Atoms, Molecules and Clusters in Motion

Book of Abstracts

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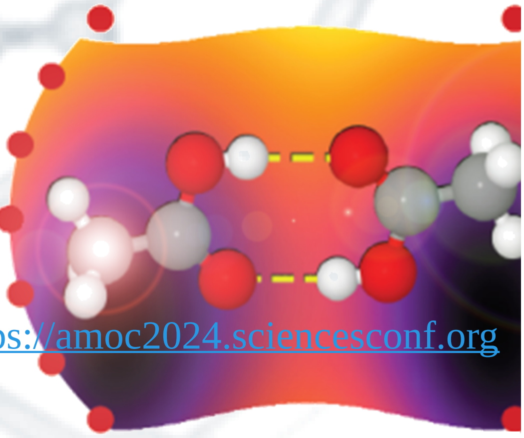
Champs-sur-Marne, France
15 – 18 April
2024



https://amoc2024.sciencesconf.org

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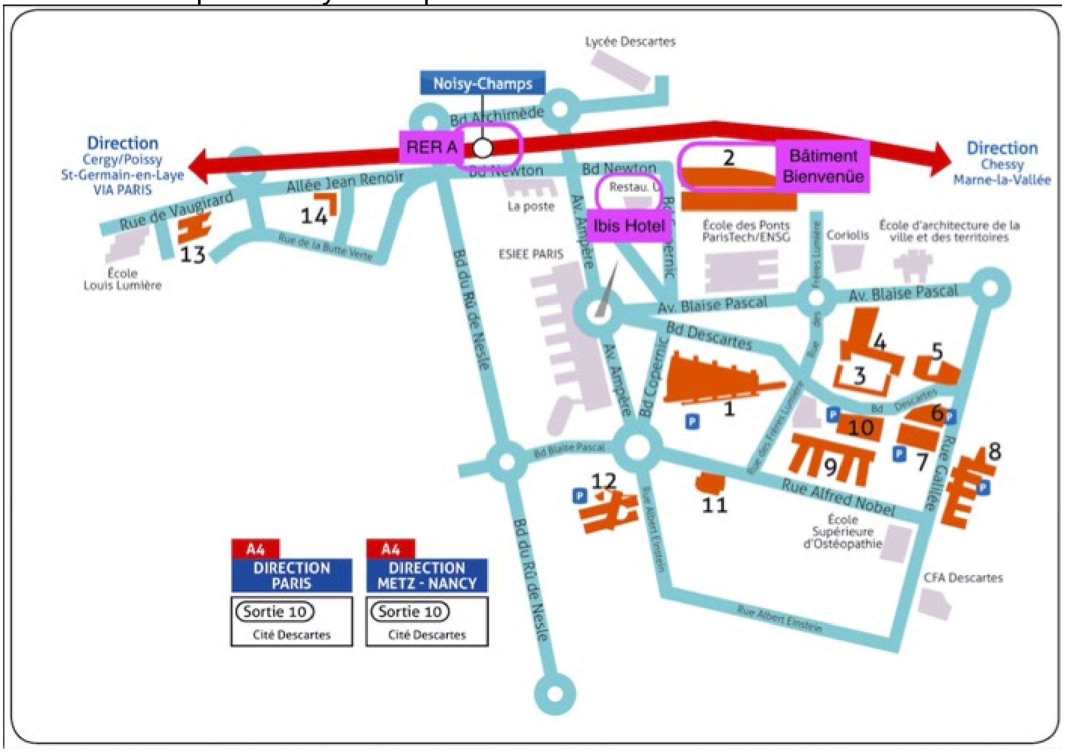
Conference program:

	Monday 15	*Tuesday 16*	*Wednesday 17*	*Thursday 18*
9h00-10h30	Registration	chair: E.-L. Zins	chair: R. Signorell	chair: S. Morisset
		M. Suhm C. Lauzin M. Schröder	A. Simon O. Roncero S. Gómez	H. Tran M. Zannese HT: I. Simko HT: L. Maillard
10h30-11h00		Coffee break		
11h00-12h30		chair: G. Worth	chair: G. Nyman	chair: V. Brenner
		B. Curchod A. Viel HT: C. Bracquart HT: B. Gervais	M. Biczysko J. Bloino HT: B. Ezra HT: L. Ibele	L. Cederbaum M. Rey Closing
12h30-14h00	Lunch			
14h00-16h00	Opening	chair: M. Suhm	chair: S. Yurchenko	departure
	chair: L. Cederbaum R. Signorell A. Hans G. Féraud	A. van der Avoird R. Wester M. Tomza T. Stoecklin	P. Çarcabal S. Grubisic A. Andersson H. Larsson	
16h00-16h30	Coffee break			
16h30-18h00	chair: M. Biczysko	chair: L. Halonen	chair: S. Grubisic	
	J. Noble V. Rivilla M Cvitaš	J. Ye W. Ubachs E. Mátyus	G. Worth S. Yurchenko F. Naumkin	
		dinner	*Poster Session* *Buffet+soft drinks*	

HT: 15-minute presentation
See the AMOC2024 website for more details.

Conference Location/meals/Conference diner:

- The conference will take place at the building Bienvenüe (bâtiment Bienvenüe) of the Gustave Eiffel University. To reach the conference, you can take the RER A and stop at "Noisy Champ".



The path from the RER A till the entrance is as indicated in the following map:

- Lunchs (12h30-13h30) will take place at the Ibis Hotel Champs. Cite Descartes, 8 Bd Newton, 77420 Champs-sur-Marne.

- The conference diner will take place in Paris downtown:
  24th floor of Tour Zamansky
  Sorbonne University, campus Pierre-et-Marie-Curie (Jussieu).
  4 Place Jussieu, 75005 Paris
  Métro ligne 7 or 10. Station Jussieu
  Meeting at 7PM, near the fountain, place Jussieu.

Presentations

The Universal Blueshift in BOMD Simulations

Åke Andersson [*] [1]

[1] Department of Physics [Gothenburg] – Sweden

Born–Oppenheimer Molecular Dynamics (BOMD) is used for many applications, one of which being the calculation of infrared spectra. Unlike fixed-geometry methods, the BOMD simulation explores the energy landscape and is inherently anharmonic. In this talk, I will explain the theoretical foundation and limitations of BOMD spectrum calculation. I will also show how to push the time step beyond what is normally required to accurately resolve dynamics, by exploting a property of the simulations I call universal blueshift.

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[*] Speaker

DFT computations benchmarked by accurate theoretical and experimental data

Malgorzata Biczysko * [1]

[1] Shanghai University – China

Accurate computations of the spectroscopic properties for molecular systems of increasing size and complexity from small prebiotic molecules of astrochemical interest (1-3) to larger bio-molecules (4) pose further challenges to the accurate description of the underlying potential energy surfaces and the treatment of nuclear motion. The reliable computational support should be able to provide a balanced description of all interactions allowing for extended mapping of the whole conformational space, including the accurate prediction of equilibrium structures, their relative positions on the potential energy surface (PES), free energies corresponding to the specific experimental conditions and the spectroscopic properties. I will discuss the status and perspective of the project based on the second-order perturbation theory (VPT2) in conjunction with PES description by QM methods ranging from density functional theory (DFT) to coupled-cluster (CC). Problems related to the description of large-amplitude motion (LAM) will be in a first approximation treated by ad hoc reduced dimensionality models. This allow for the improved treatment of weak interactions and accounting for the anharmonicity of both wave function and properties, resulting in a correct description of the intensity of non-fundamental transitions and more accurate band-shapes. The accuracy of such obtained results will be tested against the available experimental data for systems of increasing size and complexity. References (1) Y. Zhao, M. Hochlaf, M. Biczysko ”Identification of DNA bases and their cations in Astrochemical environments: Computational spectroscopy of Thymine as a test case” Front. Astron. Space Sci. 8, (2021) 757007 DOI: 10.3389/fspas.2021.757007 (2) R. Xu, Z. Jiang, Q. Yang, J. Bloino, M. Biczysko ”Harmonic and anharmonic vibrational computations for biomolecular building blocks: benchmarking DFT and basis sets by theoretical and experimental IR spectrum of glycine conformers” Journal of Computational Chemistry (2024) (3) M. Sheng, F. Silvestrini, M. Biczysko, C. Puzzarini ”Structural and Vibrational Properties of Amino Acids from Composite Schemes and Double-Hybrid DFT: Hydrogen Bonding in Serine as a Test Case” J. Phys. Chem. A 125 (2021) 9099–9114 DOI: 10.1021/acs.jpca.1c06993 (4) P. Wang, C. Shu, H. Ye, M. Biczysko ”Structural and Energetic Properties of Amino-acids and Peptides Benchmarked by Accurate Theoretical and Experimental Data” J. Phys. Chem. A 125 (2021), pp. 9826-9837. DOI: 10.1021/acs.jpca.1c06504

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*Speaker

Recent Advances Toward Accurately Predicting the Vibrational Spectra of Medium-to-Large Molecular Systems

Julien Bloino [*] [1]

[1] Scuola Normale Superiore di Pisa – Italy

Computational spectroscopy is nowadays routinely used as a predictive and interpretative tool as complement and support of experiment, providing insights of the underlying elementary phenomena responsible for the overall band-shape. With experimental techniques being able to achieve higher resolutions, standard models, such as those based on the harmonic approximation, are showing their limit(1-3). As a result, standard computational protocols can be insufficient to obtain unequivocal assignments, especially for sensitive applications like chiroptical spectroscopy. On the other hand, more sophisticated techniques have a higher computational cost, and can be complex to set up. Such considerations underline the need of carefully defining the computational protocols, starting from the selection of the most suitable level of theory. For instance, a trade-off is generally necessary between accuracy and computational cost to deal with medium-to-large molecular systems and possible environmental effects, and several strategies can be devised, with suitability varying depending on the cases.

In terms of efficiency, vibrational perturbation theory at the second order (VPT2) offers the possibility to account for anharmonic effects in the vibrational spectra of molecules comprising even dozens of atoms. It has shown to be capable of predicting even the fine details in the band-shape(1) and covering an ample spectral range into the near IR(3). However, it is also well known to be potentially unreliable because of its susceptibility to resonances. In this presentation, we will discuss how fully black-box protocols can be devised to compute reliably vibrational spectra within the VPT2 framework(4). These promising results pave the way toward considering more complex cases, including molecular flexibility and explicit interactions with solvent. We will also illustrate how VPT2 can be extended to even larger complexes through carefully designed hybrid schemes(5).

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4. Q. Yang, J. Bloino, *J. Phys. Chem. A* **126** (2022), 9276.
5. M. Fusè et al., Spectrochim. Acta A **311** (2024), 123969.

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[*] Speaker

Spectroscopic Conformer Unveiling in Gas-Phase Autoxidation Systems with Electronic Structure Calculations

Jeremy Bourgalais * [1]

[1] LRGP UMR 7274 – CNRS-Université de Lorraine – France

The autoxidation of volatile organic compounds in the gas phase is a key chemical mechanism impacting both atmospheric pollution and combustion processes in engines, where hydroperoxide (ROOH) species play important roles. These hydroperoxides, with their intricate molecular structures, are central in forming atmospheric aerosols and triggering autoignition in thermal combustion engines. Therefore, it is vital to thoroughly understand how they are formed by developing detailed chemical kinetic models, which are key in tackling their environmental and societal effects.

Yet, this requires validating these models against experimental data, a challenging task due to the difficulty in detecting and quantifying these reactive species that form in trace amounts. The employment of time-of-flight mass spectrometry using synchrotron radiation's vacuum ultraviolet photoionization (SVUV-PIMS) has made it possible to detect hydroperoxide species directly. However, accurately quantifying them is still a challenge because of the presence of many isomers and their propensity to break apart when photoionized.

In our study, we use synchrotron-based photoelectron spectroscopy combined with advanced theoretical quantum calculations to distinguish between isomers and reveal different conformations of hydroperoxide intermediates in n-pentane oxidation, a common alkane fuel. By analyzing the electronic structures, we demonstrate how insights into the photodynamics of these species can enhance combustion models. We also discuss how detecting conformers in such intricate chemical systems complicates the measurement of intermediates in gas-phase autoxidation.

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*Speaker

Towards a Strict Diabatic Basis for Coupled N-level Diatomic Systems

Ryan Brady [1], Sergey Yurchenko * [2]

[1] Department of Physics and Astronomy [UCL London] – United Kingdom
[2] Department of Physics and Astronomy [UCL London] – United Kingdom

Traditionally, the (stationary) Schrodinger equation for atomistic systems is solved using the adiabatic approach and associated adiabatic approximation. Despite being simplistic, this approach is very powerful and used in nearly all practical applications, especially when predicting near equillibrium properties of molecules.
In cases when interactions between electronic states become important, the associated non-adiabatic effects are taken into account via the first-order and second-order derivative couplings (DDRs) (also know as non-adiabatic couplings or NAC). For the diatomic case, the corresponding potential energy curves (PECs) in the adiabatic representation are characterised by avoided crossings. The alternative to the adiabatic approach is the diabatic representation, obtained via a unitary transformation of the adiabatic states by removing completely the DDRs. For diatomics, the diabatic representation has zero DDR and non-diagonal diabatic coupling (DC) ensued. The two representations are fully equivalent and so should be the rovibronic energies and wavefunctions, resulted from the solution of the Schrodinger equation in the corresponding approximation.

While the transformation for the 2-state electronic system is known analytically, we provide results on the numerically exact transformation for an arbitrarily sized N-level coupled system. We demonstrate (for the first time), the numerical equivalence between the adiabatic and diabatic rovibronic calculations of diatomic molecules, using ab initio curves of yttrium oxide (YO) (http://dx.doi.org/10.1039/C9CP03208H), carbon mono-hydride (CH), and molecular nitrogen (N2) (10.3847/1538-4357/acbef8) as examples of two-state and three-state systems, where YO and N2 are characterised by strong NACs, while CH has a strong diabatic coupling. We also showcase the potential of our solution to the diabatic problem by demonstrating equivalence for a synthetic 10-electronic state system. Rovibronic energies and wavefunctions are computed using a new diabatic module implemented in our variational rovibronic code Duo (http://dx.doi.org/10.1016/j.cpc.2015.12.021). We show that both the first and second order DDRs are important to include, with the second DDR arguably even more important than the first order DDR. We also show that there is no one choice of representation to be used within nuclear motion calculations, where the convergence of the vibronic energies can strongly depend on the representation used.

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*Speaker

Like likes like! Interaction between biomolecules and water in the gas phase.

Pierre Carcabal [*] [1]

[1] Institut des Sciences Moléculaires d'Orsay – Centre National de la Recherche Scientifique – France

Hydrogen bonding is at the centre of the interplay between biomolecules and their environment, mostly composed of water and other biomolecules. Sugars belong to one of the most important class of biomolecules and they are key actors of a variety of biological processes including molecular recognition, mediated by non-covalent interactions. These especially flexible molecules encode molecular information through their chemical composition and their conformational preferences, closely related to the direct and local environment in which they are embedded.

Using mass resolved, conformer selective double resonance vibrational spectroscopy, we can interrogate the conformational choices of isolated sugars and the effect of a controlled number of surrounding molecules. So far, in the case of sugar-water interaction studies, we have mostly focused on the effect of water on the sugar conformer.

Recent results evidencing the symbiotic structuring behaviour of solvent molecules on sugars and of sugars on the solvent. This relies on the identification of hydrated clusters of sugars structures where the water molecules and the OHs of the sugar create the same H bond networks than those that have been long studied for water oligomers. These findings echoes to the concept that sugar can be seen as "pre-organized water oligomers" with the ability of shaping and affecting its own environment. This unique property of sugars could be the fundamental key to understand the basis of their central role in molecular recognition.

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[*] Speaker

Is an efficient intermolecular energy transfer from vibrations to electronic motion possible?

