AtmChemClimate
20-21 June 2023
Montpellier

Workshop on Quo vadis theoretical modeling of gas-phase reactions: applications in atmospheric chemistry and climate change

Organised in partnership with :

Montpellier Advanced Knowledge Institute on Transitions

Laboratoire Univers et Particules de Montpellier

Université de Montpellier

20th and 21st of June 2023
Amphitheater RH of the Botanical Garden, Université de Montpellier

Réalisation : L. URANGA PINA

Welcome to the AtmChemClimate workshop in Montpellier !

We are pleased to announce the ***Workshop on Quo vadis theoretical modeling of gas-phase reactions: applications in atmospheric chemistry and climate change***, to be held in the Amphi RH of the Botanical Garden, Université de Montpellier, the 20th and 21st of June 2023, hosted by the Montpellier Advanced Knowledge Institute on Transitions (MAK'IT) and the Laboratoire Univers et Particules Montpellier (LUPM) and the University of Montpellier.

The workshop will have a two-fold objectives: the first scope will be to serve as a meeting point to bring new ideas and advance in improving current theoretical and computational methods to solve highly computational demanding quantum dynamical problems in the field of gas-phase reaction relevant to environmental physics and chemistry. We aim to cover several aspects such as, quantum mechanical modeling of reactive dynamics, energy- and time resolved molecular spectroscopy, non-adiabatic dynamics, etc. The second goal has an interdisciplinary view as we aim to gather experts from different fields tackling the question on: how the chemical-physics community can effectively help to bring new knowledge and solutions to, as well as to connect with, the atmospheric chemistry community in the context of climate change.

The aim of this workshop is to bring together researchers from the global South and Europe actively working in related fields, and to foster new interactions and collaborations within these communities. In particular, the workshop aims to consolidate the ongoing formation of a scientific network to strengthen the cooperation between researchers in Europe and the Global South on this topic. The workshop will count with the participation of leading experts in this field, and other potential stakeholders.

The programme consists of invited talks, group discussions, and poster sessions. The workshop will be held in hybrid format.

WORKSHOP AGENDA

Workshop Agenda (download)

June 20, 2023 09:00 - 22:30 CEST / Amphi 2301 OU RH (Jardin Botanique) Montpellier, France

09h00 – 09h30 Onsite registration (Welcome coffee)

09h30 – 09h40 Presentation of the MAK'IT program and venue by MAK'IT

"Atmospheric science and climate action"

Chairwoman : Dr. Bibiana BILBAO

(Professor at the Environmental Studies Department, Simón Bolívar University in Venezuela, and an active Cobra Collective CIC (Community Interest Company), UK member)

09h40 – 09h50 Introduction by the organizers (1st part)

09h50 – 10h30 Dr. Abir HADDAD (virtual)

(Legal Futurist, Founder and director of Institute for Legal Transformation (Bonn), Adjunct Professor, Universität zu Köln)

Key note talk: "Scarce Global Water Resources: A new methodological interdisciplinary approach to create sustainable regulatory frameworks for future generations by combining comparative law methods and futurism" (abstract)

10h30 – 10h50 Discussion

10h50 – 11h05 Coffee break

11h05 – 11h45 Dr. Rebecca GARLAND (virtual)

(Professor, University of Pretoria, South-Africa, specialist on atmospheric chemistry with a focus on air quality, climate change, and science-policy linkages)

Key note talk: "Improving the quantitative evidence base for air quality management in a data scarce region: perspectives from South Africa" (abstract)

11h45 – 12h05 Discussion

12h05 – 13h30 Reception (lunch)

"Theoretical modeling of gas-phase reactions in different atmospheres"

13h30 – 13h40 Introduction by the organizers (2nd part)

Chairwoman : Dr. Nadine HALBERSTADT

(CNRS Researcher, LCAR-FERMI, University Paul Sabatier, France)

13h40 – 14h10 Dr. Sergey YURCHENKO

(Professor, University College London, UK)

