into the DH + Mu channel takes place via ‘leakage’ from collisions proceeding along the DMu + H reaction path.

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P20

Velocity Map Imaging: advanced instrumentationPanos Kapetanopoulos^{1*}, Orla Kelly¹, Marc JJ Vrakking², Mike NR Ashfold³¹Photek Ltd., 26 Castleham Road, St Leonards-on-Sea, East Sussex TN38 9NS, UK²Max Born Institut, Max Born Strasse 2A, 12489 Berlin, Germany³School of Chemistry, University of Bristol, Bristol BS8 1TA, UK**E-mail: panos@velocitas-vmi.com*

Velocity Map Imaging (VMI) [1] uses optimally designed ion optics to map ions and electrons from a laser interaction with a gas target onto a 2D vacuum imaging detector. Capturing information on kinetic energy, angular distribution and signal intensity, VMI spectrometers can be used as a diagnostic tool in femtosecond and attosecond laser characterisation, or in fundamental investigations of electron processes, stereochemistry and photodissociation dynamics.

Velocitas VMI, as part of Photek [2], has been working in collaboration with leading researchers to develop state-of-the-art VMI instrumentation for a range of applications. We will present results from experiments from two different research laboratories: MBI [3] and University of Bristol [4].

From our collaborations with Prof Marc Vrakking at MBI, we will show results from high energy photoelectron spectroscopy using Velocitas VMI PRIME ion optics, including ATI of Xe and mixed colour photoionisation of Ar with IR and XUV photon sources (Figure 1).

In a second collaboration with Prof Mike Ashfold at University of Bristol, we have developed an innovative ion optics design (Velocitas VMI DOUBLE PRIME) with shaped Extractor and Repeller and stabilising electrodes for optimal field definition, permitting dc slicing (Figure 2) and large volume imaging. We will present results from state selected imaging of Br from IBr, with a comparison of inversion and dc slice imaging under the same VMI conditions.

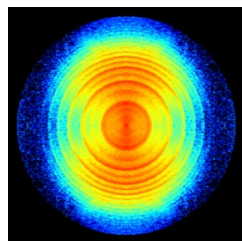


Figure 1:
Mixed colour
photoionisation of Ar
(800 nm and h. 11-29
from HHG) in Velocitas
VMI PRIME. (MBI)

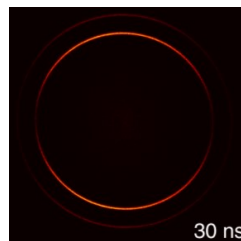


Figure 2:
30 ns slice of Br from
photodissociation of
IBr in Velocitas VMI
DOUBLE PRIME.
(University of Bristol)

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[4] Laser Chemistry, Spectroscopy & Dynamics Group, University of Bristol: www.bristoldynamics.com

P21

Photodynamics of nitrophenols Non-adiabatic ab initio molecular photodynamic study

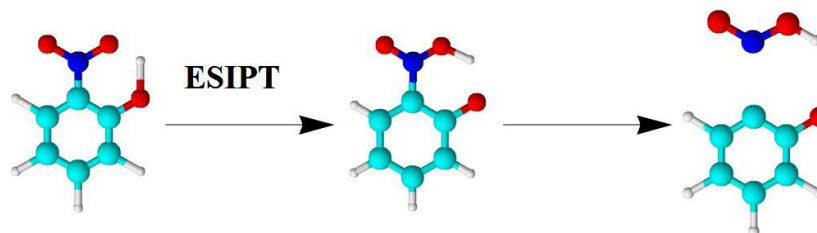
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Recently, substituted nitroaromatic molecules have been identified as possible precursors for photolytic formation of nitrous acid (HONO) in lower atmosphere [1]. The mechanism of the HONO formation remains, however, unclear.

Here, we investigate ultrafast photodynamics of *ortho*-nitrophenol, using the methods of theoretical chemistry. We particularly focus on the initial step of the HONO formation which might be the Excited State Intramolecular Proton Transfer (ESIPT) between NO₂ and OH moieties.



We have characterized the potential energy surfaces (PES) of the canonical and aci-nitro forms of the *ortho*-nitrophenol both in the ground and excited states using multireference level of theory. Furthermore, we have performed non-adiabatic (surface hopping) molecular dynamics simulations of the dynamical processes triggered by the excitation into the $\pi\pi^*$ excited state. It follows from our investigation that the excited state hydrogen transfer and aci-nitro isomer formation is energetically possible and indeed takes place within approximately 50 fs. The molecule then funnels its population back into the ground state, reconstructing the *ortho*-nitrophenol structure or staying in the one of the aci-nitro forms. From these structures, the formation of HONO is feasible.

Acknowledgement: The support by the Grant Agency of the Czech Republic via grants number P208-10-1724 and 14-08937S are gratefully acknowledged.

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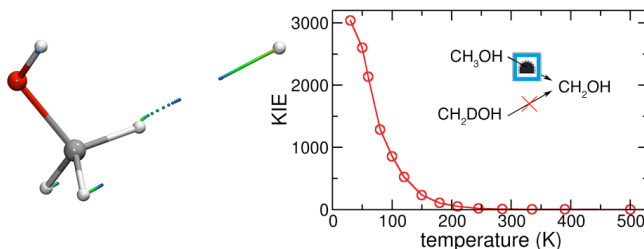
P22

Quantum Mechanical Tunneling of Atoms in Astrochemical Reactions

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Quantum tunneling of hydrogen atoms is generally accepted to play a crucial role in hydrogen transfer reactions. We use instanton theory, based on statistical Feynman path integrals, to find the most probable tunneling path and the reaction rate. This is used to investigate the formation of H₂ on the surface of carbonaceous dust grains in space [1] as well as the deuteration of interstellar methanol [2]. Large kinetic isotope effects in this and other reactions can be explained by the tunneling contribution. Tunneling paths are also calculated for the decay of substituted singlet carbenes [3] for which the different lengths of the tunneling paths distinguish the probability of two reaction channels [4]. These simulations were made possible only through algorithmic improvements in the instanton optimization. We developed a quadratically-converging optimizer as well as an adaptive partitioning of the instanton path.



Hydrogen abstraction from methanol is possible for H,
but impossible for D at low temperature.

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P23

**Coulomb explosion imaging of molecular structure on a
femtosecond time scale
using the Pixel Imaging Mass Spectrometry (PIImMS) camera**

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Coulomb explosion imaging is a powerful tool to investigate the structure of a molecule; implemented in a pump-probe scheme, it allows to study structural changes on a femtosecond time scale. The ability of the Pixel Imaging Mass Spectrometry [1,2] (PIImMS) camera to capture the full time-of-flight and velocity-map information in each acquisition cycle allows to correlate the two-dimensional momentum images of different fragments and gain insight into the structure of the parent molecule immediately prior to fragmentation, as well as into the Coulomb explosion process itself. Ion trajectory calculations based on pairwise Coulomb repulsion and their comparison with the experimental data results in a more detailed understanding of the underlying processes.

A biphenyl derivative has been chosen for this proof-of-principle work [3]. The molecules were aligned with a ns laser pulse and subsequently Coulomb exploded by a fs laser pulse. The fragment ions were velocity-mapped onto a MCP/P47 detector and imaged using the PIImMS camera. The recorded data include the complete time-of-flight and velocity-map information for all fragment ions. Any mass of interest can be selected during data analysis, and covariance images were generated that show coincidental velocity correlations between different fragments. The resulting information yields insights into the molecular structure of the biphenyl derivative, revealing the positions of the different substituents on the two phenyl rings, as well as the dihedral angle.

Furthermore, femtosecond time-resolved experiments were performed to follow the molecular dynamics after a kick pulse had initiated torsional motion in the molecules [4]. These measurements are compared to earlier experiments on a similar molecule [5], illustrating substantial advantages of the PIImMS camera over a conventional CCD camera in this application.

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P24

A comparative study of the kinetics and dynamics of the reaction of H atoms with ground-state and excited O₂

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The $\text{H}(^2\text{S}) + \text{O}_2(^3\Sigma_g^+) \leftrightarrow \text{OH}(^2\Pi) + \text{O}(^3\text{P})$ reaction has been termed the “single most important combustion reaction” [1]. Both its dynamics and kinetics has been thoroughly studied. The analogous reaction of electronically excited O₂, $\text{H}(^2\text{S}) + \text{O}_2(^1\Delta_g) \leftrightarrow \text{OH}(^2\Pi) + \text{O}(^3\text{P})$ is much less known. Generation of singlet excited oxygen has been shown to accelerate flame propagation, which was explained by the enhancement of the rate of the H + O₂ reaction, and the reaction of excited O₂ with H atoms may also be important in the higher atmosphere and in interstellar media.