Lorenz Cederbaum [*] [1]

[1] Heidelberg University – Germany

In this work we investigate the possibility of intermolecular vibrational energy transfer to electronic motion. Energy transfer of all kinds is of central importance for chemical reactivity and has been widely studied both experimentally and theoretically over many years including the transfer between the two kinds of energies, vibrational and electronic. The studies of the latter are, however, carried out in the framework of collisions where the collision complex formed and/or nonadiabatic coupling give rise to the transfer. Here, we concentrate on intermolecular vibrational energy transfer to electronic motion in weakly bound molecules, i.e., at internuclear distances at which they do not have a chemical bond and nonadiabatic coupling is negligible. We shall see that the transfer can be highly efficient.

If time is left, intermolecular vibrational energy transfer between weakly bound molecules is also addressed. Here, most of the studies were done for describing resonant vibrational energy transfer in the condensed phase. Very recently, it has been noticed that if the lifetime of the vibrationally excited molecule is much longer than that of its neighbor, efficient non-resonant vibrational energy transfer can take place.

L.S. Cederbaum, PRL 121, 223001 (2018)

L.S. Cederbaum, Mol. Phy. 117, 1950 (2019)

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[*] Speaker

Atmospheric photochemistry from a theoretical and computational perspective

Basile Curchod * [1]

[1] University of Bristol – United Kingdom

In this presentation, I will discuss 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 (transient) volatile organic compounds in the troposphere, as well as athermal ground-state processes following passage through a conical intersection.

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*Speaker

Tunneling splittings in molecules and clusters using modified WKB theory in Cartesian coordinates

Marko Cvitas *[1]

[1] Marko Tomislav Cvitas – Croatia

In molecular systems with multiple equivalent symmetry-related minima separated by potential barriers, vibrational states can delocalize over the entire system via tunneling. This phenomenon manifests itself in the energy splittings of the delocallized states in vibrational spectra. Tunneling splittings vary over many orders of magnutide depending on the type of rearrangement involved and modal excitations of the system. Calculation of tunneling splittings using variational methods for molecules larger than a few atoms is computationally prohibitive. We present a semiclassical theory for calculating tunneling spectra that works in full dimensionality and is scalable to systems of high dimensionality.

Our approach is based on a modified WKB theory on the minimum action paths connecting the symmetry related minima (1-4). We show that our approach is equivalent to the instanton theory for tunneling splittings of the ground vibrational state and that it gives an exact wavefunction in a harmonic potential for the ground and the first excited state. We test it on malonaldehyde (5) and vinyl radical molecules and apply it to calculate tunneling patterns in a number of water clusters in the ground and vibrationally excited states (6)). We also discuss an extension to calculate the splittings in rotationally excited states with an application to HO2 molecule and future direction in view of calculating tunneling rates in molecules at low temperatures.

Acknowledgements:
This work has been supported by Croatian Science Foundation under the project IP-2020-02-9932.

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[*] Speaker

UV-induced desorption of interstellar ices anologs

Géraldine Feraud * [1,2], Romain Basalgète [2], Rémi Dupuy [2,3], Daniela Torres Díaz [4], Claire Romanzin [5], Xavier Michaut [1,2], Pascal Jeseck [1,2], Laurent Philippe [1,2], Lionel Amiaud [4], Anne Lafosse [4], Samuel Del Fré [6], Alejandro Rivero Santamaria [6], Denis Duflot [6], Maurice Monnerville [6], Jean-Hugues Fillion [1,2], Mathieu Bertin [1,2]

[1] De la Molécule aux Nanos-objets : Réactivité, Interactions et Spectroscopies – Institut de Chimie - CNRS Chimie, Sorbonne Université, Centre National de la Recherche Scientifique – France
[2] Laboratoire d'Etude du Rayonnement et de la Matière en Astrophysique et Atmosphères = Laboratory for Studies of Radiation and Matter in Astrophysics and Atmospheres – Ecole normale supérieure - Paris, Institut National des Sciences de l'Univers, Observatoire de Paris, Sorbonne Université, Centre National de la Recherche Scientifique, CY Cergy Paris Université – France
[3] Laboratoire de Chimie Physique - Matière et Rayonnement – Institut de Chimie - CNRS Chimie, Sorbonne Université, Centre National de la Recherche Scientifique – France
[4] Institut des Sciences Moléculaires d'Orsay – Université Paris-Saclay, Centre National de la Recherche Scientifique – France
[5] Institut de Chimie Physique – Institut de Chimie - CNRS Chimie, Université Paris-Saclay, Centre National de la Recherche Scientifique – France
[6] Laboratoire de Physique des Lasers, Atomes et Molécules - UMR 8523 – Université de Lille, Centre National de la Recherche Scientifique, Université de Lille : UMR8523, Centre National de la Recherche Scientifique : UMR8523 – France

In the colder parts of the interstellar medium, dust grains are covered with molecular ices composed of water, carbon monoxyde, carbon dioxyde, but also of more complex molecules such as methanol. They act as the main molecular reservoir of these regions and are therefore of high interest in astrochemistry (eg (1)).

These ices evolve as they receive energy from their environment, for example when they are irradiated by UV photons. These interactions will eventually modify the ice composition, or release molecules/radicals into the gas phase. The electronic excitation of condensed molecules can thus lead to the desorption of surface molecules into the gas phase. The mechanisms at play at play during the photo-induced desorption are poorly characterized. Recent results from laboratory experiments on interstellar ice analogs exposed to UV photons from laser sources or from the Soleil synchrotron will be presented, with an effort to unveil the desorption mechanisms ((2), (3), (4)).

Références

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[*] Speaker

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Excited state quantum dynamics of PAHs

Sandra Gómez *[1]

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In this work, we study the deactivation pathways that take place after the UV excitation to the excited state manifold of coronene and circumcoronene, small moeities used as simplified models for graphene quantum dots, nanoflakes and poliaromatic hydrocarbons (PAHs). We use the wavepacket method ML-MCTDH(1) to study the time evolution of the states as well as their lifetimes.

The full-dimensional non-adiabatic dynamics results show that the different absorption spectra are only due to electronic delocalisation effects that change the excited state energies, but their structural dynamics are identical. Breathing and tilting motions drive the decay dynamics of the electronic states independently of the size of the aromatic system.(2) This promising result allows the use of coronene as a model system for the dynamics of larger polycyclic aromatic hydrocarbons (PAHs) such as graphene sheets or nanoflakes.(3)

References

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*Speaker

Investigation of charge and energy transfer processes in clusters by multi-electron-photon coincidence spectroscopy

Andreas Hans * [1]

[1] University of Kassel – Germany

During the last decades it was discovered that electronically excited states in clusters, which are created through interaction with ionizing radiation, can decay through a variety of interatomic mechanisms. Energy and charge can be transferred between the cluster's constituents, resulting in the emission of secondary electrons or photons. The details of such processes determine the final fate of the cluster and in particular its fragmentation into charged or neutral fragments. Here we present multi-electron-photon coincidence spectroscopy as a powerful tool for the experimental investigation of various interatomic decay mechanisms and discuss their role for the photochemistry of the system.

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*Speaker

Exploring the dynamics of protonated water clusters

Koki Kobayashi [1], Markus Schroeder * [1], Hans-Dieter Meyer [1], Oriol Vendrell [1]

[1] Physikalisch-Chemisches Institut, Heidelberg University – Germany

Recent advances in re-fitting potential energy and dipole moment surfaces into a sum-of-products form and made it possible to tackle large molecular systems with the Heidelberg MCTDH package. We present novel work on protonated water clusters with four constituent water molecules, namely the Eigen, and the cis- and trans Zundel isomers. In Particular we investigate isomer dependent changes in the infrared absorption spectra of these floppy systems. Special emphasis is placed on investigating the role of the coupling of various intra-molecular modes and their influence on the respective absorption line shapes.

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[*] Speaker

Tensor network states for computing vibrational and electronic states

Henrik R. Larsson * [1]

[1] University of California, Merced – United States

Mostly independently from each other, the fields of electronic structure and vibrational quantum dynamics developed powerful methods in order to accurately solve the Schrödinger equation. In particular, methods that decompose the high-dimensional wavefunction as a complicated contraction over smaller dimensional functions have attracted much attention. They have led to impressive applications for challenging quantum systems in both fields. While the underlying wavefunction representations, tensor network states, are very similar, the algorithms used to solve the Schrödinger equation for electronic and vibrational motions are very different. A systematic comparison of the strengths and weaknesses of the different approaches is missing but would allow for a better understanding and useful cross-fertilization of ideas. Here, first attempts in this direction are made (1,2).

In the first part of my talk, I will show how to use a method from electronic structure theory, the density matrix renormalization group (DMRG), for vibrational simulations (1,2). I will compare the DMRG to an algorithm used for vibrational dynamics, the multi-layer multi-configuration time-dependent Hartree (ML-MCTDH) method. I will apply these algorithms to the vibrational spectra simulation the Zundel ion, H5O2+, where a proton is sandwiched between two water units, a challenging system exhibiting large amplitude motion and Fermi resonances. For this system, I will show how the DMRG method can compute eigenstates at least an order of magnitude faster than the ML-MCTDH method. By computing 1000 eigenstates to high accuracy, I will show how subtle energetic effects will lead to a vastly different infrared spectrum of the Zundel ion (3).

In the second part of my talk, I will show how a technique widely used for MCTDH can allow for faster electronic structure DMRG calculations whenever many virtual orbitals with few electronic excitations are involved (4). With a combination of this and existing methods, I will then show how to compute a very accurate potential energy curve (PEC) of the chromium dimer, a grand challenge problem of small molecule spectroscopy, where theory and experiment have been at odds for decades. The computed PEC allows for a new analysis of the existing experimental data and hints at a new assignment of the vibrational levels of the chromium dimer (5).

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[*] Speaker

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(4): H.R. Larsson, H. Zhai, K. Gunst, G.K. Chan, Matrix Product States with Large Sites. J. Chem. Theory Comput. 2022, 18, 2, 749-762

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Spectroscopic and dynamical study of highly excited vibrational states of water containing complexes and of reference molecules.

Clément Lauzin * [1]

[1] Université Catholique de Louvain – Belgium

I will present our latest results concerning the spectroscopic characterization of water containing complexes, i.e. water-N2, water-CO2 and water-Ar. These complexes are interesting in the frame of the foreign continuum of water and present significative different dissociation energies. Experimentally, we were able to systematically increase the photon frequency over a large spectral range allowing to probe those complexes from the ground vibrational state to the second overtone of the O-H/D stretch of the water entity. These series of studies enable to sweep systematically the ratio of the frequency of excitation over the dissociation energies and to study the dynamics taking place. I plan to detail how the complex spectral signature was handled and how we plan to reach the third overtone in a near future. During this talk I also plan to briefly present most recent results and some prospects concerning the spectroscopic characterization of molecules of reference such as methanol.

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[*] Speaker

Bound-state relativistic quantum electrodynamics: a perspective for precision physics with atoms and molecules

Edit Matyus [*] [1]

[1] Eötvös Loránd University – Hungary

Precision physics aims to use atoms and molecules to test and develop the fundamental theory of matter, possibly beyond the Standard Model. Most of the atomic and molecular phenomena are described by the QED (quantum electrodynamics) sector of the Standard Model. Do we have the computational tools, algorithms, and practical equations for the most possible complete computation of atoms and molecules within the QED sector? What is the fundamental equation to start with? Is it still Schrödinger's wave equation for molecular matter, or is there anything beyond that? In my talk, I will review recent progress with the equal-time Bethe-Salpeter equation, the no-pair Dirac-Coulomb(-Breit) approximation, its high-precision numerical solution, and connections to non-relativistic QED as well as relativistic quantum chemistry. Ongoing work and future prospects for the precise computation of the pair-, retardation-, and radiative corrections to the correlated relativistic energy are outlined at the end.

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[*] Speaker

Movement of components in intermolecular complexes with charge-state dependent conformations

Fedor Naumkin * [1]

[1] Faculty of Science, Ontario Tech University / UOIT – Canada

Charge-induced shape-alterations of molecular systems could enable functioning of molecular circuits and/or actuators in nano-scale electronics and machines.

In this study, a series of complexes composed of a main-group atom and hydrocarbon molecules are theoretically developed and their structure, stability, and IR spectra analyzed.

A few system compositions are considered, including minimal species demonstrating the basic action-principle, and their structural extensions supporting its generality for a class of analogous larger systems with such core units.

The considerable geometry changes among neutrals, cations and anions involve 2-3 specific conformations associated with twisting motion within the 90-degree range.

These structures correspond to distinct IR spectra allowing their detection and differentiation in experiments.

The above suggests a possible application of such systems as intermolecular switches with a potential spectral monitoring of their performance.

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*Speaker

The evolution of ices on dust grains during the star formation process as seen in Chamaeleon I with the JWST

Jennifer Noble * [1], The Ice Age Team [2,3]

[1] Physique des interactions ioniques et moléculaires – CNRS : UMR7345, Aix Marseille Univ – France
[2] PI M. K. McClure and co-PI H. Linnartz, Leiden Observatory, Leiden – Netherlands
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http://jwst-iceage.org/ – United States

The ice mantles that build up on dust grains in cold, dense regions of the interstellar medium are the main reservoir for volatile elements. Studying the composition and structure of these ices requires not only observations in the near and mid infrared spectral region, but also dedicated laboratory astrophysics. Experiments and theory are combined to explain the physical and chemical processes occurring during star formation. The IceAge Early Release Science programme (1) on the James Webb Space Telescope was designed to trace the evolution of pristine and complex ice chemistry in Chamaeleon I – a representative low-mass star-forming region – through various stages of star formation from dense cloud to protoplanetary disk. In this talk, we will present the latest results of this programme, starting from the ice inventory towards observed lines of sight (2), and presenting the results of focussed studies looking at the structure of ices and dust grains in the quiescent cold core (3). Throughout, we will highlight the role of laboratory astrophysics in the analysis of observational data.

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*Speaker

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Construction of effective ab initio-based Hamiltonian and dipole moment operators

Michael Rey * [1]

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Precise knowledge of absorption spectra is of primary importance for various planetary applications and clearly demonstrates the necessity of having consistent line-by-line molecular databases. The current researches in the study of planetary atmospheres require knowledge of increasingly complex molecular systems over wide wavenumber and temperature ranges. Although the empirical effective Hamiltonians have greatly contributed to the golden age of the high-resolution molecular spectroscopy, they may fail to describe complex polyads, where many vibrational bands and numerous degeneracies and quasi-degeneracies are involved. Conversely, first-principles quantum mechanical calculations are well designed for applications for which completeness is crucial but in turn may fail to reproduce high-resolution spectroscopic data due to their lack of accuracy. Starting from a set of variational eigenpairs, a novel methodology(M. Rey, J. Chem. Phys. **156** (2022) 224103) is presented here for the construction of "global" *ab initio* effective rotation-vibration spectroscopic polyad models, as an alternative to algebraic Van Vleck perturbation methods. We will see how to transform first-principles calculations into a set of spectroscopic parameters to be further refined on experiment. It will be demonstrated that crucial information can be provided within a very short time, even for the so-called "dark" states which are generally a major obstacle in the more traditional spectroscopic models. Undoubtedly, the proposed approach brings a new insight into high-resolution spectra analysis and will be of great help, not only in current or future line-by-line spectra analyses of semirigid polyatomic molecules but also in the modelling of hot spectra. The case of nonrigid molecules will be also discussed.