Title : "Computing molecular line lists for atmospheric applications: completeness versus accuracy" (abstract)

14h10 – 14h40 Dr. Alejandro RIVERO-SANTAMARIA

(Professor, Laboratoire PhLAM, Université de Lille, France)

Title : "Ab Initio Molecular Dynamics calculation on NO oxidation over graphite oxides" (abstract)

14h40 – 15h10 Dr. Jean Christophe TREMBLAY (virtual)

(Professor, University of Lorraine, France)

Title : "Stochastic Simulations of Energy Exchange at Surfaces" (abstract)

15h10 – 15h40 Dr. Maikel BALLESTER-FURONES (virtual)

(Professor, Universidade Federal de Juiz de Fora, Brasil)

Title : "Vibrational relaxation and recrossing effects in the OH + SO → H + SO2 reaction" (abstract)

15h40 – 16h00 Coffee break

Chairman : Dr. Sergey YURCHENKO

(Professor, University College London, UK)

16h00 – 16h30 Dr. Sebastian FERNANDEZ-ALBERTI (virtual)

(Professor, Universidad Nacional de Quilmes, Argentina)

Title : "Vibrational Funnels for Energy Transfer during Internal Conversion in Organic Chromophores" (abstract)

16h30 – 17h00 Dr. Benjamin LASORNE

(CNRS Researcher, Institut Charles Gerhardt Montpellier, France)

Title : "Variational error in molecular quantum dynamics - a dialog between maths and chemistry" (abstract)

17h00 – 17h30 Dr. Basile CURCHOD (virtual)

(Professor, University of Bristol, UK)

Title : "Photochemistry from a theoretical and computational perspective" (abstract)

17h30 – 18h30 Cocktail & Poster Session

20h00 – 22h00 Social Dinner

June 21, 2023 09:15 - 12:30 CEST / Amphi 2301 OU RH (Jardin Botanique) Montpellier, France

Subsession : "High resolution spectroscopy and reaction dynamics"

09h00 – 09h30 Welcome coffee

Chairman : Dr. Benjamin LASORNE

(CNRS Researcher, Institut Charles Gerhardt Montpellier, France)

09h30 – 10h00 Dr. Ha TRAN (virtual)

(CNRS Resercher, Laboratoire de Météorologie Dynamique (LMD) Paris)

Title : "Collisional effects on the spectral shape and atmospheric remote sensing" (abstract)

10h00 – 10h30 Dr. Nadine HALBERSTADT

(CNRS Researcher, LCAR-FERMI, University Paul Sabatier, France)

Title : "Dynamics of superfluid helium nanodroplets" (abstract)

10h30 – 11h00 Dr. Marta I. HERNANDEZ-HERNANDEZ

(Researcher, CSIC Madrid, Spain)

Title : "Attachment of hydrogen molecules to atomic ions: role of the hydrogen rotational states" (abstract)

11h00 – 11h20 Coffee break

11h20 – 11h50 Dr. Lidice CRUZ-RODRIGUEZ (virtual)

(Postdoctoral Fellow, University College London, UK)

Title : "Forward and hybrid path-integral approaches in photoelectron holography" (abstract)

11h50 – 12h20 Dr. Pascal LARREGARAY

(Professor, Diputy director, Institut des Sciences Moléculaires, Université de Bordeaux, France)

Title : "Recent applications of the statistical approach of reaction dynamics" (abstract)

12h20 – 12h30 Concluding Remarks

ABSTRACTS

Scarce Global Water Resources:
A new methodological interdisciplinary approach to create sustainable regulatory frameworks for future generations by combining comparative law methods and futurism.

Abir Haddad[1]

[1] *Director of the Institute for Legal Transformation / UNFCCC Resilience Frontiers Initiative, Bonn, Germany*

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How can we use law to prevent bigger harm for future generations, especially those challenges we already know will occur in the future. One tool can be creating resilient laws to tackle this issue. Dr. Abir Haddad will share with you the Methodology she developed for the Resilience Frontiers Project of the *United Nations Framework Convention on Climate Change* (UNFCCC), a foresight-driven initiative that aims at harnessing the potential of paradigm-shifting frontier technologies and emerging social trends towards long-term global resilience. In this keynote you will be exploring legal instruments from different jurisdictions for opening up new possibilities of regulation, which can be implemented on a national and global level.

