XXI European Conference on the Dynamics of Molecular Systems

Toledo (Spain)

11 - 16 September 2016

MOLEC 2016

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WELCOME LETTER

MOLEC 2016

XXI European Conference on the Dynamics of Molecular Systems

Dear participants in MOLEC 2016,

Welcome to Toledo for the XXI edition of the MOLEC conference!

The series of biennial MOLEC meetings started in 1976, when the first conference was held in Trento (Italy). Since that time the conference was held in Brandbjerg Hojskole (Denmark), Oxford (UK), Nijmegen (The Netherlands), Jerusalem (Israel), Aussois (France), Assisi (Italy), Bernkastel-Kues (Germany), Prague (Chech Republic), Salamanca (Spain), Nyborg Strand (Denmark), Bristol (UK), Jerusalem (Israel), Istanbul (Turkey), Nunspeet (The Netherlands), Trento (Italy), St. Petersburg (Russia), Curia (Portugal), Oxford (UK), Gothenburg (Sweden), and now in Toledo (Spain). The present conference aims at highlighting the most recent advances in molecular dynamics, providing the appropriate forum to discuss scientific achievements at the forefront of Chemistry and Physics. Following the tradition of MOLEC conferences, the scientific program focusses on both experimental and theoretical studies of molecular interactions, collisional dynamics, spectroscopy, and related fields.

The present edition counts 107 participants from more than 20 countries, both European and non-European ones. The scientific program includes 46 talks and 67 poster contributions. We wish you a lively, fruitful, and successful conference in all respects. The time schedule allows time for informal discussions and exchange among participants. We also hope that participants there will have time to know and enjoy the beautiful and interesting city of Toledo.

We would like to thank the International Scientific Committee for suggestions on the scientific program, and all the speakers for accepting the invitation to participate in MOLEC 2016. Likewise, we acknowledge the different contributions of the remaining participants.

The conference is chaired by the Consejo Superior de Investigaciones Científicas (CSIC). The Universidad Complutense de Madrid (UCM) has also provided a valuable help in the organization of the conference. These two institutions have provided their infrastructure as well as financial support to the organization of MOLEC 2016, which we strongly acknowledge. The Real Sociedad Española de Física is also strongly acknowledged for its support. We want to thank also all the other sponsors of the conference for the different types of support they have given.

The XXI edition of MOLEC happily coincides with the 40th anniversary of the MOLEC conference, and we want to celebrate this event with a special celebration scientific session. This celebration session will open the conference, and will consist of two lectures delivered by the founders of the MOLEC conference in 1976, Professors Peter Toennies and Franco Gianturco. For this special occasion we include in the present Book of Abstracts a short history of the MOLEC conference, along with the program of the first meeting celebrated in Trento in 1976, and a table with a historical chronology of the different MOLEC editions, specifying the places, organizers, and MOLEC awards granted (courtesy of Professor Peter Toennies).

In this edition of MOLEC we also wish to award the traditional MOLEC Prize to an outstanding senior scientist. This prize has been awarded five times in previous MOLEC editions. In this edition the prize has been awarded to Professor Dieter Gerlich. In addition we have established a new MOLEC Prize (following a brilliant suggestion by Professor Peter Toennies), namely the Zdeněk Herman Young Scientist Prize, named after Professor Zdeněk Herman, to honor the great contributions that he has made to the MOLEC conference along its history. This prize has been awarded to Professor Sebastiaan Y. T. van de Meerakker. We congratulate the two winners of the prizes.

We thank the International Scientific Committee of MOLEC for their help in suggesting and voting the candidates for the two MOLEC Prizes. In particular, we want to acknowledge the help and support provided by Professors Zdeněk

Herman, Peter Toennies, and Franco Gianturco along all the process associated with the awarding of the prizes. We are strongly indebted to Professor Zdeněk Herman, who designed the medals of the two prizes with the good taste that always characterizes him. He was also guiding the process of production of the medals with sensible and smart suggestions.

Finally, we wish you a stimulating conference and a pleasant stay in Toledo.

Alberto García-Vela

Chairman, on behalf of the Organizing Committee

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MOLEC 2016

XXI European Conference on the
Dynamics of Molecular Systems

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SHORT HISTORY OF THE BEGINNING OF THE MOLEC SERIES OF EUROPEAN CONFERENCES

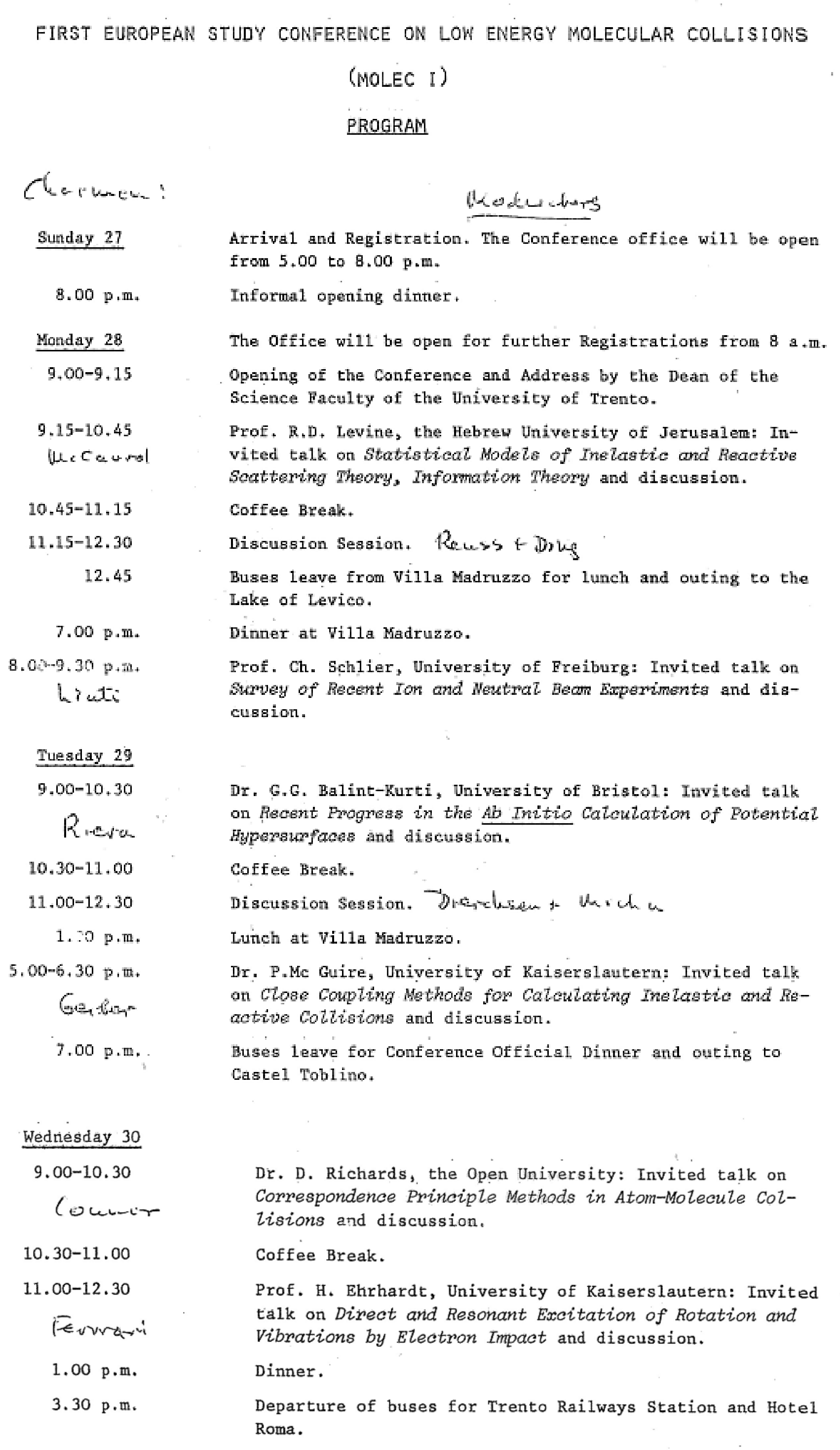
MOLEC 2016

XXI European Conference on the
Dynamics of Molecular Systems

In the early 1970’s J. Peter Toennies was coopted by the newly established Atomic Physics Board of the European Physical Society. At one of the board meetings one topic of discussion was a letter from Franco Gianturco, who had been elected Member of the EPS Council. In this letter Gianturco had suggested that a European meeting, similar to a Gordon Conference, should be established to consolidate the growing activities in the area of molecular collisions in Europe. Since the new board did not consider itself to be responsible for organizing conferences the Board suggested that Toennies, as someone working in the field, should contact Gianturco and encourage him to organize such a meeting. Gianturco, who at the time had just moved as full professor of Chemical Physics, from the University of Pisa to the University of Bari in Southern Italy, felt that it would be difficult for him to organize the meeting somewhere in Italy and also collect the abstracts while moving between places. Thus, Toennies, being already permanent at the MPI in Goettingen, and with more reliable mail services, offered to handle the correspondence and, in particular, collect the abstracts and assemble the book of abstracts. Gianturco arranged for excellent accommodations at the Villa Madruzzo, just outside Trento, Italy. Most of the participants were accommodated with meals in the villa and others in Hotel Roma in the nearby town. The lectures took place in a conference hall adjacent to the villa. Toennies carried the book with 47 abstracts for all the 83 participants in his backpack on the train trip to Trento. The conference started with an informal dinner on Sunday June 27 and lasted until the afternoon of Wednesday June 30. Each day only 1 ½ hour talks followed by a moderated discussion session, were given in the morning and afternoon. At the end of the meeting it was unanimously decided that there should be another meeting in two years. The program of MOLEC I is attached.

The 83 participants of MOLEC I came from Germany (44), Italy (13), UK (8), France (5), Sweden (3), Spain, Israel, Holland and Denmark (2) and Czechoslowakia, Portugal, Belgium and Yugoslavia (1).

14. Sept 2015: Franco Gianturco and J. Peter Toennies



FIRST EUROPEAN STUDY CONFERENCE ON LOW ENERGY MOLECULAR COLLISIONS

(MOLEC I)

PROGRAM

Chairmen! Moderators

Sunday 27	Arrival and Registration. The Conference office will be open from 5.00 to 8.00 p.m.
8.00 p.m.	Informal opening dinner.
Monday 28	The Office will be open for further Registrations from 8 a.m.
9.00-9.15	Opening of the Conference and Address by the Dean of the Science Faculty of the University of Trento.
9.15-10.45 McCourd	Prof. R.D. Levine, the Hebrew University of Jerusalem: Invited talk on *Statistical Models of Inelastic and Reactive Scattering Theory, Information Theory* and discussion.
10.45-11.15	Coffee Break.
11.15-12.30	Discussion Session. Reuss + Ding
12.45	Buses leave from Villa Madruzzo for lunch and outing to the Lake of Levico.
7.00 p.m.	Dinner at Villa Madruzzo.
8.00-9.30 p.m. [illegible]	Prof. Ch. Schlier, University of Freiburg: Invited talk on *Survey of Recent Ion and Neutral Beam Experiments* and discussion.
Tuesday 29	
9.00-10.30 Riera	Dr. G.G. Balint-Kurti, University of Bristol: Invited talk on *Recent Progress in the Ab Initio Calculation of Potential Hypersurfaces* and discussion.
10.30-11.00	Coffee Break.
11.00-12.30	Discussion Session. [illegible] + [illegible]
1.00 p.m.	Lunch at Villa Madruzzo.
5.00-6.30 p.m. Gerber	Dr. P.Mc Guire, University of Kaiserslautern: Invited talk on *Close Coupling Methods for Calculating Inelastic and Reactive Collisions* and discussion.
7.00 p.m.	Buses leave for Conference Official Dinner and outing to Castel Toblino.
Wednesday 30	
9.00-10.30 Courier	Dr. D. Richards, the Open University: Invited talk on *Correspondence Principle Methods in Atom-Molecule Collisions* and discussion.
10.30-11.00	Coffee Break.
11.00-12.30 Ferrari	Prof. H. Ehrhardt, University of Kaiserslautern: Invited talk on *Direct and Resonant Excitation of Rotation and Vibrations by Electron Impact* and discussion.
1.00 p.m.	Dinner.
3.30 p.m.	Departure of buses for Trento Railways Station and Hotel Roma.

MOLEC Conferences: 1976-2016

MOLEC	Year	Location	Organizers	The MOLEC Award (MOLEC Prizes)	Zdeněk Herman Young Scientist Prize
I	1976	Trento*	Franco Gianturco and Peter Toennies	-	-
II	1978	Brandbjerg Hojskole, DK	Udo Buck and Thor Bak	-	-
III	1980	Oxford	Mark Child	-	-
IV	1982	Hapert near Nijmegen*	Joerg Reuss	-	-
V	1984	Jerusalem	R.B. (Benny) Gerber	-	-
VI	1986	Aussois	R. (Ron) McCarrol	-	-
VII	1988	Assisi*	Vincenzo Aquilanti	-	-
VIII	1990	Bernkastel Kues*	Franz Linder	-	-
IX	1992	Prague*	Zdenek Herman	-	-
X	1994	Salamanca*	Gerardo Delgado-Barrio	-	-
XI	1996	Nybord Strand, DK*	Gert Billing	Peter Toennies	-
XII	1998	Bristol*	Gabriel Balint.Kurti	Franco Gianturco	-
XIII	2000	Jerusalem*	Michael Baer	-	-
XIV	2002	Istanbul*	Attila Askar and Ersin Yurtsever	-	-
XV	2004	Nuspeet, NL*	Stephan Stolte	Raphy Levine	-
XVI	2006	Trento*	Daniela Ascenzi, Paolo Tosi	Zdenek Herman	-
XVII	2008	St. Petersburg*	Oleg Vasyutinskii	Gabriel Balint-Kurti	-
XVIII	2010	Coimbra	Antonio Varandas	-	-
XIX	2012	Oxford	Mark Brouard	-	-
XX	2014	Gothenburg	Gunnar Nyman	-	-
XXI	2016	Toledo	Alberto García-Vela	Dieter Gerlich	S.Y.T. van de Meerakker

*Means: Toennies has documents and the program (except for MOLEC IX)

PROGRAM

MOLEC 2016

XXI European Conference on the
Dynamics of Molecular Systems

Sunday 11th September

15:30-17:00 Registration

17:00-17:15 Opening Remarks

40th Anniversary Special Celebration Session

Chair: Gerardo Delgado-Barrio *Instituto de Física Fundamental, CSIC (Spain)*

17:15-18:00 **Francesco A. Gianturco** *Innsbruck Universitaet (Austria)*

Plenary Lecture (PL1) : The puzzle of anions' formation from carbon-rich molecules in the Interstellar medium: how molecular quantum dynamics can help modelling their evolution in astronomical objects

18:00-18:45 **J. Peter Toennies** *Max-Planck-Institut für Dynamik und Selbstorganisation (Germany)*

Plenary Lecture (PL2) : Looking at molecules in very cold and gentle superfluid helium nanodroplets

18:45-19:15 MOLEC Award Ceremony

19:15-20:30 Welcome Reception

Monday 12th September

Session I: Reactive Collisions

Chair: Alexandra Viel *Institute of Physics of Rennes (France)*

09:00-09:35 **F. Javier Aoiz** *Universidad Complutense de Madrid (Spain)*

Plenary Lecture (PL3) : Quantum interferences in chemical reactions: Do they reveal classical mechanisms?

09:35-10:05 **Keli Han** *Dalian Institute of Chemical Physics (China)*

Invited Lecture (IL1) : Reactant coordinate based state-to-state reactive scattering dynamics implemented on GPUs

10:05-10:35 *Coffee Break*

Session II: Ultrafast Phenomena I

Chair: Luis Bañares *Universidad Complutense de Madrid (Spain)*

10:35-11:10 **Fernando Martín** *Universidad Autónoma de Madrid (Spain)*

Plenary Lecture (PL4) : Imaging attosecond molecular dynamics with pump-probe schemes: a theoretical perspective

11:10-11:40 **Anatoli Kheifets** *Australian National University, Canberra (Australia)*

Invited Lecture (IL2) : Time delay in molecular photoionization: Window to ultrafast electron dynamics

11:40-12:10 **Valerie Blanchet** *Université de Bordeaux (France)*

Invited Lecture (IL3) : Toward femtochemistry with circular polarized pulses

12:10-12:30 **Raimund Feifel** *University of Gothenburg (Sweden)*

Oral Presentation (OP1) : Ultrafast molecular three-electron collective Auger decay

12:30-14:30 *Lunch*

Session III: Spectroscopy I

Chair: María Luisa Senent *Instituto de Física Fundamental, CSIC (Spain)*

14:30-15:05 **Timothy J. Lee** *NASA Ames Research Center (USA)*

Plenary Lecture (PL5) : Computing highly accurate spectroscopic line lists for characterization of exoplanet atmospheres and assignment of astronomical observations

15:05-15:35 **Petr Slavíček** *University of Chemistry and Technology Prague (Czech Republic)*

Invited Lecture (IL4) : Nuclear quantum effects in spectroscopy and dynamics: ab initio simulations

15:35-15:55 **Yohann Scribano** *Université de Montpellier (France)*

Oral Presentation (OP2) : Translation-rotation dynamics of confined molecules using an efficient Smolyak Sparse-grid scheme

15:55-16:25 *Coffee Break*

Session IV: Photoinduced Processes

Chair: Raimund Feifel *University of Gothenburg (Sweden)*

16:25-17:00 **King-Chuen Lin** *National Taiwan University (Taiwan)*

Plenary Lecture (PL6) : Roaming signature in photodissociation of some carbonyl compounds

17:00-17:30 **Helen H. Fielding** *University College London (United Kingdom)*

Invited Lecture (IL5) : Time-resolved photoelectron spectroscopy of biological chromophores: from isolated molecules to dimers and liquid jets

17:30-18:00 **Mattanjah S. de Vries** *University of California, Santa Barbara (USA)*

Invited Lecture (IL6) : Photodynamics of nucleobases and their derivatives

18:00-18:20 **Etienne Gindensperger** *Université de Strasbourg – CNRS (France)*

Oral Presentation (OP3) : Spin-vibronic excited-state quantum dynamics in transition metal complexes

18:20-20:00 *Poster Session*

Tuesday 13th September

Session V: Coherence Control I

Chair: Burkhard Schmidt *Free University Berlin (Germany)*

09:00-09:35 **Regina de Vivie-Riedle** *Ludwig-Maximilians-Universität München (Germany)*

Plenary Lecture (PL7) : Quantum dynamics and control of molecular reactions: From gas phase to solution

09:35-10:05 **Cristoph Meier** *Laboratoire Collisions Agrégats Réactivité, , CNRS (France)*

Invited Lecture (IL7) : Femtosecond quantum dynamics and laser control of non-isolated quantum systems

10:05-10:25 **Ágnes Vibók** *University of Debrecen (Hungary)*

Oral Presentation (OP4) : Control by frequency chirped laser-induced conical intersections

10:25-10:55 *Coffee Break*

Session VI: Ultrafast Phenomena II

Chair: Etienne Gindensperger *Université de Strasbourg – CNRS (France)*

10:55-11:30 **Stephen R. Leone** *University of California, Berkeley (USA)*

Plenary Lecture (PL8) : An X-ray spectroscopic revolution in time-resolved molecular dynamics

11:30-12:00 **Marc J. J. Vrakking** *Max Born Institute Berlin (Germany)*

Invited Lecture (IL8) : Novel opportunities for studying atomic, molecular and cluster dynamics intense HHG sources

12:00-12:30 **Leticia González** *University of Vienna (Austria)*

Invited Lecture (IL9) : Challenges to describe intersystem crossing dynamics

12:30-12:50 **Asier Longarte** *Universidad del País Vasco (Spain)*

Oral Presentation (OP5) : Ultrafast excited state dynamics of size selected neutral molecular clusters

12:50-14:50 *Lunch*

15:30 *Visit to Toledo*

Wednesday 14th September

Session VII: Low-Energy Collisions and Reactions I

Chair: Steven Stolte *Jilin University (China)*

09:00-09:35	**Jonathan Tennyson** *University College London (United Kingdom)*
	Plenary Lecture (PL9) : Low temperature chemistry using the R-matrix method
09:35-10:05	**David W. Chandler** *Sandia National Laboratory (USA)*
	Invited Lecture (IL10) : Study of collision induced dissociation of NO_2 using crossed molecular beam scattering
10:05-10:25	**Manuel Lara** *Universidad Autónoma de Madrid (Spain)*
	Oral Presentation (OP6) : Dynamics of the $S(^1D)+o\text{-}D_2 \rightarrow SD+D$ reaction at low collision energies: revisiting the SH2 system
10:25-10:55	*Coffee Break*

Session VIII: Low-Energy Collisions and Reactions II

Chair: Jose María Fernández *Instituto de Estructura de la Materia, CSIC (Spain)*

10:55-11:30	**Sebastiaan Y. T. van de Meerakker** *Radboud University (Netherlands)*
	Plenary Lecture (PL10) : Taming molecular collisions
11:30-12:05	**Ad van der Avoird** *Radboud University (Netherlands)*
	Plenary Lecture (PL11) : Quantum phenomena in molecular collisions
12:05-12:35	**Edvardas Narevicius** *Weizmann Institute of Science (Israel)*
	Invited Lecture (IL11) : Observation of scattering resonances in neutral-neutral and neutral-ion collisions

12:35-12:55 **Alexandra Viel** *Institute of Physics of Rennes (France)*

Oral Presentation (OP7) : Bound states and inelastic scattering of $^3\Sigma_u^+$ Rb_2 - He

12:55-14:50 *Lunch*

Session IX: Coherent Control II

Chair: Ágnes Vibók *University of Debrecen (Hungary)*

14:50-15:20 **Oriol Vendrell** *Aarhus University (Denmark)*

Invited Lecture (IL12) : Coupled nuclear and electronic wave packet dynamics

15:20-15:40 **Ignacio R. Sola** *Universidad Complutense de Madrid (Spain)*

Oral Presentation (OP8) : Ultrafast population inversion by parallel transfer

15:40-16:00 **Burkhard Schmidt** *Free University Berlin (Germany)*

Oral Presentation (OP9) : Quasi-exact solvability and supersymmetry in molecular quantum mechanics: From pendular to tunneling states

16:00-16:30 *Coffee Break*

Session X: Atmospheric Chemistry

Chair: David Lauvergnat *Université de Paris-Sud (France)*

16:30-17:05 **R. Benny Gerber** *Hebrew University of Jerusalem (Israel)*

Plenary Lecture (PL12) : Mechanisms and dynamics of atmospherically relevant molecular reactions on surfaces of liquid water and of ice.

17:05-17:25 **Basile F.E. Curchod** *University of Bristol (United Kingdom)*

Oral Presentation (OP10) : Non-adiabatic molecular dynamics simulations of photochemical isoprene oxidation intermediates

17:25-18:00 *Meeting of International Steering Committee*

18:00-20:00	*Poster Session*

Thursday 15th September

Session XI: He Droplets and Clusters

Chair: Anatoly M. Pravilov *Saint-Petersburg State University (Russia)*

09:00-09:35 **Henrik Stapelfeldt** *Aarhus University (Denmark)*

Invited Lecture (IL13) : Laser-induced alignment of molecules in He-nanodroplets: Revivals, long-time coherence and breaking-loose

09:35-10:05 **María Pilar de Lara Castells** *Instituto de Física Fundamental, CSIC (Spain)*

Invited Lecture (IL14) : Ab-initio-assisted modelling of the soft, ^{4}He droplet-mediated, deposition of metallic nanoparticles

10:05-10:25 **Pablo Villareal** *Instituto de Física Fundamental, CSIC (Spain)*

Oral Presentation (OP11) : Theoretical investigations on doped rare gas clusters with neutral or ionic atomic and diatomic impurities

10:25-10:55 *Coffee Break*

Session XII: Dynamics of Complex Systems

Chair: Paolo Tosi *Università di Trento (Italy)*

10:55-11:30 **George C. Schatz** *Northwestern University (USA)*

Plenary Lecture (PL13) : Plasma enhanced dry reforming: Theoretical studies

11:30-11:50 **Sebastian Fernández-Alberti** *Universidad Nacional de Quilmes/CONICET (Argentina)*

Oral Presentation (OP12) : Excited state dynamics in carbon nanorings

11:50-12:10 **Anthony J. H. M. Meijer** *University of Sheffield (United Kingdom)*

Oral Presentation (OP13) : Investigating the mechanism of vibrationally controllable electron transfer using Density Functional Theory

12:30-14:30 *Lunch*

Session XIII: Processes at Surfaces

Chair: Anthony J. H. M. Meijer *University of Sheffield (United Kingdom)*

14:30-15:05 **Rainer D. Beck** *Ecole Polytechnique Fédérale de Lausanne (Switzerland)*

Plenary Lecture (PL14) : State-to-state scattering of methane from a Ni(111) surface

15:05-15:25 **Daniel Farías** *Universidad Autónoma de Madrid (Spain)*

Oral Presentation (OP14) : Phonon dynamics of graphene on metals

15:25-15:45 **Luca M. Martini** *Università di Trento (Italy)*

Oral Presentation (OP15) : Reactivity of fatty acid methyl esters with OH produced by a plasma Jet

15:45-16:15 *Coffee Break*

Session XIV: Spectroscopy II

Chair: José A. Fernández *Universidad del País Vasco (Spain)*

16:15-16:50 **Dieter Gerlich** *Technische Universität Chemnitz (Germany)*

Plenary Lecture (PL15) : Molecular ions in cryogenic traps

16:50-17:20 **Volker Engel** *University of Würzburg (Germany)*

Invited Lecture (IL15) : Wave-packet approach to two-dimensional vibronic spectroscopy

17:20-17:40 **Jose María Fernández** *Instituto de Estructura de la Materia, CSIC (Spain)*

Oral Presentation (OP16) : Probing molecular collisions by Raman spectroscopy

20:00 *Conference Dinner*

End of the Conference

PLENARY LECTURES

MOLEC 2016

XXI European Conference on the
Dynamics of Molecular Systems

PL-1

The puzzle of anions' formation from Carbon-rich molecules in the Interstellar Medium: how Molecular Quantum Dynamics can help modelling their evolution in astronomical objects

F. A. Gianturco

Institut für Ionen Physik und Angewandte Physik, Innsbruck Universitaet, Technikerstrsse 25, 6020, Innsbruck, Austria

Quantum computations that follow the electron attachment process at low energies (< 10 eV) to carbon-rich gaseous molecules are essential to understand the role of transient negative ions (TNIs) which can act as "doorway states" to molecular stabilization and/or fragmentation after the attachment of electrons produced in photodissociation region of interstellar space (ISM).

