Atoms, Molecules and Clusters in Motion conference
AMOC 2022
6-10 June 2022, Helsinki, Finland

www.helsinki.fi/en/conferences/amoc-2022

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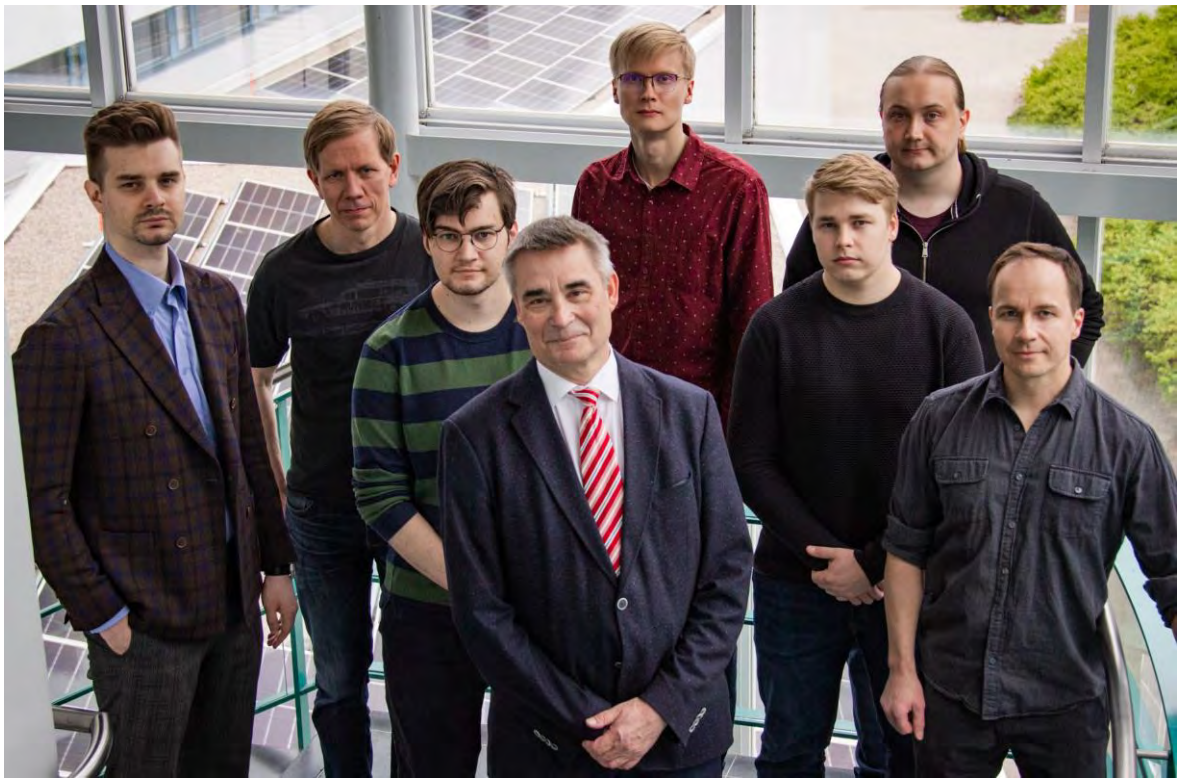
History of the Atoms, Molecules and Clusters in Motion conference

Year	Location
2012	Paris, FRANCE
2015	Madrid, SPAIN
2018	Budapest, HUNGARY
2022	Helsinki, FINLAND

Local organizing committee
AMOC 2022
June 6-10, Helsinki



From left to right: Mikhail Roiz, Markus Metsälä, Matthew Ward, Lauri Halonen, Santeri Larnimaa, Roni Vikholm, Juho Karhu, Markku Vainio

The organizers of the Atoms, Molecules and Clusters in Motion conference gratefully acknowledge the support of the following organizations and companies.

Atoms, Molecules and Clusters in Motion 2022 (AMOC 2022) conference in Helsinki and Stockholm

The first AMOC conference was arranged ten years ago in Paris (2012). I remember this very well organized event in the city center. The topic was anharmonicity in medium size molecules and clusters. The scientific standard was high as the invited speakers consisted of first class senior and junior scientists. The high quality and excellent organization continued in the following AMOC conferences in Madrid (2015) and Budapest (2018). I enjoyed both events very much.