Improving the quantitative evidence base for air quality management in a data scarce region: perspectives from South Africa

R. Garland[1]

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Global assessments estimate large impacts from exposure to poor air quality in many countries in Africa. However, these estimates have large uncertainties due to insufficient information, which often stems from the lack of ground-based measurements, as well as the lack of integration of local knowledge. The combined effect of insufficient data and uncertainties impacts not only the understanding and quantification of air pollution levels and impacts, but also affects the understanding of the climate. Many air pollutants have an impact on the climate as short-lived climate forcing pollutants (SCLPs; e.g. particulate matter, ozone).

Available monitoring data across South Africa show that ambient air pollutant concentrations often exceed South Africa's National Ambient Air Quality Standards (NAAQS), especially for PM and ozone, and have not been improving. A spatially and temporally heterogeneous mix of pollutants with varying concentrations is present, especially in the large urban areas, which makes effective air quality management a difficult task. This presentation will highlight our work that has focused on improving the evidence base for effective air quality management in South Africa despite the scarcity of available data.

Computing molecular line lists for atmospheric applications: completeness versus accuracy

S. Yurchenko[1]

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The ExoMol team at UCL is the world leader in providing spectroscopic data for hot atmospheric applications. The ExoMol database hosts molecular line lists for about 90 molecules plus many isotopologues. The ExoMol data base (www.exomol.com) has become the go to place for data on hot molecules for studies of hot environments.

Production of ExoMol line lists is based on the application of rigorous quantum mechanical methods informed by laboratory experiments, rather than on direct measurements. The ExoMol philosophy has therefore been to make a rigorous quantum mechanical formulation of the spectroscopic problem for each molecule, to use the best practicable method for solving this problem, and to then use any available experimental data to improve our spectroscopic model. We describe this as "first principles theory informed by experiment". Methods of producing highly accurate molecular line list for modern high-resolution spectroscopic applications to meet the competing demands of completeness versus accuracy will be discussed.

Ab Initio Molecular Dynamics calculations on NO oxidation over oxygen functionalized High Oriented Pyrolytic Graphite.

A. Rivero Santamaría[1], G. Alou Angulo[1], C. Toubin [1] and M. Monnerville[1]

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Nitrogen monoxide (NO) belongs to the group of the most polluting gases in the atmosphere. It serves as a critical precursor for the formation of smog and acid rain, which currently pose significant environmental and human health challenges. Carbonaceous materials have been identified as promising support to carry out the catalytic oxidation of NO to NO_2 at room temperature. After NO oxidation the NO_2 can be easily removed from the reaction chamber by the water scrubbing method allowing an efficient control of NO emissions. The understanding of the reaction mechanism involved in this complex process is fundamental to developing practical applications for this decontamination method.

We presented here ab initio molecular dynamics (AIMD) calculations on the NO oxidation over oxygen functionalized High Oriented Pyrolytic Graphite (O-HOPG) surface. Four different NO incidence energies were studied and the initial conditions were selected in order to facilitate the collision between the incident molecule and the epoxy group present at the surface. Our simulation results indicate that the reaction probability (HOPG-O + $NO_{(g)}$ -> HOPG + $NO_{2(g)}$) increase with the NO incidence energy. The correlations obtained between the initial molecule orientation and the reactivity shed light on the factors that facilitate the catalytic oxidation of NO over activated carbonaceous surfaces.

Stochastic Simulations of Energy Exchange at Surfaces

J.C. Tremblay[1]

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In this contribution, we explore the dissipative dynamics of a multidimensional system in contact with a Markovian bath in the weak and strong coupling regimes. In this endeavour, we use the recently developed stochastic Multi-Configuration Time-Dependent Hartree approach within the Monte Carlo wave packet formalism [J.\,Chem.\,Phys.\,156, 094109 (2022)]. The method proved to yield thermalized ensembles of wave packets when intramolecular coupling is weak.