It is in fact a well established fact that microscopic processes give important information about the bulk properties of the interstellar medium (ISM), and therefore control several macroscopic features of it such as temperature and density [1] and observable chemical compositions in prestellar and diffuse clouds conditions. We know already that every process of radiation-induced photoionization of the atoms and molecules which are present in the ISM yields an electron e- with a residual energy related to IP, the latter being the Ionization Potential of the species involved. This most often primarily involves H, and He. This excess amount of energy can in turn be shared between the surrounding gas and its constituents and therefore provides an important heat source within the ISM. The formation of polyatomic anions, therefore, has been predicted in astrophysical environments by earlier model studies [2,3], where it was suggested that the initial step of the electron-molecule low-energy collisions could produce a metastable species, a transient negative ion (TNI), which then further stabilizes after radiative emission: M + e - = (M_)* = M- + photon We also know that other possible paths could instead involve the loosing of the electron excess energy of the TNI complex by a dissociative electron attachment (DEA) process following Internal Vibrational Rearrangement (IVR) mechanisms: (M_)* = A + B-. Recent experimental observations of negatively charged molecular anions like C_4H^-, C_6H^-, C_8H^- and C_3N^-, C_5N^-, C_7N^-(see [4-6] and references within) have triggered the search for the possible formation of metastable TNIs in even larger systems. The excess energy brought in by the resonant electron gets transferred into the internal energy of the molecular bonds, thereby causing either the breakup of the target with the ensuing formation of stable anionic fragments (DEA), or the creation of a long-lived, full size metastable anion with little residual energy that can in turn undergo radiative electron attachment (REA) into a bound anionic molecule . The search for dynamical paths has therefore been motivated by (i) the experimental detection of stable anionic variants for the title systems in several regions of the ISM; (ii) the need to assess the possible molecular mechanisms which preside over the formation of such anions, and (iii) the identification of low-energy electron-attachment resonances and their likely competition with other chemical paths to produce the anions [7,8].

References

[1] e.g. see: J. C. Dyson and D. A. Williams, *The Physics of the Interstellar Medium* (Taylor & Francis, 1997).
[2] E. Herbst, *Nature* **289**, 656 (1981).
[3] T. J. Millar, E. Herbst, and R. P. A. Bettens, *MNRAS*, **316**, 195 (2000).
[4] F. A. Gianturco *et al., Astrophys. J. 774*, 97 (2013).
[5] F. A. Gianturco *et al*., *Astrophys. J.* **799**, 228 (2015).
[6] F. Sebastianelli, and F. A. Gianturco, *Eur. Phys. J. D*, **59**, 389 (2010).
[7] T. Grassi *et al*., *MNRAS* **425**, 1332 (2012) .

PL-2

Looking at molecules in very cold and gentle superfluid helium nanodroplets

J. Peter Toennies

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Molecular beams of superfluid helium clusters ranging in size from a few atoms up to nanodroplets with as many as 10^{10} – 10^{12} atoms are readily formed in free jet expansions. In vacuum they rapidly cool to 0.37 K and easily pick up foreign molecules thereby providing new opportunities for low temperature chemistry. High resolution spectroscopy reveals that the finite sized droplets are superfluid which enables the embedded molecules to freely rotate and translate at low velocities. Clusters with taylor-made structures, not otherwise accessible, can be constructed by adding additional identical or different molecules. In this way also bimolecular reactions can be induced. Quantum vortices, a hallmark of superfluidity, recently found inside huge droplets, can even organize metal atoms into long metal nanowires. These and other experiments have demonstrated that superfluid helium nanodroplets are by far the coldest and gentlest of all cryomatrices with remarkable properties[1].

Some recent developments include: (1) Sophisticated many-body theories which “see” the detailed motion of atoms and ions inside the droplets and how vortices are formed [2]. (2) Pulsed X-ray diffraction which has exposed unexpected shapes of very large droplets and remarkable self-organized long range structures of embedded atoms[3]. (3) Laser impulsive alignment generating rotational wavepackets followed by Coulomb explosion which has opened up a new high resolution spectroscopy of clusters with virtually no dipole moments and the possibility of reactions with aligned molecules[4]. (4) Free laser IR spectroscopy of large charged biomolecules which reveal the unzipping of the helix structures[5]. (5) High resolution spectroscopy of radical reaction products[6]. This broad range of activities illustrates how the unique environment of superfluid helium droplets opens up many new horizons in chemical physics.

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PL-3

Quantum Interferences in chemical reactions: Do they reveal classical mechanisms?

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Interferences are genuine quantum phenomena that appear whenever two seemingly distinct classical trajectories lead to the same outcome. They are common in elastic and inelastic scattering but are seldom observable in chemical reactions since it requires fully initial and final state selection and sufficiently narrow collision energy distributions. Very recently we have reported that, for certain states, interferences produce a characteristic oscillation pattern that governs the angular distributions for the $H + D_2$ reaction [1,2].

The comparison between quasiclassical (QCT) and Quantum Mechanical (QM) calculations evinces that the oscillation pattern arises when groups of partial waves than span different ranges of the total angular momentum cause scattering at the same deflection angles. Interestingly, the various groups can be assigned to different classical mechanisms that take place under certain conditions and the analysis of the quantum interferences serves to identify those mechanisms. The phenomenon is analogous to that found in the double (and multiple)-slit experiment wherein the analysis of the diffraction pattern allows us to determine the double-slit characteristics more precisely than what would have happened if the behaviour were purely classical.

Here, we analyzed the circumstances in which interferences determine the shape of the angular distribution, and how the presence of these interferences depend on the shape of the potential energy surface, the collision energy, and the initial and final states.

We have found that interferences depend on the initial rotational state j of the $D_2(v=0, j)$ reagent and diminish in strength with increasing rotation. We present here a detailed explanation for this behavior and how each dynamical scattering mechanism has a dependence on the helicity, Ω, the projection of the initial rotational angular momentum j of the D_2 reagent on the approach direction. Each helicity corresponds to a different internuclear axis distribution, with the consequence that the dependence on Ω reveals the preference of the different quasiclassical mechanisms as a function of approach direction.

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PL-4

Imaging attosecond molecular dynamics with pump-probe schemes: a theoretical perspective

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The development of attosecond laser pulses allows one to probe the inner working of atoms, molecules and surfaces on the timescale of the electronic response. In molecules, attosecond pump-probe spectroscopy enables investigations of the prompt charge redistribution and localization that accompany photo-excitation processes, where a molecule is lifted from the ground Born-Oppenheimer potential energy surface to one or more excited surfaces, and where subsequent photochemistry evolves on femto- and attosecond timescales. In this talk I will present a few theoretical examples of realistic molecular attosecond pump-probe experiments in which several molecules are ionized with a single attosecond pulse (or a train of attosecond pulses) and are subsequently probed by one or several infrared or xuv few-cycle pulses. The evolution of the electronic and nuclear densities in the photo-excited molecule or remaining molecular ions is calculated with attosecond time-resolution and is visualized by varying the delay between the pump and probe pulses. The results of these calculations [1-7] allow us to explain several experimental observations as well as to guide future experimental efforts to uncover ultrafast electron and nuclear dynamics in molecules.

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PL-5

Computing highly accurate spectroscopic line lists for characterization of exoplanet atmospheres and assignment of astronomical observations

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Over the last several years, our group has been involved in developing approaches to compute highly accurate spectroscopic constants and vibrational frequencies for small transient molecules that may be used in the interpretation and assignment of high-resolution laboratory experiments as well as high-resolution astronomical spectra. Recently, we have used the computed spectroscopic constants to simulate purely rotational and rovibrational spectra so that these may be compared directly with high-resolution astronomical observations, and we have worked on developing approaches that can be applied to much larger molecules, such as PAHs, where we can explicitly determine anharmonic corrections to vibrational modes as well as take into account intensity sharing due to resonances. Another part of our work in spectroscopic signatures involves computing highly accurate line lists for common molecules, such as CO_2, SO_2, and NH_3, which occur in many astrophysical environments, including the atmospheres of exoplanents, and often need to have their lines identified in high-resolution observations in order to determine which lines are due to other molecules. I will discuss our latest work in these areas of astrochemical spectroscopy research.

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PL-6

Roaming signature in photodissociation of some carbonyl compounds

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Photodissociation dynamics of methyl formate $HCOOCH_3$ at different photolysis wavelengths has been investigated experimentally and theoretically [1,2]. Ion imaging of CO, H and time-resolved Fourier-transform infrared (FTIR) emission spectra of CO and HCO are acquired following photolysis. The translational energy distributions of CO (v=0) yield a bimodal feature mainly contributed by the roaming and the transition state (TS) processes at >248 nm. According to quasi-classical trajectory (QCT) calculations, the CO distribution in the molecular channel is characterized by a bimodality, in consistency with the experiments. The QCT results further show that the molecular production is initiated from the $S_1(n,\pi^*)_{CO}$ transition, followed by internal conversion through conical intersection [1]. The photodissociation pathways for CO(v>0) are also investigated [2]. Next, we report photodissociation of acetaldehyde (CH_3CHO) at 308 nm. The resulting CO (v=1 to 4) fragment is acquired using time-resolved FTIR emission spectroscopy [3,4]. A branching fraction of H-roaming/CH_3-roaming/TS contribution is evaluated to be (8±3)/(68±10)/(25±5)%, in which the TS pathway was observed for the first time. Finally, a multi-center impulsive model is presented to characterize the dynamic feature of product energy distribution in photodissociation of formaldehyde, $H_2CO \rightarrow CO + H_2$ [5,6]. The model is also extended to predict the vector correlations for the fragments produced via TS and roaming path. The correlation results are consistent with those reported using QCT simulation on global potential energy surface. In contrast to the TS route, the vector properties via the roaming path are loosely correlated. This work offers an alternative method to study stereodynamics of photodissociation process.

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PL-7

Quantum dynamics and control of molecular reactions: From gas phase to solution

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Quantum dynamics simulations are the most accurate way to describe reactive molecular processes. The quantum mechanical character of the nuclei is preserved in addition to the one of the electrons. Important features like vibrational or electronic transitions induced by a laser pulse, non-adiabatic processes mediated by conical intersections or coherent control studies can be straightforwardly described. The simulations give valuable insight into the reaction mechanism and its controllability on the atomistic level. Elaborated tools for simulations in the gas phase have been developed over the years. As a large part of chemical reactions take place in solution, needs to combine the quantum system to its environment emerge.

In this talk, I will present our approach to include the solvent environment explicitly in the quantum dynamics frame work [1]. The environmental impact will be elucidated for a photoinduced bond cleavage, which is a commonly used to generate highly reactive carbocations in organic synthesis and whose reaction outcome is mediated via conical intersections. One step further is the control of a chemical reaction on the atomistic level with modulated light fields. Theoretical studies will be presented that highlight control events ranging from chemical reactions via the steering of nuclear and electronic wavepackets [2, 3, 4] over directional control of bond breaking in symmetric molecules [5] to control scenarios in solution. The examples range form diatomics to polyatomic systems and from dissociation processes to complex molecular rearrangements.

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PL-8

An X-ray spectroscopic revolution in time-resolved molecular dynamics

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Laser-produced high order harmonics are used to probe dissociating or excited atoms, molecules, and ions in time, using core level spectroscopic transitions of specific atoms in the molecule. The method is femtosecond and attosecond transient absorption in the extreme ultraviolet or x-ray spectral regime. Typical examples are investigations of the I 4d or Br 3d inner shell transitions probing to empty valence states in a molecule or atom.

Product branches are observed directly and time constants are obtained for the production of various excited states of the fragments. Energies of the lowest unoccupied molecular orbital relative to the singly occupied orbital of radical species are obtained. In addition, transient features, indicative of the x-ray spectroscopic transitions in the dissociative region of the potential curves are observed and assigned.

On ultrashort timescales, vibrational wave packets and electronic wave packets, as well as charge migration in molecules, are explored in atoms and small molecules. Shifts of core level spectral transitions with vibrational excitation are obtained. A remarkable x-ray spectroscopic ultrafast revolution presents new opportunities for molecular dynamics investigations on ultrashort timescales.

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PL-9

Low temperature chemistry using the R-matrix method

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Techniques for producing cold and ultracold molecules are enabling the study of chemical reactions and scattering at the quantum scattering limit with only a few partial waves contributing to the incident channel leading to the observation and even full control of state-to-state collisions in this regime. A new formalism is presented for tackling problems involving low- and ultra-low energy collisions. This formalism is completely general but is particularly appropriate for slow collisions occurring on potential energy surfaces with deep wells. The many resonance states make such systems hard to treat theoretically but offer the best prospects for novel physics: resonances are already being widely used to control diatomic systems and should provide the route to steering ultracold reactions.

R-matrix methods have proved outstanding successful for studies of light particle collisions [1] but have not been systematically applied to heavy particle collisions.
Our R-matrix based formalism builds on the progress made in variational calculations of molecular spectra by using these methods to provide wavefunctions for the whole system at short internuclear distances, the inner region. These wavefunctions will be used to construct energy-dependent R-matrices which can then be propagated to give cross sections at each collision energy. The methods are being used to study ultracold collisions. Initial results will be presented at the meeting.

Our R-matrix methodology is designed to treat many processes including reactive scattering, photodissociation and photoassociation, charge exchange, elastic and inelastic collisions and predissociation. It is being developed as a wrapper round several nuclear motion codes including the diatomic code Duo [2], the triatomic DVR3D [3] and the polyatomic code TROVE [4].

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PL-10

Taming molecular collisions

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The study of molecular collisions with the highest possible detail has been an important research theme in physical chemistry for decades. Over the last years we have developed methods to get improved control over molecules in a molecular beam [1]. With the Stark decelerator, a part of a molecular beam can be selected to produce bunches of molecules with a computer-controlled velocity and with longitudinal temperatures as low as a few mK. The molecular packets that emerge from the decelerator have small spatial and angular spreads, and have almost perfect quantum state purity. These tamed molecular beams allow for crossed beam scattering experiments with unprecedented levels of precision and sensitivity [2,3].

I will discuss our most recent results on the combination of Stark deceleration and velocity map imaging. The narrow velocity spread of Stark-decelerated beams results in scattering images with an unprecedented sharpness and angular resolution. This has facilitated the observation of diffraction oscillations in the state-to-state differential cross sections for collisions of NO with rare gas atoms [4,5], and the observation of scattering resonances at low-energy inelastic NO-He collisions [6].

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PL-11

Quantum phenomena in 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 [1,2]. State-to-state differential scattering cross sections are measured in a crossed molecular beam setup, with the use of a Stark decelerator and combined with velocity map imaging. Results predicted by close-coupling quantum calculations on *ab initio* intermolecular potential energy surfaces have guided the experiments. Comparison with the measured data provides a very sensitive test of the accuracy of different potentials. The high angular and energy resolution of the experiment makes it possible to discern details in the differential cross sections, such as Fraunhofer diffraction patterns. Analysis of the corresponding calculated patterns reveals a previously unknown propensity rule and enables us to extract detailed information on the stereodynamics of the collision process without pre-aligning the molecules or probing their alignment after the collision.

Scattering resonances at low collision energies, also predicted by the calculations, can be observed [3,4]. A theoretical analysis based on the multi-channel Breit-Wigner formula allows us to distinguish resonance characteristics in the integral and differential cross sections from background contributions and thus to confirm that the experiments show the resonance features. All of this is demonstrated on simple prototype systems: NO molecules colliding with various rare gas atoms.

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PL-12

Mechanisms and dynamics of atmospherically relevant molecular reactions on surfaces of liquid water and of ice

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Reactions at surface of liquid water and of ice play a major role in the chemistry of the atmosphere and other chemical disciplines. Knowledge on the molecular-level mechanisms of such processes is, however, very limited.

This lecture describes progress in understanding of the microscopic mechanisms of the reactions by Molecular Dynamics simulations using directly interaction potentials from quantum-chemical methods. One highlight of the results will be findings on acid ionization in impact on liquid water, on amorphous ice, and on defected crystalline ice.

Ionization will be shown to occur within picoseconds after impact, at the surface layer.

Formation of contact ion pairs, of solvent-separated ion pairs, and the onset of proton mobility in the medium will be described. Another highlight will be results on the formation of carbonic acid H_2CO_3 in impact of CO_2 on ice and on liquid water. This is a new predicted mechanism in the much debated issue on formation of H_2CO_3 in the atmosphere.

PL-13

Plasma enhanced dry reforming: Theoretical studies

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Dry reforming is a process wherein CH_4 and CO_2 react to give synthesis gas and/or liquid fuels. While dry reforming is less favorable than steam reforming, it has the advantage of being one of the few reactions that “captures” CO_2, if only to be recycled. Dry reforming is normally done under high temperature and pressure conditions, with a Ni catalyst, however it has recently been discovered that if a plasma is also present near the catalyst, then it is possible to get this reaction to go under modest conditions close to room temperature and atmospheric pressure. The role of the plasma in this process is poorly understood. In this talk I will describe several studies that my group is doing which are designed to describe the dynamical processes involved in plasma enhanced dry reforming, including both the role of the plasma, and the gas-surface chemistry that occurs in the presence of plasma species. There are two general directions of this work. First the plasma is known to fragment the reacting gases, especially CH_4, so we are studying the interaction of methane fragments with various Ni surfaces, to show how this enhances chemisorption, surface dissociation, and subsequent reaction with species already on the surface. Of particular importance in this work is the reaction of subsurface atomic hydrogen with adsorbed CO_2, where we connect with recent experiments. Second, the plasma provides a source of electrons that impact catalytic surfaces. Here we develop the theory of secondary electron emission, and show how this models recent experiments. We will also show that charging of the catalyst particles enhances chemical reactions involving CO_2^+ that reduces coking from adsorbed carbon. These studies have been performed with a combination of reactive molecular dynamics using semiempirical electronic structure methods and reactive force fields. We have also used electronic structure calculations in which the particles are allowed to be charged with electrons.

PL-14

State-to-state scattering of methane from a Ni(111) surface

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We report state-to-state surface scattering experiments for CH_4 colliding with clean Ni(111) as well as for graphene covered Ni(111). A molecular beam of CH_4, incident on on the target surface, is prepared in a single rovibrationally excited quantum state by infrared pumping using a single mode continuous wave optical parametric oscillator. State prepared $CH_4(\nu_3, J=2)$ then impacts on the Ni surface with controlled incident energy and angle and the scattered molecules are detected with quantum state resolution using a cryogenic bolometer in combination with infrared laser tagging. Using this setup, we measured rotational and vibrational state distributions of the scattered methane molecules. The results provide detailed information on the rotational and vibrational energy transfer between the incident $CH_4(\nu_3, J=2)$ molecules and the target surface. Efficient vibrational energy transfer is observed for incident $CH_4(\nu_3)$ leading to scattered $CH_4(\nu_1)$ where ν_3□and ν_1 are the anti-symmetric and symmetric C-H stretch normal modes of CH_4, respectively. Energy transfer probabilities to other vibrational states of CH_4 including the vibrational ground state are currently under investigation and will be reported in this contribution.

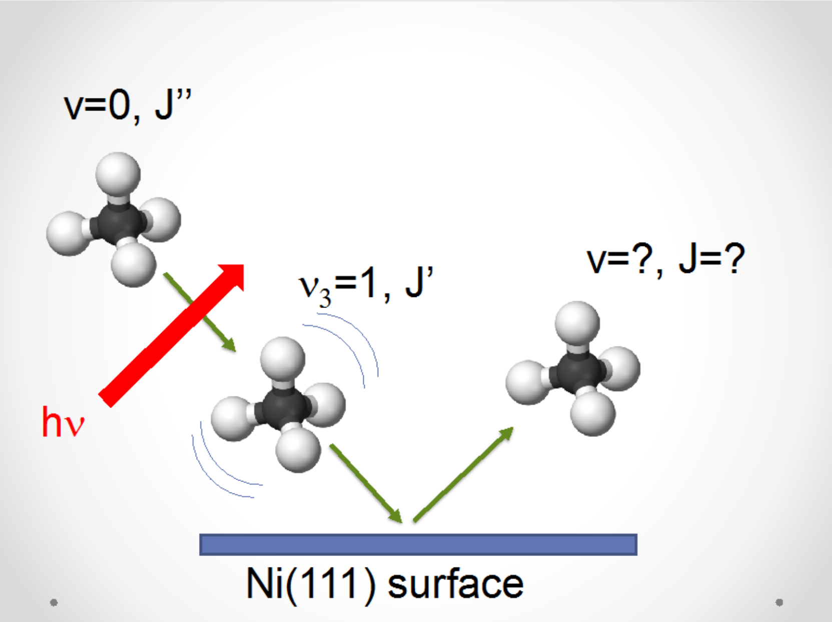

Figure 1: Schematic of the state-to-state methane scattering experiment

PL-15

Molecular ions in cryogenic traps

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Progress in molecular science strongly depends on inventions and advances in innovative tools such as molecular beams, special sources for ions and radicals, lasers, and imaging detectors, just to mention a few examples. Instruments, using fast oscillating electric fields for guiding, storing and selecting ions became very versatile. All this started in the fifties with the quadrupole mass spectrometer and the Paul trap, in 1969 the first Guided Ion Beam apparatus became operational, and in the eighties ions have been cooled in the first cryogenic ring electrode trap. More historical facts and a detailed description of the *use of inhomogeneous rf fields* can be found in Ref. [1]. In the first part of my talk, I will give a personal review of various rf based instruments which have been developed for studying the structure and reactivity of atomic and molecular ions. The sensitivity of such instruments will be illustrated by selected results for bi- and termolecular reactions, radiative association, clustering, isotope fractionation, and isomerization. Although the cryogenic 22-pole is already older than 25 years, the versatility of such traps has been recognized only after 2000.

In the second part I will focus on recent progress made with cryogenic ion traps in various laboratories. Special ion storage instruments have been developed for applications in astronomy, biochemistry, high resolution spectroscopy, and for modern applications in mass spectrometry. Especially successful has been the group of T. Rizzo to interrogate individual conformations of large *frozen biomolecular ions* using two or more lasers [2]. It was a long way to record an *electronic spectrum of* C_{60}^+ stored and cooled in a 22-pole trap: only last year the effort was coroneted by the confirmation that this ion is a carrier of several diffuse interstellar bands [3]. Evaluating high resolution *IR spectra of* CH_5^+ recorded at 10 and 4 K increased our understanding of this floppy molecule [4]. A cryogenic wire quadrupole trap, integrated into a commercial mass spectrometer, allows us today to characterize *reaction intermediates* via infrared photodissociation spectroscopy of *He-tagged ions* [5]. In many cases the perturbation of the ion via the weakly bound helium is small, whereas $He\text{-}H_3^+$ significantly differs from H_3^+ showing 100 times more lines in high resolution IR spectra [6].

Acknowledgments: I thank my hosts in Prague, Köln and Basel where I could continue to work with cryogenic traps after my mandatory retirement. I am honored that the MOLEC Committee selected me for the Senior Scientist MOLEC Prize.

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INVITED LECTURES

MOLEC 2016

XXI European Conference on the Dynamics of Molecular Systems

IL-1

Reactant Coordinate Based State-to-State Reactive Scattering Dynamics Implemented on GPUs

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A parallel code for state-to-state quantum dynamics with propagation of time-dependent wavepacket in reactant coordinates has been developed on GPUs. The propagation of wavepacket and the transformation of wavepacket from reactant to product Jacobi coordinates are entirely calculated on GPUs. A new interpolation procedure is introduced for coordinates transformation to decrease the five-loop computation to two four-loop computations. This procedure has a negligible consumption of extra GPU memory in comparing with that of the wavepacket, and produces a considerable acceleration of the computational speed of the transformation. The code is tested to get differential cross sections of H+HD reaction and state-resolved reaction probabilities of O+ HD for total angular momenta *J* = 0, 10, 20, 30. The average speedups are 57.0 and 83.5 for the parallel computation on two C2070 and K20m GPUs relative to serial computation on Intel E5620 CPU, respectively.

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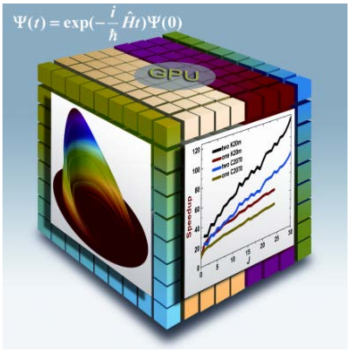
Keywords: Differential cross sections; Collision dynamics; H + HD; O + HD; Reaction probabilities; GPU



IL-2

Time delay in molecular photoionization: Window to ultrafast electron dynamics

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Attosecond physics opens a new perspective on a wide range of fundamental photo-physical and photochemical processes [1-3]. In this presentation, the following fundamental and conceptual questions of ultrafast electron dynamics in molecules will be addressed:

Attosecond time delay

- Is photoionization instantaneous or is there a finite response time of the electronic wave function to the photo-absorption event?
- Does it take longer for the electron to escape from a multi-center molecular core than from an atomic core?
- Does the emission time-delay, dependent on the relative orientation of the emission direction and molecular axis, carry information on the geometric arrangement of the atomic constituents?

Photoelectron holography

- How can the phase information be extracted from the holographic images obtained by interference of photoelectrons re-scattered from the molecular ion and those that miss the ion?

Attosecond control

- If a reaction is initiated by ultrafast ionization, how does the coherence between the ion and the continuum electron manifest?
- Does the preparation of electronic coherences in molecules allow novel pathways towards chemical control that are not available in more traditional experiments?

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IL-3

Toward femtochemistry with circular polarized pulses

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Each molecule can be recognized by its chemical composition and its structural conformation that dictates how it will interact with other molecules. Life has found an extra parameter to stock durably information: chirality. This asymmetry property appears at the molecular level when two molecules have the same chemical composition and structure but cannot be superimposed to each other by a mirror transposition. The two mirror images are called enantiomers. Enantiomers are able to regulate different biological mechanisms through their handedness. This chiral recognition is the key element in how we perceive odor and taste and is as well as of major importance in many mechanism for drug action. Chirality is as such, one of the most subtle example of broken symmetry with a huge impact in chemistry, pharmacology and biochemistry and even the origin of life.

In the photoionization of randomly-oriented pure enantiomers by circular polarization light, an asymmetry of the emitted photoelectron is observed along the photon propagation axis. This forward/backward asymmetry can reach several percentage and reverses with the handedness of the enantiomer or the helicity of the light polarization.[1] By comparing different ionization mechanisms, all using femtosecond pulses, we found that PECD exists in all regimes (single photon, multiphoton, tunneling). On the basis of these experiments, we have performed the first (to our knowledge) experimental investigation on time-dependent chiral dynamics. The time-resolved approach opens new horizons and questions on what are the most important dynamical aspects of the scattering of an electron in chiral potential that is as well evolving.

Acknowledgments: This work was financially supported by Agence Nationale de la Recherche (ANR) (ANR-14-CE32-0014 MISFITS); Labex LAPHIA and Université of Bordeaux.

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IL-4

Nuclear Quantum Effects in Spectroscopy and Dynamics: *Ab Initio* Simulations

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Nuclear quantum effects (NQEs) play an important role in molecular systems. Quantum mechanical tunneling enhances the rates of chemical reactions, zero point energy controls structure of flexible molecular systems and nuclear quantum effects strongly influence structure of hydrogen bonded liquids. Modelling thermodynamical quantities such as heat capacities is unthinkable without including the NQEs.