In this work we report on quasiclassical trajectory (QCT) calculations addressing the comparison of the detailed mechanism of the reaction of molecular oxygen with H-atom on the ground and the excited PES. According to the trajectory calculations the excitation function for the reaction starting from excited-state O₂ raises above zero at about 0.3 eV in good agreement with the exact quantum mechanical calculations by Guo et al. [2]. This reflects much larger reactivity than that of the ground state where the threshold energy is 0.6 eV and the cross sections remain much smaller than in the excited-state. At low flame temperatures the rate coefficient for reaction of singlet molecular oxygen is 4 or 5 orders of magnitude higher than for triplet one, while at high temperatures the difference is a factor of about 100. The consequence is that if 1 % of oxygen is present in the form of O₂(¹Δ_g) in a flame, then the rate of the chain-branching step is doubled.

The role of potential well and of the entrance barrier on the excited-state potential surface will be discussed in terms of complex lifetimes and angular distributions.

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P25

Inelastic scattering of NH₃ and ND₃ by Ar atomsJ. Loreau^{1*}, N. Vaeck¹, and A. van der Avoird²¹ Service de Chimie Quantique et Photophysique, Université Libre de Bruxelles (ULB)
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Inelastic collisions of ammonia with noble gases, mainly He and Ar, have attracted a lot of attention from theorists. The NH₃-He system is particularly important due to the presence of ammonia in various astrophysical and atmospheric environments as well as due to the study of NH₃ in helium nanodroplets. However, the problem is complicated by the tunnelling corresponding to the ammonia inversion motion. In the case of NH₃-Ar, the interest stemmed from the large number of experimental measurements that have been performed in the microwave and infrared on the rovibrational spectrum of the van der Waals complex (see [1] for example), which have provided insights into the weak bonding properties of ammonia. Moreover, experimental advances in the cooling of molecules have allowed measurements of inelastic differential and integral cross sections in atom-molecule collisions at low energy. NH₃ and ND₃ can be produced in specific rotational states and slowed using Stark deceleration, and collisions with He were investigated both theoretically [2] and experimentally [3].

In this work we study the NH₃-Ar system in order to calculate inelastic scattering cross sections that can be compared with experimental data. We first computed a new potential energy surface that includes the inversion motion using the coupled cluster method with single, double and perturbative triple excitations (CCSD(T)). This PES is used to calculate the rovibrational spectrum of the NH₃-Ar complex, which is in excellent agreement with all the available experimental data. We then compute differential and integral cross sections for inelastic scattering of NH₃ or ND₃ with Ar, which are compared to experimental data.

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P26

Molecular dynamics simulations of palmitic acid adsorbed on NaCl surface.

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The aerosol and gases effects in the atmosphere play an important role on health, air quality and climate, affecting both political decisions and economic activities around the world [1]. Among the several approaches of studying the origin of these effects, computational modeling is of fundamental importance providing insights on the elementary chemical processes. Sea salts are the most important aerosol in the troposphere (109T/year) [2]. Our theoretical work consists in modeling a (100) NaCl surface coated with palmitic acid (PA) molecules at different PA coverages. Molecular dynamics simulations were carried out with the GROMACS package[5], in the NPT ensemble at T= 335K. We have tested several force fields [3–4] to describe the molecular interactions in the fatty acid/salt crystal system. In this study, we focused on transition in molecular orientation of the adsorbate as a function of PA coverage, on the effect of humidity, by adding water molecules, on the organization of the fatty acid at the salt surface, and especially on the occurrence of PA isolated islands.

Acknowledgments: this research has been supported by the CaPPA project (Chemical and Physical Properties of the Atmosphere), funded by the French National Research Agency (ANR) through the PIA (Programme d'Investissement d'Avenir) under contract ANR-10-LABX-005.

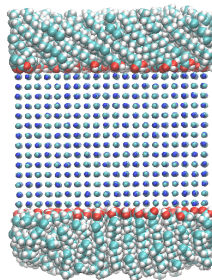


Figure 1: Monolayer of palmitic acid adsorbed on (100) NaCl.

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P27

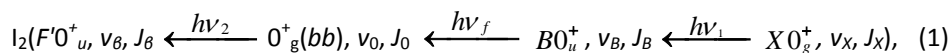
Excimer XeI(B/C) formation processes in the $\text{I}_2(F'O^+_{u'}) + \text{Xe}$ collisions

V.V. Baturo, S.S. Lukashov*, S.A. Poretsky, A.M. Pravilov

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The excimer XeI(B/C) formation processes in collisions of iodine molecule in the $\text{I}_2(F'O^+_{u'})$ ion-pair (IP) state with Xe atoms have been studied. The selected rovibronic levels of the F' state were populated by three-step three-color excitation scheme via the $B0^+_{u'}$ and $O^+_{g'}(bb)$ intermediate states correlating with the 2-nd and 3-rd dissociation limits:



Collisions $\text{I}_2(F') + \text{Xe}$ lead to formation of the $\text{XeI(B}_{1/2}$ and $\text{C}_{3/2})$ IP states or I_2 dissociation, mainly. The $\text{XeI(B} \rightarrow \text{X,A)}$ and $\text{XeI(C} \rightarrow \text{A)}$ luminescence spectra were measured after population of the $\text{I}_2(F', v_{F'}=2, 8$ and $31)$ vibronic levels. These spectra are likely than those obtained by authors of [1].

Excitation energy of $\text{I}_2(F', 2,53)$ state $E_{\text{I}_2}=52093 \text{ cm}^{-1}$ is lower than potential well of the XeI(B) state ($T_e \approx 52328 \text{ cm}^{-1}$ relative ground state of I_2 [2]). Therefore, the XeI(B) state formation in the $\text{I}_2(F', v_{F'}=2)+\text{Xe}$ collisions is energetically impossible, and we have not observed luminescence from the XeI(B) state in this case. The XeI(B) formation in the $\text{I}_2(F', v_{F'}=8$ and $31)+\text{Xe}$ collisions is available and have been observed in this work.

The principal result we have obtained is the fact, that the $\text{XeI(C} \rightarrow \text{A)}$ luminescence were observed in all the cases of population $\text{I}_2(F', v_{F'})$ vibronic states studied in this work. According to *ab-initio* calculations [3], the XeI(C) formation can be available after $\text{I}_2(F', v_{F'}>5)$ population only. Our results show other energy ordering of the B and C states of XeI , and the C state is lower by $\sim 450 \text{ cm}^{-1}$ at least relative the *ab-initio* calculations.

Radiative lifetime of the XeI(B/C) states and their formation rate constants are determined also. The most probable exit channel in the $\text{I}_2(F', v_{F'}=31)+\text{Xe}$ collisions is dissociation of I_2 , but for lower $v_{F'}$ cases probabilities of the dissociation and XeI formation processes are comparable.

The research was supported by the Russian Foundation for Basic Research (grants 12-03-31721 and 12-03-00208).

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P28

***Ab initio* multiple cloning algorithm for quantum nonadiabatic molecular dynamics**

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We present a new algorithm for *ab initio* quantum nonadiabatic molecular dynamics that combines the best features of *ab initio* Multiple Spawning (AIMS) [1] and Multiconfigurational Ehrenfest (MCE) [2-3] methods. In this new method, *ab initio* multiple cloning (AIMC), the individual trajectory basis functions (TBFs) follow Ehrenfest equations of motion (as in MCE). However, the basis set is expanded (as in AIMS) when these TBFs become sufficiently mixed, preventing prolonged evolution on an averaged potential energy surface. We refer to the expansion of the basis set as “cloning,” in analogy to the “spawning” procedure in AIMS. This synthesis of AIMS and MCE allows us to leverage the benefits of mean-field evolution during periods of strong nonadiabatic coupling while simultaneously avoiding mean-field artifacts in Ehrenfest dynamics. The AIMC method has been implemented within the AIMS-MOLPRO package [4], which was extended to include Ehrenfest basis functions.

We explore the use of time-displaced basis sets, “trains,” as a means of expanding the basis set for little cost. We also introduce a new bra-ket averaged Taylor expansion (BAT) to approximate the necessary potential energy and nonadiabatic coupling matrix elements. The BAT approximation avoids the necessity of computing electronic structure information at intermediate points between TBFs, as is usually done in saddle-point approximations used in AIMS.