Arranging the AMOC 2021/2022 conference in Helsinki and Stockholm has been challenging. In 2019, we booked the lecture theater in the University of Helsinki, the conference facility on the Silja Line cruise ship and accommodation in an economical summer hotel in the city center of Helsinki. We continued early 2020 to apply for financial support from private foundations. We invited first speakers during the spring 2020. When coronavirus pandemic started in 2020 and became serious, we had to postpone the conference and thus AMOC 2021 became AMOC 2022. Minor problems appeared, as for the new dates, the lecture theatre had already been booked for another event and the summer hotel ceased to exist. As known, very unfortunately, a serious war started in Europe in February this year. Although the distance, for example, between Helsinki and Kiev is larger than 1000 km, this incident has created uncertainty concerning travel in Europe. Moreover, quite unpredictably, there are suddenly many conferences this summer. The world has finally opened due to the excellent vaccination programs, which have made the coronavirus pandemic a minor issue.

We have slightly tuned the AMOC conference name to ‘Atoms, Molecules and Clusters in Motion’ to make the conference topic more general although anharmonicity still plays an important role. There are very interesting anharmonic large amplitude vibrational motions in molecules and clusters. Moreover, they often play a central role in chemical reactions. Indeed, there are related talks concerning chemical reactions in the present conference. We have also found it important that, besides computational and theoretical presentations, there are experimental talks that include new discoveries and compliment theory. Method development both in experiment and theory is significant and is present. In addition, applications of existing experimental and theoretical methods to interesting scientific problems are included.

Young scientists are important for the AMOC conference series. Therefore, besides the presentations of the invited, often more senior speakers, we have given an opportunity for the young generation to give contributed talks. There are also excellent posters to enjoy. The company presentations are a new aspect in AMOC. It is important that scientists and students working in universities and research institutes have contacts with company personal and equipment they offer.

Just a few days ago, I realized that 10 years have passed since the first AMOC conference was arranged in Paris. There is every reason to celebrate this. We shall have a toast for this occasion when the Silja Line cruise ship departs the Helsinki harbor.

All the best,

Lauri

AMOC 2022 Helsinki / Conference program at a glance

	Monday 06/06	Tuesday 07/06	Wednesday 08/06	Thursday 09/06	Friday 10/06	
8-9	8:00 – 8:50 Registration 8:50 – 9:00 Opening words			7:00 – 9:30 Breakfast (*Grande Buffet* restaurant)	7:00 – 9:30 Breakfast (*Grande Buffet* restaurant)	8-9
9-10	Two invited talks (chair A. Császár) 9:00 – 9:45 B. Gerber 9:45 – 10:30 M. Okumura	Two invited talks (chair M. Quack) 9:00 – 9:45 F. Merkt 9:45 – 10:30 K. Müller-Dethlefs	Go to Silja Line cruise ship Olympia terminal; Olympiaranta 1, 00140 Helsinki. Ticket pick-up in terminal 9:45 – 10:30 Boarding @ 10:45			9-10
10-11	10:30 – 11:00 Coffee & Posters (*Unicafe*)	10:30 –11:00 Coffee & Posters (*Unicafe*)			10:30 Cruise ship arrives at Helsinki harbor	10-11
11-12	Two invited talks (chair A. Császár) 11:00 – 11:45 M. Larsson 11:45 – 12:30 M. Hochlaf	Two invited talks (chair M. Quack) 11:00 – 11:45 R. Hinde 11:45 – 12:30 M. Lewerenz	Two invited talks (chair J. Tennyson) 11:00 – 11:45 D. Marx 11:45 – 12:30 K. Laasonen	Free time in Stockholm 10:00 Cruise ship arrives at Stockholm harbor 10:00 – 14:30 Free time in Stockholm City center	11:30 – 14:00 Lab visit + light lunch, Chemistry Department, Univ. Helsinki Transportation from harbor Pre-registration required by 29th of May see www.helsinki.fi/en/conferences/amoc-2022/lab-visit-on-friday	11-12
12-13	12:30 – 13:30 Lunch (*Unicafe*)	12:30 – 12:40 Group photo (all) 12:40 – 13:30 Lunch (*Unicafe*)	12:30 – 13:30 Lunch (*Grande Buffet* restaurant)			12-13
13-14	13:30 Talks: Genossar & Iyer (chair H. Kjaergaard)	13:30 Talks: Mikkonen & S.de. Oliveira (chair P. De Natale)	Two invited talks (chair M. Hochlaf) 13:30 – 14:15 G. Chambaud 14:15 - 15:00 H. Kjaergaard			13-14
14-15	Two invited talks (chair H. Kjaergaard) 14:00 – 14:45 S. Grubišić 14:45 – 15:30 J. Küpper	Two invited talks (chair P. De Natale) 14:00 – 14:45 K. Lehmann 14:45 – 15:30 M. Vainio		14:30 – 15:00 Light lunch at cruise ship (*Starlight* arena)		14-15
15-16			15:00 – 15:30 Coffee (*Starlight* arena)	Two invited talks (chair D. Nesbitt) 15:00 – 15:45 J. Ye 15:45 - 16:30 P. De Natale		15-16
16-17	15:30 – 16:00 Coffee & Posters (*Unicafe*) Two invited talks + company (chair H. Kjaergaard) 16:00 – 16:45 W. Ernst 16:45 – 17:30 M. Quack 17:30 – 17:45 Kimmy Photonics	15:30 –16:00Coffee & Posters (*Unicafe*) Invited talks + companies (chair P. De Natale) 16:00 – 16:45 D. Nesbitt 16:45 – 17:30 T. Ideguchi 17:30 – 17:45 Menlo Systems 17:45 – 18:00 IRsweep	15:30 Talks: Yachmenev & Vogt (chair M. Hochlaf) Invited talk (chair M. Hochlaf) 16:00 – 16:45 A. Császár 16:45 – 17:45 Break / Ship departs from Helsinki (Place to be: *Sun Deck*) Invited talk, poster prize (chair Hochlaf) 17:45 – 18:30 J. Tennyson 18:30 TOPTICA Poster Prize Announced	16:30 – 17:00 Coffee (*Starlight* arena) (chair D. Nesbitt) 17:00 Talks Metsälä & Rath 17:30 Conference summary (B. Gerber) 17:40 Closing words (L. Halonen)		16-17 17-18
18-19						18-19
19-20	19:00 – 20:00 City of Helsinki Reception; Old City Hall, Aleksanterinkatu 20. *Register by 30 May (see email from AMOC 2022)*		19:30 Dinner (*Grande Buffet* restaurant)	19:30 Dinner (*Grande Buffet* restaurant)		19-20