In my presentation, I will focus on the role of NQEs on molecular structure, electronic spectroscopy and dynamical processes, showing examples both for isolated molecules and for a liquid state. I will discuss methods for quantitative modelling of equilibrium nuclear quantum effects based on path integral approach to statistical mechanics and recent development in the field especially in the context of *ab initio* simulations. I will present several examples from our laboratory, in particular the role of nuclear quantum effects on acidic dissociation [1], quantitative modelling of single and two photon absorption spectra, including widths and absolute intensities [2] and the role of nuclear quantum effects in the ultrafast electronic transfer processes [3]. Finally, direct spectroscopy route to redox potentials within a framework of Marcus theory will be also discussed and tested.

Acknowledgments: This work was supported by the Czech Science Foundation GA CR project No. 13-34168S and MŠMT ČR project LD 15025.

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IL-5

Time-resolved photoelectron spectroscopy of biological chromophores: from isolated molecules to dimers and liquid jets

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Light-induced processes are ubiquitous in nature. Isolated biological chromophores are ideal starting points for studying the key elementary processes following light-absorption, free from the complications of interactions with aqueous or protein environments; however, it is important to understand the role of the environment in determining the electronic structure and dynamics. We are using a bottom-up approach to unravelling the role of the environment. Here, we begin with a description of recent work investigating the non-radiative decay dynamics of isolated small molecule chromophores[1–3] before moving on to describe our identification of a new electron transfer relaxation pathway in pyrrole dimers.[4] Finally, we describe our progress in liquid jet photoelectron spectroscopy of small biological chromophores.

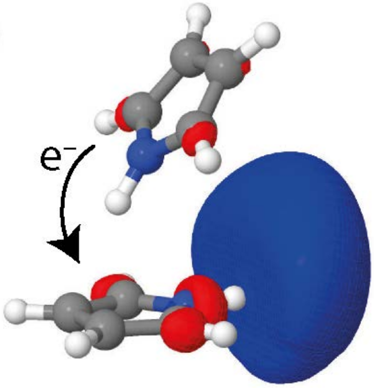

Figure: Electron transfer from the excited π-system of a donor pyrrole molecule to a Rydberg orbital localized on the acceptor pyrrole molecule, mediated by an N–H stretch on the acceptor pyrrole.

Acknowledgments: This work was enabled by support from EPSRC grants GR/T20304/01, EP/G055270/1, EP/L005646 and EP/L005697.

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IL-6

Photodynamics of nucleobases and their derivatives

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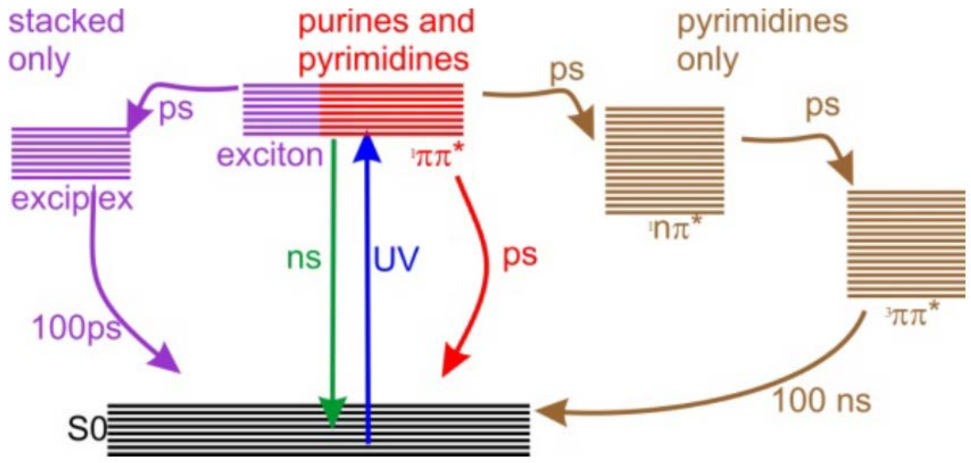
Most of the heterocyclic compounds that today are involved in replication exhibit enhanced UV photochemical stability by virtue of sub-picosecond excited state life-times. The mechanism involves rapid internal conversion through conical intersections and is exquisitely sensitive to molecular structure. This suggests the possibility of a photochemical selection of the molecular building blocks of life, as we know it, long before the advent of biological selection. It is thus conceivable that the molecular properties of nucleobases, which we study now, are relics from prebiotic chemistry that occurred 4 billion years ago.

However, additional photochemical pathways exist that compete with rapid internal conversion. Pyrimidines exhibit intersystem crossing and stacked bases can decay via exciton and exciplex formation. We explore all these processes with REMPI and IR-UV double-resonant spectroscopy in combination with *ab initio* modeling, in the nanosecond and picosecond time domains. We study the photodynamics of nucleobases, nucleobase derivatives, nucleosides, and their clusters with each other, as base pairs, and with water. From these studies an increasingly detailed picture of nucleobase excited state dynamics is now emerging.



IL-7

Femtosecond Quantum Dynamics and Laser Control of non-isolated Quantum Systems

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Laboratoire Collisions Agrégats Réactivité, IRSAMC, CNRS
Université Paul Sabatier,Toulouse, France

Optical manipulation of quantum systems by shaped laser pulses opens far reaching possibilities in many areas ranging from reactivity in chemical physics to quantum information processing. However, in most relevant cases, the quantum systems cannot be considered as isolated, and the interaction with an environment alters the dynamics and control scenario. An overview of different theoretical approaches to combine methods to propagate quantum systems subject to an environment with coherent control is presented.
In this context, two examples are given: the first is a model of Cope's isomerization of the methyl-cyclopentadienylcarboxylate dimer [1], and the second is the state-selective excitation of high-lying vibrational states of the CO stretch in hemeproteins [2].

In the first system, the isomerization reaction involves the breaking of one and the formation of another chemical bond. The modeling is based on the motion along a one-dimensional reaction path obtained by quantum chemical calculations, which is coupled to a model environment. The control is obtained by combining a non-Markovian master equation approach [2] with optimal control. As main result we find that including dissipation at the design stage is crucial for an effective control, and the underlying mechanisms on how the control field copes with the dissipation is presented [2].

The second is devoted to state-selective excitation of the CO stretch in hemeproteins, where the dynamical modeling is based on a mixed quantum/classical methodology, combined with local control theory [3]. It is shown that the excitation of selected high-lying levels can be achieved to a high degree, even for an unoriented sample and under the influence of the protein environment. Taking experimental considerations into account, we show that the thus created non-thermal distributions can be clearly measured by transient absorption. Finally, we present a novel four-wave mixing technique, which allows to directly detect vibrational coherences, a very sensitive probe of environmental influences [4].

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IL-8

Novel opportunities for studying atomic, molecular and cluster dynamics intense HHG sources

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In the last few years two novel XUV/x-ray sources have acquired an important role within atomic and molecular physics research, namely high-harmonic generation (HHG) and a new generation of free electron lasers (FELs). These two sources are of significant interest for at least two reasons. On the one hand, the short optical period of XUV/x-ray light allows the synthesis of attosecond laser pulses that can be used to study electronic processes on their natural timescale. On the other hand, the availability of very energetic photons provides opportunities for the development of novel spectroscopic techniques that are based on diffraction and/or the use of atom-specific inner shell excitation.

In my talk I will present a number of recent examples where we have exploited the opportunities offered by intense HHG sources. I will present experiments on nonlinear ionization of atoms, pump-probe spectroscopy on dilute molecular species of astrophysical interest, as well as experiments on the ionization, fragmentation and imaging of large rare gas clusters under the influence of intense XUV light pulses.

IL-9

Challenges to describe intersystem crossing dynamics

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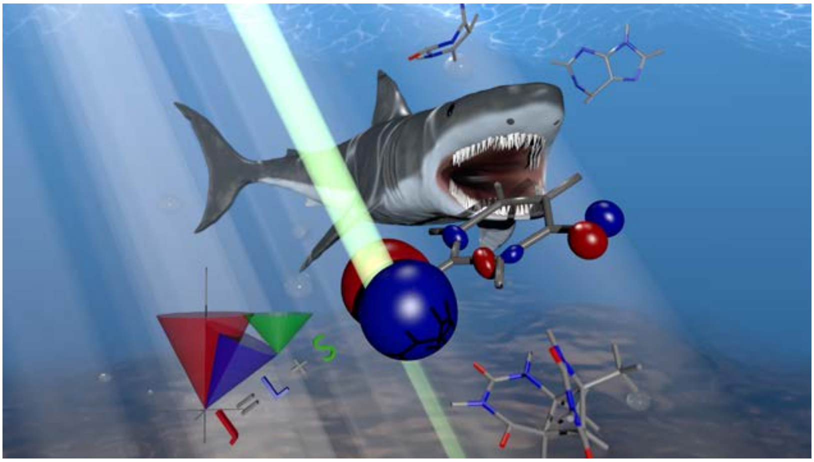
The description of electronic excited states and their dynamics is considerably more involved than that in the ground state because excited molecules possess a high density of states. Moreover, excited state potentials of same or different multiplicity can cross, breaking the Born-Oppenheimer approximation. SHARC is a generalized surface-hopping ab initio method (SHARC) [1] able to simulate ultrafast nonadiabatic molecular dynamics including both nonadiabatic couplings and spin-orbit couplings. In this talk several examples where intersystem crossing dynamics occurs in an ultrafast time scale will be presented. SHARC is currently implemented to operate with different electronic structure methods, including TD-DFT, CASSCF, MRCIS and CASPT2. How sensible are the results attending to the level of theory of the underlying on-the-fly dynamics will be also discussed.



Acknowledgments: This work has the support of the Austrian Research Fund (FWF) and the University of Vienna. The Vienna Scientific Cluster is also acknowledged for computational support.

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IL-10

Study of Collision Induced Dissociation of NO_2 Using Crossed Molecular Beam Scattering

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Collision induced dissociation of hot NO_2 is achieved by vibrationally exciting NO_2 to within a few tens of wavenumbers below its dissociation energy and then monitoring the dissociation of the NO_2 after a single collision with an Ar atom. The collision induces translational to rotation and translation to vibration energy transfer. These ro-vibraionally hot molecules then dissociate producing NO (X, J <15) state molecules and a ground state O atom. By measuring the velocity distribution of each of the NO(X, J) states produced and the dissociation branching ratio of NO_2 into each rotational state of the NO as a function of NO_2 internal energy we are able to determine the shape of the Energy Transfer Function, P(E,E') for this very vibratonally hot molecule.

The velocity of each NO J state is sensitive to energy transfer in a region equal to and above its energetic threshold. By determining the difference between the expected velocity distribution if all energies were equally populated in the NO_2^* + Ar collision and statistically distributed to the observed distribution one can determine the average energy transfer function that led to each NO rotational state. From these measurements we can piece together the shape of the energy transfer function. At low energy there is strong agreement between the theory and experiment at large energy transfer the theory over-predicts the amount of energy transfer that is observed. The experiment and differences in theory will be discussed.

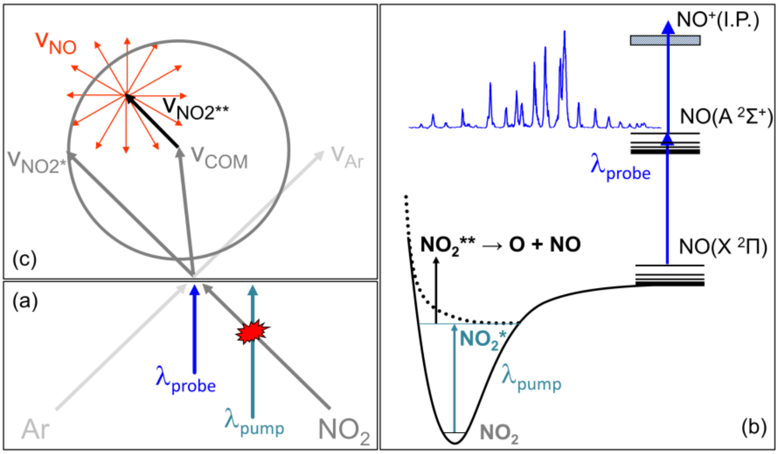

Figure 1. Schematic representation of the experiment. Panel (a) shows the spatial configuration, panel (b) shows the relative energetics, and panel (c) illustrates the key velocity components of the experiment. The Newton diagram shown in panel (c) shows the velocity components of the NO fragment as emanating from the velocity vector of the inelastically scattered NO_2^{**} molecule.

Acknowledgments: This work has the support of Department of Energy Basic Energy Sciences Gas Phase Chemical Physics program.

IL-11

Observation of scattering resonances in neutral-neutral and neutral-ion collisions

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Weizmann Institute of Science

Recent experiments with merged supersonic beams demonstrated that quantum scattering resonances can be detected in Penning ionization reactions between metastable helium and and neutral atoms and molecules at sub-Kelvin collision energies [1]. We investigated the isotope shift [2], molecular rotation effect on both shape resonances[3] and long-range forces[4]. So far the ion product energy and angular distribution information has been lost in our experiments. Here we will show that using the velocity map imaging technique we were able to detect scattering resonances at well defined energies showing strong forward-backward scattering symmetry. Resonances in He/Ar^+ collisions occur due to spin orbit coupling between different molecular ion states whereas Feschbach resonances in $He/H2^+$ collisions are traced to the coupling between vibrational and translational degrees of freedom.

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IL-12

Coupled nuclear and electronic wave packet dynamics.

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A common paradigm of femtosecond laser experiments is the generation of Franck-Condon nuclear wave packets by electronic excitation followed by their coherent evolution on one or several coupled potential energy surfaces.

Besides the generation of nuclear wave packets, the advent of ultrashort, broadband lasers with pulse durations in the attoseconds to few femtoseconds range makes it now possible to coherently excite superpositions of two or more electronic states. The electronic and nuclear dynamics initiated by the laser pulse become now intermingled in a more complex manner as compared to the dynamics started in a single electronic state.

In this contribution we discuss several examples in which the coupled evolution of the nuclear and electronic degrees of freedom strongly influences the time evolution of the system [1,2,3] and especially its electronic coherence properties [4]. Finally we provide an outlook of the other side of the coin, namely how and under what conditions electronic coherence can affect the evolution of nuclear degrees of freedom of a molecular system and to what extent some degree of control can be achieved based on those effects.

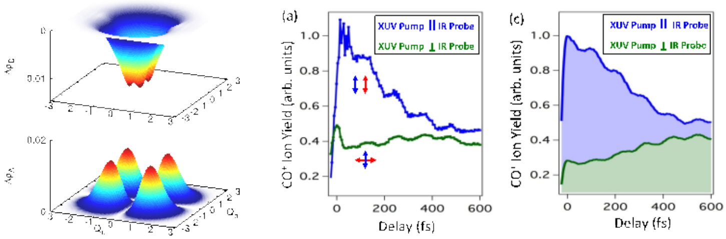

Figure: Signatures of hole wave packet dynamics coupled to nuclear vibrations in the CO_2^+ cation upon sudden ionization. Nuclear wave packet evolution (left), experimental signal (center) and calculated signal (right).

Acknowledgments: This work has the support of The Hamburg Centre for Ultrafast Imaging (CUI).

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IL-13

Laser-induced alignment of molecules in He-nanodroplets: Revivals, long-time coherence and breaking-loose

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High resolution infrared and microwave spectra of molecules dissolved in liquid helium nanodroplets display discrete rotational structure – a unique feature explained as the result of frictionless rotation of molecules adiabatically followed by a local solvation shell of He atoms [1].

The frictionless behavior did, however, not manifest itself in recent time-resolved experiments, based on femtosecond laser-induced molecular alignment techniques. In particular, the transient recurrences of alignment characteristic of freely rotating gas phase molecules was absent and the rotational dynamics was much slower than that expected from spectroscopy [2,3].

In this talk we present new experiments on femtosecond laser-induced alignment of iodine molecules embedded in helium nanodroplets showing striking new phenomena:

1) At low to moderate fluences the alignment pulse sets the molecule and a non-superfluid fraction of the He droplet into coherent motion. The coherence, although decaying, persists for many hundreds of picoseconds – long enough to allow the composite molecule-He-shell system to exhibit rotational revivals.

2) At larger fluences of the alignment pulse the molecule is accelerated to such large angular velocities that the binding to the surrounding He atoms in the droplet is broken due to the centrifugal force. Hereafter, the molecule rotates essentially freely for a few ps until the interaction with He atoms sets in again and slows the molecule down.

Our experimental observations are rationalized by classical and two-body time-dependent quantum simulations.

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IL-14

Ab-initio-assisted modelling of the soft, ^{4}He droplet-mediated, deposition of metallic nanoparticles

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The ultra-cold ^{4}He droplet-assisted synthesis and soft-landing deposition of metallic nanoparticles attracts nowadays strong attention [1-6] due to both the exciting fundamental physics behind, including quantum vorticity in superfluid ^{4}He droplets, and to the applications of the deposited metallic and bimetallic core-shell nanoparticles and nanowires. This talk is aimed to present theory, modelling and simulation to deal with these molecular processes at the interphase with quantum fluid droplets and solid surfaces of different nature [6-11]. The focus will be in a recently developed ab-initio scheme to describe He/surface, He/metal, and metal/surface dispersion-dominated interactions, and the upscaling of the simulations to large metallic nanoparticles.

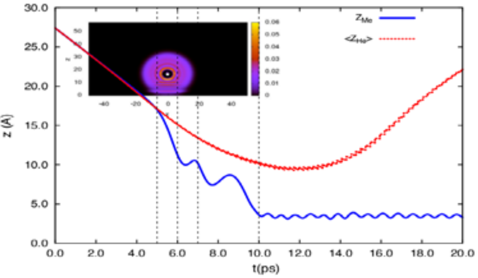

Figure : showing the soft-landing of one metallic atom inside one ^{4}He droplet: temporal evolution of the ^{4}He-surface (red line) and metal-surface (blue line) distance [8]

Acknowledgments: This work was supported by the COST Action “Molecules in Motion” (CM1405).

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IL-15

Wave-packet approach to two-dimensional vibronic spectroscopy

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Photon echo experiments use the interaction of three time-delayed laser pulses to induce a time-dependent polarization in a sample which then leads to the emission of radiation in a selected direction. Detecting a signal as a function of two times yields, upon Fourier-transformation, a two-dimensional (2D) spectrum. Such spectra are usually calculated using density-matrix theory. We present an approach which is based on wave functions. Treating first gas-phase molecules, we provide several examples which illustrate the nature of 2D vibronic spectroscopy and the reflection of coherences in the spectra [1-3]. Regarding molecules in an environment we then outline how the wave-function treatment can, under certain assumptions, be extended to situations where system-bath coupling cannot be ignored [4].

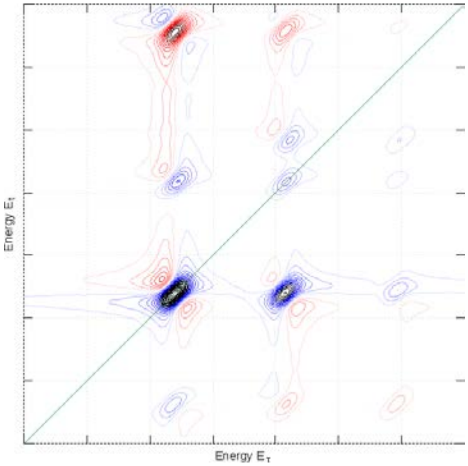

Figure 1: Real part of a 2D spectrum. The single peaks correspond to different vibronic transitions.

Acknowledgments: This work has the support of the German Science Foundation (DFG – FOR 1809).

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ORAL PRESENTATIONS

MOLEC 2016

XXI European Conference on the Dynamics of Molecular Systems

OP-1

Ultrafast molecular three-electron collective Auger decay

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A new class of many-electron Auger transitions, illustrated in Fig. 1, was initially proposed over 40 years ago for atoms [1,2], but the first tentative evidence for its real existence was only adduced by Lee *et al.*[3] in 1993 on the basis of the resonant Auger spectrum of Kr. Using a multi-electron coincidence technique with synchrotron radiation, we unambiguously showed [4] that the transition suggested by Ref. [3] really does take place, but with a rather small branching ratio. Related inter-atomic three-electron transitions in rare gas clusters were recently predicted by some of us [5] and shown by Ouchi *et al.* [6]. From consideration of the energy levels involved it seems that the basic three-electron process could occur in molecules too, wherever a double inner-valence shell vacancy lies at a higher energy than the molecular triple ionisation onset. Multi-electron coincidence experiments on CH_3F [7] reveal for the first time the existence of this new decay pathway there, and calculations show that despite its three-electron nature, its effective oscillator strength is surprisingly orders of magnitudes higher than in atoms, allowing an efficient competition with both molecular dissociation and two-electron decay channels on the ultrafast time scale. The dramatic enhancement of this *molecular* three-electron Auger transition can be explained by a partial breakdown of the molecular orbital picture of ionisation [8]. We predict that the collective decay pathway will be significant in a wide variety of molecules ionised by extreme UV and soft X-rays, particularly at Free-Electron-Lasers where double inner-shell vacancies can be created efficiently by two-photon transitions.

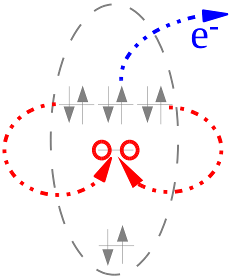

Figure1: Illustration of intra-atomic collective decay of a double inner-shell vacancy. Two valence electrons recombine into the empty orbital producing enough energy for a third electron to be ejected.

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OP-2

Translation-rotation dynamics of confined molecules using an efficient Smolyak Sparse-grid Scheme

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The quantum dynamics studies of molecular bound states are actually limited by the well known dimensionality problem. Indeed even for molecules of medium size, usual quadrature techniques have already reached their limit since a multidimensional direct-product grid can be very large. An alternative to avoid the direct-product grid is to use the Smolyak sparse-grid techniques, recently investigated by Avila and Carrington [1] for the calculation of vibrational bound states of semi-rigid molecules. Lauvergnat and Nauts [2] have proposed a new implementation of such sparse grid for the study of the torsionnal levels of methanol in full dimensionality (12D). The efficiency of this kind of grid is related to the replacement of a single large direct-product grid by a sum of small direct-product grids. We will present a recent adaptation of this kind of sparse grid for the calculation of large amplitude motion of confined molecule. In particular, we are able to use a combination of 2D-grids associated to spherical harmonic basis functions and the usual 1D-gaussian quadrature grids to form the Smolyak sparse-grid.

Preliminary results for the translation-rotation levels of $(H_2O)_{20}H_2$ (hydrogen water clathrates) in a rigid or partially flexible water clathrate cage will be presented. This system has been investigated both experimentally [3] and theoretically [4, 5] as water cages are able to store efficiently molecular hydrogen clusters in various experimental conditions or other molecules in planetary atmospheres [6, 7].

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OP-3

Spin-Vibronic Excited-State Quantum Dynamics in Transition Metal Complexes

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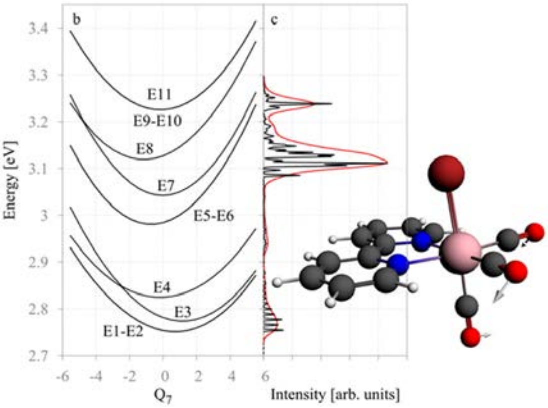
Non-radiative relaxation processes of electronically excited states are mediated by vibronic and spin-orbit coupling, depending on spin and spatial symmetry. While the former is known to lead to ultrafast relaxation (fs – ps) since many years, the latter has been recognized more recently to be able to act on the same time scale. Spin-orbit coupling may play an important role in organic compounds, but its impact become crucial in most transition metal complexes.

In order to study the excited-state quantum dynamics in such cases, we propose a model Hamiltonian comprising both spin-orbit and vibronic coupling [1]. The parameters are extracted from electronic structure calculations [2].

Applications on Rhenium α–diimine carbonyl complexes $[Re(L)(CO)_3(N,N)]^+$ are shown [3]. For Halide ligands (L = Cl, Br, I), an unexpected behavior has been experimentally observed [4]: despite a larger spin-orbit coupling constant with increasing mass of the Halide, the relaxation time increases. Our model is able to reproduce this trend, allowing use to shed new light on the ultrafast relaxation processes in this class of compounds.



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OP-4

Control by frequency chirped laser-induced conical intersections

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Controlling molecular dynamical processes is often in the focus in physics, chemistry and biology as it opens up the possibility of guided manipulation of the nuclear wave packet.

Recently we have investigated the photodissociation dynamics of the D2+ molecular ion in the presence of linearly varying frequency chirped laser pulses [1,2]. As a completion of our former work [1] a comprehensive dependence on the pulse duration and delay time is presented in terms of total dissociation probabilities.

Our numerical analysis carried out in the recently introduced light-induced conical intersection (LICI) framework [3]. Controlling via LICI is possible as the energetic position of the LICI itself can be controlled by the laser frequency and the strength of its non-adiabatic coupling by the laser intensity. Obtained results clearly show the effects of the changing position of the LICI which is induced by the frequency modulation of the chirped laser pulses. This impact is presented for positively, negatively and zero chirped short pulses.

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OP-5

Ultrafast excited state dynamics of size selected neutral molecular clusters

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Time domain studies on size controlled non-covalently bonded molecular aggregates permit to explore the photophysical/photochemical properties of the targeted molecules, under the influence of specific molecule-molecule interactions.[1, 2] In order to gain meaningful dynamical information on the processes these neutral species undergo after electronic excitation, experimental methods able to relate the recorded observables to specific size clusters are required. Herein we introduce a methodology that permits to disentangle the transient signal belonging to a particular size cluster, from the overall dynamics recorded in the ion mass channels, by associating it to a characteristic IR absorption of the targeted complex. The approach has been successfully applied to track the ultrafast electronic relaxation of different molecular complexes, containing aromatic chromophores of the form (solute)$_n$ and solute(H_2O)$_n$. The contribution will discuss some of the most relevant results obtained.

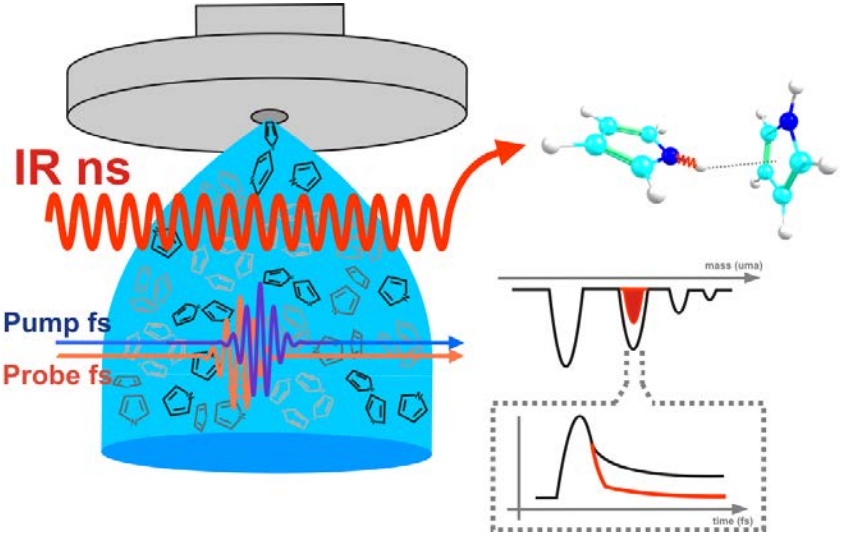

Figure: Schematic representation of the IR tagged time resolved ionization method.