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[*] Speaker

Molecular Precursors of the RNA-world in the Interstellar Medium: The G+0.693-0.027 astrochemical mine

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We still do not understand how simple molecules combined together to form large molecules essential for living organisms. Recent prebiotic experiments, based on the RNA-world hypothesis for the origin of Life, have suggested that the three basic macromolecular systems (nucleic acids, proteins and lipids) could have formed from relatively simple precursors. The detection of some of these molecules in space, thanks to the unprecedented capabilities of current astronomical facilities, has opened a new window for astrobiology from the astrochemical point of view. In this seminar I will present the most recent results of an ultradeep unbiased spectral survey towards the molecular cloud G+0.693-0.027 with the Yebes 40m, IRAM 30m and APEX telescopes. We have recently discovered 15 new interstellar species for the first time in the interstellar medium towards this molecular cloud. Among them, the first glycine isomer detected in space, glycolamide (NH2COCH2OH); key precursors of RNA nucleotides such as hydroxylamine (NH2OH); of sugars, such as the glycolaldehyde isomer 1,2-ethenediol ((CHOH)2); of proteins, such as carbonic acid (HOCOOH), ethyl isocyanate (C2H5NCO), or propargylimine (HCC-CHNH); of lipids, such as ethanolamine (NH2CH2CH2OH) and propanol (CH3CH2CH2OH); and new species with phosphorus, such as the ion PO+. I will also present several recent theoretical efforts aimed to understand how these molecules can be assembled under interstellar conditions, using quantum chemical calculations and chemical models. This amazing chemical complexity, which might be only the tip of the iceberg, means that interstellar chemistry offers an extremely rich feedstock for triggering prebiotic chemistry.

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[*] Speaker

Radiative electron attachment to rotating C3N through dipole-bound states

Thierry Stoecklin * [1], Joshua Forer , Viatcheslav Kokoouline

[1] Institut des Sciences Moleculaires, CNRS UMR 5255 – Université de Bordeaux (Bordeaux, France) – France

The role of a large dipole moment in rotating neutral molecules interacting with low-energy electrons is studied using an accurate ab initio approach accounting for electronic and rotational degrees of freedom. It is found that theory can reproduce weakly bound (dipole-bound) states observed in a recent photodetachment experiment with C3N– (Phys. Rev. Lett. 127, 043001 (2021)). Using a similar level of theory, the cross section for radiative electron attachment to the C3N molecule, forming the dipole-bound states, was determined. The obtained cross section is too small to explain the formation of C3N– in the interstellar medium, suggesting that it is likely formed by a different process.

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[*] Speaker

Photochemistry in aerosol particles

Ruth Signorell * [1]

[1] ETH Zurich – Switzerland

Photochemical processes have been identified as the main causes of degradation and oxidation of matter in atmospheric aerosol particles. When light interacts with an aerosol particle, the light intensity can be greatly amplified inside the particle as the latter acts as a light-amplifying cavity. These optical confinement effects result in an acceleration of photochemical reactions in aerosol particles compared with reactions in extended condensed matter. We have studied and quantified the acceleration of in-particle photochemistry using photoacoustic spectroscopy (1) and X-ray spectro-microscopic imaging of single aerosol particles (2).

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[*] Speaker

PAH-water clusters in a cryogenic environment: theoretical (and experimental) challenges

Aude Simon * [1]

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Institut de Chimie - CNRS Chimie, Centre National de la Recherche Scientifique, Fédération de
recherche "Matière et interactions" – France

We will present the main theoretical approaches and some results obtained for clusters involving water molecules and polycyclic aromatic hydrocarbon (PAH) units. These studies result from long term collaborative works between experimentalists and theoreticians. The theoretical efforts have been been directed towards the description of water-PAH clusters embedded in a noble gas matrix using a DFTB/FF (density functional based tight binding / force-field) scheme and to characterize their infrared (IR) fingerprints using molecular dynamics (MD) and path-integral molecular dynamics (PIMD) simulations. We will present and discuss some results obtained for planar (coronene C24H12) and non-planar (corannulene C20H10) PAHs. We will also mention some results (ionization energies and IR spectra) for larger systems involving PAH on ice, the water ice being modeled by a finite large cluster.
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[*] Speaker

Non-random vibrational resonances in hydrate complexes

Martin Suhm * [1]

[1] Universitat Gottingen – Germany

When a single water molecule solvates organic matter, its symmetric stretching vibration is characteristically shifted to lower wavenumber. This microhydration shift can be measured in cryogenically cooled water complexes. Any accurate atomistic model of hydration is expected to reproduce the experimental shift, once the ground state electronic structure and the proton dynamics of the monohydrate complex are captured sufficiently well. As long as the hydrogen bond between the solvating water and the organic solute is weak, the vibrational signature of the high frequency OH stretching mode is simple and provides a straightforward benchmark for theory. Stronger hydrogen bonds lead to resonances of the OH stretch with the 7 non-OH-stretching degrees of freedom of the water molecule which provide channels for energy flow out of the hydrogen-bonded OH oscillator and lead to characteristic patterns in the vibrational spectrum. We are trying to detect and systematically tune some of these resonances by studying monohydrates (and increasingly also dihydrates) of a large number of organic molecules. We organise blind (1) and open challenges for theory groups to match experiment. Such matches may be achieved by systematic error cancellation between the electronic structure and nuclear dynamics approaches or by machine learning strategies and can still be valuable for experimentalists as spectral assignment aids. However, the ultimate goal is to find affordable and broadly applicable full or reduced dimensionality ab initio strategies which match experiment largely for the right reasons, i,e, they get the potential energy hypersurface right as well as the anharmonicity of the quantised hydrogen motion. In this talk, a focus will be on triple quantum resonances in ketone (2) and amine monohydrates.as detected by linear infrared and Raman spectroscopy.

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[*] Speaker

Quantum resonances in ultracold atom-ion and atom-molecule collisions

Michal Tomza *[1]

[1] University of Warsaw – Poland

Cold and ultracold systems attract researchers' attention because the universe's quantum nature clearly manifests under such conditions, and research into such systems provides new insight into the quantum theory of matter and matter-light interaction. Ultracold atoms, ions, and molecules offer numerous exciting research prospects ranging from quantum-controlled chemical reactions and quantum simulations to precision spectroscopic measurements probing the fundamental laws of nature. I will present our recent results of ab initio electronic structure and multichannel scattering calculations proposing, guiding, and explaining ultracold quantum physics experiments. I will start with our efforts related to hybrid systems of laser-cooled trapped ions and ultracold atoms combined in a single experimental setup. In collaboration with experimental groups in Amsterdam and in Freiburg, we reached and explained the quantum regime of ion-atom collisions manifested via shape resonances (1) and their quantum control with an external magnetic field observed with magnetic Feshbach resonances (2). Giant second-order spin-orbit coupling is responsible for measured Feshbach resonances. I will conclude with explaining the mechanism (3) of recently observed magnetic Feshbach resonances in ultracold atom-molecule mixtures (4). In collaboration with groups at MIT and in Nijmegen, we showed that these Feshbach resonances result from spin-rotation and spin-spin couplings in combination with the anisotropic atom-molecule interaction (3). (1) T. Feldker, H. Fürst, H. Hirzler, N. V. Ewald, M. Mazzanti, D. Wiater, M. Tomza, R. Gerritsma, Nature Phys. 16, 413 (2020)

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[*] Speaker

Super-Lorentzian effects and intensity depletion due to collision by classical molecular dynamics simulations

Ha Tran [*] [1], Jean-Michel Hartmann [1], Gang Li [2], Volker Ebert [2]

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[2] Physikalisch-Technische Bundesanstalt – Germany

The integrated line shape of an absorption line is widely obtained from fit of laboratory-measured spectra assuming a line profile model. Such a laboratory-measured intensity is so far assumed to be independent of the pressure. This major assumption is now questioned: to which extent the retrieved integrated line shape is proportional to the absorber density and independent of the total pressure of the gas mixture? In this paper, the pressure dependence of the line intensities retrieved from fits of absorption spectra of HCl are investigated both experimentally and theoretically. The retrieved line intensities reveal large decreases with increasing pressure - up to 3% per atm for pure HCl. We also show that the absorptions in between successive P and R transitions are significantly larger than those predicted using the usual Lorentz profile. Requantized classical molecular dynamics simulations have been made in order to predict absorption spectra of HCl matching the experimental conditions. The pressure dependence of the intensities retrieved from the calculated spectra as well as the predicted super-Lorentzian behavior between lines are in good agreement with the measurements. Our analysis shows that these effects are essentially due to incomplete collisions, which govern the dipole auto-correlation function at very short times.

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[*] Speaker

Precision measurements of the hydrogen molecule and the search for new physics

Wim Ubachs * [1]

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The hydrogen molecule is the smallest neutral chemical entity and a benchmark system of molecular spectroscopy. The comparison between highly accurate measurements of transition frequencies and level energies with quantum calculations including all known phenomena (relativistic, vacuum polarization and self energy) provides a tool to search for physical phenomena in the realm of the unknown: are there forces beyond the three included in the Standard Model of physics plus gravity, are there extra dimensions beyond the 3+1 describing space time ? Comparison of laboratory wavelengths of transitions in hydrogen may be compared with the lines observed during the epoch of the early Universe to verify whether fundamental constants of Nature have varied over cosmological time. These concepts, as well as the precision laboratory experiments and the astronomical observations used for such searches of new physics will be discussed.

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*Speaker

Multisurface dynamics and spectroscopy of the NO_3 radical

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The nuclear dynamics and spectroscopy of the NO_3 radical is still not fully understood despite multiple theoretical and experimental investigations over the last decades. Experimentally, the Neumark group made two breakthroughs by recording in 1991 (1) the first photodetachment spectra of the nitrate anion (NO_3-) and in 2020 by providing a cryogenic cooling version of these spectra (2). Their interpretation requires a detailed and complete modelling of the five lowest potential energy surfaces of the radical.

We propose a scheme to simulate photodetachment spectra of NO_3- from first principles. It relies on the determination of accurate full-dimensional coupled diabatic potential energy surfaces adjusted to high quality ab initio energies via an artificial neural network based scheme (3). The Muti- Configurational Time Dependent Hartree approach is used to propagate full dimensional wave-packets designed such that temperature effects and the impact of near threshold detachment are taken into account (4).

The two available experiments at high and at cryogenic temperature can be reproduced in very good agreement. A prediction for the photodetachment spectrum in the energy range of the second excited state is proposed (5). It allows to study the detailed non-adiabatic dynamics by computing the population dynamics. Two behaviors are found: an ultra-fast non-statistical radiationless decay among the Jahn-Teller components, and a slow statistical non-radiative decay among the different state manifolds.

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[*] Speaker

Para-ortho H2 conversion by collisions with O2 and NO

Ad Van Der Avoird * [1]

[1] Institute for Molecules and Materials, Radboud University, Nijmegen – Netherlands

It is well known among spectroscopists that two modifications of hydrogen exist: para-H2 and ortho-H2. Pure para-H2 can be prepared by leading a 1:3 para:ortho mixture of "normal" H2 over a catalyst at low temperature, and can be kept for a long time in a gas cylinder also at room temperature. It is perhaps less well known that para-ortho H2 conversion is also accelerated by interactions with paramagnetic molecules, such as O2 and NO.

Almost ninety years ago Farkas and Sachsse(1) measured the rate coefficient of para-ortho H2 conversion in gas mixtures with the paramagnetic open-shell molecules O2, NO, and NO2. In the same year, 1933, it was proposed by Wigner (2) that it is the magnetic dipole-dipole coupling between the electron spin of the paramagnetic molecule and the nuclear spins of the two protons in H2 that is responsible for the conversion. In asymmetric collisions this coupling makes the two H-nuclei inequivalent and mixes the nuclear spin functions of para- and ortho-H2, as well as their rotational states with even and odd j values. Another mechanism, suggested to be much more effective, was proposed later: the exchange interaction with the open-shell molecule induces spin density into the electronic wavefunction of H2. In most collisions the spin density is different at the two H-nuclei, which makes them inequivalent by hyperfine interactions through the Fermi contact term.

An important and currently popular application of para-H2 is in NMR spectroscopy. By leading para-H2 gas through the sample the sensitivity of NMR can be increased by four orders of magnitude by a phenomenon called para-hydrogen induced polarization (PHIP). The effect of O2 on the conversion of para-H2 was recently remeasured in view of this application (3).

We theoretically investigated (4) the para-ortho H2 conversion by collisions with O2 in a first principles approach. Both mechanisms were taken into account and the corresponding coupling terms were quantitatively evaluated as functions of the geometry of the O2-H2 collision complex by means of ab initio electronic structure calculations. Then they were included in nearly exact quantum mechanical coupled-channels scattering calculations for the collisions between O2 and H2, which yielded the para-ortho H2 conversion cross sections and the rate coefficients for temperatures up to 400 K. The conversion rate and its temperature dependence are in good agreement with the values measured in H2-O2 gas mixtures. The calculations provide detailed insight into the conversion process.

It was also found in 1933 by Farkas and Sachsse (1) that NO is 3 to 12 times more effective in para-ortho H2 conversion than O2. This is surprising, because NO has $S = 1/2$ and O2

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[*] Speaker

has S = 1. We are currently investigating NO-H2 collisions. The calculations are much more difficult than for O2-H2, because NO has two spin-orbit states: 2 Pi_1/2 and 2 Pi_3/2. And the 2 Pi state is spatially degenerate, so that non-adiabatic coupling is important.

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Cold collisions of ions and neutrals

Roland Wester * [1]

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In this presentation I will discuss results on cold collisions and reactions of trapped ions with neutral atoms or molecules. Specifically, we have studied vibrationally inelastic collisions of trapped carbon dimer anions with molecular hydrogen and compared the quenching rate coefficients to quantum scattering calculations. In collisions of trapped oxygen and hydroxyl anions with laser-cooled rubidium atoms we have observed associative detachment reactions and investigated their dependence on the electronic state of the neutral atom. Recently, we have also studied associative detachment of the interstellar negative ions CN- and C3N- with atomic hydrogen as a function of the collision temperature.

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[*] Speaker

Non-Adiabatic Spectroscopy and Dynamics: The Linear Vibronic Coupling Model and Beyond

Graham Worth * [1]

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The Linear Vibronic Coupling (LVC) Hamiltonian is a standard model used to describe a manifold of coupled electronic states (1). It has been used with great success to simulate the absorption spectrum and underlying nuclear dynamics of a number of problems. On top of its simple descriptive power, one of its strengths lies in its mathematical form that allows it to be used for accurate solutions of the time-dependent Schrödinger equation (TDSE). However, while it is well suited for describing short-time dynamics, it is not able to treat long-range motion, such as found in photochemical change. For this reason, it is sometimes necessary to go to higher order potentials, or to find other strategies to solve the TDSE. In this presentation, examples of calculations beyond the simple LVC model will be presented. These include the photo-excited dynamics of maleimide (2) and thiophene (3), along with the photoionisation dynamics of cyclobutadiene(4).

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[*] Speaker

Quantum gas of Molecules

Jun Ye * [1,2]

[1] Joint Institute for Laboratory Astrophysics – United States
[2] National Institute of Standards and Technology [Boulder] – United States

Recently developed control and observation tools for molecules are providing new opportunities to study complex structure and interaction dynamics, and to find powerful applications for fundamental discovery. Quantum gas of molecules constitutes an outstanding experimental platform for precise quantum state engineering and control of inter-molecular interactions, enabling exploration of emergent quantum phenomena.

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*Speaker

JWST observation of small and excited molecules in the Orion Bar: evidence of chemical pumping

Marion Zannese * [1]

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Small and excited molecules such as CH^+*,* CH_3^+ *and OH, are key molecules to study physico-chemical processes in strongly irradiated environments. Their emission reveals out-of-equilibrium excitation processes that are only possible in dense, warm and irradiated regions. The study of these processes allows us to put strong constrains on those environments, either on temperature, density and on our understanding of warm chemistry. However, their emission in the infrared is very faint and has only been made possible thanks to the very high angular resolution and high sensitivity of the James Webb Space Telescope (JWST).*
Recent observations with the ERS 1288 program "PDR4ALL" (Berné et al. 2022, Habart et al. 2023, Peeters et al. 2023) have provided imaging and spectroscopy of the Orion Bar in the prototypical highly irradiated dense PDR and externally irradiated disks (disk d203-506).