A model two-dimensional Hamiltonian parameterized to represent an adsorbate-surface system is investigated to disentangle the effects of intramolecular potential coupling, of strong mode mixing observed in Fermi resonances, and of anharmonicity. Further, we simulate state-to-state scattering dynamics of NO on Au(111) to reveal important orientational effects due to vibrationally quantized relaxation.

Vibrational relaxation and recrossing effects in the $\mathrm{OH} + \mathrm{SO} \to \mathrm{H} + \mathrm{SO_2}$ reaction

Maikel Y. Ballester Furones[1], Samah Ellakkis[†] and J.D Garrido[‡]

Departamento de Física, Universidade Federal de Juiz de Fora, Brazil, [†] UNILA, Foz de Iguaçú, Brazil, [‡] Instec, Havana, Cuba

Synopsis Some details of the title reactions are presented in the frame of quai-classical dynamic studies

The understanding of elementary chemical steps in atmospheric acid rain formation is fundamental for mitigating its effects. It is believed the hydroxysulfinyl radical is an intermediate species for the production of atmospheric sulphuric acid. The present talk presents some discussions of a detailed quasi-classical trajectory study of the reaction between OH and SO radicals, considering both relaxation processes and recrossing effects [1, 2]. In the study, a global DMBE PES for the ground electronic state of the HSO$_2$ system was used. A discussion of kinetics and reaction pathways is also presented.
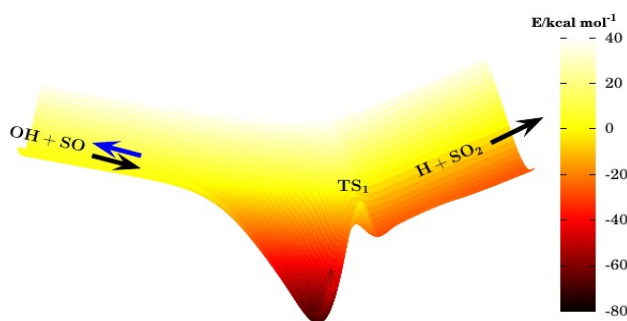
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Vibrational Funnels for Energy Transfer during Internal Conversion in Organic Chromophores

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Photoinduced electronic energy transfer in large multichromophoric molecular systems is naturally accompanied by intramolecular vibrational energy redistributions[1]. Ab initio molecular dynamics (AIMD) simulations analysed in terms of vibrational normal modes, is a widely used technique that facilitates understanding of complex structural motions and coupling between electronic and nuclear degrees of freedom[2]. Usually, only a subset of vibrations is directly involved in the process of interest. Herein, different complementary criteria are analyzed to systematically identify the subset of vibrational normal modes that actively participate on the internal conversion process of different multichromophoric conjugated molecules: chlorophylls[3], donor-acceptors[4], and dendrimers[5]. Energy transfer coordinates are analyzed in terms of state-specific normal modes defined according to the different potential energy surfaces (PESs) involved. On one hand, we identify those vibrations that contribute the most to the direction of the main driving force on the nuclei during electronic transitions, represented by the non-adiabatic derivative coupling vector between donor and acceptor electronic states. On the other hand, we monitor normal mode transient accumulations of excess energy and their intramolecular energy redistribution fluxes. We observe that the subset of active modes varies according to the PES on which they belong and these modes experience the most significant rearrangements and mixing. Besides, we apply normal mode constraints[6] in AIMD simulations as implemented in the non-adiabatic excited state molecular dynamics (NEXMD) code[7]. In this way, we directly measure the impact of normal mode constraints on the photoinduced energy transfer. Our results show that the electronic relaxation can be significantly slowed down by freezing a well-selected small subset of active normal modes characterized by their contributions in the direction of energy transfer. The application of these constraints reduces the non-adiabatic coupling between electronic excited states during the entire dynamical simulations. Furthermore, we validate reduced dimensionality models by freezing all the vibrations except a few active modes. Altogether, our analysis can be broadly used to underpin the role vibrational motion in a studied process and to formulate reduced models that describe essential physical phenomena.