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OP-6

Dynamics of the $S(^1D)$+*o*-D_2 → SD+D reaction at low collision energies: revisiting the SH2 system

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Reactive and elastic cross-sections, and rate coefficients, have been calculated for the $S(^1D)+D_2(j=0)$ [1] reaction using a modified hyperspherical quantum reactive scattering method [2]. The considered collision energy ranges from the ultracold regime, where only one partial wave is open, up to the Langevin regime, where many of them contribute. Very recently, excitation functions for the system have been measured in the near cold regime using the angle-variable crossed molecular beam technique [1]. This experiment completes the set of measurements performed in Bordeaux on the isotopic variants of the SH2 reactive system. The study, which reached unprecedented low temperatures, began in 2010 [3]. Although less resolved than the isotopologue reactions with H_2 or HD, some undulations are still visible in the medium energy domain of the title reaction. An overall good agreement is found between the experimental data and the theoretical calculations performed with different methods: quantum mechanics, semi-classical mean potential capture theory (sc-MPCT) and quasi-classical trajectory (QCT) methodology. We will show the results of extending the quantum calculations down to energies in the cold and ultracold domains. The complex scattering length will be discussed in terms of the recently published quantum defect theory by Idziaszek and coworkers [4, 5], providing some insight in the behavior of the system. Finally, the consideration of state-to-state reaction probabilities will allow the discussion of the statistical behavior of the system in the ultracold regime.

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OP-7

Bound states and inelastic scattering of $^{3}\Sigma_u^+$ Rb_2 - He

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We propose a numerical approach to solve the time-independent close-coupled Schrödinger equation based on a high-order finite element method. Our approach gives a unified description of scattering and bound state problems. The use of high-order finite element method to represent the radial functions results in a sparse Hamiltonian matrix that can be handled using state of the art sparse matrix algebra packages (PARDISO [1] , FEAST [2]).

We apply this scheme to quantum-scattering calculations of ^{4}He and ^{3}He colliding with Rb_2 with special emphasis on low-temperature dynamics [3,4]. For both isotopes, we found that the *J=1* partial wave has a strong effect on elastic and inelastic rate coefficients. In particular, a strong resonance feature of the *J=1* partial wave is responsible for an extremely efficient vibrational relaxation process. The bound states of $Rb_2{}^4$He and $Rb_2{}^3$He are determined and analyzed using the expansion of the corresponding eigenfunctions on the ro-vibrational channels. Fine details of the wave-function in full dimension can be easily accessed (see figure).

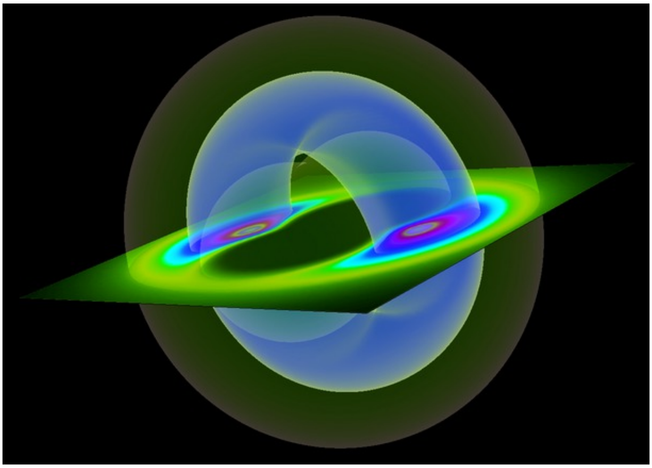

Figure: isodensity surfaces of the J=0 eigenfunction for $Rb_2{}^4$He . The volume defined by the blue-green (light-green) isosurface contains 30% (70%) of the probability to find helium. A cut of the Rb_2 He potential energy surface is also given.

Acknowledgments: This work has the support of the ANR via the COLORI contract.

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OP-8

Ultrafast population inversion by parallel transfer

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Parallel Transfer (PT) is a novel control scheme that allows ultrafast population inversion between two arbitrary states with underlying structure [1]. It is based on engineering the initial wave function before the photonic process, as opposed to shaping the laser pulse. Applied to electronic transitions in molecules, this amounts to setting the right vibrational coherences in advance, to allow multi-pathway constructive interference and minimize Stark decoupling. The outcome is full population inversion with minimal energy. The algorithm to optimize the initial state is called geometrical optimization [2]. It is a variational procedure that maximizes transition probabilities, rendering (nonlinear) eigenvalue equations. It can be applied to all sort of molecular processes triggered by light, accelerating the process or maximizing the yield of e.g. nonlinear spectroscopic signals, photoassociation, photodissociation and isomerization reactions. In this work we will concentrate on two-photon processes mediated by a sequence of two strong ultrashort pulses [3].

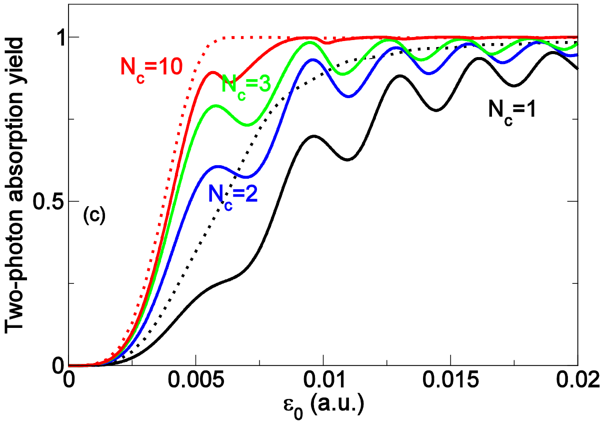

Figure 1: Two-photon absorption in the B band of Na_2 using two 40-fs (fwhm) pulses time-delayed by 20 fs in counter-intuitive order, as a function of the peak amplitude ε_0 and the initially prepared superposition state. N_c is the number of vibrational levels in the superposition. Solid lines show results when the pulses are tuned to the red of the A band, while dotted lines are for the blue-detuned (APLIP) case.

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OP-9

Quasi-exact solvability and supersymmetry in molecular quantum mechanics: From pendular to tunneling states

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Controlling the rotational degrees of freedom of molecules by external fields is of key importance for frontiers research areas such as molecular imaging or molecular reaction dynamics. For the case of pure first-order (orienting) or pure second-order (aligning) interaction, the corresponding pendular states of diatomic molecules can be expressed in terms of linear combinations of Mathieu functions (planar case) or spherical harmonics (spherical case) for which no closed-form expressions exist. However, the combined orienting and aligning interaction (arising, e. g., for permanent and induced electric dipole interactions of polar and polarizable molecules with collinear electric fields) leads to conditionally exactly solvable (CES) and quasi-exactly solvable (QES) Schrödinger equations. For a limited number of states (QES), analytic solutions can be found if permanent and induced dipole interaction parameters obey specific relations (CES) [1,2,3]. By virtue of an anti-isospectral transform, related analytic wavefunctions can also be obtained for the symmetric double well potential of Ref. 4, which can be used as a model for tunnelling in molecular physics. Using the apparatus of supersymmetric quantum mechanics and N-fold Darboux transforms, additional analytic solutions can be constructed for other pendular as well as for triple well Hamiltonians.

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OP-10

Non-adiabatic molecular dynamics simulations of photochemical isoprene oxidation intermediates

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Isoprene is amongst the most abundant volatile organic hydrocarbon compounds in the atmosphere, with annual biogenic emissions that are comparable to methane. Nevertheless, our understanding of its atmospheric oxidation sequence is not yet complete. [1] Assorted pieces of indirect evidence suggest that intermediates produced during isoprene oxidation produce OH via an as yet undetermined photochemical mechanism. [2] In this talk, I will describe new work designed to investigate the photochemical molecular dynamics (MD) of both C5-hydroperoxy-aldehyde (C5-HPALD) and C6-HPALD (a relative of C5-HPALD which has been synthesized and measured in the laboratory). [3] C5-HPALDs are isoprene oxidation intermediates which have been hypothesized to photolytically produce OH. Using a range of excited state quantum chemistry methods, we have characterized the excited electronic states of both C5 and C6 HPALD, and calculated their corresponding excited state absorption cross sections. Our results quantitatively reproduce experimentally measured photolysis rate coefficients for C6-HPALD. [3] For both C5 and C6 HPALDs, a weak S_1 $n \rightarrow \pi^*$ absorption feature is largely responsible for the photolysis rate coefficient observed under ambient atmospheric conditions. Exploiting a fast GPU-accelerated TDDFT framework, we ran semi-classical non-adiabatic MD simulations initialized in the C5 HPALD S_1 state. The results indicate two competing mechanisms which are responsible for picosecond-timescale population transfer out of the S_1 state: (1) internal conversion via avoided crossing to an S_2 state with σ^* character, and (2) intersystem crossing to a low-lying triplet state with σ^* character. Both of these states appear to lead to fast bond dissociation and OH production. In order to understand how the *in vacuo* MD kinetics map onto atmospheric temperatures and pressures, we have used the MESMER non-equilibrium statistical mechanics package to construct an energy-grained master equation of C5-HPALD using a non-adiabatic variant of microcanonical transition state theory (TST). The non-adiabatic master equation framework allows us to investigate the photochemical kinetics of C5-HPALD photochemistry under typical atmospheric temperatures and pressures, and provides direct evidence for OH production in near unity quantum yield.

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OP-11

Theoretical investigations on doped rare gas clusters with neutral or ionic atomic and diatomic impurities

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Helium clusters formed with up to N ~ 70 atoms doped with an impurity X have been studied by means of Monte Carlo (MC) simulations and classical optimization algorithms [1]. The dopants under consideration are neutral atoms (Ca) [2,3] and diatoms (Rb_2) [4-7], and anionic species He^{*-} and He_2^{*-}[8]. Energetics and structure of the corresponding He_N-X systems has been analyzed for different temperature ranges with a path integral MC (PIMC) approach. A variety of interaction potentials have been employed and the effect of their strength was studied in detail. Special emphasis is made on general issues such as the position of the impurity with respect to the helium cluster and the role of its internal degrees of freedom such as rotation.

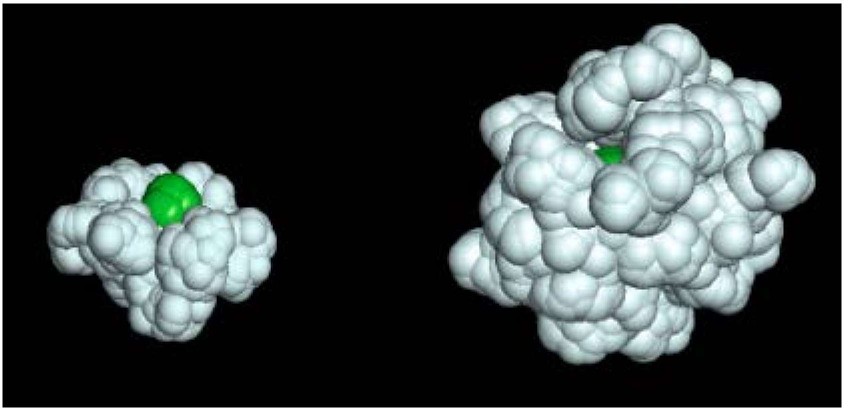

Figure: Snapshots from PIMC calculations for HeN-Ca, N=10 (left) and 40 (right), at T=1 K using the Kleinekathöfer He-Ca potential, *Chem. Phys. Lett*. 324, 403 (2000).

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OP-12

Excited state dynamics in carbon nanorings

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Cycloparaphenylenes ([nCPP] (n=9-16)) and related nanohoops represent the smallest possible fragments of armchair carbon nanotubes.Due to their cyclic and curved conjugation, these nanohoops own unique photophysical properties[1]. Herein, the internal conversion processes of cycloparaphenylenes of sizes 9 through 16 are simulated using Non-Adiabatic Excited States Molecular Dynamics[2] at both low temperature (10K) and room temperature (300K). The photoexcitation and subsequent electronic energy relaxation and redistribution lead to different structural and dynamics changes such as planarization of the chain, electron-phonon couplings, localization, and intra-ring migration of exciton. A quantitative analysis of the exciton self-trapping is reported. Our simulations reveal fluctuations in the localization/delocalization of the exciton once it reaches the lowest S_1 excited state.

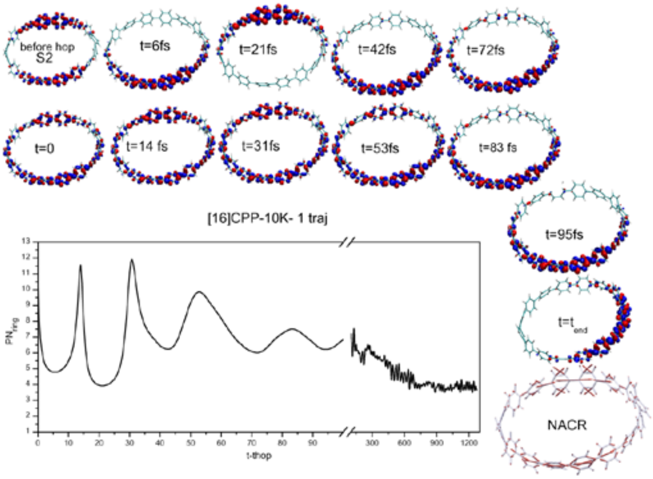

Figure: Exciton intra-ring migration on S_1 state as a function of delay time for a typical NA-ESMD simulation of [16]CPP at 10K. The nonadiabatic coupling vector(NACR) at the moment of non-adiabatic $S_2 \rightarrow S_1$ transition is also shown.

After that, a randomized intra-ring migration involving most of phenyl rings is observed. The exciton localization is not merely a static contraction of the electronic wavefunction. These results can be connected to unpolarized emission observed in single-molecule fluorescence experiments.

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OP-13

Investigating the mechanism of vibrationally controllable electron transfer using Density Functional Theory

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Recent experiments have shown that excited state electron transfer (ET) can be influenced by the excitation of specific vibrational modes in solid state[1] and solution phase[2,3]. This phenomenon, dubbed "IR control", provides a pathway to controllable ET: a long standing aim in chemistry. Understanding the mechanisms by which these effects occur is a vital part of achieving this goal.
Whilst previous work has focused on chemically asymmetrical Donor-Bridge-Acceptor systems, recently we have exploited selective isotopic labeling to construct a D-B-A-B-D Platinum(II) *cis*-acetylide complex that is chemically symmetrical but has spectroscopically distinct ET pathways[4].

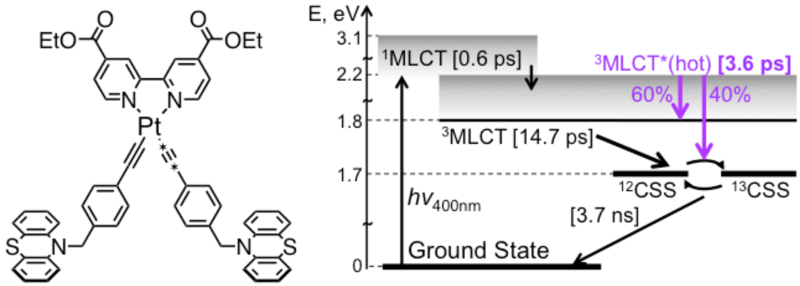

Figure 1: Pt(II) complex investigated and summary of experimentally determined electron transfer dynamics. (✶ = ^{13}C)

We use Density Functional Theory (DFT) and Time-Dependent DFT (TD-DFT) to develop a simple model to explain the observed IR control behavior in the compound (Figure 1).

Acknowledgments: We thank the EPSRC and the University of Sheffield for funding, and the STFC for access to facilities.

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OP-14

Phonon dynamics of graphene on metals

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The study of surface phonon dispersion curves is motivated by the quest for a detailed understanding of the forces between the atoms at the surface and in the bulk. In the case of graphene (Gr), additional motivation comes from the fact that thermal conductivity is dominated by contributions from acoustic phonons, while optical phonon properties are essential to understand Raman spectra. The system formed by Gr on metal surfaces provides a good example of how small changes in the strength of the Gr-substrate interaction modify the corresponding phonon dispersion curves. Thus, phonon spectra may provide valuable information on the bonding of Gr with the substrate as well as on the electron–phonon coupling [1].

We review recent progress made in the experimental determination of phonon dispersion curves of Gr grown on several single-crystal metal surfaces [1]. The two main experimental techniques usually employed are high-resolution electron energy loss spectroscopy (HREELS) and inelastic helium atom scattering (HAS) [2]. The different dispersion branches provide a detailed insight into the Gr-substrate interaction. Softening of optical modes and signatures of the substrate′s Rayleigh wave are observed for strong Gr-substrate interactions, like on Gr/Ni(111) and Gr/Ru(0001) [3-5], while acoustic phonon modes resemble those of free-standing Gr for weakly interacting systems like Gr/Cu(111) [6]. The later allows determining the bending rigidity and the Gr-substrate coupling strength, a piece of information difficult to get with other experimental techniques.

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OP-15

Reactivity of Fatty Acid Methyl Esters with OH Produced by a Plasma Jet

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Lipid oxidation is an important research field in biology, combustion, and atmospheric chemistry. Radical-initiated oxidation processes can be investigated by using atmospheric-pressure plasma jets, which allow generating reactive oxygen species (ROS), such as OH, O, O_3 and $O_2(a^1\Delta_g)$. In our experiment, the jet plume impinges over the surface of a liquid target, composed of fatty acid methyl esters (FAME). We choose this class of compounds as a simplified model of cellular membrane constituents. As shown by model calculations, OH is the most abundant species in He-H_2O plasmas, while other ROS are lower by a factor of 2-3 [1]. The addition of O_2 greatly enhances the production of O, O_3, and $O_2(a^1\Delta_g)$ [2]. Thus, we can select two extreme relative ROS concentrations: (a) OH about two times larger than that of the other ROS; (b) O, O_3 and $O_2(a_1\Delta_g)$ concentration more than one order of magnitude larger than OH. The treatment of fatty acids in the two conditions results into strikingly different products In the first case, the main result is the reduction (hydrogenation) of FAME and the formation of dimeric species. In the second condition, we observed the presence of several oxidized products. The appearance of these species is typical of lipid autoxidation [3]. We carried out LIF measurements [4] over the surface of the target in order to assess a correlation between the OH flux and the FAME reactivity. In addition, methyl oleate and methyl linoleate have been used as models of the FAME in some DFT calculations. The reactions considered have been limited to H, OH, and $^3O_2$, and several possible combinations have been considered.

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OP-16

Probing Molecular Collisions by Raman Spectroscopy

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Molecular collisions are involved in a number of phenomena in gases: inelastic collisions are responsible for the transport properties and the thermal relaxation in gases, and contribute to the broadening of spectral lines; in turn, cohesive collisions give rise to the formation of molecular clusters. These collisions play an important role in the out-of-equilibrium environment of supersonic gas jets [1], and can be successfully probed by quantitative high-performance Raman spectroscopy with high space (few microns) and time resolution [2].

The experimental setup and methodology developed in our laboratory will be described, and some recent results on inelastic collisions of H_2O [3,4] and O_2 with He, and of clustering of ortho-D_2 [5] will be shown. Rotational populations and number densities, both of isolated molecules or clusters, can be measured along the jet axis with time resolution of nanoseconds. Rotation-translation energy transfer by inelastic collisions can be tracked by means of the time evolution of the rotational populations, and interpreted by using a Master Equation in terms of the state-to-state rate coefficients [3]. The formation of small clusters and their structure can also be tracked with high temporal resolution from the very beginning of condensation (the dimer) [5].

Acknowledgments: This work has been supported by the Spanish Ministerio de Economía y Competitividad (MINECO), grants FIS2013-48275-C2 and CONSOLIDER-ASTROMOL CSD2009-0038.

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POSTERS

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P-1

Environmentally relevant ion-molecule processes: Non-adiabatic collisions in ground state N_2O and CO molecules with Na^+ and Li^+ in the 0,10-5,00 keV energy range

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N_2O and CO gases produced at the tropospheric level from many sources can drift to the ionosphere where they can collide with high-energy alkali ions coming from meteoric ash [1]. These collisions can lead to charge transfer reactions producing excited alkali atoms and also eventually excited molecular ions. Using crossed beams techniques, the $Na^+(^1S) + N_2O(X\ ^1\Sigma^+)$ and $Li^+(^1S) + CO(X\ ^1\Sigma^+)$ systems have been studied in the 0,10-5,00 keV energy range, a series of exit channels having been characterized by analyzing and measuring fluorescent emissions from the excited species formed, and the corresponding excitation functions of the exit channels have been determined. In order to obtain information on the manifold of potential energy surfaces (PESs) involved in these experimental non-adiabatic processes, a complete active space interaction configuration (CSASCI) study has been performed by using restricted Hartree-Fock electronic structure calculations. The active space was build up considering 6 molecular orbitals and 6 active electrons. CASCI (6 m.o., 6 e^-) calculations were made for different ion-molecule orientations. A qualitative interpretation of the experimental data from calculated PESs and simple dynamical models is given.

Acknowledgments: This work has the support of the MINECO Project CTQ2013-41307-P), the AGAUR Project 2013SGR25 and the CESUC-FCR supercomputing time.

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P-2

Radio Frequency Guided Ion Beams (RF-GIB) study of ion-molecule reactions having environmental, astrochemical and prebiotical relevance at the few eV energy range

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Ion-molecule reaction kinetics, both in solution and in gas phase, have always been a "hot topic", this interest having recently experienced a renewal due to their application to the study of biological systems and since many ionized molecules of capital astrochemical importance have been detected spectroscopically in the interstellar medium. It is thought that gas-phase *ion-molecule reactions* can lead to complex, biologically-relevant, organic *molecules* leading to prebiotic systems [1]. Using a RF-GIB setup (developed by us in collaboration with the Atomic & Molecular Physics group at Trento University), we have studied some of these processes in the past few years [2]. A newly-designed electron bombardment ion source has allowed us to produce a series of atomic and molecular ions that, after characterization, have been made to collide with neutral molecules under single collision conditions, giving many different products. In order to characterize as much as possible the interactions between the colliding reactants, ab initio quantum chemistry studies complement the experiments by allowing at least a qualitatively interpretation to be made of the reaction dynamics in terms of the potential energy surface features. Detailed information on different reactive collision systems (Ar^+, N_2^+, H_2, C_2H_4, N_2O…) will be given at the meeting.

Acknowledgments: This work has the support of the MINECO Project CTQ2013-41307-P), the AGAUR Project 2013SGR25 and the CESUC-FCR supercomputing time.

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P-3

Theoretical study of oxides of pure and mixed dimers of transition metal atoms

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We study the atomic, electronic, and magnetic structure of neutral and charged complexes, $XY_m^{0/\pm}$, formed by two transition atoms (X,Y= Fe, Co, Ni) and up to m=6 oxygen atoms, by means of DFT/GGA first principles calculations. The effect of hybridization between the electronic states of X≠Y complexes, compared to the cases with X=Y, on the electronic properties is studied, as well as the evolution with the oxygen coverage. In particular, the magnetic moments of the X≠Y neutral complexes results to be enhanced with respect to the X=Y cases, and remain nearly constant when the oxygen coverage increases. The role of the charge transfer between X and Y atoms is important for the properties of charged complexes. The binding energy per atom saturates at m=4 oxygen atoms for neutral and charged complexes, and at m<4 for the mixed transition dimer complexes. For m>4, the binding of additional oxygen atoms is very week.

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R.H.A-T acknowledges the financial support provided by the University of Valladolid for the participation in this conference and a fellowship from CONACyT (Mexico, scholarship 415121).

P-4

Adiabatic and non-adiabatic electron-nuclear motion: quantum and classical dynamics

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Using a model for coupled electronic-nuclear motion [1] we investigate the range from negligible to strong non-adiabatic coupling. In the adiabatic case, the quantum dynamics proceeds in a single electronic state, whereas for strong coupling a complete transition between two adiabatic electronic states takes place. It is shown that in all coupling regimes the short-time wave-packet dynamics can be described using ensembles of classical trajectories in the phase space spanned by electronic and nuclear degrees of freedom. We thus provide an example which documents that the quantum concept of non-adiabatic transitions is not necessarily needed if electronic and nuclear motion is treated on the same footing [2].

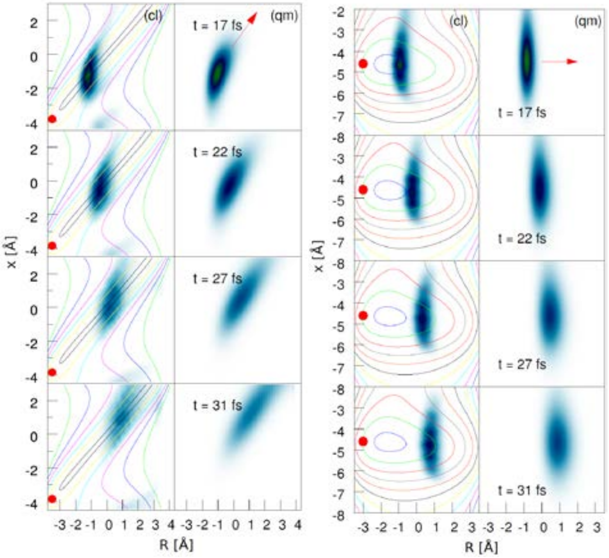

Figure 1: Adiabatc (left) and non-adiabatic (right) wave-packet motion along the electronic (x) and nuclear coordinate (R). Compared are classical (cl) and quantum mechanical (qm) densities.

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P-5

Dependence of elution order on the valine enantiomer configuration in the molecular dynamics simulation of their separation by β-cyclodextrin

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Cyclodextrins (CDs) are macrocyclic molecules composed of glucose units (7 for β–CD) forming truncated cone-shaped compounds [1]. Amino acids are biologically important organic compounds whose physicochemical properties are extensively studied in order to better understand proteins [2]. In molecular dynamics (MD), the movements of particles during the simulation time (trajectories) are determined by solving their classical equations of motion [3, 4]. These are differential equations whose solutions depend on the initial conditions of variables. Among the starting values, velocities are the same for both enantiomers but the initial atomic positions of L- and D-amino acids in each trajectory never can be the same because they are mirror images. It is convenient to reduce the number of factors that artificially cause differences in the simulation of each enantiomer, other than its interaction with β–CD. Different methods to select the initial configurations of valine enantiomers are proposed in this work, and their influence on the interaction energy, elution order and capacity of forming inclusion complexes is studied. The energy values obtained in the simulation differ from one method to another, although this difference is not big enough to modify the elution order. The capacity of forming inclusion complexes is hardly affected and the guest tends to locate in the same areas of β–CD but with different orientations according to initial configuration.

Acknowledgments: We are grateful to the Ministerio de Economía y Competitividad (FIS2013-41532-P) for their generous financial support.