The efficiency of AIMC is demonstrated on the nonradiative decay of the first excited state of ethylene, the simplest molecule with a C=C double bond that has been extensively studied both experimentally and computationally, and on a detailed computational simulation of photodissociation of pyrrole. Large statistics accumulated for pyrrole allows to calculate and to analyze total kinetic energy release (TKER) spectrum and Velocity Map Imaging (VMI) in good agreement with experimental data [5]. Both TKEER spectrum and the structure of VMI are well reproduced.

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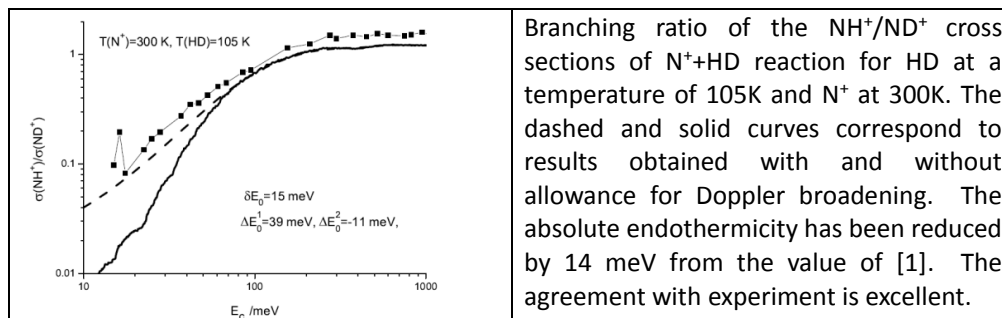
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P29

The NH^+/ND^+ branching ratio in reactions of N^+ with HDTasko P. Grozdanov¹, Ronald McCarroll²¹Institute of Physics, University of Belgrade, 11080 Belgrade, Serbia,²Laboratoire de Chimie Physique, Université Pierre et Marie Curie, 75231-Paris, France

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The experimental cross sections [1] for the production of NH^+ and ND^+ in collisions of N^+ with HD at low energies present an interesting challenge for a theoretical interpretation in view of the widely held belief that branching ratios of reaction products are poorly described by statistical models. But recent work [2] has shown this not to be the case. In this work, the standard statistical model is used to treat the N^+ -HD reaction, using only polarization interactions in the reactant and product channels. The relative endothermicities of the NH^+ and ND^+ reaction products are known from spectroscopic data but their absolute value is subject to an uncertainty of about 0.03 eV in the dissociation energy of NH^+ . Dependence on $D(\text{NH}^+)$ is studied.



State-to-state cross sections for N^+ ($^3\text{P}_j$) in collision with $\text{HD}(v=0, J)$ are calculated for a range of collision energies from 1 meV to 1 eV. These results are then averaged over a thermal distribution of HD at 300K and 100K. For the final states of NH^+ and ND^+ both vibration and rotation states must be considered. Account is also taken of Doppler broadening to take account of the random thermal motion of the reactant HD molecules. As in the experiments, the fine structure states of N^+ are initially populated at a temperature of 300K. It is assumed that in the collision complex the fine structure states are statistically mixed.

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P30

**Interactions of sodium atom with atmospheric aerosols
– collision simulations and equilibrium structures**

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Neutral sub-nanometer aerosol particles are known to play a significant role in the atmospheric chemistry [1]. Experimental characterization of these particles is, however, difficult. Only recently, sizing and structural characterization of small aerosols using sodium doping on the aerosol particles have been developed [2]. It is, therefore, highly desirable to understand details of the interaction between sodium and pure or doped water particles. Here, we employ theoretical chemistry methods to investigate these systems.

We have studied energetics, structure, and reactivity of sodium with nitric acid, nitric acid-water clusters and pure water clusters using *ab initio* and DFT methods [3]. In addition, we have performed on-the-fly *ab initio* molecular dynamics simulations. A sodium atom deposited on pure water clusters releases a surface hydrated electron which can be further ionized. This process is used for the cluster sizing and structural characterization [4]. In contrast, processes in HNO₃ doped water clusters are more complex. We observe a reaction of sodium atom with HNO₃, leading to the formation of NaOH and NO₂. Alternatively, charge transfer between a sodium atom and a doped cluster takes place, leading to the formation of Na⁺...HNO₃⁻(H₂O)_n complexes. In both cases, the particles formed cannot be ionized with low energy UV radiation and the mass spectrometric characterization with tunable laser light is thus not possible.

We have also simulated collision of larger water clusters with sodium atom under defined conditions, estimating the effective cross section for these particles.

Acknowledgement: The support by the Grant Agency of the Czech Republic via grants number P208-10-1724 and 14-08937S are gratefully acknowledged.

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P31

Double impulse effects in scattering of ions by molecules and clusters

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The hard-shell model [1] and the hard-potential model [2-3] have been extensively applied to describe the energy transfer and angular momentum transfer in atom (ion)-molecule collisions. In these models, an impulse is exerted at a point on the hard-shell, which is given by the equipotential surface at the collision energy. Here we discuss the possibility of the *double impulse* effect in a single collision event within the framework of the hard-shell model. This may occur if the collision energy is almost exhausted in the first impulse and if the shell anisotropy is large [4]. In the figure, we show examples of trajectories for double impulse mechanism in $K^+ - N_2$. Here the hard-shell is given by a sum of monopole and quadrupole deformations as $r_s(\gamma) = r_0(1 + \beta_2 P_2(\cos \gamma))$ with the anisotropy parameter $\beta = 0.3$ (0.4) in the left (right) panel. The trajectories before and after the first contact are shown in a molecular frame. As shown figures, it is assumed that the initial velocity of the projectile is normal to the hard-shell. We observe that the projectile contacts the shell again in the right panel, while it does not in the left panel. We find that the double impulse mechanism is likely to occur when the anisotropy is large. We expect that such a phenomenon would be widely observed in the collision of atoms (ions) with molecules and clusters.

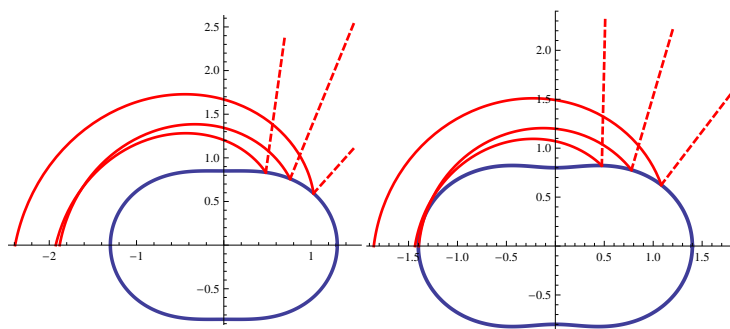


Figure 1: The hard shell and trajectories before (dashed lines) and after (solid curves) the first impulse for K^+ scattered by N_2 in a molecular frame where the horizontal axis is always taken to be the direction of molecular axis.

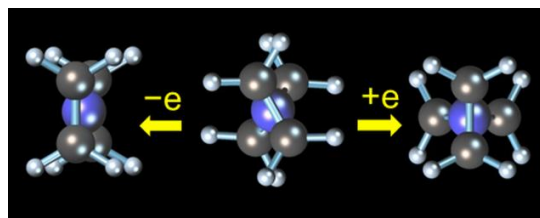
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P32

**Electronic-perturbation induced structural dynamics
of metal-organic molecular sandwiches**Fedor Y. Naumkin^{*1} and Kayla Fisher¹¹ Faculty of Science, UOIT, Oshawa, ON, L1H 7K4, Canada**E-mail: fedor.naumkin@uoit.ca*

Interfaces between metal atoms and organic molecules are key units of many important metal-organic systems. Presented are results [1] of systematic computational studies for a series of complexes of light main-group metal atoms sandwiched between small unsaturated hydrocarbon molecules. Evolution of the system structure and stability is investigated for varying metal atoms, as well as upon excitation, ionization and electron attachment. Predicted interesting features include cooperative stabilization, unusual geometries, reversible charge- or excitation-governed structural dynamics, including cycle-closing isomerization. The features exhibit similarities for isoelectronic systems. The predicted variety of properties suggests potential applications of such species as intermolecular junctions and units with charge- or spin-controlled shapes (switches, etc.) in molecular devices and/or machines. The system can be selected to facilitate a desired geometry and function of such a dynamic junction. Possible extensions to systems with larger organic molecules, in particular those with a few unsaturated fragments [2], and related property modifications are also considered. Directions of future studies involving potential development of larger frameworks built of multiple such blocks and designed for more elaborate operations are discussed as well.