Venues

Metsätalo (Forest House) Univ. of Helsinki
Address: Unioninkatu 40, 00170 Helsinki.
(5 min to "University of Helsinki" metro st.)

Silja Line Cruise Ship (Helsinki – Stockholm route), *Starlight* arena (decks 7 – 8)

Time zones

UTC + 3 h

UTC + 2 h

www.helsinki.fi/en/conferences/amoc-2022

General Information

Invited and contributed presentations

Invited presentations are 40 minutes long + 5 minutes are reserved for the questions. Contributed presentations are 13 minutes long + 2 minutes for the questions. Please bring your presentation (Power Point and/or pdf) on a USB flash drive and copy it to the lecture room computer well before your own session. If you are planning to use your own computer for the presentation, please check before the session that everything works smoothly.

Posters

If your contribution has been selected as a poster presentation, please hang up the poster on Monday (6 June) during the on-site registration (before 9 am). The posters should be on display the entire Mon-Tue; the schedule of poster sessions can be found on the Program page. Please remove your poster at the end of the day on Tuesday (7 June). If you are a student and taking part in the best poster contest, be prepared to present your poster at least during the Tuesday poster sessions (morning and afternoon), when the committee goes through the posters.

Venue

June 6 - 7, 2022 (Mon-Tue): Metsätalo (Forest House), University of Helsinki, Helsinki city centre. Address: Unioninkatu 40, 00170 Helsinki. Entrance through the main doors, in the courtyard, see the photo below.

The closest metro station is "University of Helsinki". Take exit B (opposite to all other exits) and walk about 300 m to Metsätalo. For details about public transportation (metro, buses, trams, city bikes), see the journey planner at https://www.hsl.fi/en.

June 8 - 10, 2022 (Wed-Fri): Silja Line Symphony cruise ship from Helsinki to Stockholm and back. (Cruise, including accommodation and meals, is included in the conference registration fee.) The ship leaves on Wed afternoon from the Olympia terminal, downtown Helsinki. Important information:

- Cruise ship tickets/cabin keys will be distributed on Wednesday (6th of June) morning in the terminal between 9:45 and 10:30. (Look for a separate desk with "AMOC" sign in the check-in lobby). The boarding takes place at 10:45. In case you arrive late, you can pick up your ticket/key at the check-in counter of group passengers.
- In order to enter the cruise ship, you need a passport, EU ID or an EU driver's license.