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P-6

Single photon K-shell double ionization

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Single photon multiple ionization of atoms and molecules in which a single photon ejects several electrons is a weak but fundamental process relying on electron correlation. It is only in the last five years that it became possible to detect double photoionization in the deeper inner-shell orbitals. We studied in details double ionization in the K-shell, using synchrotron radiation and a magnetic bottle time-of-flight electron spectrometer.

Two possibilities arise in molecules: either the two electrons are ejected from the same K shell of a given atom in the molecule (1-site Double Core Holes (DCH) or K^{-2}) or they originate from two different K-shells, that is from two different atoms in the molecule (2-site DCH or $K^{-1}K^{-1}$). It is the multi-electron coincidence technique, which made possible the experimental observation of these weak cross section processes. [1] K^{-2} double ionization is typically 10^{-3} compared to the single ionization K^{-1}, while the weaker $K^{-1}K^{-1}$ double ionization drops to a typical 10^{-5} value.

The most recent development is the study of the closely related process in which a single photon simultaneously ionizes a K-shell electron and excites another one (noted $K^{-2}V$). [2] We will present several studies for this process as for example CO_2 molecule [3].

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P-7

Dynamic Stark control of ammonia photodissociation with strong femtosecond laser pulses

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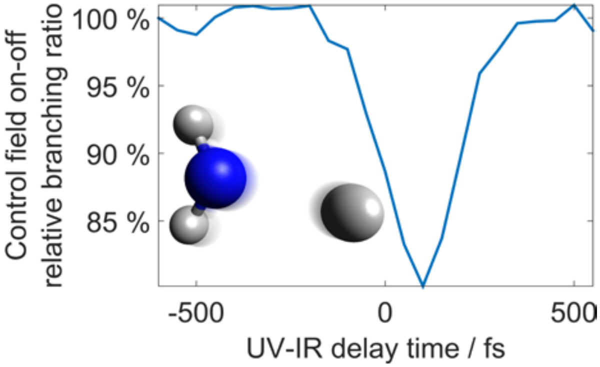
Chemical reactivity is known to be substantially altered by strong laser fields (tens of TW/cm^2). In 2006, Stolow and coworkers, using the non-resonant dynamic Stark effect (NRDS), showed that it is possible to modify the Br($^2P_{3/2}$)/Br*($^2P_{1/2}$) product branching ratio in the photodissociation of IBr [1]. Control was achieved because the non-perturbative electrical field distorts the potential energy curves in the region of the conical intersection between the two excited electronic states involved in the photodissociation process. In our group, we have recently been able to extend the strong laser field control to the photodissociation of a polyatomic molecule. Specifically, we have used strong IR laser pulses to modify the I($^2P_{3/2}$)/I*($^2P_{1/2}$) branching ratio in the CH_3I photodissociation, as well as the kinetic energy that the fragments acquire in the process [2]. In this case, the effect is caused by the generation of a light induced conical intersection (LICI) between the ground and the excited surface where the reaction takes place. The present work will show recent advances we have made in the strong laser field control of the photodissociation of ammonia (NH_3). We have tracked the photodissociation of NH_3, from the 2_0^4 vibronic level at 201 nm, which yields NH_2 in the ground X (non-adiabatic) and the first electronically excited A (adiabatic) states of the NH_2 fragment in correlation with H atoms, under the effect of strong IR femtosecond laser pulses. Employing velocity map imaging (VMI) and resonance enhanced multiphoton ionization (REMPI), we have measured kinetic energy release distributions of the H-atom. A reduction of the $NH_2(A)/NH_2(X)$ branching ratio is observed when the control IR laser pulse arrives around 100 fs after the UV pulse that triggers the reaction, which suggests the effect occurs mainly in the region of the conical intersection and it is attributed to a NRDS effect in agreement with the theoretical work by Worth *et al.* [3].



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P-8

A velocity-map imaging study of the non-resonant multiphoton ionization detection of methyl photofragments from the photodissociation of CH_3I in the *A*-band

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The development of the velocity map imaging (VMI) technique [1] in combination with pump-probe schemes has permitted an important advance for the study of the dynamics of chemical reactions. The widespread use of resonance enhanced multiphoton ionization (REMPI) has allowed the efficient detection of ro-vibrationally state-selected photofragments. On the contrary, non-resonant multiphoton ionization (NRMPI) detection is scarce because of its much lower efficiency. In such case, however, ionization of every quantum state of the photofragments could provide final quantum state distributions of the products in the same way as in the case of one-photon VUV ionization "universal" detection [2,3].

The main goal of this work is to study the sensitivity of the NRMPI to a fragment vibrational distribution arising from a molecular photodissociation process. We revisit the well known photodissociation of methyl iodide in the *A*-band at about 280 nm using the VMI technique in conjunction with non-resonant MPI of the methyl fragment [4]. The detection wavelength, carefully selected to avoid any REMPI transition, was scanned between 325 and 335 nm in order to look for evidences of a direct effect in the distribution of vibrational states detected (i.e. the translational energy distribution) as well as in the angular distributions of the observed channels. The experimental results have been compared with quantum dynamics calculations carried out on available *ab initio* potential energy surfaces using three- and four-dimensional models [5].

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P-9

A velocity map imaging study of the CH_2BrI photodissociation dynamics in the first and second absorption bands

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The photodissociation dynamics of alkyl bromides has attracted a lot of interest because of its relevant role at destroying stratospheric ozone [1]. Numerous studies on monohalogen alkyl photodissociation have already been reported over the years [2]. A non-adiabatic crossing governs the reaction dynamics in the first absorption band and determines the observed product distributions. However, multihalogen alkyl compounds photodissociation dynamics have been much less studied. In particular, bromo-iodomethane (CH_2BrI) photodissociation has been investigated almost exclusively by Butler, Lee and coworkers [3] in the late 1980s using the photofragment translational spectroscopy technique, highlighting a possible bond selective photochemistry.

We report here a velocity map imaging (VMI) study of the photodissociation dynamics of CH_2BrI in the two first absorption bands. A pump-probe scheme using resonance enhanced multiphoton ionization (REMPI) to detect the iodine and bromine fragments produced is employed in combination with the VMI and slicing techniques [4,5]. Excitation wavelengths were set at around 266 and at 210 nm corresponding to the maximum of the first and second absorption bands associated to the promotion of an electron in the iodine atom and in the bromine atom to an antibonding orbital on the C-I and C-Br bonds, respectively.

The results will be presented in terms of translational energy distributions and fragment angular distributions and will be discuss in order to propose photodissociation mechanisms involving primary and secondary dissociation processes.

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P-10

Femtosecond velocity-map imaging study of the photodissociation dynamics of CH_2ClI and CH_2BrI in the first absorption band

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Interest for halomethanes has substantially grown up in recent years because of their relevant role in atmospheric photochemistry. Investigations on their photodynamics permit to establish their potential environmental impact, especially at destroying the stratospheric ozone [1-2]. Monohalomethanes photochemistry has been extensively studied using both experimental and theoretical methods. Photodissociation in the first absorption band leading to the C-X cleavage has been completely characterized in terms of the branching ratios between different channels taking into account the spin-orbit splitting and of the involved excited states and non-adiabatic couplings [3]. On the contrary, studies on dihalomethanes photodynamics are scarcer. Their photodissociation leads generally to the formation of a halogen atom and a halomethyl radical [4]. This radical may experience a further photodissociation and produce a second halogen and a methyl radical. In this way, primary and secondary photodissociation processes are in competition.

The aim of this work is to study the halogen substituent effect on the dihalomethanes photodynamics. Specifically, we have studied CH_2ClI and CH_2BrI photodissociation in the first absorption band at an excitation wavelength of 268 nm. The experimental results could indeed be compared to the well known methyl iodide photodissociation. For this, we have performed femtosecond time-resolved velocity map imaging measurements on CH_2ClI and CH_2BrI in conjunction with a (2+1) Resonance Enhance Multiphoton Ionization (REMPI) scheme to detect the iodine atoms. The results will be presented in terms of translational energy distributions and transients and will be discussed in relation to the femtosecond photodissociation dynamics.

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P-11

Charge transfer reactions with Ar^+ and various neutrals

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The crossed-beam technique has become the method of choice for the analysis of reaction dynamics [1] as it allows to precisely assess the complete kinematics of both reactants and products. In the last decade, it could be extended from neutral partners to ion neutral reactions [2]. The combination with three-dimensional velocity map imaging has allowed us to obtain energy- and angle-differential cross sections for the $Ar^+ + N_2$ charge transfer reaction [3], opposing previous experimental results and in agreement with theoretical predictions [4]. Recently, a radio-frequency ion trap has been added to our setup that allows to achieve an improved energy resolution of the ion beam.

Here, we present the status of experiments that extend our previous work on the charge transfer reaction with Ar^+ to various neutral partners starting with H_2, D_2, CO and O_2. While state specific reaction cross sections have already been investigated for the individual spin-orbit states of Ar^+ [5, 6], our measurements of differential cross sections reveal the specific excitation of vibrational levels of the product ions. The prediction of an energy resonance in the charge transfer reaction with H_2 but not with D_2 [5] is already supported by first results with hydrogen that show a dominant vibronic coupling between the $Ar^+(^2P_{1/2}) + H_2$ ($\upsilon = 0$) entrance and $Ar + H_2^+$ ($\upsilon = 2$) exit channel. Such a near resonance of the energy levels of initial and final states is not present with the other neutral partners. Yet, the qualitatively different ratios between the $P_{1/2}$ and $P_{3/2}$ cross sections for N_2 (<1), CO (>1) [6] and O_2 (near 1) [7] suggest interesting differences in the dynamical features of the proposed reactions.

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P-12

IR-driven asymmetric molecular frame angular distributions upon photoionization with XUV pulses.

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We theoretically investigate the use of XUV-IR pump-probe schemes with ultrashort pulses to explore electron dynamics in small molecules. These techniques have been widely employed in photoionization experiments with atomic [1,2] and molecular targets [3,4], where an attosecond XUV pulse triggers ionization and an IR field traces and drives the photoelectron. Particular interest is focused on the role of autoionization in this IR-induced dynamics [2,3]. In this context, we propose a theoretical study of hydrogen molecule using a combination of a single attosecond UV pulse with a moderately intense femtosecond IR pulse to explore laser-assisted ionization. We use an ab-initio theoretical method to compute total and energy differential ionization probabilities for both dissociative and non-dissociative ionization channels. Features found in the energy differential electron-ion coincident maps, including the IR-modified autoionization signature, can be explained in terms of perturbative transitions involving a UV and several IR photons. In the photoelectron distributions, we observe the streaking patterns, shifting the electron momentum in time with the IR vector potential. The streaking patterns appear very clear in the non-dissociative channel, while they are modified in the dissociative ionization channel where autoionization has a larger contribution. Finally, we explore the asymmetry in the molecular frame photoelectron angular distributions (MFPADS) as a consequence of populating states of both gerade and ungerade symmetries associated to the same ionic state. The asymmetric electron ejection is controlled with the delay and relative phase between the UV and the IR pulse.

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P-13

Mechanism of Methanol and Water Photocatalytic Dissociation on TiO_2(110)

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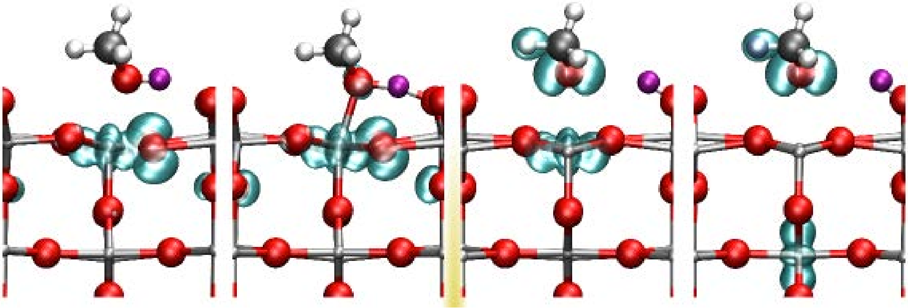
Heterogeneous photocatalysis is very important because of its potential applications in energy and environmental technologies. Methanol and water on single-crystal rutile TiO_2(110) interfaces are model systems for ultra high vacuum surface studies aimed at revealing its basic principles [1,2]. Using spin-polarized density functional theory with a hybrid exchange-correlation functional (HSE06), we study the photocatalytic dissociation of methanol and water adsorbed at coordinately unsaturated Ti sites of the TiO_2(110) surface as excited-state processes with triplet spin multiplicity. The photocatalytic dissociation corresponds to a proton coupled electron transfer mediated by hole transfer from the substrate to the adsorbate and simultaneous proton transfer in the opposite direction. In the case of methanol, the product is a methoxy radical that can further react to formaldehyde, and we discuss whether the overall reaction from methanol to formaldehyde may correspond to a one-photon process. We also discuss the higher photocatalytic activity of CH_3OH compared to H_2O.



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P-14

The formation of chemically bound argon via photoexcitation of Ar-I_2 van der Waals complex

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Van der Waals complex Ar-I_2 is a benchmarking model for a study of the influence of weakly bound environment on molecular photochemistry and photophysics. Previous studies with this complex were focused mainly on the processes with I_2 molecule excited in the lowest excited electronic states. In the current work mechanism of photodissociation of Ar-I_2 complex has been studied with excitation of high-lying Rydberg states (E≈9.2 eV) of I_2 molecule via two-photon (*hν*≈4.6 eV) process. Photodissociation of free I_2 with this level of excitation has been studied earlier with the use of velocity map imaging technique [1]. Channels of dissociation of this highly excited I_2 via ion-pair state giving rise to pair I^++I^- as well as via lower lying Rydberg states giving rise to all energetically accessible Rydberg states of I atom have been detected. In the present work influence of Ar on these processes in van der Waals complex Ar-I_2 has been investigated. Complex Ar-I_2 has been generated in supersonic molecular beam. Besides channels observed earlier for free I_2 the new complex-specific channels have been detected which give rise to Ar^+ and ArI^+ ions. The four-photon ionization of Ar (IP=15.7 eV) is negligible in our nanosecond experiments. Image of velocity map of Ar^+ ions shown in Figure 1 indicates formation of molecular precursor containing chemically bound Ar. Mechanism of photodissociation of highly excited complex Ar-I_2 is suggested.

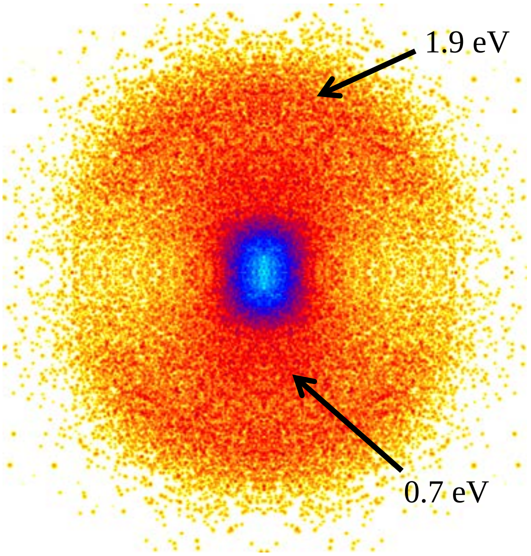

Figure 1. Velocity map image of Ar^+ ions.

Acknowledgments: This work has been supported by Russian Foundation for Basic Research (grants 16-33-00303 and 16-53-12025).

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P-15

Ab initio study on the photodissociation of CH_3O and CH3S radicals : The effect of spin-orbit coupling.

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The methoxy family CH3X (X = O, S) is a series of very interesting radicals from several perspectives [1]. They are important compounds in environmental and combustion chemistry, in astrophysics and atmospheric reactions. Numerous references to the practical importance of these radicals have been compiled [2]. Although the literature on CH_3O and CH3S is quite extensive, the most germane works from the viewpoint of photodissociation dynamics are the spectroscopic [3] and theoretical investigations [1,4] of the electronic structure of methoxy. In the present work, new ab initio data have been calculated on the ^2E, $^2A_1$, $^2A_2$, ^4E, and $^4A_2$ five electronic states of CH3O and CH3S that correlate with the asymptotes $O(S)(^3P) + CH_3$ and $O(S)(^1D) + CH_3$, including spin-orbit coupling for the first time. Potential energy surfaces for the above electronic states have been computed as a function of CO(CS) distance and OCH(SCH) angle under C_{3v} symmetry, using multireference internally contracted single and double excitation configuration interaction method with the aug-cc-pCVQZ basis set. The possible photodissociation mechanisms of CH3O and CH3S are discussed in the light of these potentials.

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P-16

Theoretical study of the photodissociation of the ethyl radical from the 3s and 3p Rydberg states.

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Ethyl radical, C_2H_5, is an intermediate of central importance in hydrocarbon combustion [1]. As one of the simplest alkyl radicals, ethyl represents an important prototype for more dynamically complicated radicals. There have been numerous studies on the photodissociation process of this radical in order to elucidate its dissociation dynamics [2,3]. The photodissociation of the ethyl radical takes place by exciting the system to predissociative 3s or 3p Rydberg states, which can then decay into three product channels : CH_3+CH_2, CH_2CH_2+H and $CHCH_3$+H.

To gain some insight on the possible photodissociation mechanism, high level ab initio electronic structure calculations were carried out using multireference internally contracted single and double excitation configuration interaction method, with AVTZ basis sets. The adiabatic potential energy curves of the excited electronic states involved in the process have been calculated for the above three dissociation channels for the first time. The possible dissociation mechanisms are discussed.

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P-17

Theoretical Spectroscopic Characterization of Gaseous Ethylene Glycol Isotopologues at Low Temperatures

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To complete the molecule characterization, after an initial study of ethylene glycol (EG) [1], we have studied three isotopologues containing deuterium, $DOCH_2$-CH_2OH, $HOCH_2$-CH_2OD, and $DOCH_2$-CH_2OD, to determine the effect of deuteration on the spectroscopic properties. Isotopic displacements ensure the correct assignment.

Ethylene glycol shows three conformers of very low energy, G_1, G_2 and G_3. Two of them stabilize by the formation of one intramolecular hydrogen bond. The full-dimensional anharmonic analysis performed with vibrational second order perturbation theory (VPT2) provides first approximate spectroscopic constants for the O-H modes. The effect of the weak intramolecular forces on the OH stretching is prominent. The computed rotational and centrifugal distortion constants are in good agreement with microwave experimental investigations [2, 3].

For the most stable conformer G1, anharmonic OH-stretching frequencies were calculated to be ν_1 = 2715 cm^{-1} and ν_2 = 3629 cm^{-1} ($DOCH_2$-CH_2OH), ν_1 = 3681 cm^{-1} and ν_2 = 2676 cm^{-1} ($HOCH_2$-CH_2OD), and to be ν_1 = 2715 cm^{-1} and ν_2 = 2676 cm^{-1} ($DOCH_2$-CH_2OD). Band center displacement of ~900 cm^{-1} with respect to the main isotopologue for which ν_1 = 3680 cm^{-1} and ν_2 = 3628 cm^{-1}, are obtained. In addition, the effect of the deuteration produces large displacements of ~400 cm^{-1} in the COH bending transitions. The deuteration alters the relative order of some modes.

The isotopic effect is important on the torsional energies and their splittings. The assignments of the main isotopologue levels have been discussed in our previous work performed using a variational procedure. For the deuterated species previous experimental spectra are available [4]. Variational calculations allow to discuss previous assignments.

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P-18

Selectivity of Imidazole for CO_2 Capture in a Rich Atmosphere in Greenhouse Effect Gases CH_4 and SF_6

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The search of new materials of low cost and high efficiency for the capture and storage of pollutants is the object of many studies focused to the development of new technologies. Electronic structure calculations are applied to the study of the Zeolitic Imidazolate Frameworks (ZIF) [1] selectivity for gas capture in rich atmospheres in the greenhouse effect gases CO_2, CH_4 and SF_6 [2]. Van-der-Walls complexes of these adsorbates with imidazole are explored considering the imidazolate rings simplest models for the study of the nature of host-guest interactions in ZIF's. The minimum energy paths for complexation are described by determining global interaction potential energy surfaces. The number of the complex stable geometries, depending on the size and polarity of the adsorbate, makes more probable its adsorption. The calculations prove that capture by imidazole is energetically favored for the three adsorbates; CO_2 displays the largest ability for binding imidazolate rings. CH_4 and SF_6 can be expected to be strong competitors while the molecular size of SF_6 can yield to important steric effects.

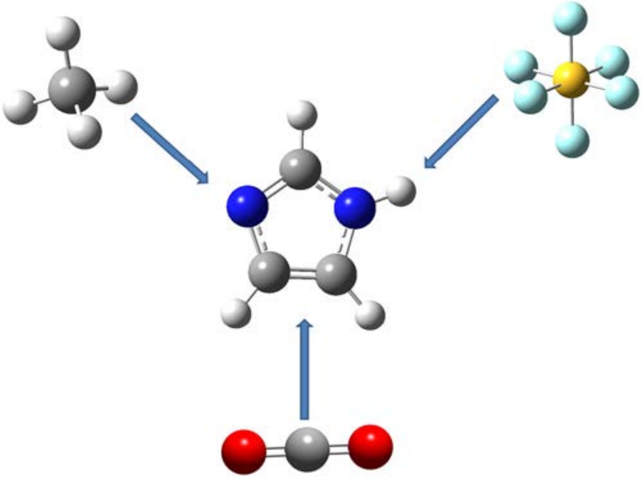

Figure: Scheme Describing Imidazole + (CO2, SF6, CH4) Complexes Formation.

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P-19

Crossed molecular beam studies of the O(^{3}P) + 1,2-butadiene reaction

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The reactions of O(^{3}P) with unsaturated hydrocarbons (alkenes, alkynes and dienes) play a central role in our understanding of combustion processes and oxidation mechanisms of hydrocarbons. These reactions exhibit several competing product channels, some of which can only take place via intersystem crossing (ISC) from the entrance triplet to the underlying singlet potential energy surface (PES).[1]

Even though the overall kinetics of many of these reactions have been investigated in depth, the identity of primary products as well as the branching ratios (BRs) are much less known. From a kinetics point of view, there are interesting studies with synchrotron radiation detection at 298 K.[2a] On the other hand, the most suitable technique to reveal unambiguously the primary products, the BRs and the detailed dynamics of these reactions is "crossed molecular beams" (CMB) scattering technique with mass-spectrometric detection and time of flight analysis, improved with soft ionization by tunable low energy electrons[1] (or VUV synchrotron radiation[2b]). The capabilities of the CMB technique have been well illustrated in recent, experiment/theory synergic studies of the reactions O+ethyne[3a], O+ethene[3b], O+propene[4], O+allene[5], O+propyne[6] and O+1-butene, where the product BR and extent of ISC were quantified.

In this contribution, CMB studies were extended to a reaction with a higher diene: O(^{3}P)+1,2-butadiene, at a collision energy of 10.0 kcal/mol. From product angular and velocity distributions at different mass-to-charge ratios we have identified primary products attributable to eight competing channels leading to H and H_2 elimination and to C-C bond breaking pathways forming CO+C_3H_6, HCO+C_3H_5, CH_3CO+C_2H_3, CH_2CHO+C_2H_3, HCCO+C_2H_5, C_3H_3O+CH_3. Estimates of product branching ratios as well as electronic structure calculations of the triplet and singlet PESs (in collaboration with C. Cavallotti, Polytechnic of Milan) are currently under way.

Acknowledgments: Financial support by "Fondazione Cassa Risparmio Perugia" (Project Codes 2014.0253.021 & 2015.0331.021 Scientific and Tecnological Research) and University of Perugia ("Fondo Ricerca di Base 2014") is gratefully acknowledged.

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P-20

Shear viscosity of *n*-alkanes in the zero density limit

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The shear viscosity of *n*-alkanes in the zero density limit has been calculated by the classical-trajectory method that has been successfully used to predict the viscosity of real dilute gases [1]. The *n*-alkane molecules were modelled as rigid linear chains consisting of n_c-1 spherical segments (n_c being the number of carbon atoms) that interact through a combination of site-site Lennard-Jones (LJ) 12-6 potentials [2]. The moment of inertia of each *n*-alkane was used to determine the site-site separation. It is shown that it is not possible to find a unique pair of LJ parameters, ϵ and σ, to reproduce the measured viscosity values of *n*-alkanes. However, based on the best fit values of ϵ and σ, for C_3H_8, C_4H_{10}, C_6H_{14} and C_7H_{16}, it was shown that the ratio $\sqrt{\epsilon}/\sigma^2$ is a linear function of n_c. Hence, a model was developed that predicts the viscosity values to within ±5 % of experimental ones for alkanes from C_3H_8 to C_9H_{20} (Figure 1) and within ±5-10 % for longer alkanes. As a limiting case of the site-site potential, we also considered representation by an effective, spherical LJ 12-6 potential. This correlative approach, that makes use of a semi-empirical relationship for the LJ parameter σ, yields viscosities to within ±2-3 % of experimental ones. The effective LJ parameter ϵ exhibits a smooth increase with increasing n_c.

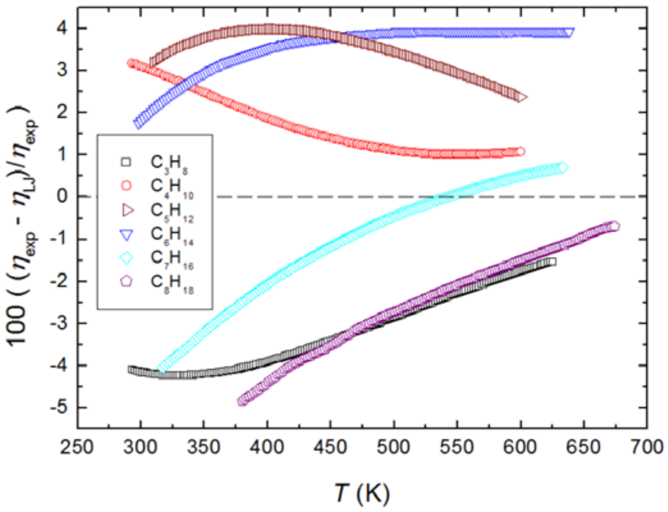

Figure 1: Percentage deviations between the calculated and experimental viscosity.

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P-21

Comparative Stereodynamics of NO($A^2\Sigma^+$) Rotational Energy Transfer with Atomic and Molecular Colliders

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We have used crossed-molecular beam scattering with velocity-map imaging, combined with optical state-selection, to study the stereodynamics of rotational energy transfer of NO($A^2\Sigma^+$, v = 0, N = 0, j = 0.5) with both rare gas and molecular colliders.[1] We present full state-to-state resolved differential cross sections and angle-resolved rotational polarization moments for collisions with He and D_2 for product states N' = 3, 5-12, together with quantum scattering calculations using an *ab-initio* NO($A^2\Sigma^+$)+He potential. Careful control of the molecular beam conditions ensured identical collision energies, resulting in experiments with atomic and molecular colliders with identical collision kinematics. We observe quantitative agreement between experiment and theory for scattering from He, with systematic deviations from purely hard-shell scattering dynamics. Comparison of the D_2 and He results then provides information on the previously unknown NO(A)+H_2 potential. We will also present results from the extension of this technique to collisions of NO(A) with more strongly interacting colliders, e.g. N_2, O_2 and CO, which provides a new probe of potential surfaces that result in electronic quenching.