In this contribution, I will present the first NIRSpec and MIRI detection of vibrationally excited CH^+*,* CH_3^+*, OH in the Orion Bar and our modeling efforts to interpret these observations. In particular, I will show how to leverage the high spatial and good spectral resolution of NIRSpec and MIRI to resolve the distribution of these excited species and conduct detailed analysis of their excitation.* CH^+ *and* CH_3^+ *are indeed detected in very different environments throughout the Orion Bar, both in the disk d203-506 (Berné et al. 2023) and the interstellar PDR (Zannese et al. in prep) and show a good spatial correlation with excited* H_2*. This last result and study of their excitation are in favor of* CH^+ *(resp.* CH_3^+*) being formed and chemically pumped by the reaction* $C^+ + H_2 \rightarrow CH^+ + H$ *(resp.* $CH_2^+ + H_2 \rightarrow CH_3^+ + H$*). In the case of* CH^+*, where the state-to-state data are available, I will show the good agreement between quantum dynamical models of chemical pumping and observations. I will also present a similar excitation process observed with PDRs4All in the ro-vibrational emission of OH detected in the disk d203-506 (Zannese et al. 2024). Chemical pumping is thus seen in the excitation of various species and is particularly handy in constraining the physical parameters of the regions. Thus, I will highlight the need for new quantum calculations to build state-to-state astrochemical models in the JWST era.*

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Zannese, M. et al., OH as a probe of the warm-water cycle in planet-forming disks, Nature Astronomy (2024)

Comments:

I would like to explain this submission as it might look a bit out of topic for this conference. Alexandre Faure was contacted to give a talk on chemical pumping but as he cannot be there, he encouraged me to submit an abstract. I am obviously not an expert on the subject of the conference as I am an astrophysicist, specialized in observations. However, I think this talk showing how the data calculated by people in the assembly is essential to the understanding of observations with JWST would be very interesting. With this study on CH+, CH3+, OH detected in the Orion Bar, we revealed the importance on collaboration with quantum experts to fully analyze observed spectra. That is why I think it is highly important that I share my results in this conference even if it is a bit far from what other attendees will present.

Kind regards,
Marion Zannese

Hot Topics

INVESTIGATION OF THE MICROSOLVATION OF SECONDARY ORGANIC AEROSOL PRECUSORS: MICROWAVE SPECTROSCOPY OF NITROMETHOXYPHENOLS HYDRATES

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Mhamad Chrayteh [1], Goubet Manuel [2], Arnaud Cuisset [1]

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Atmospheric aerosol particles strongly influence the Earth s atmosphere, and their contribution to climate change is versatile. Especially, Secondary Organic Aerosols (SOAs) play a major role in the radiative budget and the clouds formation through their hygroscopic properties and atmospheric chemistry (1). Methoxyphenols (lignin s monomer) represent a significant part of biomass burning emissions. Recent works have shown that SOAs are formed by oxidation of methoxyphenols such as guaiacol and nitro-guaiacols (NG) are the main oxydation products yielding to SOAs with an hydrophobic character (2). We present here the rotational spectroscopy of 4- and 5-NG isomers studied using a free jet Fabry-Perot Fourier-transform microwave (FP FTMW) spectrometer (2 to 20 GHz) with the support of quantum chemistry calculations. The observation of the hyperfine structure induced by the presence of a 14N nucleus allowed us to simulate the nuclear quadrupole coupling constants in addition to the Watsonian rotationnal parameters. Each isomer shows only one planar conformer stabilized by an intramolecular hydrogen bond as already observed for guaiacol (3). However, the position of the nitro-group seems to influence the global stability of the molecule. The microsolvation of 4-NG with water has been investigated, unveiling only one monohydrate complex in agreement with the demonstrated hydrophobic character of 4-NG aerosols (3). The study of the hydration of 5-NG is ongoing as well as the study of the less volatile 4-nitro-syringol, a precursor with more hydrophilic SOAs than NG (4).

(1) doi:10.1016/B978-0-12-257060-5.X5000-X, Barbara J. Finlayson-Pitts and James N. Pitts, Jr., Chemistry of the Upper and Lower Atmosphere, Academic, 951 (2000)

(2) doi:10.1364/AO.56.00E116, W. Ahmad et al., Infrared spectroscopy of secondary organic aerosol precursors and investigation of the hygroscopicity of SOA formed from the OH reaction with guaiacol and syringol, Applied Optics, 56, E116-E122 (2017)

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[*] Speaker

(3) doi:10.1063/1.5089426, A. Jabri et al., Conformational landscape and inertial defect of methoxyphenol isomers studied by mm-wave spectroscopy and quantum chemistry calculations, The Journal of Chemical Physics, 150,10, 104303 (2019)

(4) This work is supported by the LabEx CaPPA (11-LABX-0005-01) and by the CPER ECRIN.

Ab initio quantum analysis of the strong field dissociation process - angular momentum analysis

Bar Ezra * [1], Shimshon Kallush [2], Ronnie Kosloff [1]

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Simulating photo-dissociation processes from first principles is a challenging task. The difficulty is due to the vast Hilbert space dimension that is required for a full quantum description. Coupling the external electromagnetic field and the transition dipole moment induces transitions between electronic states. Each electronic transition is accompanied by an angular momentum change of one unit of . Thus, the dissociation process achieved by a strong field leads to a significant change in the angular momentum. Therefore, the exact calculation has to include all angular momentum quantum states.

We presented a first principle model, which includes a numerical exact solution of the time-dependent Schrödinger equation (1). All nuclear rotational and vibrational states and the coupling between them are included. The simulation aims to describe the full physical process that initiates at a finite temperature. Therefore, the initial conditions of the system were set to be thermal and to include different rovibrational states. The simulation outcomes are analogous to experimental observables, such as the momentum angular distribution of the photo-fragments.

The random phase thermal wavefunction (RPTW) method is used to overcome the challenge of the large Hilbert space. It replaces the density operator calculations by a finite sample of random phase thermal wavefunctions. We developed methods to

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*Speaker

calculate the full asymptotic photo-fragment distribution, and studied the convergence of the calculation with respect to the number of RPTW employed. Typically, in the RPTW theory the convergence of the observables scale with the number of realizations, , and the Hilbert size, , as (2). We want to investigate the prefactor of this scaling, or particularly know what the number K of RPW that is required to converge a specific observable to experimental accuracy (3).

We used the freedom of setting the model to explore fundamental processes and simplify the full complexity into a two-electronic-state system. The simplified model enables clear and informative benchmarking before going down the rabbit hole of the complete and detailed simulations of the photo-dissociation process. The model complexity will be increased by steps. The modular construction will allow to sort out the different contributions to the process and allow direct analysis of experiments.

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(3) Bar Ezra, Ronnie Kosloff, and Shimshon Kallush. "Simulating photo-dissociation in strong field by the random phase thermal wavefunction approach". In: arXiv preprint arXiv:2110.12458 (2021).

Exciton model for Ar clusters: a puzzle?

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Rare gas solid are perhaps the simplest solids to study the structural changes induced by electronic excitation. The paradigm of exciton formation summarizes the underlying process of electronic energy transfer to the lattice and the localization of the excitation. In a rare gas solid, exciton is usually assumed to lead to formation of a diatomic excimer, which can migrate through the solid if its lifetime is long enough, and eventually relax by luminescence or lead to sputtering when it is close to a surface. We present a study of exciton formation for small Ar clusters by means of the popular diatomics-in-molecule (DIM) method and by means of a Hole-Particle Pseudopotential (HPP) formalism introduced by Dupláa and Spiegelmann. Two different pictures emerge from these two methods. The DIM method favours the formation of a symmetric D2h trimer inherited from the structure of Ar3+ and surrounded by ground state Ar atoms. On the contrary, the HPP formalism suggests the formation of an Ar2* surrounded by ground state Ar atoms excimer, in agreement with common assumptions used in sputtering models. Thus, Ar3* structure is apparently a puzzle which deserves further exploration, but it comes at the cost of more cumbersome wave function calculations.

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[*] Speaker

Efficient Prediction of Gas Adsorption in Nanoporous Materials through Force field based Molecular Simulations

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The crystalline hybrid porous materials such as Metal-Organic Frameworks (MOFs) have potential to help address health challenges and environmental challenges like, water and sustainable energy due to their high degree of porosity, functional tunability, chemical and structural versatility. However, translating metal organic framework basic research from laboratory to industrial applications is still hampered by the lack of precise control over their structure, properties and performance from the molecular-level framework to three dimensional porous materials. In this talk I will focus on the development and modelling of new nano-scale MOF materials based on the structures of zinc- triazolate and zinc- triazolate- oxalate complexes for several high-need applications such as gas storage and separations. To achieve this, computational methods (combining force field based grand canonical Monte Carlo (GCMC) simulations and density functional theory (DFT) calculations) have been used to improve structure-property predictions and to calculate the adsorption isotherms of investigated gases with and without the presence of water. The crystal structures of alpha - CALF-20 and its polymorph derivative were fully geometry-optimized (atomic positions and cell parameters relaxed) at the periodic DFT level without imposing any constraints in terms of topology/geometry. Force-field parameters and derived atomic partial charges of the MOFs have been validated by an excellent agreement between the CO2 and N2 adsorption isotherm simulated for alpha-CALF-20 with the corresponding available experimental data in the pressure domain of 0–1 bar. In addition, we have calculated gas adsorption isotherms for β-CALF-20. We observed that investigated MOFs show good adsorption performance for CO2, SO2 and H2S capture. The nature of the interactions between investigated gases with the pore surface cavities was examined at the microscopic level. More details can be found in Ref. 1-5. The GCMC simulations were performed using RASPA code on PARADOX IV supercomputing facilities (6).

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6. PARADOX IV supercomputing facility at the Scientific Computing Laboratory of the Institute of Physics Belgrade.

The nature of topological and geometric phases in coupled electron-nuclear dynamics - an exact factorization perspective

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The exact factorization of the electron-nuclear wavefunction proposes to represent the dynamics of a molecule in the excited state as a single time-dependent nuclear wavefunction, evolving under the action of a single time-dependent potential energy surface and a single time-dependent vector potential (1). Concepts, such as conical intersections and transition dipole moment, do not exist in this formalism.

In this presentation, I will discuss processes in the vicinity of a conical intersection within the standard Born-Oppenheimer representation and the exact factorization picture (2, 3). I compare the influence of the conical intersections on the dynamics of the wavepacket when passing through and around the conical intersection (4). The observable nature of topological phases related to conical intersections in molecules is addressed, highlighting numerically the fundamental difference between topological and geometric phases. Such topological phases should be ubiquitous in physical chemistry, but their elusive character has made them a topic of extensive discussion in recent years. Topological phases are related to the adiabatic representation of the electrons and are, thus, not observable. In contrast, geometric phases naturally arise from the coupled electron-nuclear dynamics and are robust physical observables.

In addition, I will highlight the challenges that different trajectory based formalisms face to describe the intricate nature of lwo-energy dynamics around a conical intersection. (5)

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[*] Speaker

Nested Sampling for exploring Lennard - Jones clusters

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[3] Laboratoire de Chimie Théorique, Sorbonne Université, CNRS, Paris, France – Sorbonne Université, CNRS, Laboratoire de Chimie Théorique – France
[4] Laboratoire Jacques-Louis Lions, Sorbonne Université and ANGE, INRIA Paris, France – Laboratoire Jacques-Louis Lions, Unkown Labs [Inria] – France

Although much heavier than electrons, light nuclei exhibit Nuclear Quantum Effects, such as tunnelling and zero-point energy, that can have a large impact on the structure and the dynamics of materials. The standard method to account for them when simulating the static properties at equilibrium is the use of path integrals. However, this method considerably increases the number of degrees of freedom with a consequent increase of the parameter space to study. An efficient algorithm to explore those materials is therefore necessary. Here, we consider the nested sampling (1,2) algorithm which explores the space from higher energy levels to lower energy levels, providing an estimate of the density of states while doing so. It can therefore compute the partition function and its derivatives and provide information about the system studied. Firstly, we study classical Lennard - Jones clusters for which the partition function can be computed at all temperatures with only one run of nested sampling. Following we study quantum Lennard - Jones clusters by the development of a new method. In particular, we look at the interplay between the zero point energy and the depth of the potential well for different values of the de Boer parameter.

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[*] Speaker

HCl trimer: HCl-stretch excited intramolecular and intermolecular vibrational states from 12D fully coupled quantum calculations

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Investigating H-bonded molecular complexes helps to understand the effect of H-bonding interaction on structure and dynamics. Molecular trimers are the smallest systems where non-additive three-body interactions (cooperative H-bonding) can be studied.

We performed rigorous fully coupled, full-dimensional quantum calculations to determine the inter- and intramolecular vibrational states of HCl trimer. The computation is based on the partition-contraction method (P. M. Felker, Z. Bacic, J. Chem. Phys. 158, 234109 (2023)), where the 12D Hamiltonian is partitioned into a 9D inter- and a 3D intramolecular Hamiltonian, and a remainder term. The inter- and intramolecular Hamiltonians are diagonalized separately, and their eigenstates are employed to create a product contracted basis in which the complete Hamiltonian is diagonalized.

Since all coupling is included in the model, comparing the computed energies with experimental values allows the assessment of the quality of the potential. The calculations reveal the coupling between different vibrational modes and also that the three-body interaction has a significant effect. Furthermore, we were able to identify states localized in the secondary minimum of the potential.

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*Speaker

Poster Session

1 - Vibrational transitions of H2Cl+: Potential energy surface and anharmonic computations

Kokou M. Robert Afansounoudji * [1], Rabiou Issa [1], Komi Sodoga [1], David Lauvergnat [2]

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A new three-dimensional potential energy surface of the electronic ground state of the chloronium ion, H2Cl+, based on the explicitly correlated coupled cluster method with a triple zeta basis set adapted to this method has been expanded in an analytical representation. This potential energy surface is later incorporated into our home-made Fortran code to compute variationally the vibrational levels, zero-point ground average structural parameters and the rotational constants of the chloronium ion and several isotopologues. Our results(1) show a good agreement with experimental(2) and theoretical(3) data and that our results will help to detect H2Cl+ isotopologues in the interstellar medium(4).

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[*] Speaker

2 - Ozonolysis of 2-methyl-2-pentenal: new insight from Master equation modelling

Alexander Alijah [*] [1], Najoua Derbel [2], Struan H Robertson [3], Carmen Kalalian [1], Estelle Roth [1], Abdelkhaleq Chakir [1]

[1] GSMA, Groupe de spectrométrie moléculaire et atmosphérique – Université de Reims Champagne-Ardenne, Centre National de la Recherche Scientifique – France
[2] Laboratoire de Spectroscopie Atomique, Moléculaire et Applications – Tunisia
[3] Dassault Systemes [Cambridge] – United Kingdom

The ozonolysis reaction of 2-methyl-2-pentenal was investigated theoretically from the results of accurate density-functional (M06-2X) and ab initio (CCSD(T)) computations, employing the AVTZ basis set. The sequence of reaction steps was established and the system of kinetics equations modelled using MESMER. In the first step, a primary ozonide is formed, which then decomposes along two pathways. The principal ozonolysis products are propanal, methylglyoxal, ethylformate and a secondary ozonide. An interesting competition between sequential reaction steps and and well-skipping is found, which leads to an inversion of the expected methylglyoxal/propanal product ratio at temperatures below 210 K. The mechanism of the ”hot ester” reaction channel of the Criegee intermediate was revisited. The computed ozonolysis rate constant and product branching ratio arein excellent agreement with the experimental data. N. Derbel et al., J. Phys. Chem. A, in press, https://doi.org/10.1021/acs.jpca.3c04965

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[*] Speaker

3 - Pairwise Model Potential and DFT Study of Ne_n^-Li ˆ+ Clusters (n = 1–20): The Structural, Electronic, and Thermodynamic Properties

Hamid Berriche * [1], Nisrine Mabrouk [2], Bejaoui Mohamed [2], Jamila Dhiflaoui [2]

[1] American University of RAK and University of Monastir – United Arab Emirates
[2] UNIVERSITY OF MONASTIR – Tunisia

Abstract: The geometrical structures and stability of clusters with n=1-20, have been investigated using pairwise potentials determined at CCSD(T) level of calculation. The potential energy surface employed in these calculations is based on the , and V3B interactions (1). For this, we tested a set of bases with the CCSD(T) method to reproduce accurately the experimental and potential energies curves. In addition, both potentials have been fitted by the analytical expressions following Tang and Toennies (TT) (2) and Lennard-Jones (LJ) (3) formula. The results show that the most stable structures of clusters up to n = 20 have been optimized using the Basin-hopping Monte Carlo method. Furthermore, these structures are determined through ab initio optimization techniques at CCSD (T) and DFT level of calculations with B3LYP functional combined with the 6–311 + + G (2d,2p) basis sets and using Molpro (4) and Gaussian packages (5). The relative stabilities of these clusters are discussed by calculating the binding energy, the fragmentation energy and the second order energy difference to determine the corresponding magic numbers that could be. The electronic and thermodynamic properties were determined to improve that the formation process of clusters is endothermic and non-spontaneous.
Keywords: Clusters; Stability; Optimization; ab initio; DFT; Basin Hopping.