WiFi at AMOC

At the venue in Helsinki (Metsätalo, University of Helsinki), WiFi is available through the "HelsinkiUni Guest" network (password: uniguest). The network can be used for 5 hours at a time, after which you need to reaccept the terms of use (the number of sessions is not restricted). The session is disconnected after 30 min if the user is not using the network.

At the Silja Line cruise ship, standard WiFi is available throughout the ship via a code that is given on your cruise ticket. Please note that the connection speed is limited. In addition, a Premium WiFi network will be available at the Starlight area where the conference presentations will be held. The code for the Premium network will be shared to the participants onboard the ship on Wednesday.

AMOC 2022 program

Monday, June 6 — Helsinki

08:00 – 08:50 **Registration**: Metsätalo (Forest House), University of Helsinki. Address: Unioninkatu 40, 00170 Helsinki

08:50 – 09:00 Conference opening

09:00 – 10:30 **TWO INVITED PRESENTATIONS**
Session chair: Attila Császár

09:00 **Mechanisms and dynamics of atmospheric reactions in clusters and in liquid water** *Benny **Gerber**, University of Jerusalem, Israel*

09:45 **Atmospheric radical reactions studied by frequency comb spectroscopy**
*Mitchio **Okumura**, California Institute of Technology, USA*

10:30 – 11:00 **COFFEE AND POSTERS**

11:00 – 12:30 **TWO INVITED PRESENTATIONS**
Session chair: Attila Császár

11:00 **Symmetry breaking and chirality in molecular physics**
*Mats **Larsson**, University of Stockholm, Sweden*

11:45 **Spectroscopy and dynamics of small molecular systems relevant for astrophysics, environment and biology**
*Majdi **Hochlaf**, Université Gustave Eiffel, France*

12:30 – 13:30 **LUNCH**

13:30 – 14:00 **TWO CONTRIBUTED PRESENTATIONS**
Session chair: Henrik Kjaergaard

13:30 **Ring opening and tunneling inversion in the cyclopropyl radical and cation**
*Nadav **Genossar**, Ben Gurion University of the Negev, Israel*

13:45 **Ozonolysis of α-pinene: Biradical route**
*Siddharth **Iyer**, Tampere University, Finland*

14:00 – 15:30 **TWO INVITED PRESENTATIONS**
Session chair: Henrik Kjaergaard

14:00 **In silico design of new metal organic frameworks for gas adsorption**
*Sonja **Grubišić**, University of Belgrade, Serbia*

14:45 **Ultrafast dynamics in microsolvated biomolecules**
*Jochen **Küpper**, University of Hamburg, Germany*

15:30 – 16:00 **COFFEE AND POSTERS**

16:00 – 17:45 **TWO INVITED PRESENTATIONS AND A COMPANY PRESENTATION**
Session chair: Henrik Kjaergaard

16:00 **Mixed metal clusters - core-shell structures, phase transitions, and nano alloying**
*Wolfgang **Ernst**, Graz University of Technology, Austria*

16:45 **Symmetries and time scales for molecular primary processes between yoctoseconds and days**
*Martin **Quack**, ETH, Zürich, Switzerland*

17:30 **Kimmy Photonics presentation**
*Kim **Grundström**, Kimmy Photonics*

19:00 – 20:00 City of Helsinki Welcome Reception at Old City Hall (Empire Room). Address: Aleksanterinkatu 20

Tuesday, June 7 Helsinki

Venue: Metsätalo (Forest House), University of Helsinki. Address: Unioninkatu 40, 00170 Helsinki.