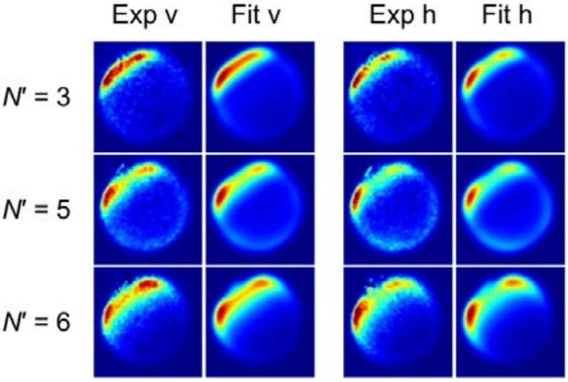

Figure: Example experimental and fit images for NO(A)+D_2 scattering for product states N' = 3, 5 & 6, acquired with probe polarization in-plane (h) or orthogonal (v).

Acknowledgments: This work is supported by a grant from the UK EPSRC (EP/J017973/01) and by Heriot-Watt University (James Watt Scholarship for T.F.M.L).

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P-22

Molecular-beam scattering of OD radicals from atmospherically relevant liquid surfaces

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We present the first results from a new experimental apparatus, designed to measure the dynamics of scattering of Hydroxyl radicals with well-defined collision energies and rotational temperatures from the surfaces of atmospherically relevant liquids. OD radicals are generated in the expansion region of pulsed molecular beam, by a pulsed DC-discharge (Δt = 10 μs) in D_2O seeded in either He or Ne carrier gas. This provides a short temporal packet of rotationally cold OD with a lab-frame collision energy of either 26 kJ mol^{-1} (He) or 6.1 kJ mol^{-1} (Ne). The OD packet is incident on a continually refreshed liquid surface, generated by rotating a stainless steel wheel through a bath of either an inert reference perfluorinated polyether (PFPE, Krytox® 1506), or the potentially reactive liquids squalane ($C_{30}H_{62}$, 2,6,10,15,19,23-hexamethyltetracosane) and squalene ($C_{30}H_{50}$, trans-2,6,10,15,19,23-hexamethyltetracosa-2,6,10,14,18,22-hexaene). The in-going OD packet, and the OD products of inelastic scattering at the liquid surface are detected by LIF. Measurements of time-of-flight profiles and excitation spectra allow determination of the sticking coefficients for OD on squalane and squalene, as well as dynamical information on the scattering process.

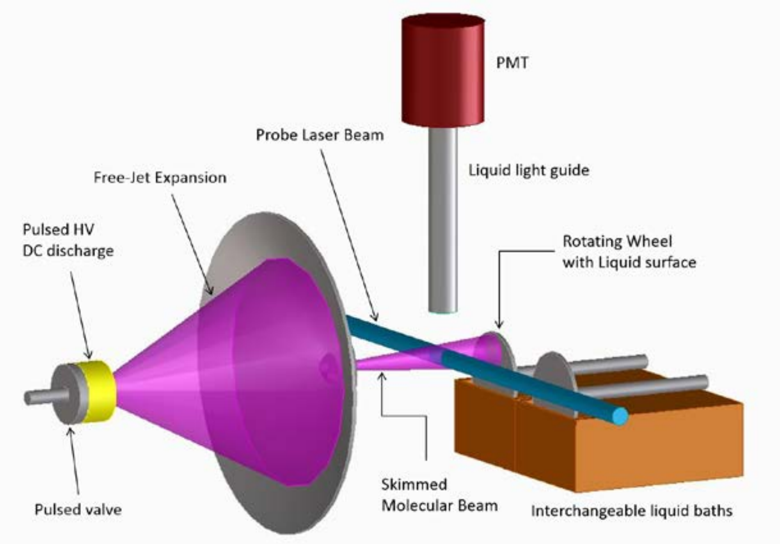

Figure: A schematic of the pulsed OD molecular beam / liquid-surface scattering apparatus.

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P-23

Time-Resolved Photoion Yield Spectroscopy of Hydroxyindoles

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Rapid and efficient energy redistribution processes in biological chromophores following ultraviolet (UV) absorption are believed to be a vital ingredient in providing biological photoprotection. Important examples include the DNA bases and the melanin pigments. Gas-phase spectroscopic techniques provide a valuable insight into the fundamental dynamics of these mechanisms, free of intermolecular and solvent effects [1]. However, many large molecules of interest have low vapour pressures, with a propensity to decompose under vigorous heating, making gas-phase spectroscopy difficult.

This work presents a soft thermal desorption technique [2], incorporated within a time-of-flight mass spectrometer (TOFMS), facilitating studies of the UV-photoprotection in non-volatile model biological chromophores. Back irradiation of a thin metallic foil by a CW laser produces neutral plumes of the molecule of interest. Relaxation dynamics following UV absorption in the eumelanin building blocks, 4, 5,and 6-hydroxyindole and 5,6-dihydroxyindole, have been investigated using time-resolved pump-probe photoion yield measurements. Further work includes the design of a novel nozzle system to facilitate molecular pick-up, increasing sample concentration and producing partial molecular cooling.

Acknowledgments: This work was made possible by financial support from the Leverhulme Trust Research Project Grant RPG-2012-735. SWC thanks Heriot-Watt University for PhD funding.

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P-24

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

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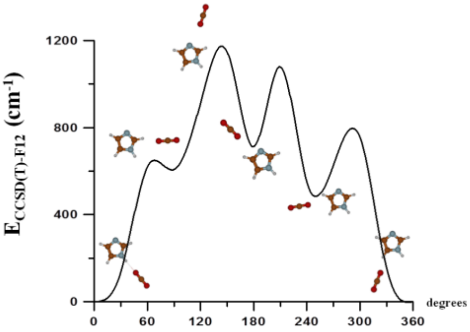
Due to the problem of global warming caused from mass emissions of greenhouse gas and pollutants, such as CO_2, NH_3, SO_2, CO and N_2O new gas capture and gas sequestration materials need to be designed. The aim of this work is the study of the Van-der-Walls complexes of these gases with imidazole,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

We present all the possible structures of the imidazole-NH_3, imidazole-SO_2, imidazole-N_2O, and imidazole-CO complexes, as well as, the binding energies and the interaction potential energy surfaces. Harmonic frequencies are provided to demonstrate the minimum energy character of the structures. Further work on studying the three-body systems type NH3-imidazole-CO_2, SO_2-imidazole-CO_2, N_2O-imidazole-CO_2 and CO-imidazole-CO_2 confirms the probability of simultaneous attachments.



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P-25

Theoretical Spectroscopic Characterization at low Temperatures of C_2H_3NO and its Isomers

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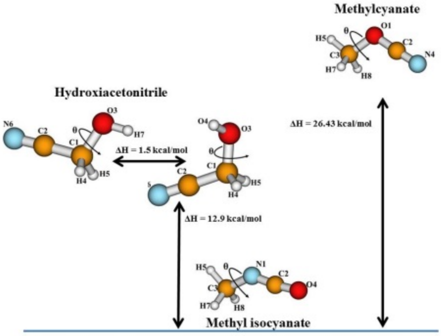
Relevant astrophysical molecules of empirical formula C_2H_3NO are characterized using explicitly correlated coupled cluster methods (CCSD(T)-F12/AVTZ-F12). We present results for four species: the most stable methyl isocyanate (CH_3NCO), as well as, methyl cyanate (CH_3NCO), acetonitrile oxide (CH_3CNO) and hydroxyacetonitrile ($HOCH_2CN$).

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

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

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



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P-26

Ab initio based potential energy surface for the OH + GeH_4 reaction. Kinetics study

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The construction of potential energy surfaces (PES) in polyatomic systems increases the difficulty with molecular size and number of electrons, and it is a research field of current interest and in continuous development. The use of analytical functions represents an interesting and economical alternative to quantum-mechanical methods, which present higher computational and temporal costs.

For the title complex system (which presents 45 electrons as compared with the 19 electrons in the prototype OH + CH_4), we present in this communication a hybrid approach in three steps: i) as input information we used high-level ab initio calculations to describe the most important features of the reactive system (stationary points, reaction path and reaction swath); ii) we chosen a valence-bond molecular mechanics (VB-MM) type surface, an adequate functional form which depends on several parameters; and finally, iii) we fitted the input information to obtain these parameters using a semi-automated multi-beginning least-squares optimization procedure.

Using the CCSD(T)/cc-pVTZ single-point ab initio level as input information, we applied this methodology to the gas-phase OH + GeH_4 hydrogen abstraction reaction and analyzed the quality of the results using two tests: first, a test of auto-consistency, which showed that the different features of the PES (geometry, vibrational frequency, and energy) correctly reproduce the input ab initio information used in the fitting; second, we tested the quality of the PES by comparing the kinetics results with experimental measurements. In general, the results reproduce the experimental information available, where the tunneling effect is negligible given the very small barrier in this very exothermic reaction.

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P-27

Exploring the dynamics of the spin-forbidden reaction $FeO^+ + H_2 \rightarrow Fe^+ + H_2O$

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Activation of hydrogen by the iron oxo cation FeO^+ is a very simple model for the oxidation of related iron-oxo species. This reaction is of particular interest as it involves participation of two spin surfaces in the rate-determining step [1,2]. The reactants and the products both have a sextet ground state whereas the two transition states and the intermediate lie lower in energy on the quartet surface. Reaction on the sextet surface would be extremely slow, and is not in line with experimental results. This gives rise to an interesting question, which is to ask whether the steps in which spin-state change occurs represent the bottleneck of the reaction, and if not, how do these steps affect the kinetics of the reaction.

We embarked on a molecular dynamics study of this reaction. We constructed two analytical potentials for the quartet and sextet surfaces using a modified version of the polynomial expansion suggested by Braams and Bowman [3] corrected with Gaussian functions following a procedure recently developed by one of us [4]. We found this hybrid approach to yield very accurate and efficient potentials, enabling us to generate dozens of *reactive* trajectories in just a few hours.

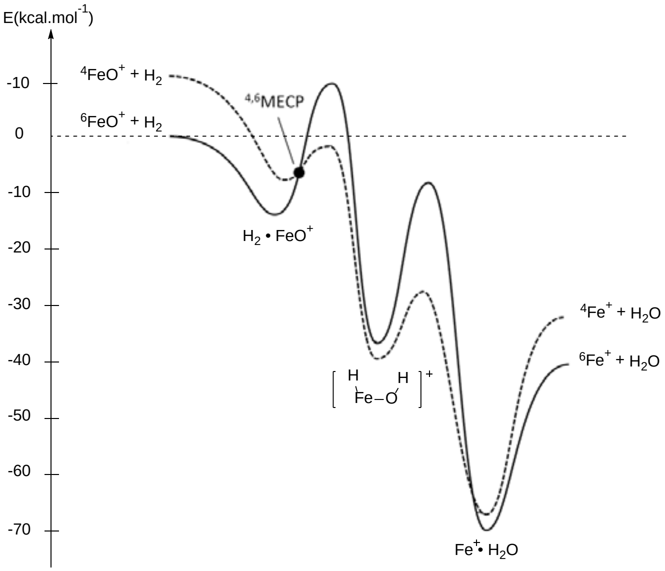

Figure: Schematic potential energy surfaces.

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P-28

Cold Radical Chemistry with Buffer-Gas Beams

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Cryogenic buffer-gas beams (CBGB) have gained popularity as bright, low-temperature molecular sources for spectroscopy and reaction studies. They have been shown to be especially productive for creating certain radical species, such as CH. We have used a CBGB as a source of radicals for two separate cold molecule experiments. First, we have determined a method for efficiently loading a significant fraction of the buffer-gas beam into a traveling-wave Stark decelerator, which used time-varying inhomogeneous electric fields to decelerate polar molecules [1]. Second, we have used a CBGB to create a matrix isolated sample for reactions with other molecules such as O_2.

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P-29

Modeling the Histone-DNA Interactions Using Computational Chemistry and a Reductionist Approach.

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Paracetamol (n-(4-hydroxyphenyl)ethanamide is one of the most widely used mild analgesics. However, how it works is not completely clear, although it is commonly accepted that its action is related to COX-2 enzyme. Once ingested, it is absorbed mainly in the gastrointestinal tract and starts a trip until the molecule finds its target or it is filtered and metabolized by the liver. In such trip, paracetamol encounters all kinds of metabolites and proteins, with which it interacts, in some cases producing undesired effects. In others, it is simply chemically modified, losing its analgesic properties. Understanding the relationship of paracetamol with those molecules may shed light on its mechanism of action and on the origin of its secondary effects. Here, we explore the interaction of paracetamol with three glucose derivatives: α/β-methyl-D-glucopyranose and β-phenyl-D-glucopiranose, using a combination of mass-resolved excitation spectroscopy and computational methods.

A laser desorption jet-cooled system was used to obtain the isolated molecules and aggregates in a supersonic expansion. Next, the beam was explored using a combination of REMPI and IR/UV techniques to extract structural information. Comparison of such experimental results with the output from DFT calculations at M06-2X/6-31+G(d) and M06-2X/6-311++G(d,p) levels allowed us to assign the experimental spectra to a calculated structure.

Two of the four conformers of paracetamol were detected in the expansion, in good agreement with previous publications. Both isomers present similar interaction energies with the sugar molecules. According to our results, interaction with the glucose molecules is not localize in one of the substituents of the aromatic ring but it extends to the aromatic ring, promoting the CH-π hydrophobic binding.

P-30

Exploring the Interaction of Glucopyranose Anomers in Isolated Phase Using Mass-Resolves Excitation Spectroscopy

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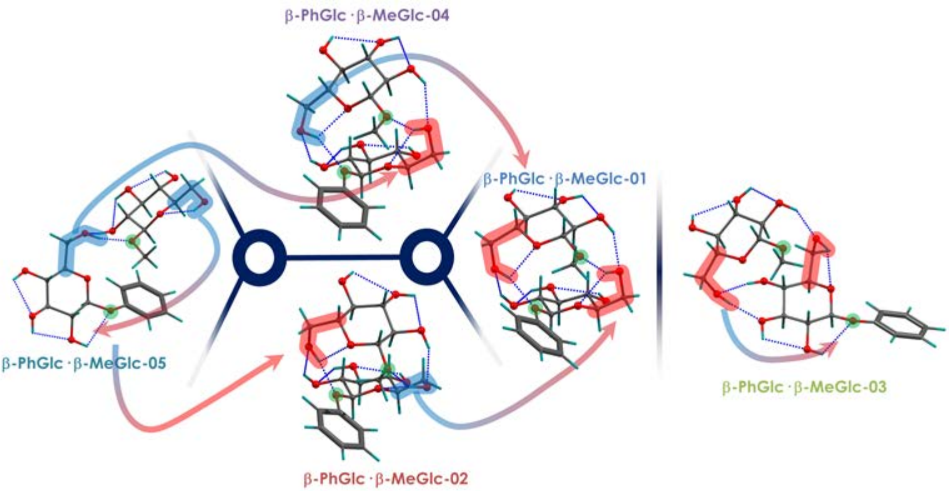
Sugars are essential in living beings not only for energy management but also for some basic functions such as immunity and signaling. Those functions are guided by the intermolecular interactions between sugar units and other biomolecules. Here we analyze how the anomeric substituent influences the ability of glucopyranose to aggregate, using a combination of mass-resolved laser spectroscopy in supersonic expansions and computational simulations. The results obtained clearly demonstrate that the small stability difference between the α/β anomers of glucopyranose is inverted and amplified during molecular aggregation because the small geometry differences between α and β anomers allow the latter to form highly symmetric aggregates in which each molecule incorporates in the cooperative hydrogen bond network formed by the hydroxyl substituents of the interaction partner. This may also be the cause of specificity on carbohydrates and the differences in affinity of synthetic receptors for one of the two anomers or for macroscopic properties such as the differences in solubility between starch and cellulose.



P-31

Modeling the Histone-DNA Interactions Using Computational Chemistry and a Reductionist Approach.

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The DNA is not found free in the cellular nucleus, but wrapped around some proteins called histones forming what is called the nucleosome. Such complex plays a crucial role in the stabilization of DNA but also controls its replication and transduction. Such complexes are formed by the interaction between a histone octamer with a superhelix of 146 base pairs of DNA. Despite the number of studies on the structure of the complex, it is not clear what forces guide the DNA-histone association. Clearly, the frequency of DNA base-amino acid contacts show large variations with the nature of the amino acid. So is the complementarity between the DNA and a given histone what finally guides the association process? Is the histone designed to associate with a given section of the DNA? Or any histone can associate with any sequence of DNA, independently of its sequence of bases?

Using a reductionist approach, we divided the histone-DNA interactions in amino acid-DNA base pairs, which may be analyzed using high-level quantum chemistry methods. We will present a systematic study on the conformational behaviour and the nature of several interactions in DNA base pairs – amino acid systems, using a combination of molecular mechanics and DFT calculations

The results indicate a clear correlation between the strength of the interaction between individual amino acid-DNA base and the frequency of contacts. Therefore, the sequence of the amino acids in the histone is designed to allow the interaction with the DNA double helix in a pre-fixed way.

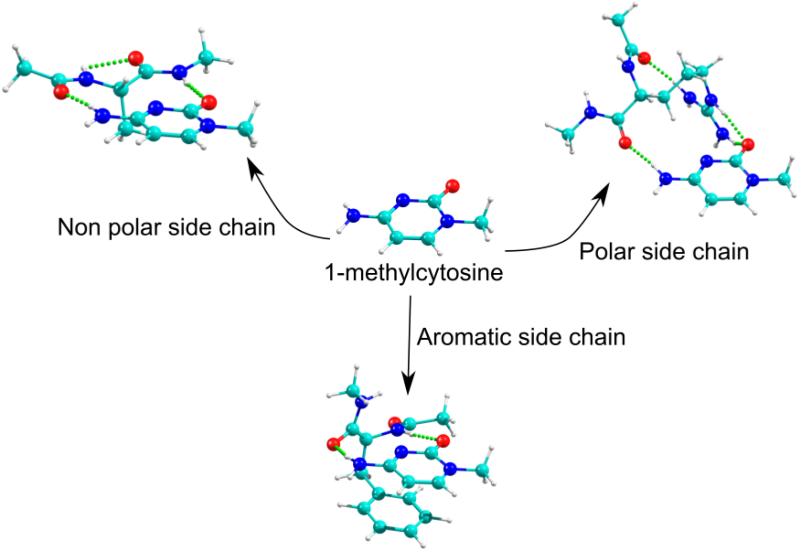

Figure: 1-methylcytosine interacting with the non-polar side chain of alanine, the polar side chain of arginine and with the aromatic side chain of phenylalanine.

P-32

Spin-vibronic quantum dynamics of ultrafast intersystem crossing in $[Re(CO)_3(phen)(imi)]^+$, a building unit for long-range electron transfer in modified blue-copper proteins

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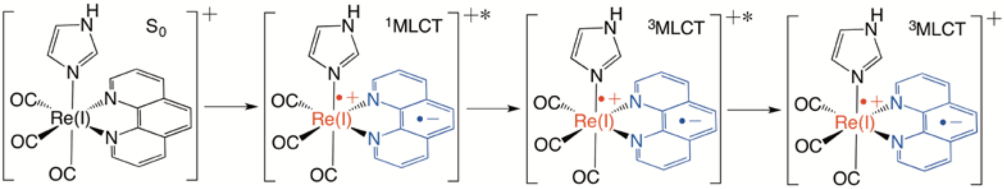
Re^I tricarbonyl complexes constitute an important family of molecules for their application as luminescent probes due to their long-lived emissive metal-to-ligand charge transfer (MLCT) states. However, the redox activity of the excited states (EE) has also been widely exploited to trigger long-range electron transfer (ET) reactions through biological systems. Remarkably, investigations of metal-modified derivatives of a blue-copper protein *Pseudomonas aeruginosa* azurin revealed that these ET processes can be highly accelerated if an appropriate intervening redox center is used. This is the case of $Re^I(CO)_3(dmp)(H^{124})\div(W^{122})\div AzCu^I$, in which rapid formation of Cu^{II} was detected after photoexcitation of $Re^I(CO)_3(dmp)(H^{124})$ [1]. In the present work, the ultrafast intersystem crossing (ISC) in $[Re(CO)_3(phen)(imi)]^+$ is investigated by means of wavepacket propagations based on the multiconfiguration time-dependent Hartree (MCTDH) method [2]. On the basis of time-dependent density functional theory (TD-DFT) electronic structure data, the luminescence decay is simulated by solving a 14 electronic states multimode problem including both vibronic and spin orbit coupling within the linear vibronic coupling (LVC) model [3]. A careful analysis of the results provides the key features of the mechanism of the primary ISC in this complex long-range ET process that occurs within the protein.



Scheme of the excited-state relaxation mechanism of $[Re(CO)_3(phen)(imi)]^+$.

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P-33

Conformation-specific effects in gas-phase neutral and ionic bimolecular chemical reactions

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Many complex molecules posses multiple conformers (rotational isomers) which often have distinct chemical reactivities. Despite of the ubiquity of conformations in complex molecular systems, studies of conformation-specific bimolecular reactions under single-collision conditions have been sparse. The reason for this lies in the difficulties of isolating individual conformers in the gas phase which can often interconvert into one another over low barriers at room temperature. Recently, methods were developed for the spatial separation of distinct conformers in a supersonic molecular beam by electrostatic deflection [1]. We have combined this technique with a linear Paul ion trap that contains Coulomb crystals of cold ions [2] for studying conformation-selective ion-molecule reactions [3, 4]. By implementing a high-resolution time-of-flight mass spectrometer for the analysis of the reaction products, we are now able to investigate complex conformation-specific reactions with multiple reaction channels [5]. For studies of conformational effects in neutral reactions, we are currently building a crossed-molecular-beam (CMB) setup with conformationally selected molecular beams [1]. Velocity-map imaging (VMI) will be used to detect the quantum-state and angular distributions of the products. We will present the latest results from these experiments, focusing on conformational effects in reactions of importance for organic chemistry such as the Diels-Alder reaction as well as reactions with free radicals.

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P-34

Potential Energy Surface and Dynamical Properties of the Astrochemical Reaction $C+CH^+ \rightarrow C_2^+ + H$

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The title reaction is a prototype model for the formation of the carbon-carbon chemical bond in the interstellar clouds and it involves two astrochemical relevant species: the ubiquitous throughout the interstellar space methylidyne cation CH^+ and the dicarbon cation C_2^+, an important precursor for the production of hydrocarbons. Presently available estimates for the rate coefficient of the title reaction are based on the Langevin capture model and accordingly the thermal rate coefficient is independent of the temperature.

In this work, we carried out high-level ab initio calculations of the electronic structure of C_2H^+ on an optimal space-reduced bond-order grid [1], the fitting of an accurate potential energy surface by using the Aguado & Paniagua method [2], quasiclassical calculations for evaluating state-specific cross sections, state-specific rate coefficients and fully thermal rate coefficients.

The calculated state-specific cross sections decrease when the energy (either translational or internal) increases, as expected for a barrierless reaction. This constant decrease results in state-specific rate coefficients which first rise from a very small value to a plateau as the temperature increases from 5 K to a value varying from 500 to 1000 K and then decrease from such maximum as the temperature further increases. The fully thermal rate coefficients show a trend similar to that of the state-specific rate coefficients, contrary to the present value quoted in astrochemical databases. In particular, for the temperature of 10 K (the temperature of the interstellar medium) the database value overestimates by a factor of two the one obtained by us (thus improperly enhancing the destruction route of CH^+ in astrochemical kinetic models. Moreover, the temperature dependence of the thermal rate coefficient is better described by the ‘deformed Arrhenius’ of Aquilanti & Mundin [3] than the popular Arrhenius-Kooij formula.

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P-35

Valence to Rydberg Transitions in the Photodynamics of Pyrrole and Methylated Derivatives

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Rydberg states are widely considered to not influence the dynamics of molecules that are photoexcited into the valence manifold. However, recently Mori et al [1] and Sellner et al [2] proposed the involvement of the π3s Rydberg state in the photochemical dynamics of ethylene upon excitation to the lowest lying ππ* state, and this was experimentally confirmed by Champenois et al [3] using time-resolved photoelectron spectroscopy (TRPES).

Here, we present a TRPES study of pyrrole and its methylated derivatives: N-methyl pyrrole (NMP) and 2,5-dimethyl pyrrole (2,5-DMP), where we find the involvement of the $\pi 3p_y$-Rydberg state in the dynamics of all three molecules after their excitation into the lowest lying ππ*-state with 200 nm photons. The Rydberg states are populated after about 25 fs, from where they subsequently decay further to the lowest lying excited state, which has πσ*-character, after another 25 fs. After 100 fs (both pyrrole and 2,5-DMP) to 160 fs (NMP), the molecules return to the ground state, indicating that a similar mechanism is responsible for all three species, which is likely to be N-H (N-C) dissociation [4].

This study emphasizes that Rydberg states might play an important role in the photodynamics of medium sized molecules when excited to higher lying states, and we speculate that they push the molecules towards one specific reaction/relaxation channel on the lowest lying potential energy surface.

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P-36

Scattering involving identical entities: examples from quantum dynamics at the molecular scale

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Very generally, scattering between groups of identical particles, or identical fragments, deserves special attention and careful examination. The most general way to take this fact into account would be the use of a scattering formalism entirely based on second quantization, in which symmetry requirements to be satisfied by indistinguishable entities would be incorporated from the outset [1,2]. However, while theoretically elegant, it is difficult to effectively implement it numerically. Moreover, in the case of relatively small systems, like three-body (possibly reactive) collisions, it is possible to adapt the specific method used in explicitly computing the cross sections (like the time-independent formalism we use, based on hyperspherical coordinates for rearrangement collisions) in incorporating the correct permutation symmetry. Another possibility is to post-symmetrize the cross sections obtained when neglecting the indistinguishability of the three particles, by any method (time-independent or time-dependent).

Within the frame of molecular quantum mechanics, we present various examples of scattering observables for three-body systems with identical nuclei either with zero spin, such as ${}^{16}O + {}^{16}O{}^{16}O$ [3] and ${}^{18}O + {}^{18}O{}^{18}O$ [4], or nonzero spin like $H^+ + H_2$ [5] or ${}^{17}O + {}^{17}O{}^{17}O$ [6]. These systems were all treated by a full quantum-mechanical time-independent formalism. To this end, we have used recent global potential energy surfaces for the ground electronic state developed by other groups [5,7]. This kind of study is computationally intensive and takes properly into account the indistinguishability of the three identical atoms. It yields accurate cross sections and rate constants as functions of collision energy and temperature.

While always correctly accounted for in the realm of particle and nuclear physics, it seems that the proper inclusion of permutation symmetry has been missing in many studies in quantum molecular dynamics. These new findings therefore suggest that previous dynamical calculations on these or related systems need be carefully revised. Indeed, interpretation of the dynamics of this type of systems with three nuclei considered as distinguishable, such as in statistical theories, (quasi-) classical methods or approximate quantum approaches, may lead to erroneous conclusions.