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4 - The mean square displacement of a ballistic quantum particle

Oussama Bindech [1], Fabien Gatti [2], Mandal Souvik [*] [1], Roberto Marquardt [1], Lei Shi [2], Jean Christophe Tremblay [3]

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A commonly used quantum mechanical formulation of the mean square displacement $\delta_x^2(t)$ is based on the quantum correlation function of the position operator. While this quantity yields the classically expected result $\delta_x^2(t) \propto t^2$ for a ballistic particle in the interval topology, it is found here to diverge at essentially all times, when evaluated on infinitely large rings. A somewhat different formulation of the mean square displacement in quantum mechanics was proposed in a previous work (R. Marquardt, Mol. Phys. 119, e1971315 (2021)) and yielded the result $\delta_x^2(t) \propto t$ for the ballistic particle on an infinitely large ring. Here, it is shown analytically that that formulation yields $\delta_x^2(t) \not\equiv 0$ for the ballistic particle on an infinitely long interval. The two formulations define two different, topology dependent quantities that have the dimension of an area and that could in principle be determined from the same experiment, following a measurement idea proposed in the aforementioned work. That idea is critically reviewed here.
Ref: (1) O Bindech, F Gatti, S Mandal, R Marquardt, L Shi, JC Tremblay, Molecular Physics, doi: 10.1080/00268976.2024.2322023

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[*] Speaker

5 - Theoretical study of the CH3Br(X1A1) + N2(1Σ_gˆ+) van der Waals complex: potential energy surface and applications

Driss Ben Abdallah * [1], Ikbel Mejdi [1], Hassen Aroui [??]

[1], Majdi Hochlaf [??]

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The first five-dimensional potential energy surface (PES) for the CH3Br + N2 atmospheric weak bond complex is presented in this work. This surface is developed from a large number of ab initio energies where the CH3Br (X1A1) and N2 (1) monomers are treated as rigid rotors. Computations were done using the DCSD/aug-cc-p-VTZ level of theory. For Br atom, we used the corresponding aug-ccpVTZ-PP correlation consistent basis set together with the appropriate Stuttgart/Köln ECP10MDF pseudopotential, where the 3s23p64s23d104p5 electrons are processed explicitly while the (Ne) electrons are part of the core. The equilibrium structure of the CH3Br-N2 complex found when N2 is lying near the plane formed by the C3 axis and the C–H bond at the intermolecular separation of 7.75ao. The corresponding well depth is -288 cm–1. As a first application, this new 5D-PES is used for computing the temperature dependence of second virial coefficients of the CH3Br + N2 pair. Experimental values for a dimer CH3Br-N2 gas mixture are not available to our knowledge. However, the data reported here will hopefully motivate this type of experiments, and will also serve as a future test of the quality of our surface. As a second application, this PES is fitted to an analytical function through a procedure that combines spline, least-squares and projections for later evaluation of the pressure broadening coefficients of the spectral lines of Methyl bromide CH3Br in N2 bath. These data will be helpful to a precise estimation of CH3Br abundances in planetary atmosphere spectra.

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*Speaker

6 - Addressing Discrepancies Between Theory and Experiment in the NF3 Photoelectron Spectrum

Megan R. Bentley [*] [1,2], Peter R. Franke [1], Kaila E. Weflen [1], Branko Ruscic [3], John F. Stanton [1]

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[3] Chemical Sciences and Engineering Division [Argonne] – United States

Due to a large change in geometry upon ionization of NF3, the corresponding photoelectron spectrum observed by Berkowitz and Greene exhibits a long vibrational progression spanning roughly 1.5 eV. The ionization threshold is assigned at 13.0 eV, consistent with previous experimental determinations but at considerable odds with mid-level calculations which predict an ionization energy nearly 0.4 eV lower. We perform high-accuracy thermochemical calculations (HEAT) to determine the ionization threshold and find it is consistent with previously calculated estimates, a fact which is not entirely surprising given the difficulty in determining the onset experimentally due to small Franck-Condon factors in the vicinity of the origin in ionization processes associated with a significant geometry change. More interestingly, the width of the overall progression is enough to surmount the barrier to planarity in NF3+ , assigned experimentally to an observed change in vibrational spacing on either side of the peak maximum. Again, high-accuracy calculations determine a value much lower in energy (0.24 eV) than that predicted by experiment, throwing into question the explanation for the change (or loss) of observed spacing on the higher energy side of the peak maximum. Attempts to alleviate discrepancies between calculated and experimental assignments, relying on the aforementioned thermochemical calculations and Franck-Condon simulations are discussed.

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[*] Speaker

7 - Electronic Dynamics in liquid phase

Geoffrey Carneiro [*] [1,2], Jérôme Palaudoux [2], Hugo Marroux [3]

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Photoemission delays in liquid water have been measured by Jordan**[1]** *et al.* The goal of our work is to extend these measurements to solvated species. In order to do that we use the well known RABBIT technique which is attosecond interferometry between XUV (obtained by High Harmonic Generation) and intense IR beams (from titanium-sapphire laser). Two photon transitions occur between the harmonics and the IR giving birth to sidebands. By scanning the XUV-IR delay we can measure the oscillations of the sidebands and then retrieve photoemission delays. (1): I. Jordan *et al.* Science **369** (6506), 974-979.

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[*] Speaker

8 - UV-spectrum and photo-decomposition of peroxynitrous acid in the troposphere

Wiem Chebbi * [1,2], Najoua Derbel [1], Alexander Alijah [2], Thibaud Cours [2]

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Peroxynitrous acid HOONO was first observed in an Argon matrix (1). It is an unstable species and has not been seen in the gas phase at ambient pressure and temperature because of its short lifetime of a few seconds (2).
The thermolysis and photo-decomposition mechanisms of HOONO are not well-understood, so we studied its photochemical decomposition and non-adiabatic dynamics in this work. We used various theoretical methods to calculate the UV spectra of the two most stable conformers, namely the cis-cis and trans-perp conformers.

We have reanalysed the experimental UV spectrum of peroxynitrous acid recorded by W.J. Lo and Y. P.Lee (3) forty years ago, it was computed at the B3LYP/AVTZ level. the maxima in the simulated spectra are displaced from the positions of vertical excitations due to large-amplitude vibrational motions of this molecule.

Since the excited electronic states are repulsive, the molecule will disintegrate upon UV absorption, yielding HO2 + NO as the principal photolysis product, compared to thermal decomposition, which mainly yields NO2 + OH. We have computed the rate constant for atmospheric photo-decomposition for the first time in this work, using the statistics of trajectories computed at MCSCF/AVTZ level employing the fewest switches surface hopping algorithm (4). We found that near the tropopause, the photolysis rate constant

J= 6*10-4 s-1, which shows that photo-decomposition is significantly more rapid than thermal decomposition (k $\approx$ 10-6 s-1) (5).

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[*] Speaker

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9 - Simulation of rovibrational spectra of sulphur containing molecules of astrophysical relevance

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The detection of new molecules in the interstellar medium and circumstellar envelopes has gained increasing interest in the recent past. The sulphur counterparts of oxygen-containing molecules, which have already been detected in space, are promising further candidates. We have studied thioformyl cyanide and thiopropynal. The equilibrium geometries were determined using CCSD(T)-F12b, i.e. explicitly correlated coupled-cluster with single, double, and perturbative triple excitations, in combination with an augmented triple zeta basis set. The multidimensional potential energy surfaces were obtained using a truncated n-mode expansion up to 4th order, with the equilibrium geometry as the reference point for expansion. Vibrational configuration interaction (VCI) calculations based on the non-rotating Watson Hamiltonian was used to determine vibrational wave functions of fundamental transitions, overtones and combination bands. Rovibrational configuration interaction (RVCI) calculations were performed using vibrational basis sets obtained from the preceding VCI calculations along with Wang combination-type rotational basis functions. Hot bands have been considered throughout. The resulting infrared spectra were color-coded to identify the states involved in the transitions. Temperature effects on the spectra were also studied.

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*Speaker

10 - Hydrogen Sticking on Graphene

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The H sticking on graphene is investigated using Hybrid TRAJectory (HyTRAJ), a mixed quantum classical method. A single potential with well-defined barrier, physisorption and chemisorption well are obtained by including VanderWaal's interactions and the study of phonon vibrational modes using PWSCF method in Quantum Espresso.

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*Speaker

11 - Rovibrational ab initio line lists of triplet and singlet methylene

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[2], Dominika Viglaska ??

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Methylene molecule (CH2) is a short-lived radical with lacking data on its spectral line intensities. Although the lifetime of CH2 is extremely short under the Earth's conditions, it exists in a free form in interstellar media. CH2 is an important intermediate species in chemical reactions associated with the formation and destruction of complex hydrocarbons. We present the rovibrational line lists of CH2 in its ground triplet and first excited singlet electronic states constructed from the developed *ab initio* potential energy (PES) and dipole moment surfaces (DMS). The *ab initio* potential energies were calculated using the single-reference coupled cluster approach (CCSD(T)) in a combination with the extrapolation to the complete basis set (CBS) limit based on the correlation-consistent orbital basis sets with the core-valence electron correlation (aug-cc-pCVXZ, X = T, Q, 5, and 6). In addition, the contributions to the correlation energy from highly-excited Slater determinants (CC(n), n=3–5) were included as well as the scalar relativistic effects and DBOC. Finally, the most accurate description of the experimental band origins of triplet and singlet CH2 was achieved for the energy region where impact of the nonadiabatic coupling due to the Renner-Teller effect can be neglected. To obtain the probabilities of the rovibrational transitions, the *ab initio* DMSs were developed using the CCSD(T)/aug-cc-pCVQZ approach. Finally, the rovibrational spectra of both species were predicted from the variationally computed line lists. This work was supported by the Russian Scientific Foundation (RSF, No. 22-42-09022) and Agence Nationale de la Recherche (ANR, French National Research Agency, Grant No. 21-CE30-0053-01).The support from the ROMEO computer center of Reims-Champagne-Ardenne is also acknowledged.

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*Speaker

12 - Application of photoelectron spectroscopy to uracil and bromouracil molecules in liquids

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The knowledge of the electronic structure and the ionization energy are shaping the behaviours of molecules. Our study is two fold. First, we want to determine the influence of solvation on the electronic structure of uracil, a RNA nucleobase and one of its derivatives, the 5-bromouracil. Then, we are interested in the influence of the chemical environment. For this, soft X-rays electron spectroscopy has been used. The measurements have been performed using synchrotron radiation (synchrotron SOLEIL) and an under-vacuum liquid jet, coupled with and electron spectrometer, available on PLEIADES beamline. With this configuration, it is possible to probe about three molecular layers at the surface of the liquid, which means that our measurements are very are surface-sensitive. The 1s electronic core level of carbon and nitrogen have been probed in two different pH conditions (basic and neutral). The recorded photoelectron spectra of solvated uracil in neutral condition are closely similar to the ones obtained on water-uracil clusters. The comparison between photoelectrons spectra at each pH condition reveals some binding energies differences of the peaks in the photoelectron spectra that could illustrate a modification of the chemical environment in addition to deprotonation. Our experimental observations are supported by theoretical calculations. Additionally, information on the Lowest Unoccupied Molecular Orbital (LUMO) electronic level has also been retrieved. A tentative of deciphering the different de-excitation pathways following a photoexcitation of a 1s electron, from carbon or nitrogen, to the LUMO, highlighted the complexity to interpret such data obtained in liquid phase.

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[*] Speaker

13 - 3D-QSAR Studies of Pyrimidine derivatives, molecular docking and ADMET properties

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Neuropathic pain syndrome exerts a profoundly negative and agonizing influence on the lives of those affected by it. The quest for an effective treatment for this condition has led to extensive and meticulous scientific research, which has revealed that the $\sigma 1$ receptor stands out as a promising target for therapeutic agents. The development of 3D-QSAR models utilized the method of comparative molecular similarity indice analysis (CoMSIA). The results of these investigations underscored the robustness of the CoMSIA model, as evidenced by an impressive R2 train value of 0.96 and Q2 value of 0.54, ensuring accurate prediction of the activity of diverse compounds. Through the integration of valuable insights obtained from experts in the field of 3D-QSAR modeling and the implementation of molecular docking studies focusing on the potent compound C48, a total of sixteen novel compounds were successfully engineered to showcase heightened efficacy against neuropathic pain. Apart from the comprehensive 3D-QSAR scrutiny, the freshly synthesized compounds underwent a thorough assessment encompassing absorption, distribution, metabolism, excretion, and toxicity considerations. This evaluation was designed to appraise the pharmacokinetic and toxicological profiles of the compounds, furnishing essential information for prospective in vitro inquiries. The substantial progress achieved in this study ought to act as a compelling impetus for forthcoming in vitro investigations centered on these innovative compounds. **Keywords:** $\sigma 1$ receptor antagonists; Pyrimidine derivatives; 3D-QSAR; Molecular Docking, ADMET.

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*Speaker

14 - Efficient Generation of Torsional Energy Profiles by Multifidelity Gaussian Processes for Hindered Rotor Corrections

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Hindered rotations (HR) play an important role in the prediction of thermochemical properties for various applications. With a sufficiently accurate potential energy surface (PES), the one-dimensional hindered rotor (1DHR) model helps to deal with these anharmonic motions. The quality of 1DHR models, however, depends on various factors: a) the accuracy of the modelling of the moments of inertia of rotating tops, b) the treatment of harmonic oscillators outside the 1DHR system, and c) the quality of the Fourier fit to an accurate 1D PES (1). An oscillation-free fit for the 1D PES can be obtained with TAMkinTools (1), which is an extension of an existing Python package that can solve molecules for the 1DHR model. The accuracy of its predictions depends on the level of theory used to generate the PES scans it uses. With a low-level theory such as DFT, the PES is not accurate enough, but with a higher level theory such as coupled cluster theory, predicting an accurate PES is expensive. Because thermochemical properties are much more dependent on lower-energy regions and minima, the state of the art until now has been to combine low-level computations with selected high-level calculations around minima to predict the thermochemical parameters accurately without compromising on the cost of the calculation.