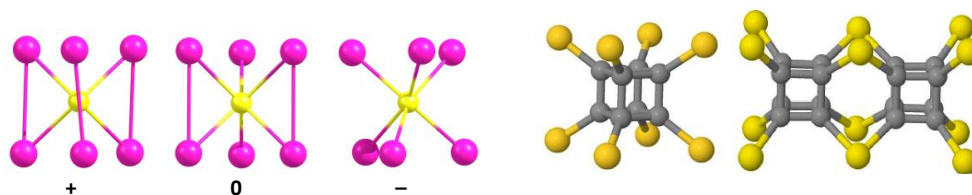
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P33

**Core-shell metallocarbons:
Property alteration and charge-controlled structural dynamics**Fedor Y. Naumkin*¹ and Ramachandran Chelat¹¹ Faculty of Science, UOIT, Oshawa, ON, L1H 7K4, Canada*E-mail: fedor.naumkin@uoit.ca

A series of carbon-doped noble-metal clusters C_mM_n are studied computationally at a DFT level [1,2]. Structures and stabilities are compared for a few isomers. The lowest-energy isomers are found to range from core-shell species for systems with a single carbon atom at centre to side-attached segregated carbon and metal components of larger counterparts. For smaller systems, structural dynamics is tracked upon electronic excitation, ionization, and electron attachment, indicating a range from a relatively weak to a considerable reversible geometry alteration. For larger systems, variations of corresponding energies relative to those of the pure metal clusters are related to shape change of the metal shell or its interaction with the carbon core. Trends in the variations of these energies, as well as of the dissociation energies for different channels, with cluster size are investigated and compared with those of pure metal counterparts. For larger systems the strongest property variations are observed for core-shell isomers. Feasibility of assembling these systems into aggregates of such units and related property and structural dynamics evolution are considered from the viewpoint of promoting desirable changes (accumulation vs cancellation of contributions from the individual units). Related potential applications of such systems are discussed, including, but not limited to, areas of new materials, catalysis and molecular electronics.



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P34

Study of the Direct Dissociative Recombination (DR) Dynamics of H_2O^+

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The direct Dissociative Recombination (DR) process of H_2O^+ is here studied theoretically. This is a process whereby a low energy electron collides with the H_2O^+ ion to form a highly excited neutral state. Since this is an unstable state, it can then dissociate to neutral fragments, which can be either a two-body or a three-body breakup. In the process, autoionization is possible while the potential energy surface of the resonant excited state has not crossed the ion ground state surface. However, once the surface have crossed, autoionization is no longer possible, and the molecule continues to dissociate. This is known as the direct DR mechanism. Some experimental studies of the process have been carried out, measuring both total cross section and branching ratios[1,2]. However, there is lack of a theoretical understanding of the details entailing the process, like the dominance of three-body fragmentation and isotope dependence of the reaction. We compute potential energy surfaces and autoionization widths of resonant states using structure and electronic scattering calculations. A "quasidibatisation" is performed by removing electronic states that have a dominant Rydberg configuration. Wave packets are propagated on the complex resonant state potential energy surfaces. The wave packets are propagated including different nuclear degrees of freedom, varying them from one to three degrees of freedom. For the multi-dimension wave propagation, the MCTDH program[3] is used.

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P35

Quantum Chemistry Calculations on Excited States of Small Molecular Systems

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The Born-Oppenheimer (BO) approximation is a common scheme in molecular physics that greatly simplifies the task of computing the wavefunction of a molecular system by factorizing it into an electronic and a nuclear part. However, a number of physical phenomena—including the process of mutual neutralization—cannot be explained in the framework of the BO approximation. Indeed, in such *nonadiabatic* processes, the degree of interrelation between the vibrational nuclear and the electronic motions is too high.

The main task of this project is to compute the potential energy surfaces corresponding to the ground state and the first few excited states of small molecules such as LiF and LiHF as well as the *nonadiabatic couplings* between those states. Such *nonadiabatic couplings*, which are essentially the matrix elements of the nuclear derivative operators, represent an effective measure of the degree of interrelation between the vibrational and the electronic motions. In order to reach numerical estimates of the aforementioned physical quantities, calculations were performed with such quantum chemistry methods as the *Complete-Active-Space Self-Consistent Field* (CASCF), and the *Multi-Reference Configuration Interaction* (MRCI) schemes, which are implemented in the software package MOLPRO [1].

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P36

Thermodynamics of rare gas–water clusters under pressure: the $\text{Ar}(\text{H}_2\text{O})_{20}$ case

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Classical parallel-tempering Monte Carlo simulations in the isothermal-isobaric ensemble were carried out for the $\text{Ar}(\text{H}_2\text{O})_{20}$ clusters, over a wide range of temperatures (30–1000 K) and pressures (3 kPa–10 GPa) [1], in order to study their thermodynamical properties and structural changes. The TIP4P/ice water model is employed for the water-water interactions, while both semiempirical and *ab initio*-based potentials are used to model the rare gas– H_2O ones.

Temperature-pressure phase diagrams for these clusters were constructed by employing a two-dimensional multiple-histogram method [2]. By analyzing the heat capacity landscape (see Fig. 1 (left panel) black dots corresponding to its maximum values), and the Pearson correlation coefficient profile for interaction energy and volume (see Fig. 1 (left panel) red dots correspond to its maximum values, while blue ones to its minimum), structural changes were detected (see Fig. 1 (right panel)). Those at high pressure correspond to solid-to-solid transitions and are found to be related with clathrate-like cages around the Ar atom (see Figure 1–left panel). It is also shown that the formation and stability of such structures are determined by the intermolecular interaction between the rare-gas and host molecules.

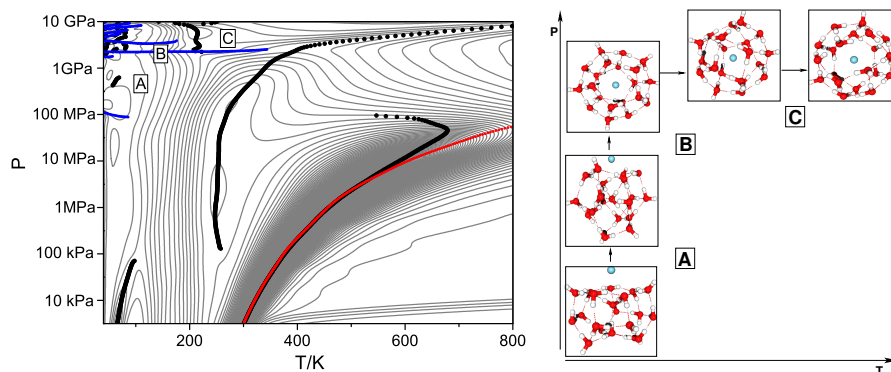


Figure 1: Phase diagram (left panel), and indicated structural changes (right panel)) for the $\text{Ar}(\text{H}_2\text{O})_{20}$ cluster.

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P37

Ab initio description of the fragmentation of $\text{H}_2\text{O}^+(\tilde{B}^2\text{B}_2)$

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The single ionization of water molecules by collisions with photons, electrons or ions leaves H_2O^+ in several possible electronic states: $\tilde{X}^2\text{B}_1$, $\tilde{A}^2\text{A}_1$ and $\tilde{B}^2\text{B}_2$. The first two states are obtained after removal of essentially non-bonding electrons from H_2O , and the corresponding cations do not fragment; however, the energy of the third estate lies above the dissociation limits of the first two ones and it has been measured [1] that about 92% of the ions formed in that state do fragment.

In this work [2], we consider $\text{H}_2\text{O}^+(\tilde{B}^2\text{B}_2)$ ions produced by a vertical transition from the ground vibrational state of the water molecule and we solve the nuclear TDSE using the Grid-TDSE method [3]. The calculation takes into account the lowest three doublet states of H_2O^+ and the non-adiabatic couplings between them, featuring a conical intersection between $\tilde{A}^2\text{A}_1$ and $\tilde{B}^2\text{B}_2$ states and the Renner-Teller coupling between $\tilde{X}^2\text{B}_1$ and $\tilde{A}^2\text{A}_1$ at linear geometries. We also calculate the contribution of the lowest quadruplet $\tilde{a}^4\text{B}_1$ to the dissociation yield by including the spin-orbit interactions with $\tilde{A}^2\text{A}_1$ and $\tilde{B}^2\text{B}_2$ states.

Figure 1 illustrates the probability density of the wave function at $t = 0$ and after 28 fs.