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P-37

Microsecond Kinetic Measurements for Catalytic Surface Reactions *via* Ion Imaging

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We describe the use of ion imaging to study molecular beam-surface scattering. Imaging detection allows the efficient measurement of the laboratory frame angular and speed distributions of products from direct inelastic scattering [1], trapping desorption, or catalytic reactions on the surface. The technique can be extended to provide direct information about the rates of desorption and reaction as a function of surface temperature. The measured rates, in turn, yield information about the barriers controlling the chemical reactivity on the surface.
We present results for the prototypical catalytic oxidation of CO by O_2 on Pt(111). We find evidence for two different reaction channels which produce CO_2 with different final scattering velocities. The separation of the product channels provided by the imaging detection technique allows the kinetics and reaction barriers of the different channels to be measured independently.

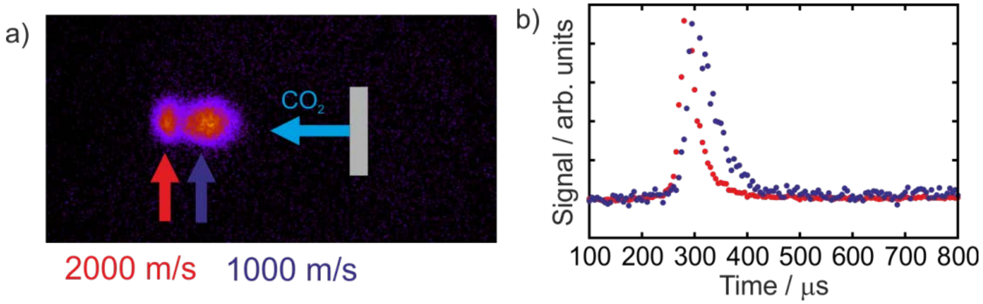

Figure 1. a) Ion image showing two different velocity components for CO_2 formed on the Pt(111) surface. b) The time dependence of the signal in the different channels measured by the delay between the molecular beam pulse and the ionization laser.

These experimental techniques can be applied to a wide range of chemical reactions occurring at surfaces, providing benchmark data for comparison with theory or for use in kinetic models. The speed and efficiency of the technique also make it suitable for reactivity screening.

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P-38

Exploiting Transient Absorption Spectroscopy for Mechanistic Insight into Photoredox Organocatalysis

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Recently photoredox catalysis merged with organocatalysis has been proven to be a very powerful technique for some elusive chemical transformations, e.g., α-alkylation of aldehydes [1]. Nevertheless, a mechanistic explanation with spectroscopical evidence for these reactions is still lacking. It is widely believed that the systems are too complex to be studied with transient absorption (TA) spectroscopy [2]. We now go beyond this belief by reporting a detailed investigation of α-alkylation of octanal with the photocatalyst naphthaldiimide (NDI) and the organocatalyst imidazolidinone. By using the TA spectrometer of our own design [3] and a novel quantum yield determination system [4], we track the generation and quenching of the NDI singlet, triplet excitation and radical anion under selective influence of the individual reactants in catalysis. Time ranges from low picoseconds to hundreds of microseconds are found.

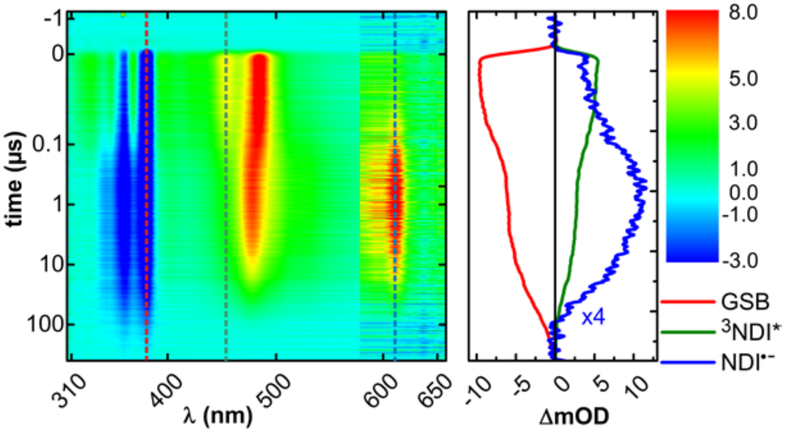

Figure 1: Transient absorption for NDI catalyzed α-alkylation of octanal.

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P-39

Multilayers embedded silver nanoparticle generated by femtosecond pulsed laser deposition

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Deposits of exposed and embedded silver nanoparticles were grown on Si(100) and silica substrates by laser ablating high-purity silver and SiO_2 targets in vacuum using a femtosecond Ti:sapphire laser delivering 45 fs pulses at 804 nm and 1 kHz repetition rate. The effect of the laser fluence and irradiation time on the obtained nanostructures was investigated using several fluences between 650 mJ/cm^2m and 3.2 J/cm^2 and deposition times in the range of 1-20 minutes. Optical response of the deposits was characterized using optical absorption spectroscopy and the surface morphology was studied by scanning electron microscopy (SEM). Samples with the optimal optical response were obtained by depositing three successive Ag/SiO_2 bilayers at the main laser wavelength (804 nm) under vacuum at substrate room temperature. They were composed of silver nanoparticles with an average diameter of 6 nm and a narrow size distribution; each layer of these nanoparticles was then separated by silica layers of approximately 100 nm. The laser fluence and deposition time for Ag (SiO_2) were 650 mJ/cm^2 (3.2 J/cm^2) and 1 min (10 min), respectively.

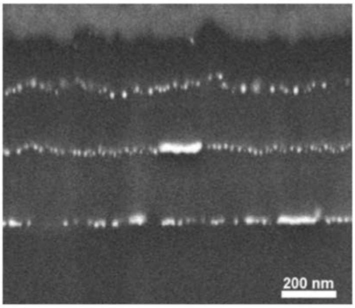

Figure 1.: SEM micrograph of the transversal section of a multilayer structure ($Ag/SiO_2/Ag/SiO_2/Ag/SiO_2$) deposited on a silica substrate.

P-40

Surface morphology modifications of titanium alloy (Ti-6AL-4V) induced by femtosecond laser pulses

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Ultrashort laser micro-machining is a widely used technology to obtain surface textures of materials [1]. While most of the studies have focused on investigations using femtosecond laser pulses centred at the peak wavelength of Ti:Sapphire lasers at 800 nm [2], experiments at other wavelengths would be timely to generate a wider morphological collection of microstructures in materials.

Titanium alloy (Ti-6Al-4V) provides a high corrosion and temperature resistance with an extraordinary strength-to-weight ratio, which makes it attractive for many biomedical [3], aeronautical or industrial applications. In this work, the effect of femtosecond laser parameters (fluence and wavelength) on the resulting micro/nano-structures generated on titanium alloy (Ti-6Al-4V) has been studied. A Ti-6Al-4V plate has been irradiated with a Ti:Sapphire amplified laser system centred at 800 nm, with an energy of 1 mJ/ pulse, a frequency of 1 kHz and a temporal duration of 90 fs. Irradiation has been carried out also at 400 nm and 266 nm, by frequency doubling and tripling the fundamental. The micro/nano-structures produced at the different wavelengths and fluences have been characterized by confocal microscopy and scanning electron microscopy (SEM).

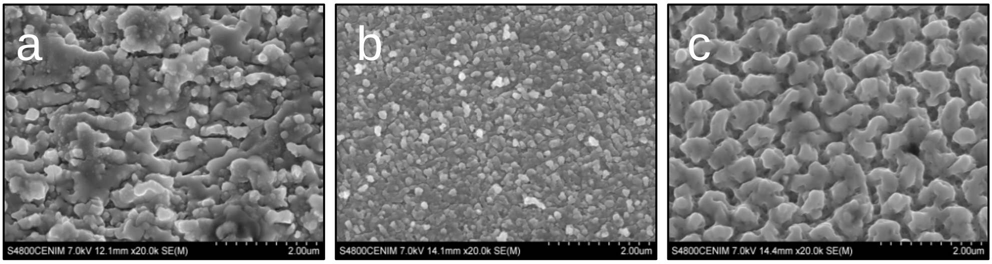

Fig 1. SEM micrographs of titanium alloys irradiated with a) 800, b) 400 and c) 266 nm.

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P-41

Λ-doublet ratio for the O(^{3}P)+D$_2$ reaction: the imprint of Stereodynamics

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It has been longer assumed that the ratio between the Λ-doublet levels Π(A') and Π(A") should be directly related to the cross sections whenever there are two concurrent potential energy surfaces (PESs) of A' and A" symmetries. For the O(^{3}P) + D$_2$ reaction, where both PESs have the same barrier and the A" displays a broader “cone of acceptance’’, it should be therefore expected that Π(A") levels would be more populated.

However, recent experiments carried out by Minton and coworkers [1, 2] has challenged theoreticians by showing a strong propensity towards the Π(A') regardless of the collision energy and final rovibrational states considered. To account for these experiments, we have developed a rigorous method to calculate the Λ-doublet populations from the cross sections on the A' and A" PES [3]. The results obtained are in very good agreement with the experiments and show how the different reaction mechanisms present for the two concurrent PESs have a decisive effect on the Λ-doublet populations that strongly depend on the alignment of the product’s internuclear axis onto the recoil direction.

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P-42

Ro-vibrational bound states near the dissociation limit for the H_3^+-system and the influence of non-adiabaticity on the spectrum

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It is generally accepted that radiative association of ions with molecules plays an important role in the molecular synthesis in the super-cold, low-density environment of the interstellar medium. Cosmic rays ionize atoms and molecules by radiation, which provides sufficient energy to initiate a chain of chemical reactions. Mostly positive ions are observed including the simplest triatomic one, H_3^+.

One of the crucial steps in the investigation of cross-sections for radiative association is the calculation of the ro-vibrational bound states and resonances near the dissociation limit. Because H_3^+ has a binding energy of ca. 35000 cm^{-1}, the accurate determination of the highest bound energy levels can be demanding. In the present work preliminary results, how we plan to perform calculations for the radiative association of a strongly bound molecule will be presented: we need a good potential energy and dipole surface, an efficient time-independent reactive scattering implementation and an efficient way of calculating high-lying bound states and resonances.

In this work we demonstrate that using the Lanczos algorithm [1,2] it is possible to calculate energy levels of bound states of H_3^+ and its isotopologues up to highest allowed J values. Iterative methods obviate the need to store the Hamiltonian matrix and therefore make it possible to use large basis sets. They are especially attractive when using a product basis. H_3^+ is extremely floppy and therefore not a good candidate for contracted basis methods. Non-direct product basis functions are products of functions of a single variable, but with a shared index, and therefore efficient matrix-vector products are possible. We obtain energy levels that agree well with those of previous calculations (on the same surface) and we are also able to compute levels for larger values of J than was heretofore possible. The non-direct product basis provides a compact representation of the wave functions. In order to compete with experimental results, non-adiabatic effects have to be included by using coupled surfaces or effective nuclear masses [3,4] that depend on internuclear distances

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P-43

Modeling Photoionization of DNA Components in Aqueous Solution

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Redox characteristics of nucleobases (i.e. their ionization and reorganization energies and redox potentials) play an important role in understanding of DNA interaction with high energy radiation as well as for understanding of charge transfer processes in nucleic acids. High energy photons can cause oxidation of DNA leading to cell mutation and cancer growth. However, ionization characteristics are difficult to obtain both by experiment and theory. Quantitative measuring of ionization energy in liquid phase was enabled by photoelectron spectroscopy with liquid microjets a decade ago; yet, the molecular picture can be provided by theoretical calculations.[1] In this presentation we focus on modeling photoelectron spectra of nucleobases and other DNA components in aqueous solution. Following experience gained in our calculations in minimum geometry [2, 3], we now present photoelectron spectra and other redox quantities calculated using MD simulations. We investigate the effect of classical and *ab initio* dynamics based on Generalized Langevine Equation (GLE) [4] combined with semi classical reflection principle on vertical and adiabatic ionization energy and then on reorganization energy and spectral width. The relations between these quantities will be discussed. The solvation effects were modeled using the direct approach, non-equilibrium polarizable continuum model and combination of both methods.

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P-44

Associative detachment of alkali hydroxide

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Sympathetic cooling of molecular ions using ultracold atoms is one of the possible way to reach the ultracold regime for molecular species. The co-trapping experiment of OH^- and Rb is currently under investigation by the HAITrap team of the university of Heidelberg. Their experimental setup consist of a radio frequency ion trap with a magneto optical trap (MOT) that allows the OH^- cloud to be immersed in a ultracold Rb cloud. In such environment, elastic and inelastic (including reactive) collisions can occur. This system is expected to show very large internal de-excitation rates [1]. The first published experimental results showed a measure of a loss of OH^- which was attributed to the associative detachment reaction $Rb(^2S)+OH^-(^1\Sigma^+)\rightarrow RbOH(^1\Sigma^+)+e$ [2]. They obtained a rate constant of 2^{+2}_{-1} $cm^3.s^{-1}$ for 200-600K, which is 10 time smaller than the expected Langevin capture rate.

We have performed high level *ab initio* calculations on the RbOH and $RbOH^-$ systems and show that the potential energy curves crosses in the repulsive region of the potential energy surfaces. The crossing defines the autodetachment region where the anion can spontaneously eject an electron. This crossing lays above the energy of the entrance channel at some geometry, a certain amount of energy is therefore needed for the associative detachment reaction to occur. We have used a simple Langevin based model [3] to model the dynamics and showed that the rate constant only slightly changes with temperature, which means that the reaction would also occur in the cold regime. However, the rate constant strongly depends on the position of the crossing point [4].

We have extended our work to several other alkali atoms (Li, Na, K and Cs) which are also routinely used in MOT. Our results indicated that the associative detachment reaction rate increases with size of the alkali. The rate constant is appreciable for Rb and Cs but is almost 0 for K, Na and Li. This implies the absence of associative detachment reaction and means that the loss of ions could be avoid by switching from Rb to K, Na or Li in the MOT.

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P-45

Acetone multi-channel photofragmentation dynamics studied by time-resolved photoelectron-photoion coincidence spectroscopy

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The excited state dynamics of isolated acetone molecules initiated by two-photon (269 nm) excitation to high-lying Rydberg states has been investigated with time-resolved photoelectron-photoion coincidence techniques (PEPICO). As shown in the figure, we observe three distinct pump-probe ionization pathways because of different relaxation processes triggered by the excitation pulse. The high differentiability of PEPICO detection allows us to observe the fragmentation and relaxation behavior of each channel separately. The first channel proceeds via the excited S_n Rydberg states to the unfragmented molecular ion. A second channel via the S_3 state leads to fragmentation after ionization due to electronic-to-vibrational energy conversion in the neutral molecule, as evidenced by the simultaneous presence of parent and acetyl fragment PEPICO signals. The populations of these excited states undergo an exponential decay with the same (147 ± 28) fs time constant. A third, persistent pure-fragment PEPICO signal indicates the ionization of neutral, excited acetyl radicals, which are presumably formed through Norrish type I dissociation on excited state surfaces.

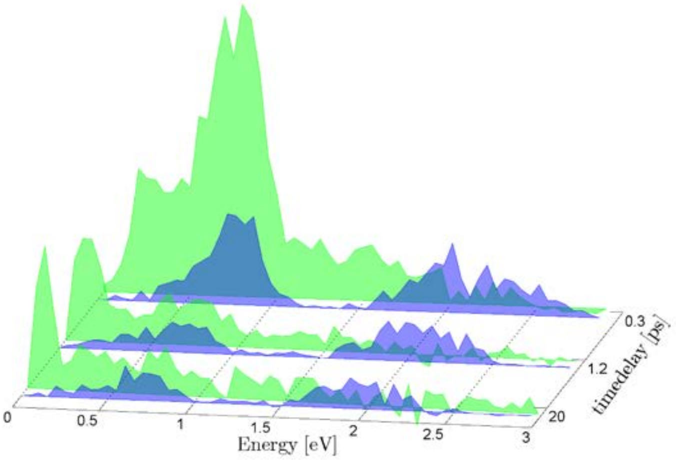

Figure: Temporal evolution of the pump (4.6 eV) – probe (3.1 eV) PEPICO signals associated to the acetone parent ion ($C_3H_6O^+$, 58 u, blue curve, front) and the acetyl fragment ion ($C_2H_3O^+$, 43 u, green curve, back). The three PEPICO bands at 0.1, 0.7 and 2.1 eV correspond to three different pump-probe ionization channels.

P-46

Time-resolved photoelectron imaging of mixed Rydberg/valence states

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The excited states of organic molecules prepared via ultraviolet light absorption often follow a complex, non-adiabatic evolution. Among others, photosynthesis and human vision are two examples in which non-adiabatic dynamics are central to chemical function. Developing a better understanding of the ultrafast molecular dynamics operating in model bio-molecular chromophores, which are considered to be the building-blocks of life, can give a deeper insight into the photostability of those larger systems. Recently, the dynamical role played by electronic states of mixed Rydberg/valence character has been the focus of much attention [1-5] and has been also investigated in this work.

Time-resolved photoelectron imaging (TRPEI) is a powerful pump-probe technique, providing time-, energy-, and angle-resolved information. Our present measurements also exploit the generation of femtosecond pulses in the vacuum ultraviolet region of the spectrum using non-collinear four wave mixing of the fundamental frequency (800 nm) of a Ti:Sapphire and its third harmonic (267 nm) in an argon-filled cell [6]. The dynamics of several small anime and ether systems have been investigated and the subsequent photo-physical/chemical processes are discussed. In particular, the photoelectron angular distributions afforded by the TRPEI approach offer considerable mechanistic insight.

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P-47

Enhancing high-order harmonic generation in light molecules by using chirped pulses

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The process of generating high-order harmonics is a result of the non-linear response of the electrons in a strong laser field, leading to the emission of light of much higher frequency than that of the driving laser. One of the most appealing applications of this technique is the generation of attosecond pulses of light, which can in be used in time-resolved pump-probe experiments, to resolve physical processes at such timescales.

Nowadays, extending the harmonic production to increasingly high energies while maintaining the efficiency of the high harmonic emission represents an important challenge [1]. In this work, we show that the combined effect of linearly chirped pulses and nuclear dynamics in light molecules allows one to achieve this goal. The effect is only observed for down chirps and for IR pulses that are long enough to induce nuclear wave packet dynamics able to bring the molecule well outside the Franck-Condon region. The observed extension and enhancement of the HHG spectrum derives from an adequate timing of the low-frequency cycles with respect to the molecular stretching.

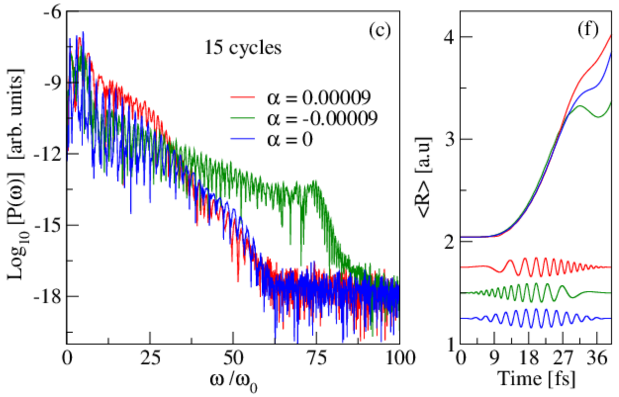

Figure: (Left) High harmonic spectra of H_2^+ obtained with chirped pulses of 40 fs, which correspond to an unchirped pulse ($\alpha = 0$) of 15 cycles, $\lambda = 800$ nm and peak intensity $I_0 = 3 \times 10^{14}$ W/cm^2. The pulse is said to be up-chirped if $\alpha > 0$ or down-chirped if $\alpha < 0$. (Right) Pulses used to obtain the corresponding harmonic spectra as well as the mean value of the internuclear distance, as a functions of time.

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P-48

Role of nuclear dynamics in ultrafast charge migration

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Electron dynamics can be nowadays observed with sub-femtosecond time resolution in ever-increasing molecular systems [1]. The possibility of inducing ultrafast charge migration along the skeleton of large biological molecules upon their photoionization was already predicted more than 15 years ago [2], yet its experimental confirmation has only been achieved very recently using a XUV-pump/IR-probe scheme [1]. A theoretical method based on a density functional theory (DFT) approach, but properly accounting for the scattering states of the ionized system [3], was used to describe the electronic wave packet created after the interaction with the attosecond pulse in [1]. This wave packet described the motion of a highly delocalized hole that gives rise to charge fluctuations occurring in less than 4-5 fs, in good agreement with the experimental findings. Nevertheless, several issues remain open such that the role of nuclear motion in the observed hole dynamics or the dependence with the UV pulse parameters. Here we will address these issues using as target the glycine molecule. We employ a new approach to include the nuclear degrees of freedom combining our ab initio DFT-based methods [3] with time-dependent density functional theory plus Ehrenfest dynamics. In principle, one could assume that the much slower nuclear motion will have a negligible effect at the early stages of the electron wave packet evolution, as shown for benzene in [4]. However, it has also been shown in similar targets that nuclear dynamics could strongly affect the coherence between two electronic states beatings in less than 10 fs in situations where the molecular state after photoionization falls not far from a conical intersection [5]. Since conical intersections are a common feature in large molecules, can we really assume that nuclear motion does not play any role in the early stages of the charge migration process? In this communication, we aim at theoretically answering this question.

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P-49

Resonant photoionization of atoms and molecules using quantum chemistry packages: the XCHEM approach.

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Current quantum chemistry packages (QCP), such as MOLCAS [1], implement sophisticated methods to describe electronic correlation in bound states of atoms and molecules. Recent advances in the generation of extreme ultraviolet (XUV) and x-ray attosecond pulses have now made it possible to follow correlated electron dynamics in real time [2, 3]. Such pulses, however, can also liberate one electron from the atoms and molecules with which they interact, a process whose theoretical interpretation goes beyond the capabilities of QCPs, as it requires to represent the ionization continuum of the target in a wide energy range. So far, this representation has only been achieved with ad hoc codes for selected small systems, such as He and H_2 [4-7]. For more complex systems, however this approach is impractical, and it disregards the advanced methods already available for bound-state calculations.

To overcome these limitations we follow a novel approach based on the merge between existing QCPs and state-of-the-art numerical scattering methods. As customary in close-coupling methods, the electronic configuration space is divided in a short-range and a long-range region. The wave function in the short-range region is fully described in terms of Gaussian functions, which are compatible with standard QCPs. In the long-range region, a single electron interacts with a finite number of correlated parent ions. The state of this electron is expressed in terms of a hybrid basis which combines mono centric Gaussian functions with B-splines (GABS)[8], which are appropriate to represent the continuum. Here we present the results for the resonant multichannel ionization of the He atom and of the H_2 molecule, as a first step towards more complex systems. The positive results, together with the great flexibility of QCPs, position our method as a strong candidate for the theoretical study of the ionization of poly-electronic systems.

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P-50

Continuum extension of quantum chemistry tools: the photoionization of neon.

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Recent breakthroughs in the generation of extreme ultraviolet (XUV) and x-ray attosecond pulses [1, 2], have made it possible to study electron dynamics at its natural time scale. Many numerical approaches can accurately reproduce the ionization processes triggered by these pulses in small atomic and molecular targets [3-6]. Problems arise, however, when tackling more complex systems, due to the correlated short-range structure of polyelectronic functions. Whereas sophisticated methods to compute the electronic structure of bound molecular states are implemented in standard quantum chemistry packages (QCP) (e.g., MOLCAS [7]), equivalent general tools for the electronic continuum are not available yet.

To tackle this problem we are developing a merge between existing QCPs and current numerical scattering method (XCHEM code). In our approach, the electronic configuration space is separated in a short-range region, which can host all the interacting electrons, and a long-range region in which one outer electron interacts with a finite number of correlated parent ions. This outer electron is expressed in terms of a hybrid basis (GABS) which combines short-range Gaussian functions, compatible with standard QCPs, with B-splines [8], which are appropriate to represent the continuum. Using this approach, we have already obtained good results for He and H_2, whose parent ions contain a single electron. Here, we illustrate the capabilities of the XCHEM code for the neon atom, a more complex system with multi-electronic parent ions. We use XCHEM to compute multichannel eigenphases as well as the photoionization cross section, and find good agreement with the results obtained using the STOCK code [9].

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P-51

Imaging the complex influence of the leaving group on nucleophilic substitution reactions

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Predicting the outcome of a reactive encounter is of fundamental importance for processes in synthetic chemistry, catalysis or astrochemistry. Our group has investigated the dynamics of several gas phase bimolecular substitution S_N2 reactions of the type $X^- + CH_3Y$ where X (nucleophile) and Y (leaving group) are halide atoms and has identified a number of distinct dynamical features [1], than just the classic backside attack.

Here, we report on the influence of the leaving group on the dynamics of S_N2 reactions [2]. Our experimental approach combines crossed beam scattering with 3D velocity map imaging. This allows us to record differential scattering cross sections which contain the full three dimensional velocity information. Specifically, we have studied the reaction of F^- with CH_3Cl. We expected similar dynamics as for $F^- + CH_3I$ [3] because both systems show very similar energetics in the entrance channel. However, we found a significantly different dynamical behavior in case of chlorine as leaving group. High level chemical dynamics simulations revealed that the differences in interaction of the nucleophile F^- and the respective leaving group leads to this distinct differences in the dynamics [2].

Recently, we extended our investigations of gas phase organic reactions to the competition of based induced elimination E2 with bimolecular nucleophilic substitution S_N2 reactions. These two reaction channels are in constant competition, if the molecule contains at least two carbon atoms in its backbone. To disentangle both channels by experimental methods is challenging because the same ionic product is formed in both S_N2 and E2 reactions. We used ion imaging to identify the dynamical fingerprint of the E2. First results will be shown on the transition from S_N2 to E2 dynamics.

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P-52

Competing relaxation channels of N-methylpyrrole: C-N dissociation *vs* internal conversion

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N-methylpyrrole (NMP) is an excellent model to study the photochemistry of $\pi\sigma^*$ states involving C-N bonds [1]. We have explored its relaxation after electronic excitation, by combining femtosecond time resolved ion/electron detection methods and high level *ab initio* calculations [2]. The recorded dynamics, remarkably different to that observed for pyrrole and other aromatic systems, is explained in terms of two alternative decay channels: intersystem crossing followed by C-N bond dissociation and ground state internal conversion along the out-of-plane ring deformation. Important implications for more complex molecular systems can be derived.