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[5] *"Analysis of state-specific vibrations coupled to the unidirectional energy transfer in conjugated dendrimers"*, Miguel A. Soler, Adrian E. Roitberg, Tammie Nelson, Sergei Tretiak, and Sebastian Fernandez-Alberti. J. Phys. Chem. A, 116, 9802-9810,(**2012**)

[6] *"Photoinduced dynamics with constrained vibrational motion: FrozeNM algorithm"* H. Negrin-Yuvero, V. M. Freixas, B. Rodriguez-Hernandez, G. Rojas-Lorenzo, S. Tretiak, A. Bastida and S. Fernandez-Alberti[a] submitted (**2020**)

[7] *"NEXMD Software Package for Non-adiabatic Excited State Molecular Dynamics Simulations"* W. Malone, B. Nebgen, A. White, Y. Zhang, H. Song, J. A. Bjorgaard, A. E. Sifain, B. Rodriguez-Hernandez, V. Manuel Freixas, S. Fernandez-Alberti, A. E. Roitberg, T. R. Nelson, and S. Tretiak, J. Chem. Theory Comput., J. Chem. Theory Comput. 16, 9, 5771–5783 (**2020**).

Variational error in molecular quantum dynamics — a dialog between maths and chemistry

Benjamin Lasorne[1]

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In this talk we shall discuss how to handle estimates of the variational error inherent to simulations in molecular quantum dynamics from the joint perspective of mathematical physics and physical chemistry. In this context, scale identification is common practice, especially within the context of the electronic-nuclear Born-Oppenheimer approximation, but also for uncorrelated approximations relying on a vibrational system-bath type partitioning. This will be illustrated on the prototypical case of a two-mode system experiencing tunnelling along a reaction coordinate and a cubic coupling with a harmonic bath [1,2].

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Photochemistry from a theoretical and computational perspective

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What happens to a molecule once it has absorbed UV or visible light? How does the molecule release or convert the extra energy it just received? Answering these questions clearly goes beyond a pure theoretical curiosity, as photochemical and photophysical processes are central to numerous domains like energy conversion and storage, radiation damages in DNA, or atmospheric chemistry. A plethora of theoretical tools have been developed over the past decades to address these questions by simulating the excited-state dynamics of molecules. These methods are often tested and theoretically validated on reduced-dimensionality models or rather simple molecules.

In this seminar, I will show a series of examples where studying the photophysics and photochemistry of real-life molecules helped spotlight the limitations of current theoretical methodologies and stimulate the development of new strategies for excited-state dynamics. In particular, I will focus on the sunlight-induced reactivity of volatile organic compounds in the troposphere, as well as athermal ground-state processes following passage through a conical intersection.

Collisional effects on the spectral shape and atmospheric remote sensing

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Atmospheric remote sensing is entirely based on spectroscopy, the physical and chemical properties of the atmospheres being derived from the interpretation of spectra. The analysis of the measured data, mostly done through the so-called "inversion" procedures, requires the knowledge of the intrinsic spectroscopic parameters of absorption lines (positions, intensities, spectral shapes). The collisions between the molecules have to be considered as their effects yield a modification of the line shape for most of the atmospheric physical conditions (pressure, temperature).

It is now well known that the widely-used Voigt profile does not well describe absorption line shapes of molecular gases. This is due to several collision effects which are neglected by the use of the Voigt profile such as the Dicke narrowing, the speed dependences of collisional parameters, collisional interferences between lines, non-Markovian collisions. A short review on the recent theoretical approaches, models and results on the topic of spectral shapes will be reviewed with examples of their effect on atmospheric spectra analysis.