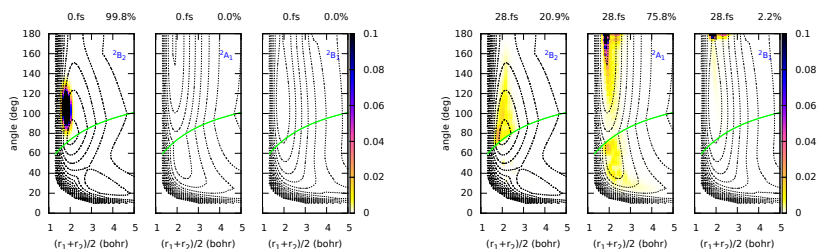


Figure 1: Probability density as a function of the radius $\xi = (r_1 + r_2)/2$ with $\zeta = 0 = (r_1 - r_2) = 0$. At $t = 0$ s, the wave packet is fully located on the $\tilde{B}^2\text{B}_2$ state (first panel). At $t = 28$ fs, the wave packet has crossed twice the conical intersection seam (green solid line) and it is spread over the three electronic states: $\tilde{B}^2\text{B}_2$, $\tilde{A}^2\text{A}_1$ and $\tilde{X}^2\text{B}_1$.

Acknowledgements

This work is funded by the project ENE2011-28200 (Secretaría de Estado de I+D+i, Spain) and is carried out under the computational support of the Centro de Computación Científica of UAM.

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P38

ortho-para-H₂ conversion by proton exchange in astrophysical media

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The ratio of *ortho*-H₂ to *para*-H₂ (OPR) plays a crucial role in understanding the astrochemistry behind star formation. The dark interstellar cloud (~ 10 K to 20 K) is cooled mainly by colliding H₂ molecules and this cooling causes the interstellar gas to clump to high densities. When the density of these clouds reaches a certain critical value, they collapse under their own gravity leading to the protostars. Noteworthy point here is that the rate of cooling of these dark interstellar clouds depends on the OPR of H₂ [1] which can determine the excitation of the other colliding molecular species [2]. Further, it is assumed that reactive collisions with H⁺ or H₃⁺ are the main source of *ortho* to *para* conversions in the most astrophysical environments [3].

We present the rotationally resolved reaction probabilities, integral cross sections and rate constants calculated for the H⁺ + H₂ ($v=0, j=0$ or 1) \rightarrow H₂ ($v'=0, j'$) + H⁺ reaction [4, 5] using a time-independent quantum mechanical method and two recent potential energy surfaces [6, 7]. Emphasis is put on the conversion of *ortho*-H₂ ($j = 1$) to *para*-H₂ ($j = 0$) via proton transfer as it seems to be the most dominant reaction path determining the OPR of H₂ in the cold interstellar clouds. Integral cross sections and rate constants obtained on the two potential energy surfaces considered here show remarkable differences in terms of magnitude which can be attributed to the subtle differences observed in the topography of the surfaces near to the entrance channel.

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P39

Investigation of chiral bio-molecules in the gas phase using high and low energy collisions with chiral target

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Study of biomolecules in the gas phase using mass spectrometry represents a promising approach to investigate their structure and properties. The chirality phenomenon has now become a top-class subject for academic research as well as for pharmaceutical development. Homochirality is believed to be not only a consequence of life but probably a precondition for it. An important and much discussed astrophysical question concerns the mechanism leading to the formation and processing of interstellar organic compounds and the role of different physical mechanisms in formation of different enantiomers [1].

In this work we present the first results of the project aimed to the investigation of fundamental principles of chiral recognition and selection. Collisions of keV energy ion beams of L- and D-forms of protonated amino acids with non-chiral and chiral targets were studied using an ion accelerator [2] at the Department of Physics, Stockholm University. The results show that the fragmentation process appears to be statistical, i.e. the collision leads to a statistical distribution of the energy over the available vibrational modes. The fact that no difference between the two enantiomeric forms of the cations was observed suggests that the three-point model [3, 4] is not applicable in this case; the activated ions retain no memory of the interaction with the chiral selector when they dissociate.

Low energy (0.3 – 4 eV) collision induced dissociation experiments were performed on a commercially available quadrupole time-of-flight mass spectrometer at the Department of Chemistry, University of Oslo. No difference in the fragmentation pattern of different enantiomeric forms of amino acids was observed. It was also found that low energy collisions of mass selected ions of amino acids with chiral target gas result in formation of ion-molecule complexes. An investigation of the complex formation process for different enantiomeric forms of amino acids with racemic and (S)-(+)-butanol were made.

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P40

A multilayer approach to the coupled coherent states method

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The method of coupled coherent states (CCS) is a powerful approach to deal with versatile multidimensional problems in molecular dynamics and in other fields of chemistry and physics. CCS is a member of the family of Gaussian-based methods: the wave function is expanded in coherent state basis, yet due to the coupling between the quantum amplitudes, it gives a fully quantum mechanical description of the system. The most important advantage of CCS is that it does not scale directly with the degrees of freedom (DOF).

Multilayer variants of existing numerical methods in multidimensional quantum mechanics offer greater flexibility and better scalability for the description of complex quantum systems. With such a scheme, different dynamical descriptions can be used for different subsystems of a composite system, and these configurations can be coupled together with an upper-level quantum amplitude.

The scheme was tested on a 20-dimensional, asymmetric double well potential where a tunnelling mode is coupled to a 19-dimensional bath. The quantum tunnelling is described by the CCS method and the dynamics of the bath modes is determined by Ehrenfest-trajectories. The results from the new scheme are compared with results obtained from CCS and other benchmarks. The multilayer scheme can be further extended to employ other type of trajectory-based approaches, such as the variational multiconfigurational Gaussians (vMCG) method.

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Control of chemical reactivity through spatial separation of molecular conformations

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Many molecules have multiple conformations (rotational isomers), which can exhibit different reactivities, opening up perspectives to manipulate chemical reactions by selecting specific molecular conformations [1]. However, a detailed understanding of the role of conformations in gas-phase chemical reactions still has to be established. In a recent experiment we studied the reactive collisions between conformationally selected 3-aminophenol and a Coulomb crystal of laser-cooled Ca⁺ ions [2,3]. This reaction was chosen as a model system. 3-Aminophenol exhibits two different conformations (cis and trans) with different permanent dipole moments. Their interaction with external inhomogeneous electric fields enables the two conformers to be spatially separated in a molecular beam passing through an electrostatic deflector [4]. Coulomb-crystals of spatially localized Ca⁺ ions stored in an ion trap [5] provide a suitable stationary target for the conformer-selected molecular beams enabling the study of conformer-specific reactive collisions with extremely high sensitivities down to the level of single reaction events.

By tilting the molecular beam machine mechanically with respect to the ion trap, conformationally pure components of the molecular beam have been overlapped with the ion trap. The progress of the reaction was monitored by imaging the laser-induced fluorescence of unreacted ions. The observed rate constant for cis-3-aminophenol is a factor of 2 larger than the one measured for the trans-3-aminophenol. These results agree well with the results from adiabatic capture theory calculations [6], indicating that the dynamics of the Ca⁺ - cis/trans-3-aminophenol reaction are mainly controlled by conformer-specific differences in the long-range ion molecule interaction potential.

In a new experiment, we want to study short-range reactive effects in an ion-molecule reaction. We are investigating the reaction of conformationally selected methyl vinyl ketone (MVK) with CO⁺ ions and the reaction between MVK and MVK⁺. These are Diels-Alder like cycloaddition reactions that should show significant differences in the dynamics for different conformations. To analyze the products of this reaction, we designed a new time of flight mass spectrometer that will be coupled to the ion trap. On the poster we present a summary of the Ca⁺ - Aminophenol experiment as well as first results and simulations regarding the new experiment.

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Excited state dynamics simulations using the AI-MCE methodKenichiro Saita^{1,2*}, Dmitrii V. Shalashilin¹¹ School of Chemistry, University of Leeds, Woodhouse Lane, Leeds LS2 9JT, UK² School of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK

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We have been developing the new ab initio multiconfigurational Ehrenfest (AI-MCE) method [1]. The basic idea is similar to the original MCE method [2], but here we introduce the working equations of MCE theory combined with the adiabatic electronic wavefunctions. AI-MCE method is named after the direct (on-the-fly) ab initio dynamics, and it has been developed in order to make the technique easily applicable to large molecular system. The benchmark of the excited state dynamics of ethylene gives pictures which include the nonadiabatic transitions through the twisted and pyramidalised conical intersections and hydrogen atom migrations. Our results are consistent with those obtained by ab initio multiple spawning (AIMS) technique and we use several approximation against demanding computational cost, however, the results are semi-quantitative. Strongly nonclassical nature of the Ehrenfest trajectories provides natural treatment of the coupled electronic states and can be an advantage in strongly quantum regimes.