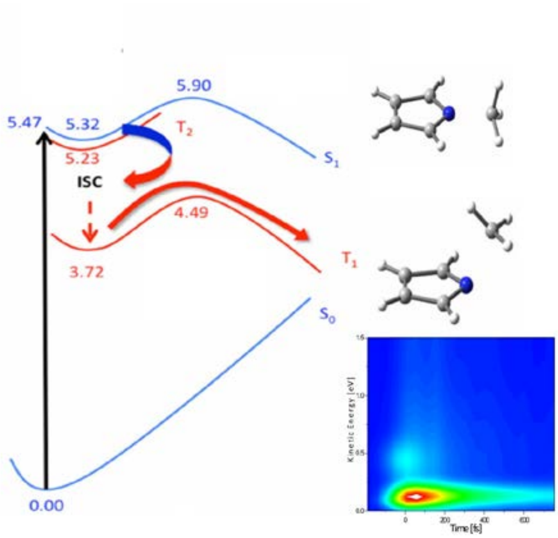

Figure: Schematic representation of the NMP photochemistry

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P-53

Sampling initial states for quasiclassical trajectory calculations using adiabatic switching

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The quasi-classical trajectory (QCT) method is widely used in the state-resolved theoretical investigations of elementary reactions in gas phase. In the QCT method, the motion of the atoms is simulated classically, and the only quantum effect considered is that the initial vibrational states of reactant molecules are semiclassically quantized. Preparation of initial states is usually based on the harmonic approximation to the Hamiltonian, which reduces the problem of quantization to independent normal modes.

A sensible expectation is that the initial ensemble of classical molecular states generated this way should be stationary, similarly to the quantum state it is supposed to represent. We demonstrate that normal mode sampling provides a nonstationary ensemble even for a simple rigid molecule like methane (CH_4). Because of the nonstationarity, QCT cross sections for reaction R1: $CH_4+H \rightarrow CH_3+H_2$ oscillate periodically as a function of the initial distance of the colliding partners. We proposed an *ad hoc* correction, in which reactivity parameters are calculated by averaging over a period of the oscillation [1].

Primitive semiclassical theory and Ehrenfest's theorem of adiabaticity provides a physically more established means, called adiabatic switching (AS), to prepare initial states with semiclassical quantization of the uncoupled Hamiltonian [2,3]. However, the applicability of Ehrenfest's theorem is not guaranteed for molecules with chaotic and/or resonant motion [4]. Previous application of AS to CH_4 were unsuccessful [5]. We revisited the problem [6] and here we report on successful convergence of semiclassical energies and we show that normal mode quantum numbers are conserved only if some level of separability is assumed between the modes. By running QCT simulations of reaction R1 we also demonstrate that the CH_4 ensembles obtained by AS are stationary.

Recently, we evaluated the Palma-Clary (PC) reduced-dimensional model in QCT simulations of reaction R1 using normal-mode sampling of initial states [7]. Here we report on applying AS to quantize a hierarchy of reduced-dimensional models of CH_4 in order to prepare initial states and investigate their reactivity in reaction R1.

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P-54

Reactive Collisions of Sodium Atoms with Doped Water Clusters

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Tagging molecular clusters with sodium atoms can be used for sizing the clusters; sodium atom upon the uptake on polar clusters releases hydrated electron which can be photo-ionized in a fragmentation free process and standard mass spectrometry techniques can be used for the cluster detection. In this way, e.g. the onset of crystallization in water clusters was observed [1]. The hydrated electron can however also react with another molecule within the cluster. Here we study the structure and reactivity of the hydrated electron on a small ice cluster using methods of *ab initio* chemistry and *ab initio* molecular dynamics. The energy transfer between the colliding sodium atom and the cluster molecules leads to formation of different cluster isomers [2]. We also discuss the effects of non-sphericity of the clusters resulting in higher effective cross section of the collision compared to spherical clusters with the same number of molecules. We further investigate reactivity of sodium with nitric acid HNO_3 [3] and nitrous oxide N_2O. It is shown that the hydrated electron is attached to the nitrogen compound within a few picoseconds upon the uptake. This process is characterized by a marked increase in the ionization energy of the system. The anion formed then almost immediately decomposes and further reacts with the solvent molecules.

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P-55

Attosecond transient absorption spectroscopy above the N=2 threshold of helium

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Time dependent processes, such as chemical reactions, are controlled by the time evolution of electrons. This gives an incentive to study time resolved electron dynamics. Previous work, such as 1 and 2, has made use of attosecond transient absorption spectroscopy (ATAS) in order to study two-photon beatings in helium. ATAS allows the study of coherent superpositions of atomic states by looking at the beating between excited states. It makes use of two pulses, a short extreme ultraviolet pulse (XUV) that populates the high energy states of the atom, and a longer pulse of visible light (VIS) which induces population transfer between the excited states. The dipole response is then observed to gain information about the electron dynamics. By varying the time delay between the pulses, a time resolved image emerges.

In this communication numerical ab initio calculations of ATAS in helium were made with a B-spline basis. The spectrum was then computed from the Fourier transform of the dipole response. The response near the pulse was transformed numerically, whereas for times after the pulses had died down, the response was transformed using the analytical Fourier transform along with the computed state vector.

This work is an extension of references 1 and 2 to energies above the N=2 threshold. It uses a VIS pulse with a wavelength of ~798nm to studies the four-photon beating between the 2s3p+3s2p state and the 3s3p state in helium.

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P-56

The RgI$_2$(ion-pair states) van der Waals complexes

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We report on the first measurements of excitation spectra of luminescence as well as luminescence spectra themselves of predissociation products of the RgI$_2$(ion-pair, IP, states), Rg = He, Ar, van der Waals (vdW) complexes.

New experimental set up consisting of supersonic beam equipment, Quantel laser system and registration system described in [1] was utilized in the experiments. A pulsed supersonic molecular beam was crossed with two counter-propagating temporally overlapped laser beams at ~ 5-8 mm downstream distance from the nozzle. Two tunable dye TDL90 lasers ($h\nu_1$ and $h\nu_2$) pumped by second harmonic of theYG981C Nd:YAG laser ($2h\nu_f$) were utilized. The *T*-shaped HeI$_2$(B,v_B=19) and ArI$_2$(B,v_B=20) complexes were populated by $h\nu_1$ laser beam. These complexes and products of their vibrational predissociation (VP) (I$_2$(B,v_B) were excited by the $h\nu_2$ laser beam.

High concentrations of the RgI$_2$(IP) complexes and large $h\nu_1$, $h\nu_2$ laser pulse photon irradiance $E_{h\nu}$ (photon/(s·cm^2)) enable us to measure excitation spectra of luminescence of the RgI$_2$(IP) complexes predissociation products I$_2$(IP), IP = $D0_u^+$, $D'2_g$, $\beta 1_g$, $E0_g^+$ and even their luminescence spectra with spectral resolution sufficient for determination of vibrational distributions of the products. To understand in which optical transitions, from the I$_2$(B,v_B) molecules or RgI$_2$(B,v_B) complexes, luminescent species are populated, we measured excitation spectra with $h\nu_2$ laser pulses 20 ns temporally delayed relative the $h\nu_1$ one. The RgI$_2$(B,v_B) complexes have to disappear in this time scale.

The principal results we have obtained can be described briefly as follows:
ArI$_2$(IP):
1. The ArI$_2$(E,v_E=0-3 ← B,20) transitions are the strongest in the $\nu_1 + \nu_2 \approx 41300 – 41900$ cm^{-1} energy range under study with subsequent ArI$_2$(E,v_E=0-3)→Ar+I$_2$(E,v_E=0-2) VP and electronic ArI$_2$(E,v_E=0-3)→Ar+I$_2$(D, β, D') predissociation (EP). Rate of VP is ~ 10 times less than total rate of the EP.
2. The larger v_2 value is, the higher vibronic levels of IP states which populated in EP of the ArI$_2$(E,v_E) complexes and following VP of the ArI$_2$(IP,v_{IP}) complexes are.
3. We have determined the spectroscopic parameters of the ArI$_2$(E,v_E=0-3) complexes.
HeI$_2$(IP):
1. The HeI$_2$(E,v_E=0-2 ← B,19) transitions are the strongest in the $\nu_1 + \nu_2 \approx 41300 – 41600$ cm^{-1} energy range under study with subsequent HeI$_2$(E,v_E)→He+I$_2$(E,v_E=0-1) VP and HeI$_2$(E,v_E)→He+I$_2$(D, D') EP.
2. Relative probabilities of VP and EP depend on populated state; rate of HeI$_2$(E,v_E) EP yielding the I$_2$(D') is much less than that of I$_2$(D).
3. Dissociation energies of the HeI$_2$(E,v_E=0-2) complexes have been determined.

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Quantum Hydrodynamics of the Electron in Vibrating H_2^+

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Ultrafast vibrating hydrogen molecular ions H_2^+ are produced when intense strong laser pulses interact with neutral hydrogen molecules H_2. When these molecular ions are analyzed with field-free Born-Oppenheimer (BO) dynamics, then their vibrations will normally be described by the movements of nuclear wave packets in the electronic non-degenerate ground state. It is intuitively clear that these vibrations cause electron motions which can be characterized both by the electron density and by the electron current density depending on time and space. However, in the Born-Oppenheimer approximation (BOA), the electron current density vanishes incorrectly for vibronic wave packets in a single electronic state. Nevertheless, electron currents – which are electron current densities integrated over areas – can be calculated within the BOA by integration of the time derivative of the electron density over reasonably chosen areas (see [1]). In order to circumvent this problem, our new idea is to calculate electron current densities by applying quantum hydrodynamics (QHD) (for the fundamentals of QHD see [2,3]). That is, we solve numerically an equation called quantum Navier-Stokes equation (QNSE) numerically to obtain non-vanishing electron current densities. This approach includes the use of a time-dependent wave function as an input to the QNSE. We analyze if the use of an approximated BO wave function instead of the exact one is a reasonable input for the QHD simulations. This yields to a condition which has to be checked with exact wave functions. For the H_2^+ molecule, we can calculate these exact wave functions with the methods explained in [4] and use them for a check of this condition.

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P-58

Controlled reactions of methyl cations with hydrocarbons

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The methyl carbocation is a reactive species whose presence has been detected in a lot of gaseous environments fed by high energy sources, such as the interstellar medium, planetary ionospheres and laboratory plasmas for methane conversion into higher hydrocarbons for instance. Its reactivity with hydrocarbons is generally well-known, yet the corresponding literature mainly concerns the cation in its ground state although excited species are likely to be present in the different environments of interest.

Here, new results on the reactivity of the methyl carbocation obtained with the CERISES setup (a guided ion-beam experiment) will be presented. The originality of these experiments is to investigate the effect of internal degrees of freedom (vibrational, electronic) on the reactivity of the CH_3^+ cation with different hydrocarbons. This is made possible by producing the CH_3^+ ion *via* direct photoionization of a molecular beam of $CH_3\cdot$ radicals. The radicals are formed by pyrolysis of an appropriate precursor molecule (here CH_3NO_2) in an additional chamber coupled to the standard CERISES set-up [1] and further ionized thanks to VUV photons delivered by the DESIRS beamline at the synchrotron SOLEIL [2]. Variation of the photon energy thus allows to produce the ion within a controlled degree of internal excitation.

Branching ratios and absolute reaction cross-sections have been obtained for the $CH_3^+ + CH_4$ reactive system. Reaction dynamics and its dependence on the vibrational excitation of the parent-ion will be discussed. Results obtained with other small hydrocarbon targets (C_2H_2, C_2H_4, C_2H_6…) will also be reported.

Note that, thanks to the radical source now available on this setup, other radicals such as $C_2H\cdot$, $C_2H_3\cdot$, $C_2H_5\cdot$… can be produced and the reactivity of their excited cations (C_2H^+, $C_2H_3^+$, $C_2H_5^+$…) studied.

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Adding exchange and multiple splitting terms to correct the long range in the H_3^+ potential surface

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The description of the long range interaction in potential energy surfaces is a hard task that has to be carefully study for every system. Particular care must be taken if the potential energy surface will be used in cold and slow collisions.

The high interest that H_3^+ produces, due to his presence in the interstellar medium[1], is evident from the large number of studies on its spectroscopy and formation by different methods (collisions, etc...). Theoretical studies require as a first step the calculation of the potential energy surfaces and in the literature there are several global potential energy surfaces for the ground[2,4] and some of the excited states[3,5] of H_3^+. However the accuracy of these surfaces is high, the intermediate and long range description is not as high as certain calculations may require, being in most of them higher than 10 cm^{-1}.

In this poster contribution we present the new terms that we are adding to the potential fit of the H_3^+ surface including the exchange splitting of the interaction energy between H and H^+, and the multipole expansion, accounting for the long range interaction between an ion (H^+) and a homonuclear neutral molecule (H_2). This expansion is added to the diagonal terms of the DIM matrix, fitted and after diagonalised to obtain the ground electronic state of H_3^+ with an accuracy lower than 1 cm^{-1} for the whole surface.

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P-60

Identification of phase transitions of a mixed system of electronically excited species and liquid helium by studying the pressure dependence of lineshift, linewidth and line intensity of visible and near infrared fluorescence

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The ability to record spectra with rotational resolution at cryogenic temperatures provides exceptional sensitivity for investigating solute – solvent interactions. For example, infrared spectroscopy of foreign molecules in helium droplets has uncovered manifestations of nanoscale superfluidity [1]. These studies also showed remarkable temperature effects on the spectral features when 0.4 K cold ^{4}He droplets were replaced by 0.15 K cold mixed ^{3}He – ^{4}He droplets. The promise of pressure and temperature effects motivated our study.

To investigate solute – solvent effects in a larger temperature range and as a function of pressure we have generated He_2^* excimers in bulk helium by means of a corona discharge. Corona discharges allow for electronic excitation and ionisation of helium in a very wide pressure range. Using this technique, we have recently shown the formation, growth and compression of ionic helium clusters [2]. In bulk liquid helium He_2^* excimers have been studied before, but the state of solvation remained unclear.

Spectra were recorded between 3.8 K and 5.0 K and 0.2 bar and 5.6 bar. Intense fluorescence in the visible and near infrared regions showed the rotationally resolved $d^3\sum_u^+ \rightarrow b^3\prod_g(0-0)\ and\ D^1\sum_u^+ \rightarrow B^1\prod_g(0-0)$ transitions of He_2^*. Also we observed Fluorescence of the $3s^3\ S \rightarrow 2p^3\ P\ and\ 3s^1\ S \rightarrow 2p^1\ P$ of atomic transitions. Upon increasing the pressure the lines broadened and merged into a continuum. The lines were also found to shift in frequency towards short wavelength when the pressure was increased; the intensity distribution shifted towards the lowest rotational state and within the resolution the B - constant was unchanged.

Lineshift, line broadening and the line intensity ratio of Q and averaged P lines (without - P 2) coefficients were derived by fitting Lorentzian functions to the rotational and atomic lines. We observed that for the Q -band these showed discontinuities at pressures and temperatures close to the saturated vapour pressure of helium. Whereas the discontinuities were not observed for the P and R-bands indicating that the sharp P and R-lines were due to excimers reside in gas bubbles generated by local Joule – heating of the corona discharge although the temperatures were below the critical point and within the liquid region of the phase diagram. For other transition including the atomic transitions is qualitatively similar results we obtained, but the exact position of the discontinuities deviated. So the detection of the discontinuities gives rise to identify the saturated vapour pressure curve for each individual mixed system. Hence, the possibility of cluster formation can be studied by the exact position of the saturated vapour pressure curves.

This would provide an important benchmark for theory to test interaction potentials of excimers and He atoms in different excited states in helium. Also the demonstration of rotationally resolved spectroscopy in the bulk phases of He is important for a better understanding of superfluidity at the nanoscale.

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P-61

Ab initio study of the simplest Criegee intermediate CH_2OO

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Criegee intermediates are formed by ozonolysis of alkenes and they play a key role in tropospheric chemistry as they are responsible for the removal of volatile organic compounds from the atmosphere.[1] However, their experimental characterization is difficult due to their extremely short lifetime.[2] Alternatively, Criegee intermediates can be studied by means of theoretical chemistry.

This work focuses on the quantitative *ab initio* description of the simplest Criegee intermediate CH_2OO. The primary objective is to describe both ground and excited states of CH_2OO and to obtain its high quality UV absorption spectrum. Particular attention is paid to the development of sophisticated modeling methods and to the dual nature of Criegee intermediates which exhibit both biradical and zwitterionic character. It was found that commonly used methods are inadequate to describe Criegee intermediates due to their complex electronic structure. Therefore, advanced simulation protocols mainly based on the coupled clusters theory are presented in this work. UV spectra are modeled using *ab initio* molecular dynamics and reflection principle. Quantum effects are incorporated by combining path integral molecular dynamics and quantum thermostat based on Generalized Langevin Equation.

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P-62

Conical intersection dynamics of NO_2 probed with a time-preserving XUV monochromator

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A newly-developed XUV monochromator for HHG is used to investigate the conical-intersection and dissociation dynamics of NO_2 [1] by time-resolved photoelectron and photoion spectroscopy. Using 3.1 eV (400 nm) pulses of ~40 fs duration the molecule is excited to the A^2B_2 state which leads to internal conversion and partial dissociation into NO and O fragments. Time-resolved photoelectron spectra are recorded with XUV pulses centered at 20.2, 23.3 and 26.3 eV (results shown in panel a) with ~30 fs duration. The unique novelties of XUV time-resolved photoelectron spectroscopy, compared to its traditional variant, are its ability to (i) project the photoexcited neutral-molecule wave packet onto multiple electronic states of the cation and (ii) to probe wave-packet components returning into the electronic ground state following internal conversion. Both innovations are optimally exploited in the present study. Property (i) leads to a much more complete characterization of the photoexcited wave packet, which becomes apparent when noticing the profound differences between the time-resolved signals shown in panel b. Property (ii) enables internal conversion to be followed over its entire temporal evolution, revealing wave-packet dynamics in the electronic ground state. These results are shown in panel c. These experimental results will be discussed by comparison with high-level ab initio calculations of the electronic structures of NO_2 and NO_2^+ and full-dimensional wave-packet calculations.

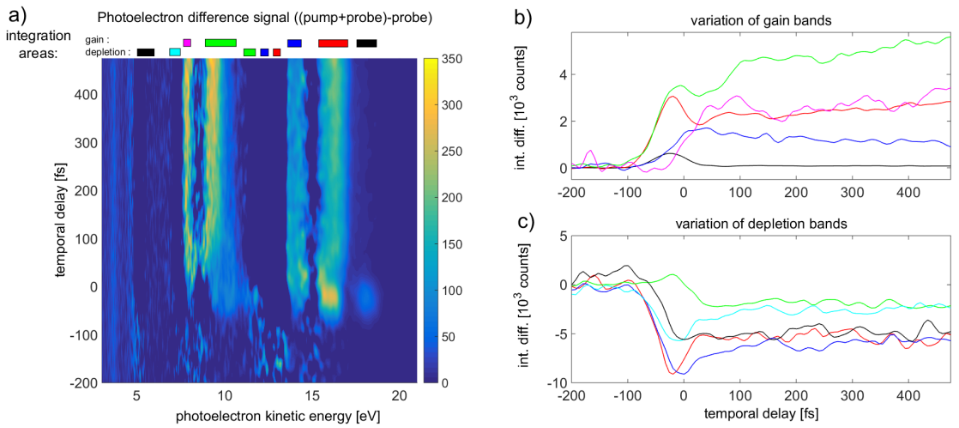

Figure: Time-resolved photoelectron spectra of NO_2 following excitation at 3.1 eV (~40 fs) and ionization at 26.3 eV (~30 fs). Panel a shows the positive contributions to the difference spectrogram acquired through single-shot referencing. Panels b and c show spectrally-integrated gain and depletion bands, respectively, according to the color code of the rectangles displayed above panel a.

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P-63

Cold ion-molecule collisions in a cryogenic hybrid trap

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In recent years, collisions of cold atoms with atomic and molecular ions have been studied intensively. The development of “hybrid traps” which allow for the simultaneous trapping of cold neutral atoms and ions have paved the way for gaining insights into the nature of ion-atom collisional processes at very low temperatures [1].

We are currently developing a cryogenic trap for the simultaneous confinement of cold neutral molecules and cold molecular ions. Translationally cold neutral molecules are produced by Stark deceleration and loaded into a magnetic trap [2]. The magnetic trap’s center can be mechanically displaced and superimposed with the center of an RF ion trap. The interaction of room temperature black body radiation (BBR) results in rotational excitation of the OH leading to trap loss after few seconds. To alleviate this effect, the hybrid trap is cooled down to 7 K to be shielded from room temperature BBR, which is increases the lifetime of the trapped molecules by several orders of magnitude, commensurate with the trap lifetime of the ions.

This new setup will allow for the first time studies of ion-molecule collisions in the millikelvin regime. We will present a detailed characterization of the experiment and first results on cold ion-molecule collisions.

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P-64

Multi-step reactions mechanism of F and N atoms interactions with SiOCH low-*k* films

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Elementary stages of etching processes widely used in plasma processing are not fully understood. Multi-step mechanism of F atoms interactions with nanoporous low-*k* organosilicate glass (OSG) films used in advanced interconnects of ULSI devices is proposed on the base of *ab initio* DFT static and dynamic simulations and experimental study [1]. A brief review of state-of-the-art approaches to such simulations is presented.

Coherent picture of SiOCH films damage and etching processes is provided to describe the experimentally observed stages: fast fluorination, damage and etching [1]. Quasi-chemisorption of F atoms and complex redistribution of electron density resulting in appearance of pentavalent Si states on SiOCH surface play an important role in these processes. It was revealed that pentavalent Si atoms induce the weakening of adjacent Si–O bonds and their further breaking under incident fluorine atoms. A set of elementary chemical reactions of successive appearance and removal of various CH_xF_y surface groups followed by the fluorinated SiO_x matrix etching is described. The similar DFT approach was applied for the interactions of N atoms with OSG films to analyze experimental data on appearance of C-N and N-H bonds.

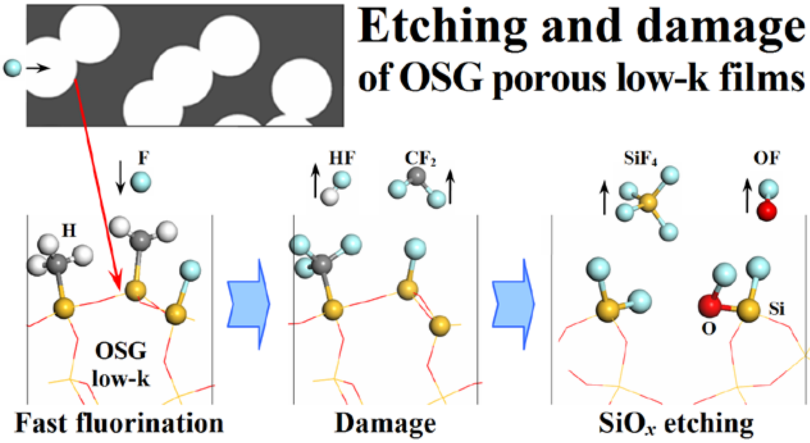

Fig. 1: Schematic stages of OSG films etching and damage by fluorine atoms.

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P-65

Quantum-mechanical binary approach: sputtering of amorphous Si by Ar atoms.

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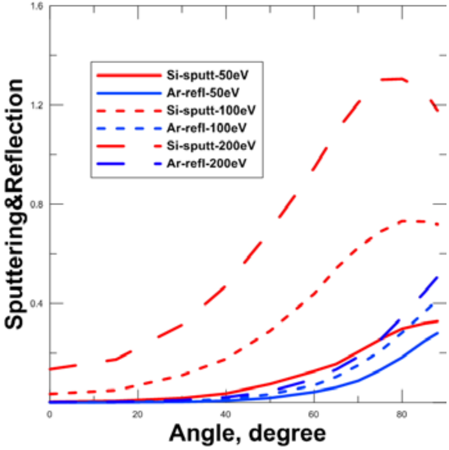
Molecular dynamics (MD) is the most suitable tool to model sputtering of amorphous materials under atomic bombardment in the range of energies from just above of threshold to a few hundreds eV, see Ref.1 and Ref.2. However it is still time consuming for industrial applications and below we present a binary Monte Carlo (MC) model that is close to compete with MD at low energies. Unlike traditional MC approaches based on mean free path equaled to interatomic distance in a solid and classical calculation of a scattering angle our model uses quantum-mechanical integral atom-atom elastic cross sections (ICS) for a mean free path calculations and differential cross section (DCS) for computation of a scattering angle.



We have calculated *ab initio* interatomic Ar-Si potential with help of multireference Hartree-Fock method and the DCS and ICS for this potential, see Ref. 3. The obtained cross sections were applied to MC modeling of Ar atom interaction with amorphous Si. The obtained dependences of Si sputtering and Ar reflection coefficients on angle of bombardment are presented on Fig.1. We expect the obtained data to be useful for modeling of such plasma processing technologies as zero-defect and atomic layer etching (ALE) by fast atoms.

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Fig.1. Dependence of Si sputtering and Ar reflection as a function of Ar bombardment angle to the normal to silicon surface

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P-66

Steric effect in the F + aligned-$CHD_3(v_1=1)$ reaction

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The steric requirement of reagent approach geometry is one of the key concepts for fully understanding and controlling chemical reactions [1]. Recently, a benchmark study on full three-dimensional (3D) characterization of such steric effect has been reported by acquiring the dependence of product angular distributions on the spatial alignment of the C-H bond in the vibrationally excited CHD_3 (v_1=1) + Cl reaction, in which the initially prepared alignment state of CHD_3 is preserved up to the reaction barrier due to the relatively weak long-range interaction in the entrance valley [2, 3]. In contrast to such investigation on purely actively controlled steric dynamics, we study steric effect in the F + vibrationally excited CHD_3 (v_1=1) reaction, in which strong long-range anisotropic interactions in the entrance valley [3, 4] may strongly stir initially prepared reagent approach geometry. Here, we report a complete 3D characterization of steric effect in the title reaction in a crossed-beam, time-sliced imaging experiment. The complete set of polarization-dependent differential cross-sections (PDDCSs) [5] of the F + aligned-$CHD_3(v_1=1)$ reaction are deduced from the vibrationally state-resolved product angular distributions in a series of reagent alignment configurations in the laboratory. The relatively small, yet finite, values of PDDCSs imply anticipated influences of long-range interactions in the entrance valley of the title reaction on initially prepared reagent alignment. In addition, the renormalized PDDCSs for both DF(v=4) + $CHD_2(1_1)$ and DF(v=3) + $CHD_2(1_1)$ product pairs show similar trends over the full range of scattering angles. Moreover, PDDCSs deduced from different types of alignment preparations of $CHD_3(v_1=1, J=1)$ using R(0) and Q(1) excitation transitions present partially different dependences of polarization effects on product scattering angles.

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P-67

Quantum State Resolved Scattering of NO from Molten Metal and Ionic Liquid Surfaces

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Nonadiabatic collision dynamics at the gas-liquid interface are explored with state-to-state resolved molecular scattering of NO. Complete rotational and electronic populations of scattered NO are extracted, which provide insight into energy transfer and scattering pathways at the surface. Additionally, the multiple low-lying electronic states of NO allow the electronic properties of the surface to be explored by observing spin-orbit excitation in the scattering event, which is of particular interest in molten metals and molten salts via electron transfer mechanisms.

Dynamics at the gas-liquid interface are investigated as a function of (i) scattered angle, ranging from $\theta_{scatt} = -60^{\circ}$ to 60° with respect to surface normal, (ii) incident collision energy, (iii) liquid identity, specifically room temperature ionic liquids (RTILs) and molten metals (Ga, In, Au), and (iv) surface temperature. Results from these experiments show strong correlations between liquid identity and spin-orbit state population distributions, which provide insight into the nature of the NO-liquid surface collision dynamics.

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