We present a multi-fidelity (MuFi) strategy for the combined approach, allowing us to efficiently predict the high-fidelity (HiFi) data points from inexpensive low-fidelity (LoFi) data points. To achieve this optimized combination of HiFi and LoFi data points, we used Gaussian process regression (GPR) with Bayesian Prediction (BP). This allowed us to transfer much of the accuracy of highly-accurate model chemistries like CCSD(T) down to efficient DFT PESs for 1DHR and N×1DHR treatment of larger molecules and complexes. The accuracy of the MuFi model depends primarily on three important contributions. First, the model is very sensitive to what training data is used. In our case, this was complete torsional scans at the LoFi level paired with one or two SPEs of the torsional profile taken at the HiFi level. The accuracy of GPR also relies on the choice of the kernel function. We opted for the Matérn32 kernel over the RBF and Fourier kernels (2). Finally, to predict the thermodynamic data, an appropriate acquisition function must be chosen. In this study, we developed and used our own, problem-oriented acquisition function inspired by thermodynamic functional relations. All the previously mentioned methods were combined to develop an algorithm to predict optimal locations of HiFi points alongside their uncertainties. This algorithm was later used in concert with TAMkinTools to

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*Speaker

calculate the accurate PESes and therefore the thermodynamic properties for chemical systems like ethanol monomer, tetrahydrofuran, and 2-methylfuran-methanol complex.

From the study, we were able to successfully include the HiFi calculations within a MuFi approach to efficiently construct a PES. We also used BP to increase the effectiveness of sampling for collecting data both HiFi and LoFi data points. Additionally, we learned that including a few more higher-energy data points dramatically improves the prediction of HiFi data points from the LoFi dataset. Overall, we estimate to have reduced the computational resources necessary for a 1DHR calculation for dimethoxymethane by up to 27%, and this was done without compromising the accuracy of the calculation. These savings are expected to increase for higher dimensions within a coupled NDHR treatment scheme that would ordinarily require exponentially more samples compared to 1DHR schemes.

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15 - Probing vibronic structure of formic acid cation and its further decomposition: Theory and Experiment

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Formic acid (HCOOH) is the simplest and most abundant carboxylic acid in the atmosphere. It participates to acid rain formation1. It is mainly produced *in-situ* from VOCs oxidation/decomposition chemical reactions. Its atmospheric burdens are still underestimated since its physical chemistry is still not fully understood2,3, in particular in higher layers of the atmosphere. The HCOOH photoabsorption cross-sections measurements (with photons having $4.7 \leq hn \leq 10.8$ eV) showed that solar photolysis is an important destruction process of HCOOH above 30km of altitude4. While under an altitude of 30 km, the reaction of HCOOH with OH· is the dominant degradation pathway. Moreover, HCOOH was detected in active interstellar regions where ionizing rays are abundant, leading, for instance to the formation of HCOOH+ cation and its subsequent unimolecular decomposition. Although some experimental and theoretical studies were treating these specie5–7. The dissociative photoionisation of HCOOH is still not fully understood. At present, we combine state-to-the-art theoretical first principles methodologies and He I TOF-PEPICO experimental technique to shed light into the spectroscopy of the HCOOH+ ion in its lowest electronic states, their couplings and their further state-to-state evolution. Experimentally, we use a HeI light source (21.21 eV) coupled to a magnetic bottle TOF spectrometer8 to record the photoelectron and photoion spectra of HCOOH cation ionized at 21.21 eV. Theoretically, we generated the photoelectron spectra of HCOOH+, where we optimized the geometries of HCOOH and its cation in its 5 lowest electronic states. Thus, we were able to simulate some photoelectronic bands, whereas the other exhibit strong vibronic coupling that go well beyond the simple monoconfigurational picture. We also investigated theoretically the state-to-state fragmentation of HCOOH+. Besides, the ionization energy of HCOOH was calculated accurately using an advanced composite scheme method. These computations were done using GAUSSIAN 169 and MOLPRO 201510.

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16 - ON NON-SEPARABLE ANHARMONIC VIBRATIONS IN ALUMINA CLUSTERS

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This study investigates the effect of non-separable anharmonic vibrational motions in aluminium oxide clusters (Al2O3)n. Second-order vibrational perturbation theory is employed to obtain anharmonic vibrational densities of states which are then compared to the commonly used harmonic vibrational densities of states. The ratio shows that the significance of anharmonicity within the alumina clusters grows with both size of the clusters and internal energy.

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*Speaker

17 - Revisiting core polarization pseudopotential: toward an effective Hamiltonian for Alkali-rare gas molecules.

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Following an idea put forward by Sinanoglu, we present a development of an effective Hamiltonian based on the core-valence separation to study alkali-rare gas molecules. Such a separation is common to all pseudo-potential and model potentials for atoms and we consistently assume that the core orbital overlap is negligible. To take into account the core-valence correlation, we consider the configurations made of one core hole and two valence electron and treat them by means of second order Van Vleck perturbation theory. We identify two kinds of term in the perturbation expansion. The first series is made of purely atomic terms and we can substitute their perturbative approximation by a more accurate parameterization obtained from very accurate scattering experiments and

calculations for the rare gas and from the Rydberg state energy levels for the alkali. The remaining terms express the couplings of the rare gas and alkali in the combined field of the valence electron and the alkali cationic core. We take into account small exchange effects, which modify the polarisation effects. Our parameterization has some resemblances with the *ab initio* model potential developed by Huzinaga and by Seijo and Barandiaran as it respects the nodal structure of the valence orbitals in the core region. This allows us to take into account the scalar relativistic effect in the Douglas-Kroll-Hess approximation (DKH2) and of the spin orbit couplings in a non-empirical way. We show that the developed model yields accurate predictions in the elementary case of alkali-helium dimers. Our analysis reveals that exchange term plays a non-negligible role to reproduce accurately reference coupled cluster single double and perturbative triple excitations (CCSD(T)) calculations.

SINANOGLU : https://doi.org/10.1063/1.1731359

VAN VLECK : https://doi.org/10.1143/PTP.53.1641

HUZINAGA : https://doi.org/10.1063/1.1681443

BARANDIARAN/SEIJO : https://doi.org/10.1142/9789812815156_0002

DKH : https://doi.org/10.1021/cr200040s

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[*] Speaker

18 - Hagedorn Wavepackets and Time-Dependent Schrodinger Equation on Ground and Excited States.

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The simulation of molecular quantum dynamics is done by numerically solving the time-dependent Schrödinger equation. There are several ways to rep- resent the solution of this equation. The traditional way is to project it on a time-independent basis. Another way is to represent it on a time-dependent basis. In this last category, there are several techniques such as semi-classical method proposed by Heller (1), MCTDH (2), Hagedorn wavepackets tehnics (3), DD-vMCG(4) etc... We are developing a simulation code based on the Hagedorn wavepackets technics for which, the basis set and the grid move over time following the evolution of the wavepackets. We make applications on models potential (HenonHeiles 6D) and on non-adiabatic models. We show that this way of carrying out propagation makes it possible to optimally reduce the num- ber of primitive basis functions and delay exponential growth. Therfore, it is possible to save time and IT resources.

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*Speaker

19 - Potential energy surface for the BN$^-$ (X$^2\Sigma^+$) + He ^{1}S) system

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A new potential energy surface (2D-PES) for the interaction of He (^{1}S) with the BN$^-$ (X$^2\Sigma^+$) anion in its ground state is computed using the self-consistent field method (CASSCF) with full valence in active space, followed by the multireference single and double interaction configuration method with Pople correction for quadruples, MRCISD(Q), in the aug-cc-pCV5Z basis set for B and N and aug-cc-pV5Z for He (442 contractions), for further calculations of the scattering cross sections.

The rigid BN$^-$ anion in the ground state X$^2\Sigma^+$ has the internuclear equilibrium distance of 1.2884 $\AA$ with $r_B = 0.7272$ $\AA$ and $r_N = 0.5612$ $\AA$ from the center of mass, the dipole moment of -1.0000 Debye directed from N to B and a rotational constant of 49.899960 GHz calculated with average atomic masses. The Jacobi coordinates were used, where the R coordinate is the distance of He from the center of mass X of the BN$^-$ and the theta angle He-X-B is set to 0 degrees at the linear He$cdots$BN$^-$ configuration and 180 at the linear BN$^- \cdots$ He. The PES was calculated from R=2.5 up to R=20 $\AA$, with a step of 5 degrees in theta angle.

The complex has 15 electrons and the ground state $^2\Sigma^+$, which is close to the first excited state of the same symmetry, about 1 eV above it. To avoid convergence problems due to flipping between two roots, the CAS was averaged for two states with weight 1 for the lowest one and then used for the subsequent CI calculations. The zero energy corresponds to the splitting of the BN$^-$ and He fragments at R=100 $\AA$. At each point, the basis set superposition error (BSSE) for BN$^-$ and He fragments was calculated by the counterpoise correction.

All calculations were performed in the point group C_S with the MOLPRO 2012.1.(1)

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*Speaker

20 - Ground and Excited electronic states of C$_5$N and C$_7$N radicals and their anions predicted by multireference methods

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Last year, the C_7N^- anion was discovered towards the starless core TMC-1 and the carbon-rich evolved star IRC +10216 (1). The question of possible radical detection is open, but the arrangement of the ground and low-lying excited valence electron states is controversial due to the closely spaced $^2\Pi$ and $^2\Sigma^+$ states in these carbon chain species. The former state has a very small dipole moment of about 0.8 Debye, the later a large one of about 4.3 Debye in C_7N. If the radical has a large dipole moment, above a critical value, it can bind an extra electron to form a dipole-bound electronic state, and we have predicted the existence of such states in the C_5N^- anion.(2)

Excited states were calculated using multireference methods: the complete active space self-consistent field (CASSCF) as a reference function for the subsequent multireference configuration interaction with singles and doubles (MRCISD), also with the Pople correction for quadruples, MR-CISD(Q), the multireference averaged quadratically coupled cluster method MR-AQCC, and CASPT2 in the standard basis sets aug-cc-pVT(Q)Z. The full active space was chosen to include 13σ, 14σ, 2π, 3π, 4π and 5π molecular orbitals in C_5N and 17σ, 18σ, 3π, 4π, 5π and 6π molecular orbitals in C_7N and their anions. All calculated states with a total spin value, including the neutral doublet ground state, were averaged using the CASSCF method with equal weights to obtain the orthogonal states. The calculations were performed using the quantum chemical ab initio programs MOLPRO (3) and ORCA (4).

MR-CISD(Q) predicts the ground $^2\Sigma^+$ for C_7N, similar to the case of C_5N, but in contrast to some previous results, e.g. ref (5). However, due to the mixing of these states, we can calculate the average value of the dipole moment, which may be important for the detection.

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[*] Speaker

21 - Generating the Potential Energy Surfaces for complexes relevant to astrochemistry

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Generating Potential Energy Surfaces (PES) for complexes relevant to astrochemistry is a challenging endeavor. Obtaining accurate PES for noncovalently bound molecular dimers presents two primary challenges. Firstly, there is the computational cost associated with accurately calculating interaction energies. Secondly, the number of grid points required increases exponentially with the problem's dimensionality. One potential solution to the computational cost issue is to transition from established methods like CCSD(T) or CCSD(T)-F12 to SAPT or even more cost-effective SAPT(DFT). Both SAPT and SAPT(DFT) have demonstrated reliability in describing noncovalent interactions. Addressing the challenge of the exploding number of grid points can be achieved by seamlessly integrating short-range interactions (calculated within a given approximation) with long-range interactions (using multipole expansion).
Additionally, rather than using evenly spaced grid points, selecting grid points based on physical information obtained from earlier versions of potentials for a given system can lead to significant savings in computational resources. These solutions have been implemented in the autoPES(1) code developed in Szalewicz's group. This presentation will cover some technical aspects of the autoPES code and its successful applications, such as the recently published studies on the benzonitrile-He(2) and HCN-H2O(3) systems.

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*Speaker

22 - Study of the influence of microhydration on a sugar-peptide complex structure with pump-probe laser spectroscopy.

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Sugars are a family of biomolecules that plays numerous roles in biological processes of living organisms such as energy transfer, or structural roles. Among those roles stands molecular recognition, allowed by the flexible structures adopted by sugars that can reorient themselves and non-covalently bond to other molecules thanks to an extended hydrogen bonding network. Some sugars can then be selectively recognized by some proteins which plays a key role in the immune system and some diseases. It is then interesting and important to understand the structural properties of this key-lock association and the role of water that can strongly influence those structures. We studied in environment-free conditions the association of a functionalized mannose molecule with a functionalized glutamic acid that reproduces a peptide bond. With double resonance laser spectroscopy in the far-IR and mid-IR range, we compared the structure of this dimer with a micro-hydrated one to which one water molecule was added. The resulting spectra are selective in mass and conformer specific. By comparing those spectra to a theoretical study conducted at the B3LYP-D3/def2-TZVPP level of theory of the density functional theory, we obtained a correct match for the two most stable structures observed for the dimer and for the mono-hydrated dimer. The water molecule appears to be inserted between the mannose and the glutamic acid in two different ways leading to a complete reorganization of the hydrogen bonding network, with some very explicit differences in vibration signatures.

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*Speaker

23 - Formation of dimethyl ether ion from protonated methanol clusters: an intracluster reaction of astrophysical interest

Hector Lissillour *[1], Laura Parrado Ospina [1], Denis Comte [1], Leo Lavy [1], Thibaud Salbaing [1], Paul Bertier [1], Linda Feketeova [1], Bernadette Farizon [1], Michel Farizon [1], Florent Calvo [2], Tillmann Mark [3]

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Abstract

The abundance of extra-terrestrial methanol makes the reaction between methanol molecules, in a molecular cluster, a possible key step in the search of mechanisms for the formation of more complex molecules, under the conditions of the interstellar medium as well as circumstellar and planetary atmospheres (1,2). The dimethyl-ether formation, resulting of the reaction of a methanol molecule interacting with a protonated methanol ion via the elimination of a water molecule, is a basic mechanism in the formation of complex organic molecules.

The Molecular-Cluster Irradiation Device (DIAM) (3) (4), set-up at the Institut de Physique des 2 Infinis de Lyon is devoted to perform experiments under conditions that reproduce some aspects of interstellar, circumstellar or planetary atmospheric environments. In order to investigate the occurrence and competition of various fragmentation and intramolecular processes, as evaporation, dissociation, or formation of further complex organic molecules (COMs), we have performed single collision experiments of 8-keV mass-selected protonated methanol clusters.

Focusing especially on the post-collisional relaxation of the protonated methanol dimer and trimer ions after high-energy single collisions, the results indicate a strong size selectivity favoring the occurrence of this reaction only in the dimer ion. To elucidate this behavior, the velocity distribution of the eliminated water molecule was measured using an event-by-event coincidence analysis (5). These results are interpreted using quantum chemical calculations of the dissociation pathways. It turns out that in the dimer case two transition states are able to contribute to this intracluster reaction (6).

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24 - Photofragmentation of cyclobutanone simulated using non-adiabatic dynamics

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The modeling of photochemical molecular dynamics using theoretical chemistry has been a longstanding challenge due to the consideration of quantum effects on both nuclei and electrons. The objective of this study is twofold: First we further our understanding of cyclobutanone photochemistry through a detailed simulation of its excited states molecular dynamics (1), and second the capabilities of our excited state dynamics as predictive models for the outcome of photoinduced processes will be tested thanks to new ultrafast electron diffraction experiments (2). The Tully surface hopping (TSH) (3) mixed quantum-classical non-adiabatic dynamics method was our choice to propagate the nuclei, where the electronic energy is evaluated on-the-fly using TDDFT and CASSCF electronic structure methods.

A strong difference between both methods has been found for the deactivation pathways followed by the excitation to the n-3s excited state. Moreover, gas-phase ultrafast electron diffraction signals have been computed for both electronic structure methods to reveal the reliability of each of them for predicting photoinduced processes in organic molecules.