Recently we studied the photodissociation dynamics of pyrrole using the AI-MCE method [3]. Photodissociation of pyrrole has been investigated and has proven to be an interesting case, prototypical of many heteroaromatic systems in which low energy heteroatom centred $\pi\sigma^*$ states occur in the singlet manifold. These states result from the close degeneracy of the 3s Rydberg orbital of the heteroatom with the repulsive σ^* orbital of the heteroatom to substituent bond, which leads to strong mixing. Where the substituent is simply H, N-H bond fission is the primary decay mechanism for pyrrole molecules excited to this $\pi\sigma^*$ state. In the dynamics, the nonadiabatic transitions play an important role via conical intersections of ${}^1\pi\sigma^*$ (1A_2 or 1B_1) states with the ground (1A_1) state, which are known to be responsible for N-H bond fission, and via the intersection between 2A_2 and 2B_1 states of the resulting molecular radical after the departure of the H atom. The latter intersection, which is effectively between the two lowest electronic states of the pyrrolyl radical, may play significant role in explaining the branching ratio between the two states observed experimentally. The exchange between the two states of pyrrolyl occurs on a much longer scale than that of N-H bond fission. All the 30 DOF were considered in our simulation, which was associated with SA3-CAS(8,7)-SCF/cc-pVDZ electronic calculations.

We present here recent progress of the AI-MCE simulations.

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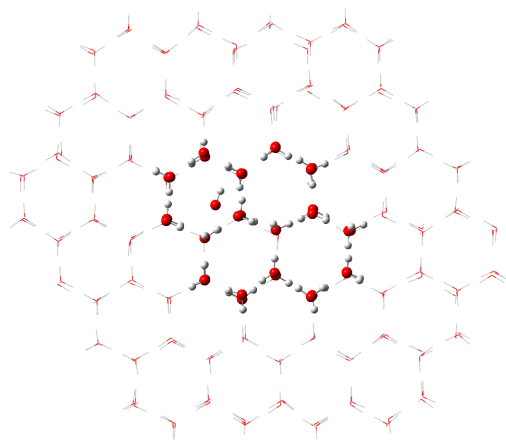
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Hybrid QM/MM Methods for Interstellar ChemistryW. M. C. Sameera,^{*1,2} Stefan Andersson,^{2,3} Gunnar Nyman,²¹Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto 606-8103, Japan.²Department of Chemistry and Molecular Biology, University of Gothenburg, Kemivägen 04, Gothenburg, SE-412 96, Sweden.³SINTEF Materials and Chemistry, P.O. Box 4760, NO-7465 Trondheim, Norway

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In hybrid quantum mechanics/molecular mechanics (QM/MM) methods, electronically most important region (e.g. binding site, reaction center) can be described by QM, while MM description is used for the remaining part that acts in a perturbative fashion.^{1,2} Therefore, QM/MM methods can provide accurate results, and the computational cost is kept manageable. However, hybrid QM/MM methods are not popular to model the chemical processes on ices. This is due to limited availability of force fields in most practical QM/MM implementations. We have developed the "Shell Interface for Combining Tinker With ONIOM" (SICTWO) program to overcome this limitation.^{2,3} SICTWO supports several polarizable and non-polarizable force fields that are suitable for modeling ices with ONIOM(QM:MM).



QM/MM model structure of an ice cluster ('ball and stick' model represents the QM region and 'Wireframe' model represents the MM region)

On the practical side, we have combined the AMOEBA polarizable force field with the ONIOM(QM:MM) approach to rationalize adsorption preference of the interstellar molecules (H₂O and benzene) and the radicals (HO and HCO) on crystalline water ice (I_h). Our calculations indicate that the dangling-oxygen (*d*-O) and dangling-hydrogen (*d*-H) on the ice surface play an important role on the binding preference.

The ONIOM(QM:AMOEBA) calculations on OH radical diffusion quite surprisingly suggested that diffusion on crystalline ice might be slower than on amorphous water ice.³ These studies indicate that hybrid QM/MM methods will be useful for the interstellar chemistry in future.

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On the influence of the C=O-groups on the excited state dynamics of small, organic molecules

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Studying light induced dynamics of small, organic molecules is central for understanding the dynamics of large synthetic and bio-molecules upon photoexcitation. Of special importance is the role of specific functional groups attached to the carbon backbone and the complex interplay between them. In this contribution, we specifically address the influence of the C=O-group on a delocalized π -system. We used time-resolved photoelectron spectroscopy and *ab initio* computation to investigate the excited state dynamics in substituted α,β -enones which have a basic structure of HC=CH-CH=O [1,2], and furan which is substituted in 2- and 3-position with an aldehyde group (2- and 3-furaldehyde). Our experiments show a clear deceleration of the dynamics by an order of magnitude after attachment of the extra C=O-group. The reason for this behavior is revealed by *ab initio* calculations: Through the addition of a C=O-group, the molecules obtain an additional low lying $n\pi^*$ -state. In cyclopentenone, it is accessed upon excitation of the bright $\pi\pi^*$ -valence states. Conical intersections (CoIns) between the $n\pi^*$ -state and the molecular ground state tend to lie significantly above the minimum energy of the $n\pi^*$ -state which reduces the speed in which it can be accessed. This decrease may allow the wave packet to evolve to a close lying triplet state on a few picosecond timescale. In furaldehyde, however, *ab initio* trajectory calculations show that most of the population remains in the $\pi\pi^*$ -valence state. Here, the reason for the deceleration is an increase of the potential energy of the CoIn with the ground state as compared to furan which also agrees with a faster decay of 3-furaldehyde as compared to 2-furaldehyde.

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Mixed Quantum/Classical Theory of rotationally inelastic scattering: calculations of cross sections in a broad range of collision energies

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In the presented work we have carried out Mixed Quantum/Classical calculations^[1] of rotationally inelastic scattering cross sections for two diatomic + atom collision systems: He + H₂, with the light induced mass of the system, Na + N₂ where the masses of the collision partners are relatively high^[2] and triatom + atom system: He + H₂O. The comparison between calculated cross sections and the exact quantum values^{[2][3]} shows that the obtained results are accurate and hard to distinguish from the full quantum results in many cases. The method is computationally cheap and particularly accurate at higher energies, heavier masses, and larger densities of states. Thereby Mixed Quantum/Classical Theory (MQCT) represents a useful alternative to the standard full-quantum scattering theory.

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Diffusion of Hydrogen and Deuterium on interstellar ices and tunneling

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Diffusion or mobility of atoms on the surface of ice grains play an important role in understanding the formation of H₂ and more complex molecular structures in the interstellar medium. H and D atoms mobility have been extensively discussed in the Astrochemistry community from both theoretical and experimental perspectives[1-10]. I will present our theoretical insight on the mobility of H and D atoms on crystalline water ice (I_h) and amorphous solid water (ASW) at very low temperatures[11]. We have calculated the barrier heights, rate constants and diffusion coefficients. The harmonic transition state theory (HTST) was used to obtain the rate constants and the harmonic quantum transition state theory (HQTST) was used for the tunnelling correction. The diffusion coefficient was calculated using the Einstein Smoluchowski equation and the kinetic Monte Carlo method.

The classical barrier heights are smaller on I_h than on ASW. Similarly, the vibrationally adiabatic ground state (VAG) barrier heights are smaller on I_h than on ASW. The well depths and barrier heights (classical and VAG) are distributed over a range of energies, in line with previous experimental observations. The surface morphology strongly influences the well depth. Quantum tunneling becomes important below 10K. The diffusion coefficient is lower on ASW than on I_h.

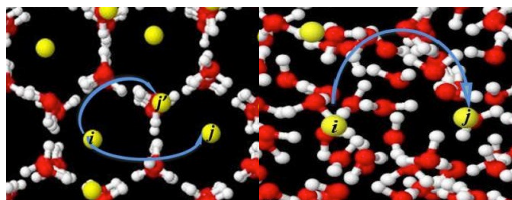


Figure: One hop on the surface of ice. i and j (or j') are the initial and final minima of the hop. Yellow dots in panels (a) and (b) are the local minima.

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Non-statistical Fragmentation of Fullerenes and Polycyclic Aromatic Hydrocarbons

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Non-statistical fragmentation processes are important when Polycyclic Aromatic Hydrocarbon molecules (PAHs), fullerenes, or other large molecules collide with atoms and atomic ions at center-of-mass energies from a few tens to a few hundreds of eV and typically result in the prompt, billiard-ball-like knockout of single atoms.