Clustering dynamics in superfluid helium nanodroplets: A theoretical study

FRANÇOIS COPPENS,[1] ERNESTO GARCÍA ALFONSO,[1] NADINE HALBERSTADT,[1*] MARTÍ PI,[2,3]
MANUEL BARRANCO,[2,3]

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In this work we study the collision of heliophilic atoms with a superfluid helium droplet, followed by their solvation and clustering. ^{4}He nanodroplets are intriguing, quantum fluid objects of finite size (typically several thousands of ^{4}He atoms) [1]. They exhibit very "exotic" properties, including superfluidity, very low temperature (0.38 K), high energy dissipation rate, quantum vortices,... They constitute an interesting medium to study molecules at very low temperatures, even lower than the interstellar medium. Because of their very high energy dissipation rate, they can trap collisional complexes in local, metastable configurations which may be of interest for comparison with, eg, photo-association complexes when the ground, thermodynamic configuration is not attained.

We use time-dependent Helium density functional theory (^{4}He-TDDFT), which has proven to be the best compromise between accuracy and feasibility to study the stability and real time dynamics of doped helium droplets with a size comparable to experiments.[2]

We also investigate the effect of the presence of a quantum vortex on the pickup and clustering process, in relation with the pioneering experiment by Vilesov's group which used atom doping to visualize quantum vortices.

Our simulations[3, 4] reveal rather surprising final cluster configurations, very different from the gas phase ones. This is due to the fast cooling property associated to superfluidity, which quenches metastable configurations, and to the high density shell building around each dopant atom which can prevent dopant-dopant bond formation. They also reproduce the attractivity of dopant atoms to the vortex lines, with a cluster building along them but in a final configuration very different from the gas phase one. We also compare the results of ^{4}He-(TD)DFT simulations in vortex free nanodroplets with particle-based methods which have been used for these systems.[5]

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References

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Attachment of hydrogen molecules to atomic ions: role of the hydrogen rotational states

M. Hernández-Hernández[1]

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Interactions between molecular hydrogen and ions are of interest in cluster science, astrochemistry and hydrogen storage. In dynamical simulations, H_2 molecules are usually modelled as point particles (pseudoatoms), an approximation that can fail for anisotropic interactions. Here we apply an adiabatic separation of the H_2 rotational motion to build effective pseudoatom-ion potentials and in turn study the properties of $(H_2)_n Na^+/Cl^-$ clusters. The potentials are based on high-level *ab initio* calculations and improved Lennard-Jones parametrizations, the subsequent dynamics being performed by Difussion Monte Carlo calculations. By comparisons with simulations explicitly describing the molecular rotations, it is concluded that the present adiabatic model works very well. Interestingly, we find differences in the cluster stabilities and coordination shells depending on the spin isomer considered (para- or ortho-H_2), specially for the anionic clusters.

Forward and hybrid path-integral approaches in photoelectron holography

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We propose a strong-field path integral method with full Coulomb distortion. The electrons' orbits are forward propagated, and we contrast the results with those from a hybrid forward-boundary approach. In the forward method, we derive a non-adiabatic ionization rate from the Coulomb quantum-orbit strong-field approximation (CQSFA), which includes sub-barrier Coulomb corrections. We show that the sub-barrier Coulomb corrections broaden the resulting PMDs and improve the agreement of the rate-based method with the hybrid forward-boundary CQSFA and direct solution of the time-dependent Schrödinger equation. We assess the influence of biased sampling on the holographic patterns and explain our results using the initial to final momentum mapping.

Recent applications of the statistical approach of reaction dynamics

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The state and spatial distributions of the products of elementary gas-phase processes are among the most finely tuned pieces of information about chemical reactivity. Predicting and understanding the shape of these distributions is therefore a major goal of theoretical chemistry.

In the last decades, the statistical approach has been widely developed and applied to rationalize the dynamics of complex forming chemical reactions. After reviewing the main assumptions, I will present some examples highlighting its validity and interpretative power within the framework of atom-diatom chemical reactions.