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[*] Speaker

25 - Rotational Excitation and De-Excitation of Interstellar Chloronium Cation in Collisions with Helium Atoms

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Chloronium, H2Cl^{+}, is detected in astrophysical media. It is key chemical intermediate for understanding of the physical chemistry of chlorine species there. At present, we compute the collision rates for the rotational excitation and de-excitation of ortho- and para-H2Cl^{+} colliding with He for $T \leq 150$ K, relevant for the interstellar medium (ISM) conditions. Prior to that, we generated the 3D interaction potential of the weakly bound H2Cl^{+}-He complex along the Jacobi coordinates. For electronic structure computations, we used a post-Hartree-Fock explicitly correlated method at the CCSD(T)-F12/aug-cc-pVTZ level. The analytical expansion of this potential was incorporated into close coupling computations of the cross sections for the rotational excitation and de-excitation of ortho- and para-H2Cl^{+} colliding with He and for collision kinetic energies Ek ≤ 1000 cm^{-1}. The rates were obtained after averaging these cross sections over a Maxwell-Boltzmann distribution of kinetic energies. Our data show that the $\Delta j = \Delta ka = \Delta kc = -1$ de-excitation transitions exhibit the largest values, in particular those used to identify this cation in the surveys. Besides, our results should help for determining more accurate abundances of H2Cl^{+} in the ISM and, thus, better modeling the chlorine chemistry there.

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[*] Speaker

26 - Exploring the Excited States of the HPS+ Cation through Electronic and Spin-Rovibrational Spectroscopy

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Using post Hartree-Fock multi-configuration interaction *ab initio* approaches, the six (four) doublet (quartet) lowest electronic states of thioxophosphane cation, HPS+, are treated. These electronic states are mapped along the internal coordinates, including the HP, PS distances and in-plane HPS bending angle. Several potential minima are located where long-lived HPS+ ions can be found. Also, computations show that the (2A', 12A", 22A", 12A', 14A' and 14A") states are bound, for which we generate their 3D-potential energy surfaces (3D-PESs). After nuclear motion treatments, we determine the rotational and vibrational constants of these states and the pattern of their rovibrational levels up to 4000 cm^{-1} above the corresponding vibrational ground state level. For instance, the RCCSD(T)/aug-cc-pV(5+d)Z anharmonic frequencies for HPS+(2A') are computed ω= 2237.7, ω=543.0, ω= 686.8 (in cm^{-1}). For the lowest electronic excited state (HPS+(12A")), these frequencies change to ω= 2330.5, ω= 254.6 and ω= 749.6 (in cm^{-1}). Several anharmonic resonances are identified. Besides, a very accurate adiabatic ionization energy of HPS (= 9.3173 eV) is deduced using the (U)CCSDT(Q)/aug-cc-pV(T+d)Z approach and where the core-valence (ΔCV), scalar relativistic (ΔSR) and zero point vibrational energy (ΔZPE) corrections are included. Our spectroscopic data should be useful for identifying this ion in laboratory and in media where reactive collisions between PS/PS+ + H+/H or HP/HP+ + S+/S are taking place.

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[*] Speaker

27 - Identification and treatment of large amplitude motions in chiral metal complexes

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The recent IR and vibrational circular dichroism (VCD) measurements of a ferrocene derivative, ferrocene diethylmethylamine (FDMA) in the xenon provide a challenging case for computations. The flexibility of the ferrocene moiety and the side chains lead to the existence of nine distinct conformers here. Moreover, due to the sensitivity of VCD, whose signal is about 104 less intense than IR absorption, the quality of the level of theory is critical.
In theory, DFT coupled with the second-order vibrational perturbation theory (VPT2) can provide the necessary accuracy, provided the computational protocol is carefully set up. For VPT2, two major challenges arise. First, the resonances must be carefully identified and treated. Second, the flexibility of the side chain can give rise to the so-called large amplitude motions (LAMs), generally poorly described at the VPT2 level. It is thus necessary to properly identify those vibrations. The definition of LAMs is not straightforward and comprehensive protocols are lacking.

In this contribution, we will present several metrics developed to identify LAMs, to build a black-box, automated protocol to identify them with minimal or no input from the users. The devised protocol combines topological analysis, such as the hindered rotation analysis, and numerical analysis based on anharmonic constants and VPT2 core quantities. The impact of these criteria on the definition of the LAMs will be illustrated through the simulation of IR and VCD spectra of FDMA. Paths toward a full protocol to compute VPT2 spectra in the presence of LAMs will also be sketched.

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*Speaker

28 - Towards the quantum dynamics of the reactive scattering of CH4 on Ni(111) in 13D with MCTDH and compact Canonic Polyadic representation of the potential

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Understanding the atomic-level mechanism of the dynamics of dissociation of methane upon collision with a metal has significance from both industrial and academic points of view. From an industrial perspective, breakage of a C-H bond is the rate-limiting step in steam reforming, a main route for the production of molecular hydrogen. From an academic standpoint, the relatively small size of the polyatomic system makes it ideal for benchmarking and studying the mechanism of heterogeneus catalisys in general. Our approach to the study of this system is based on quantum dynamical calculations using the powerful Multiconfiguration Time-Dependent Hartree (MCTDH) method (1). To fully leverage the computational efficiency offered by MCTDH, it is crucial to express all the quantities in the sum of product (SOP) form. While the kinetic energy operator can be readily formulated in a separable form when the suitable coordinates are employed (in our case, polyspherical coordinates), the potential energy is often given in the form of a multidimensional function thus requiring its re-expression in SOP form of the lowest rank possible (smallest possible number of terms). Various grid-based algorithms that turn potential into Tucker format are available for this purpose. Given the dimensionality of the system (15/13D) and the grid size necessary for this system (≈ 10ˆ19 grid-points), the compact Canonical Polyadic (CP) representation of the potential is more suited. In this respect, the recently proposed Monte Carlo Canonical Polyadic Decomposition (MCCPD) (2) has emerged as a particularly promising approach for refitting high-dimensional surfaces.

In this contribution, we present our results for the above-mentioned system in 13D, that is, including all the vibrations and rotations of the molecule, but limiting the impact site to the top of Ni atom. To prepare the available PES (3) in a form suitable for the dynamics, we use the MCCPD method (2). Despite the fact that it performs the decomposition on a subset of the full tensor and the nature of the given potential (unbound potential with significantly different regions of interest: asymptotic, physisorption, transition states), by using a judiciously chosen subset one can ensure the global and accurate representation of all the regions relevant for the dynamics. Moreover, given that the density needed to obtain well-converged results of quantum dynamical calculation is not known a priori, we subsequently transform the obtained CP expression of the PES into analytical form. (4) To this end, we express low-dimensional terms of

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[*] Speaker

the CP expansion (so-called single-particle potentials, SPPs) in terms of Chebyshev polynomials (hence finite basis representation, CP-FBR (5)) Finally, by performing the quantum dynamical calculation on the obtained low-rank representation of the potential, we illustrate that despite the standard tests of the quality of the CP approximation, the wave-function propagation may indicate some additional issues which require the iterative process of improvement.

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29 - Unravelling the OH stretch spectrum of formic acid

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Recent combined multi-experimental and theoretical vibrational spectroscopic efforts have tremendously contributed to and extended our understanding of the internal dynamics of formic acid (HCOOH), the smallest carboxylic acid (1). One important result is that the well-known $\nu_5 - 2\nu_9$ OH bend-torsion Fermi resonance plays a far more important role than previously believed (2). The OH stretch has long been known to be strongly perturbed by several resonances, leading to a significant intensity redistribution. However, the analysis of its rotationally-resolved spectrum was achieved only as recently as 2023 (3), almost two decades after its first measurement (4). Using high-level full-dimensional perturbative (Canonical Van Vleck) and variational (GENIUSH-Smolyak) vibrational models in combination with full-dimensional potential energy and property surfaces, it is found that the perturbers belong to a large network of coupled vibrational states that build on the well-known $\nu_5 - 2\nu_9$ Fermi resonance. Many of the observed OH stretch perturbers are highly-excited multi-quantum vibrational states ($n \geq 3$) so that normal mode labels become inadequate to properly label the bands. The question arises of how – if at all – the interaction can be understood in chemical bonding terms which is addressed in light of the underlying OH bend-torsion $\nu_5 - 2\nu_9$ Fermi resonance.

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[*] Speaker

30 - Collision Induced Fragmentation of Protonated Pyridinium–Water Clusters

Laura Parrado Ospina *[1], Hector Lissillour ??

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The role of impurities in water cluster growth is a crucial step in the early stage of aerosol and cloud formation (1). A large number of molecules are present in the earth atmosphere and some of them are key to aerosol formation in the atmosphere. The concentration of some of these organic molecules, such as pyridine, has recently increased significantly (2, 3 and 4) due to human activities and therefore may contribute significantly to a change in atmospheric aerosol formation. Pyridine (C5H5N) is a hydrophobic molecule and the pyridinium-water clusters are thus of interest since water plays a key role in the aerosol nucleation (5, 6).

The Molecular-Cluster Irradiation Device (DIAM) at the Institut de Physique des 2 Infinis de Lyon is dedicated to the study of out-of-equilibrium mass- and energy- selected molecular cluster ions (7, 8, 9). The evaporation of water molecules from out-of-equilibrium pyridinium–water cluster ions was investigated using the correlated ion and neutral time-of-flight (COINTOF) mass spectrometry technique in combination with a velocity-map imaging (VMI) device (10). This combination COINTOF-VMI allows the direct measurement of the velocity distribution of the water molecules evaporated from excited clusters after high-velocity cluster – atom collision.

The role of the pyridinium versus hydronium ion in such water nanodroplets is investigated in the present study. The evaporation of water molecules from excited clusters is found to be much slower when the cluster is doped with a pyridinium ion. Therefore, the presence of a contaminant molecule in the nascent cluster changes the energy storage and disposal in the early stages of gas-to-particle conversion, thereby leading to an increased rate of formation of water clusters and consequently facilitating homogeneous nucleation at the early stages of atmospheric aerosol formation. (9,11).

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31 - Temperature-Dependent Photodissociation Cross Sections and Rates for H2S

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The photodissociation of molecules influences the chemical composition and dynamics of many atmospheric and interstellar systems. In the study of exoplanets and other hot astronomical bodies, it is thus important to understand the effect of temperature on such dissociative processes. With increased interest in sulfur chemistry in the JWST era, the photodissociation of the triatomic molecule H2S is of particular importance. Here, we present preliminary temperature-dependent photodissociation cross sections and rates for H2S in its first absorption band centered at around 195 nm. These data were generated through triatomic nuclear motion calculations in the EVEREST computational suite (1) using ab initio potential energy and transition dipole moment surfaces from Chen et al. (2). We compare our results to experimental measurements at room temperature (3, 4) and calculate temperature-dependent photodissociation rates using several radiation fields.

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*Speaker

32 - Improved Stratified Sampling Approach for Monte Carlo Integration for Solving High-Dimensional Integrals

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High-dimensional integrals are commonly encountered when dealing with problems involving the motions of nuclei, and the difficulties they create regularly end up dictating the final approaches taken for a given scenario dealing with such motions. Within the field of anharmonic thermochemistry, a class of approaches that has been recently gaining traction takes a direct approach instead of the traditional way of grossly simplifying the anharmonic problem to avoid dealing with these integrals. Methods like MCPSI (1), Wang-Landau (2), and CIMCI (3) instead rely on a technique called Monte Carlo integration to directly calculate the high-dimensional integrals needed for fully anharmonic thermochemical densities-of-states and partition functions. While efficient, these approaches all still require potentially billions of single point energy calculations even for systems the size of a few nuclei. The core shortcoming is that there so far has not been a known Monte Carlo integration method that is both suitable for obtaining thermochemical data and is also efficient enough to avoid needing massive amounts of calculations for molecules large enough to display interesting thermochemical properties.

We present a suite of novel improvements to the well-known MISER variant of Monte Carlo integration (4) that is shown to be orders of magnitude more efficient than its predecessor. Bundled into a method preliminarily called "Tarot", this suite combines the previously reported improvements of PMISER and RMISER (5) with a fundamental reworking of how to determine which subregions should be sampled and at what density. Compared to MISER, Tarot is up to ca. 10000x more efficient with its sampling budget utilization, with greater gains specifically coming from tighter integrals defined across more dimensions. Additionally, thanks to its much stronger theoretical grounding compared to the more empirically designed MISER, Tarot is also able to avoid critical pitfalls of MISER where MISER will sometimes have high statistical confidence in very inaccurate results. While Tarot was developed primarily with CIMCI in mind, its improvements are all general enough to be applicable to other uses of Monte Carlo integration as well, such as calculating Feynmann path integrals (6).

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33 - A biogenic organic molecule involved in the formation of secondary organic aerosols: microwave and millimeter-wave spectroscopy of 3-methylcatechol backed by quantum chemistry

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3-methylcatechol is likely to be found in the atmosphere during biomass burning episodes. The molecule exhibits three large amplitude motions: the torsions of its two hydroxyl groups and the internal rotation of the methyl group. Microwave and millimeter-wave spectra were recorded. Their analysis was supported by quantum chemical calculations. The theoretical three dimensional torsional potential suggests the existence of three rotamers, of which only two were detected, confirming the results of Hazrah *et al.* (A. S. Hazrah, M. H. Al-Jabiri and W. Jäger, Structure and conformations of 3-methylcatechol: a rotational spectroscopic and theoretical study, J. Mol. Spectrosc. 390, 111715 (2022), doi: 10.1016/j.jms.2022.111715). The V3 and V6 coefficients involved in the internal rotation of the methyl group were determined by fitting one-dimensional potential curves. The rotational spectrum was investigated by using a coaxially oriented beam-resonator arrangement (COBRA) pulsed jet Fourier-transform microwave (PJ-FTMW) spectrometer covering 2-20 GHz at Chongqing university. The millimeter-wave spectrum (70-110 GHz) was recorded at 323 K using an amplified multiplication chain from Virginia Diodes Inc. and a new heated absorption cell designed for the study of semi-volatile organic compounds. The new microwave and millimeter-wave data was combined with the assignments published by Hazrah et al. to produce a new global fit.

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*Speaker

34 - Toward an automated calculation of anharmonic vibrational frequencies in arbitrary internal coordinates

Moritz Schneider * [1]

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The calculation of anharmonic vibrational frequencies in arbitrary internal coordinates requires the computation of the kinetic energy as well as the evaluation of a multidimensional potential energy surface. Due to the myriad definitions of internal coordinates, writing an automated algorithm for this purpose is a challenging task. The various properties of the coordinates require a high degree of flexibility in the calculation of the potential energy surface to handle the key elements as choosing fitting functions, positioning of grid points, exploitation of symmetry, or the elongation of the surface. Also for the subsequent frequency calculation, which consists of high dimensional integrals due to the coupling within the kinetic energy, constraints like a n-mode expansion of the Wilson G matrix need to be used to allow for a general implementation of the Podolsky operator. To proof the concepts of the implemented algorithms, the HOPO molecule is used as a benchmark system, to highlight the benefits of the internal coordinate with respect to large amplitude motions.

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*Speaker

35 - Modified Spectroscopic Models for Formaldehyde Isotopologue Spectra

Oleksiy Smola *[1], Sergey Yurchenko [1], Jonathan Tennyson [1], Avanija Menon [1]

[1] UCL – United Kingdom

We present methods of computing ro-vibrational isotopologue spectra, applied to the formaldehyde isotopologues H2CO-13 and D2CO. For both isotopologues, the semi-empirical AYTY (1) H2CO-12 spectroscopic model is adapted. In the case of H2CO-13, we apply a mass optimisation procedure, fitting the carbon nuclear mass to empirical MARVEL (2) energies, to produce a line list consisting of around 12.5 million states and 9.7 billion transitions with frequencies up to 10000 cm-1. The H2CO-13 line list is also improved through MARVELisation, wherein the empirically derived energies are used to compute transition frequencies where available. For D2CO, we add an empirical mass dependent correction term to the AYTY H2CO-12-fitted potential energy surface, which reduces back to the ATTY surface for the parent isotopologue. Nuclear motion calculations were carried out using the TROVE (3) FORTRAN 90 code and intensities are computed using the GAIN GPU code (4).