The primary *statistical fragmentation* channels for PAHs are H-, H₂, and C₂H₂-loss with dissociation energies of 5-7 eV, while for fullerenes C₂-loss dominates, with a dissociation energy of about 10 eV. These processes typically dominate when molecules are excited by photon absorption or electron impact. The dissociation energies for losses of single carbon atoms are substantially higher - typically 15 eV for fullerenes and 11-17 eV for PAHs. The single carbon atom loss channel is thus a clear signature of non-statistical fragmentation of these molecules.

We have performed an extensive set of experiments in order to further understand the importance of the non-statistical knockout process, focusing on collisions between PAH or C₆₀ cations and He atoms at center-of-mass energies around 100 eV. Density Functional Theory and Molecular Dynamics simulations are employed to interpret our results. For PAHs, we find the contribution from knockout reactions to be surprisingly large. Indeed, single carbon loss (insignificant in statistical processes) becomes the dominant carbon loss channel for large PAHs such as coronene C₂₄H₁₂[1]. We also observe larger differences in the fragmentation patterns of PAH isomers than is typically seen with other means of excitation. For C₆₀ the observed single carbon loss channel is much weaker, mainly due to the three-dimensional structure of the molecule.

Non-statistical fragmentation yields different, more reactive fragments than statistical processes and may thus play an important role in the formation of larger molecules. This has been observed when knockout occurs inside clusters of C₆₀ molecules, yielding a C₅₉⁺ fragment which quickly bonds with a nearby C₆₀ to form dumbbell-shaped C₁₁₉⁺[2].

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**The modified Quasi-Quantum Treatment of rotationally inelastic NO(X)-
He scattering**Xia Zhang,¹ Chris J. Eyles,² Dajun Ding^{1*} and Steven Stolte^{1,3,4*}¹*Institute of Atomic and Molecular Physics, Jilin University, Changchun, 130012, China*²*Institut für Chemie und Biochemie, Freie Universität Berlin, Takustrasse 3, 14195, Berlin, Germany*³*Institute for Lasers, Life, and Biophotonics, Vrije Universiteit, de Boelelaan 1083, Amsterdam 1081 HV, The Netherlands.*⁴*Laboratoire Francis Perrin, Bâtiment 522, DRECEM/SPAM/CEA Saclay, 91191 Gif sur Yvette, France*

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Abstract

A Modified Quasi-Quantum Treatment (MQQT) of the rotationally inelastic scattering problem has been developed to improve on the so-called Regular QQT (RQQT), in which the potential energy surface (PES) $V(R, \gamma_R)$ is replaced by its hard shell contour $V(R, \gamma_R) = E_{col}$. The MQQT presented here overcomes the limitations imposed by a single contour PES. It is replaced by $V(R, \gamma_R) = E_{col} \cdot \cos^2 \beta$, so that the potential is equal to the collision energy E_{col} provided by the component of the incoming momentum vector \mathbf{k} directed anti parallel to the shell surface normal \mathbf{n} . Consequently the component of \mathbf{k} parallel to the shell surface at the moment of impact remains conserved and the full range $0 \leq V(R, \gamma_R) \leq E_{col}$ of repulsive PES contours is taken into account. The MQQT rotationally inelastic state-to-state DCSs and ICSs of He + NO(X) at $E_{col} = 508 \text{ cm}^{-1}$ have been compared with those resulting from RQQT and from numerically exact QM calculations. The MQQT DCSs resemble the QM DCSs more closely than the RQQT DCSs for $j' \leq 5.5$ up to a scattering angle of $\theta \approx 60^\circ$. The MQQT and RQQT inelastic DCSs are quite similar for all other inelastic transitions and θ ranges. These results have been attributed to the specifics of the anisotropic Legendre expansion coefficients $C_n(\cos \beta)$ of the contours of the He + NO(X) V_{sum} PES. In the particular case for which the bond length or geometry of a molecular collider changes with the proximity of the collision partner due to charge transfer, the short range anisotropic terms will depend strongly onto the intermolecular distance, which can be accounted for by MQQT but not by RQQT.

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Formation of the hydroxyl radical by radiative association

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Radiative association is a typical process for the formation of molecules in the interstellar medium. The hydroxyl radical is a molecule of much astrochemical interest. For these reasons this study is made to acquire the reaction rate constant, at different temperatures, for the radiative association possibly resulting from the collision of an oxygen atom and a hydrogen atom.

A combination of different methods have been used to get a result. For direct radiative association a quantum mechanical perturbation theory [1, 2], a semiclassical method [3], and a classical method [4] were used. The perturbation theory can handle shape-resonances, but to the (semi)classical results Breit-Wigner theory [5, 6] was added to account for those. For a possible inverse predissociation pathway the contribution to the rate constant was calculated from reaction widths and lifetimes gathered from several sources [7, 8, 9, 10].

These results will contribute to the improvement of astrochemical models.

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High-Order Harmonic Generation with the Coupled Coherent States method

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High-order harmonic generation is a phenomenon in which an electron bound to a nucleus responds highly non-linearly to a strong input near-infrared laser field releasing radiation at high harmonics of the input field, reaching the extreme ultraviolet to soft x-ray regime [1]. The spectrum of harmonic photons generated by this interaction can be calculated by use of the time-dependent Schrödinger equation, however this is only suitable for one-dimensional single electron systems due to the exponentially increasing numerical effort encountered at larger degrees of freedom. More often, the spectrum is calculated using the strong field approximation. While this is often sufficient in many cases, due to the approximation of the continuum by a field-dressed plane wave serious difficulties arise in situations where the interplay between the Coulomb potential and the external field becomes important.

In light of these problems an alternative calculation method is desired. One such is the Coupled Coherent States method^[2], an orbit-based method which allows the simulation of multidimensional many-body quantum dynamics. In this method the wavefunction is projected onto a basis of trajectory-guided coherent states coupled through time propagation equations. These trajectories are guided not by a classical potential in the manner of many semiclassical methods but instead are guided by a quantum average over the guiding coherent state. In this way, the Coupled Coherent States equations describe a method which is, in principle, formally exact and capable of simulating non-classical events with a good degree of accuracy.

We show that through the periodic reprojecting of the wavefunction and through dynamically altering the basis set size the Coupled Coherent States method can account for a wavefunction which spreads out to cover a large area in phase space, such as that of the High Harmonic system, while still keeping computational cost low. As a proof of principle a one-dimensional single electron system is modelled and the resulting High Harmonic spectrum compared against that obtained from solving the time-dependent Schrödinger equation, showing a good level of agreement.

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Low-temperature Inelastic Collisions of Water with Helium. Theory versus Experiment

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State-to-state rate coefficients for *ortho*-H₂O:He and *para*-H₂O:He inelastic collisions have been investigated in the 20 to 120 K thermal range on the basis of a novel experimental procedure [1]. This procedure is based on the use of a kinetic Master Equation which describes the evolution of populations of *ortho*-H₂O and *para*-H₂O rotational levels along a supersonic jet of H₂O highly diluted in helium. The Master Equation is expressed in terms of experimental observables and rate coefficients for *ortho*-H₂O:He and *para*-H₂O:He inelastic collisions. The primary experimental observables are the local number density and the rotational populations of *ortho*-H₂O and *para*-H₂O, quantities which are determined along the jet with unprecedented accuracy by means of Raman spectroscopy with high space- and time-resolution. Secondary experimental quantities, which are inferred from the primary observables, are the translational temperature, the flow velocity, and the time evolution of the rotational populations of H₂O along the supersonic jet. All these data are employed in the Master Equation, where the only remaining unknowns are the state-to-state rates. Scaling of preexisting theoretical rates to best matching with respect to the experiment leads to empiric rates of better than 10 % accuracy in average.

In a first step the rates from the literature [2] and from present close-coupling calculations based on different H₂O-He potential energy surfaces (PES)[3,4] have been tested against the experiment. The state-to-state rates involved in the evolution of populations of the eight lowest rotational energy levels of *ortho*-H₂O and *para*-H₂O calculated by Green *et al.* [2] are about 50 % too low compared to experiment. The rates calculated here from Hodges *et al.* PES [3] are about 20 % lower than the experimental ones, while most rates calculated from Patkowski *et al.* PES [4] agree with the experiment within 15 % .

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Ultra-cold methane - nitrogen mixtures under irradiation: formation of monocarbon and dicarbon cationic clusters

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The goal of our study is to understand the clusterization processes in methane – nitrogen mixtures under irradiation. We examine formation of monocarbon and dicarbon clusters from the N₂/CH₄ mixtures, since both methane and nitrogen are omnipresent in terrestrial and extraterrestrial environments. Nitrogen is an essential component of the ocean water, large volumes of frozen methane are stored beneath the sea floor in the form of methane hydrate, methane is found in the soil due to its role as a dominant end-product in the processes of mineralization. Both gases are present in the earthen atmosphere. Furthermore, they are unambiguously found in the atmospheres of exoplanets, as well as in our solar system: in the atmospheres of Mars and Titan and on meteorites.

Ultra-cold helium nanodroplets are a very useful medium for assembly and study of reactions in various molecular complexes due to their high ability to be doped and their superfluidity. In our study, processes related to molecule and cluster formation in irradiated gaseous methane-nitrogen mixtures in helium droplets are investigated at the temperature of 0.37K.

Molecular structures formed from N₂/CH₄ mixtures of different concentrations were trapped by means of an ultracold environment of helium nanodroplets. A beam of low-energy electrons (70 eV) was used for the irradiation. Afterwards, the results of irradiation were analyzed by the TOF mass spectrometer. From the experiment, it can be deduced that all the monocarbon clusters studied are most likely to be formed in the range of 5%–30% of methane in the mixture. A number of clusters and molecules were observed with the mass to charge ratio up to 80 Da. The synthesized structures were analyzed by quantum chemical calculations using the CCSD(T)/6-311G(2d,p)//CCSD/6-311G(2d,p) method.

Formation of chemical bonds in C₂H₂⁺, C₂H₃⁺, C₂H₄⁺, C₂H₅⁺, C₂H₆⁺, N₄⁺, CHN₂⁺, CH₂N₂⁺, CH₃N₂⁺ similar to bonds in typical organic molecules was observed – it is a clear indication of possibility of synthesis of a true chemical bond under the low-energy electronic irradiation. Molecular complexes CHN₂⁺, CHN₄⁺, and CH₂N₂⁺ exhibit a strong energetical favorability towards C=C-N ring formation. Molecule CH₃N₂⁺ has the greatest ion yield and a rather high binding energy of 1.57 eV. Otherwise, there is little correlation between the ion yields and the associated binding energies, indicating that kinetic control is more important than thermodynamic control for forming the clusters in most cases.

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Strongly aligned and oriented molecules for internal dynamics studies

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For many applications in physics and chemistry fixed in space samples of molecules are highly desirable. The behavior of molecules subject to strong laser fields and the resulting alignment and orientation has been a rapidly growing topic in molecular physics and chemistry during the last years. The anisotropic interaction between an isolated molecule and static electric and non-resonant laser field creates pendular states, i. e., directional superpositions of field-free rotational states [1]. While state selection and brute-force orientation has been used traditionally to create oriented samples [2] a stronger control, also in 3D, in the degree of orientation has been achieved by the use of a combination of weak electrostatic and strong non resonant laser fields [3,4].

We unravel the rotational and pendular state wave packet dynamics of quantum state selected carbonyl sulfide (OCS) molecules [5]. Features in the transition from impulsive, non-adiabatic to adiabatic alignment and orientation were disentangled. A strong oscillation in the degree of alignment is observed, which resembles the motion of a pendulum. This behavior holds as well for internal rotations in molecules and has therefore implications on the switching behavior of fast molecular switches in non dissipative media. In addition, we demonstrated how the combination of quantum state selection and rotational coherence spectroscopy allows for a complete measurement of magnitude and polarization of angular momenta of molecules in field-free space.

Furthermore, we will present molecular frame photoelectron angular distributions (MFPADs) of strongly 3D-aligned and oriented molecules. These static images are the first step to study rearrangement processes in molecules like internal rotations via MFPADs which will be used to determine structural information while the molecule is changing its shape upon laser excitation in the near future.

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Towards atomic resolution diffractive imaging of isolated molecules with x-rays and electrons

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Controlled-molecule imaging increases the amount of information accessible in molecular dynamics studies by x-ray or electron diffraction. We report experimental results and a detailed analysis of a new bottom-up approach of diffractive imaging of isolated molecules [1-3]. The experiment was performed in the CAMP experimental chamber [4] extended by a modern state-selective molecular beam injector [1,5] at the Linac Coherent Light Source (LCLS) x-ray free-electron laser (XFEL) [6]. An ensemble of the prototypical target molecule 2,5-diiodobenzonitrile ($C_7H_3I_2N$, DIBN) was cooled in a supersonic expansion, quantum-state selected using the electrostatic deflector [5], strongly laser-aligned by nanosecond pulses from a nonresonant near-infrared Nd:YAG laser [7,8], and subsequently probed by the femtosecond pulses of the LCLS in order to collect x-ray diffraction data of the ensemble of isolated molecules.

We obtained diffractive imaging signals of strongly aligned ensembles of DIBN above experimental noise. The extensive analysis of the experimental data included spectroscopic discrimination of x-ray and optical photons, and the analysis of radiation damage based on ion and photon data. The molecular alignment observed in the diffraction patterns is in agreement with Coulomb explosion ion images. The structural information, i. e., the heavy-atom distance derived from the diffraction patterns, is consistent with theoretical calculations. The results confirm necessary steps toward diffractive imaging of weakly-scattering molecular samples such as, e. g., the ability to deliver quantum-state selected ensembles of molecules to the interaction volume of the XFEL, to strongly laser-align them for the diffraction experiment, and to perform single-photon detection with the pnCCD cameras, even above severe background levels. We point out that the angular anisotropy in the diffraction from aligned DIBN was preserved during the measurement time of several hours. The approach is suitable for studies of ultrafast dynamics of small isolated molecules utilizing the femtosecond x-ray pulses from XFELs together with femtosecond pulses from optical lasers in pump-probe experiments.

Here we will present our first electron diffraction images on solid state samples. These results are used to characterize a new photoelectron gun, which will be used for future electron diffraction molecular dynamics experiments on fixed in space molecules in the gas phase.

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P55

**Full-dimensional state-to-state reaction probabilities
for $H + CH_4 \rightarrow H_2 + CH_3$**

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Understanding chemical reactivity is one of the fundamental goals in chemical physics. Full-dimensional state-to-state differential cross sections can be calculated for triatomic and selected tetratomic systems. In the last decade impressive experiments studied polyatomic reactions in full detail. Reactions of methane with atoms like H , F , Cl and O provide prototypical examples studied. Most theoretical studies rely on quasi-classical trajectory calculations while advanced wave packet calculations employ reduced dimensional models explicitly including six of the twelve coordinates. For six atom reactions, only thermal rate constants and initial state-selected reaction probabilities could be studied by rigorous theory.

Full-dimensional state-resolved reaction probabilities for the $H + CH_4(\mathbf{v}_{CH_4}, j, m) \rightarrow H_2(\mathbf{v}_{H_2}) + CH_3(\mathbf{v}_{CH_3})(J = 0)$ reaction are presented. These calculations are facilitated by flux correlation functions, the quantum transition state concept, the multi-layer extension of the multiconfigurational time-dependent Hartree (MCTDH) approach and an efficient scheme to evaluate the accurate Shepard interpolated potential energy surface on modern graphics processing units (GPUs). The mode-selectivity of the title reaction and the influence of rotational energy will be discussed. Furthermore, product distributions will be examined.

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Quantum dynamics of CH_5^+ and the Pauli principle

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The theoretical investigation of the ro-vibrational quantum dynamics of molecular systems has been a central task in molecular physics and physical chemistry since the foundation of quantum mechanics. Systems with two or more potential minima connected by shallow barriers can be especially demanding in this context since they show floppy dynamical behaviour. Here, the fundamental concept of one reference structure known from rigid molecules has to be abandoned.

Presumably the most prominent example of a highly floppy or fluxional molecule is the CH_5^+ cation. It has been intensively investigated by theory and experiment since its discovery in the 1950's. Its potential energy surface shows 120 equivalent minima which are separated by relatively small barriers. Thus, the detailed investigation of the structure and dynamics of CH_5^+ is a challenging subject. The IR spectrum of CH_5^+ could be measured in low resolution in the frequency range from about 500 to 3200 cm^{-1} and was studied by classical and quasi-classical ab initio molecular dynamics simulations. A full-dimensional potential energy surface was developed and low-lying vibrational eigenstates have been calculated quantum mechanically.

Here, full-dimensional quantum dynamics calculations employing the multiconfigurational time-dependent Hartree (MCTDH) approach are presented which obtain a large number of vibrational and ro-vibrational eigenstates of CH_5^+ . The calculations rigorously consider the Pauli principle and the nuclear spin statistics. The low-temperature IR spectrum in the frequency range from 0 to about 2000 cm^{-1} is calculated and compared to experiment. The Pauli principle is found to have a severe impact on the computed spectrum. Furthermore, a complete breakdown of the separation of rotational and vibrational motion is found which can be attributed to fundamental symmetry properties.