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[*] Speaker

36 - Ultrafast Excited-State Non-Adiabatic Dynamics in Pt(II) Donor-Bridge-Acceptor Assemblies: A Quantum Approach for Optical Control

Mandal Souvik [*] [1], Chantal Daniel [??]

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The ultrafast non-adiabatic excited state dynamics of (PTZ-N-benzyl-acetylide) (trans-bis-trimethylphosphine) Pt(II) (acetylide-NDI-bis-methyl), representative of a series of Pt(II) Donor-Bridge-Acceptor assemblies experimentally studied by Weinstein group, University of Sheffield, is investigated by means of wavepacket propagations based on the multiconfiguration time-dependent Hartree (MCTDH) method. On the basis of electronic structure data obtained at the time-dependent density functional theory (TD-DFT) level, the sub-ps decay is simulated by solving an eleven electronic states multimode problem, up to eighteen vibrational normal modes, including both spin-orbit coupling (SOC) and vibronic coupling. A careful analysis of the results, within the diabatic representation, provides the key features of the spin-vibronic mechanism at work in this complex, distinguishing between the spin-orbit and vibronically activated ultrafast processes within the excited states manifold. The knowledge of the key active normal modes that promote selectively the population of specific electronic excited states opens a route toward optical control by selectively exciting these modes in order to drive the associated non-adiabatic processes. Relevant simulations, over 2 ps, are proposed to assess the impact of these selective vibrational excitations on the branching ratio between the primary photoproducts, namely bridge charge-transfer and/or acceptor localized (CT/LC) electronic states and acceptor-donor charge-separated (CS) states. Contrary to the commonly accepted hypothesis, the excitation of the localized acetylide bridge C-C bond stretching does not modify drastically the population of the low-lying electronic states within the first two ps. In contrast, vibrational excitation of the out-of-plane twisting motion of the N-benzyl group linked to the donor entity favors the population of the CS states at the expense of the lowest LC/CT states. Ref: (1) Souvik Mandal, Chantal Daniel, Phys. Chem. Chem. Phys, 2023, **25**, 18720-18727

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[*] Speaker

37 - Benchmark 12D vibrational computation of methanol and search for enhanced parity violation effects in substituted methanol compounds

Ayaki Sunaga * [1], Gustavo Avila [1], Edit Mátyus [1]

[1] Eötvös Loránd University – Hungary

Parity violation (PV) effects (1) are known to be enhanced by the presence of heavy elements. According our pilot 1D computations, large-amplitude motions (LAM) can also enhance PV effects, since the quantum dynamics samples very different areas of the potential energy surface, providing various PV energies. A systematic study was recently started for substituted methanol compounds, CXYZOH with X,Y, Z = H, F, Cl, Br, I, among which the most promising candidate will be studied in full-dimensional rovibrational quantum dynamics computations.

A full-dimensional rovibrational computation of a six-atomic molecule with one large-amplitude motion using a spectroscopic quality potential energy surface is nowadays becoming possible (2). To prepare the ground for the PV enhancement search in substituted methanol compounds, the GENIUSH-Smolyak methodology (3-5) was used for CH3OH on an ab initio potential energy surface developed by Qu and Bowman (6) and using one torsional (LAM) and eleven path-following curvilinear normal coordinates to describe the quantum dynamics. All vibrational energies and corresponding wave functions are converged to better than 0.5 cm-1 up to 2000 cm-1 beyond the vibrational zero-point energy. Most of the computational predictions are in excellent agreement with available experimental vibrational band origins, which confirms the good quality of the potential energy surface. This vibrational data provides a benchmark set for further computational developments for methanol, and with further extension to rotationally excited transitions may contribute to astrochemistry (7) and the proton-to-electron mass ratio variation searches in the outer space (8).

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[*] Speaker

38 - ROVIBRATIONAL STATES CALCULATIONS OF THE N2O–CO VDW COMPLEX.

Herve Tajouo Tela [*] [1], Ayda Badry [2], Richard Dawes [3], Steve Alexandre Ndengué [4], Majdi Hochlaf [5], Adrian Batista Planas [3], Ernesto Quintas-Sánchez [3]

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[4] Department of Physics, Trinity College, Hartford, CT, USA – United States
[5] COSYS/ISME, Université Gustave Eiffel, Champs sur Marne, France – French Southern Territories

N2O and CO are two of the most common species in space and the atmosphere with the ability of binding to form dimers such as N2O–CO. Due to their importance as potential greenhouse gases or the potential role of N2O in the creation of NOx , numerous experimental studies have been carried out to characterize the infrared spectroscopy of this system. In our presentation we will complement these work by presenting, what we believe to be for the first time, a calculation of the rovibrational states of this cluster. To obtain these results, two sets of Potential Energy Surfaces for this complex have been built. We will present the surfaces, describe our calculations that were carried out with the MCTDH code, and explain our procedure.

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[*] Speaker

39 - Ab Initio Study of AlnNmq+ Molecules (n=1-3; m=1-3; q=0-2)

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[3] Laboratoire Instrumentation, Modélisation, Simulation et Expérimentation (IMSE) – Université Gustave Eiffel – France

Aluminum nitride (AlN) material is widely investigated due to their excellent physical and chemical properties, such as chemical and thermal stability, microelectronics, high-frequency (wide band communications), ultrasonic and semiconductor. A complete study of the spatio-temporal evolution of the different plasma species of AlN ceramic material ablation at different experimental conditions has been presented before (1). The main processes contributing to atomic and molecular formations in laser-induced AlN plasma include shock wave formation, recombination, electronic excitation/de-excitation, dissociation, and ionization of particles by electronic impact. In this work we present an *ab initio* study of AlnNmq+ (n=1-3; m=1-3; q=0-2) molecular species to propose plausible explanation of our experimental results obtained in laser induced AlN plasma into nitrogen ambiance (1). For that we have investigated their equilibrium structures in their lowest respective potential energy surfaces (Figure 1) and their vibrational frequencies with the aim of determining their single and double adiabatic ionization and dissociation energies. Which may help to characterize those species spectroscopically. We performed our calculations using the Complete Active Space Self Consistent Field (CASSCF) method followed by the explicitly correlated Multi Reference Configuration Interaction (MRCI-F12) method using the MOLPRO (version 2015) program suite (2). Besides, our work showed that commonly used Coupled Cluster (CCSD(T)) approach is inappropriate due to the multi-configurational character of the molecular species under consideration.

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*Speaker

40 - Analyses of ”forbidden” spectra of methane isotopologues CH4, CH3D, CHD3 in the terahertz range recorded at SOLEIL synchrotron

Vladimir Tyuterev * [1], Jean Vander Auwera [2], Andrey Nikitin [1], Michael Rey [3], Thibault Delahaye [4], Attila Tajti [5], Olivier Pirali [6], Laurent Manceron [6]

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[4] LMD, – LPICM, CNRS, Ecole Polytechnique, Université Paris-Saclay, 91128, Palaiseau, France – France
[5] Budapest University – Hungary
[6] Ligne AILES – Synchrotron SOLEIL, Gif sur Yvette, France – France

Highly symmetric molecules such as methane do not have a permanent dipole moment in the nuclear equilibrium configuration. As a result, their rotational spectrum would be ”forbidden” as stated in the Herzberg book (1). Intramolecular interactions in methane isotopologues make these spectra allowed (2-5), giving rise to extremely weak bands, which are sensitive to molecular symmetry and to various types of coupling between nuclear and electronic motion. Previous experimental and theoretical works on this subject have led to somewhat contradictory results (3-5) concerning particularly the role of non-Born-Oppenhemer (BO) contributions (6). The present study aimed at measuring weak bands of cold and hot bands of methane 12CH4 as well as deuterated isotopologues CH3D and CHD3 in the THz range (40 – 370 cm–1) with a resolution of 0.001 cm-1. Synchrotron radiation in conjunction with a White-type cell set to 152 m optical path length and a Bruker IFS125 HR FTIR spectrometer at the AILES beam line (7) of the SOLEIL synchrotron led to the observation of very weak rotational bands. Hot bands due to transitions among vibrationally excited states were also detected. The long-term aim of this work is to understand effects of the symmetry breaking Td => C3v (point groups) due to deuterated isotopic substitutions H => D. In this work, we report the analyses of the recorded spectra and the comparison with high-level ab initio calculations (8-10), including effects of breakdown of BO approximation in line intensities of these ”forbidden” bands. New line lists are proposed based on the modeling of observed spectra using empirically fitted parameters of the effective Hamiltonian and effective transition dipole moments. Support from the ANR-RNF TEMMEX project (grants RSF 22-42-09022 and ANR-21-30CE-0053-01) is acknowledged.

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[*] Speaker

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41 - RECENT PROGRESS IN THE FULL-DIMENSIONAL CALCULATIONS OF INTRA- AND INTERMOLECULAR ROVIBRATIONAL STATES OF H2O-HF AND H2O-HCl FROM POTENTIAL ENERGY SURFACES

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Molecular complexes play an important role in the chemistry of planetary atmospheres. H2O-HF and H2O-HCl are of considerable interest because of two Cs equivalent minima separated by a very low inversion barrier (70 and 50 cmˆ-1, respectively).

The recent methodological advances based on the full-dimensional calculations of intra - and intermolecular rovibrational states have significantly improved the understanding of molecular dynamics of Van der Waals complexes (XG. Wang, T. Carrington, J. Chem. Phys., 2023, 158(8), 084107; P.M. Felker, Z. Bacic, Phys.Chem. Chem. Phys., 2022, 24, 24655). The rigid-monomer approximation is a good compromise when intramolecular frequencies are much higher than intermolecular frequencies but their application is often not sufficient for the high-resolution molecular spectroscopy.

In particular, we show that for H2O - HF dimer, the coupling between the intra- and intermolecular modes is not negligible (few cmˆ-1 of difference between 5D and 9D calculations) and should be taken into account to predict accurately all the transition frequencies and tunneling splittings.

All our calculations are based on a full dimensional ab initio potential energy surface (D. Viglaska, XG. Wang, T. Carrington, D.P. Tew, J.Mol. Spectrosc. 384 (2022), 11158; Y.liu, J. Li, P.M. Felker, Z. Bacic, Phys. Chem. Chem. Phys., 2021, 23,7101).

The kinetic energy operator discussed initially by Brocks et al. (G. Brocks et al., Mol. Phys. 50,1023 (1983)) and written in terms of angular momentum operators defined in monomer- and dimer-fixed frames is used.

A G4 symmetry-adapted Lanczos algorithm and an uncoupled product basis are employed.

All computed results were confronted with available experimental data.

The agreement between theory and experiment is clearly improved when 9D calculations are

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[*] Speaker

considered and confirms our suggestion of a possible reassignment for two bands of H2O-HF. H2O-HX dimers are excellent candidates for more experimental high-resolution studies.

42 - Pre-dissociative spectroscopic model of AlH in its A electronic state and accurate description of the A-X band in Proxima Cen

Sergey Yurchenko * [1], Jonathan Tennyson [2], Wojciech Szajna [3], Rafal Hakalla [3], Mikhail Semenov [2], Yakiv Pavlenko [4,5], Mirek R. Schmidt [6]

[1] Department of Physics and Astronomy, University College London (UCL) – United Kingdom
[2] Department of Physics and Astronomy, University College London – United Kingdom
[3] Materials Spectroscopy Laboratory, Institute of Physics, University of Rzeszow – Poland
[4] Instituto de Astrofísica de Canarias (IAC) – Tenerife, Spain
[5] Main Astronomical Observatory, Academy of Sciences of the Ukraine – Ukraine
[6] Nicolaus Copernicus Astronomical Center, Polish Academy of Sciences – Poland

An accurate first-principle model of the A-X system of AlH and AlD is constructed using a mixture of diabatic and adiabatic representations. The shallow potential energy curve of the A state can only hold two vibrational states in AlH (v=0,1) and three vibrational states in AlD (v=0,1,2). Because of the small potential barrier, the A rovibronic states are increasingly pre-dissociative. The ab initio spectroscopic model of AlH is refined to experimentally derived energies using the nuclear-motion code Duo and used to study the pre-dissociative effects in the A-X system. The lifetimes of the pre-dissociative states are estimated and compared to the experiment. The rovibronic A-X spectrum is shown to reproduce the experimental spectra of both AlH and AlD well, and to describe the AlH absorption in the recently reported Proxima Cen spectrum, including the strong pre-dissociative line broadening.

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*Speaker

43 - Choice of molecular frame in variational calculations of rotation-vibrational spectra of ammonia isotopologues

Sergey Yurchenko [*] [1], Oleksiy Smola [2]

[1] Department of Physics and Astronomy, University College London (UCL) – United Kingdom
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Here we present a variational rotation-vibrational study of istopologues of ammonia NH3, ND3, NH2D and ND2H. When constructing a kinetic energy operator, the choice of the molecular frame is important, especially for a non-rigid molecule as ammonia with a lower barrier in its umbrella motion. We follow the Hougen-Bunker-Johns (HBJ) approach in conjunction with the Eckart and Sayvetz conditions to represent the molecular frame as a non-rigid reference configuration. For the symmetric isotopologues (NH3 and ND3), the z axis is chosen parallel to the trisector with the umbrella coordinate as the trisector angle. For the non-symmetric isotopoluges, the orientation of the non-rigid reference frame xyz is defined by the principle axis system conditions at any instantaneous value of the umbrella coordinate, which is also a trisector angle. In the case of the heavier asymmetric molecule ND2H, its moments of inertia flip as the molecule goes through the umbrella motion. The effect of the choices of the molecular frame on the variational calculations such as convergence will be discussed. Results of calculations of molecular spectra of 15NH3, ND3, NH2D and ND2H will be presented.

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[*] Speaker

List of participants

- Afansounoudji Kokou M. Robert
- Ajili Yosra
- Alijah Alexander
- Andersson Åke
- Ben Abdallah Driss
- Bentley Megan
- Berriche Hamid
- Biczysko Malgorzata
- Bloino Julien
- Braams Bastiaan
- Bracquart Colwyn
- Brenner Valérie
- Carcabal Pierre
- Carneiro Geoffrey
- Cederbaum Lorenz
- Chebbi Wiem
- Cigrang Leon
- Cours Thibaud
- Cuisset Arnaud
- Curchod Basile
- Cvitas Marko
- Das Subhasish
- Dhiman Mukul
- Dhont Guillaume
- Dupuy Rémi

- Egorov Oleg
- Ezra Bar
- Fattouche Maroua
- Fedor Naumkin
- Féraud Géraldine
- Fournier Marine
- Gervais Benoit
- Gloriod Antoine
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- Halonen Lauri
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- Issa Rabiou
- Jaidane Nejmeddine
- Jerosimić Stanka
- Kedziera Dariusz
- Kossov Arsène
- Larsson Henrik
- Lauvergnat David
- Lauzin Clément
- Linguerri Roberto
- Lissillour Hector
- Maillard Lune
- Martín Santa Daría Alberto
- Matyus Edit
- Morice Adrien
- Morisset Sabine

- Nadoveza Natasa
- Noble Jennifer
- Nyman Gunnar
- Palaudoux Jérôme
- Parrado Ospina Laura
- Perri Armando Nicola
- Rath Gabriel
- Rauhut Guntram
- Reinhardt Peter
- Rey Michael
- Rivilla Victor M.
- Roncero Octavio
- Rutkowski Lucile
- Schneider Moritz
- Schroeder Markus
- Signorell Ruth
- Simko Iren
- Simon Aude
- Smola Oleksiy
- Souvik Mandal
- Stoecklin Thierry
- Suhm Martin
- Sunaga Ayaki
- Tajouo Tela Herve
- Tomza Michal
- Tran Ha
- Tyuterev Vladimir
- Ubachs Wim
- Van Der Avoird Ad
- Viel Alexandra
- Viglaska Dominika
- Wester Roland

- Worth Graham
- Ye Jun
- Yurchenko Sergey
- Zaghari Ines
- Zannese Marion
- Zins émilie-Laure