09:00 – 10:30 **TWO INVITED PRESENTATIONS**
Session chair: Martin Quack

09:00 **Cold ion chemistry within the orbit of a highly excited Rydberg electron**
*Frédéric **Merkt**, ETH, Zürich, Switzerland*

09:45 **Observation of a periodic many-body system**
*Klaus **Müller-Dethlefs**, University of Manchester, UK*

10:30 – 11:00 **COFFEE AND POSTERS**

11:00 – 12:30 **TWO INVITED PRESENTATIONS**
Session chair: Martin Quack

11:00 **Molecular dynamics in pristine and defective parahydrogen matrices**
*Robert **Hinde**, University of Tennessee, USA*

11:45 **Atomistic modelling of the dynamics of soft liquid nano-droplets**
*Marius **Lewerenz**, Université Gustave Eiffel, France*

12:30 – 12:40 **AMOC 2022 GROUP PHOTO**

12:40 – 13:30 **LUNCH**

13:30 – 14:00 **TWO CONTRIBUTED PRESENTATIONS**
Session chair: Paolo De Natale

13:30 **Detection of gaseous nerve agent simulants with photoacoustic Fourier transform spectroscopy**
*Tommi **Mikkonen**, Tampere University, Finland*

13:45 **Double-resonance spectroscopy of methane in the 3v3 ← v3 region using a frequency comb probe**
*Vinicius S. de **Oliveira**, Umeå University, Sweden*

14:00 – 15:30 **TWO INVITED PRESENTATIONS**
Session chair: Paolo De Natale

14:00 **Intracavity 2-photon and double resonance spectroscopies**
*Kevin **Lehmann**, University of Virginia, USA*

14:45 **Cantilever-enhanced photoacoustic spectroscopy (CEPAS) for highly sensitive detection of gas-phase molecules and light-absorbing aerosols**
*Markku **Vainio**, University of Helsinki, Finland*

15:30 – 16:00 **COFFEE AND POSTERS**

16:00 – 18:00 **TWO INVITED PRESENTATIONS AND COMPANY PRESENTATIONS**
Session chair: Paolo De Natale

16:00 **High resolution spectroscopy of molecular transients: From cosmochemistry to COVID**
*David **Nesbitt**, JILA, USA*

16:45 **High-speed mid-infrared spectroscopy and microscopy**
*Takuro **Ideguchi**, University of Tokyo, Japan*

17:30 **Menlo Systems presentation**
Sandra de Vega, Menlo Systems

17:45 **IRsweep presentation**
Jakob Hayden, IRsweep

Wednesday, June 8 Helsinki-Stockholm

Venue: Silja Line Symphony cruise ship in Helsinki.
- Ticket pick-up at 9:45 – 10:30 in terminal, from "AMOC" desk. (Address: Olympia terminal; Olympiaranta 1, 00140 Helsinki. If you arrive late, please pick up your ticket from the check-in counter of group passengers.
- **Boarding at 10:45**
- Presentations in the *Starlight* arena (decks 7 and 8)
- The ship leaves the Helsinki harbor at 17:00
- Helsinki time zone: UTC + 3

11:00 – 12:30 **TWO INVITED PRESENTATIONS**
Session chair: Jonathan Tennyson

11:00 **Quantum solvation of fluxional molecules: From tagging to superfluid helium**
*Dominik **Marx**, University of Bochum, Germany*

11:45 **Ab initio molecular dynamical simulations of electrochemical reactions Hydrogen reactions on Pt(111) surface**
*Kari **Laasonen**, Aalto University, Finland*

12:30 – 13:30 **LUNCH**

13:30 – 15:00 **TWO INVITED PRESENTATIONS**
Session chair: Majdi Hochlaf

13:30 **Interaction and reactivity of molecules on activated surfaces**
*Gilberte **Chambaud**, Université Gustave Eiffel, France*

14:15 **Spectroscopy and Gibbs energy of bimolecular complexes**
*Henrik **Kjaergaard**, University of Copenhagen, Denmark*

15:00 – 15:30 **COFFEE**

15:30 – 16:00 **TWO CONTRIBUTED PRESENTATIONS**
Session chair: Majdi Hochlaf

15:30 **Calculation of molecular vibrational states using neural networks**
*Andrey **Yachmenev**, DESY, Germany*

15:45 **Vibrational band shapes in hydrogen bound complexes: From jet-cooled to room temperature**
*Emil **Vogt**, University of Copenhagen, Denmark*

16:00 – 16:45 **INVITED PRESENTATION**
Session chair: Majdi Hochlaf

16:00 **Clusters in motion**
*Attila **Császár**, Eötvös Loránd University, Hungary*

16:00 – 16:45 **BREAK – CRUISE SHIP DEPARTURE FROM HELSINKI**

17:45 – 18:35 **INVITED PRESENTATION AND POSTER PRIZE**
Session chair: Majdi Hochlaf

17:45 **Accurate molecular line list for studies of hot atmospheres**
*Jonathan **Tennyson**, University College London, UK*

18:30 **Announcement of the poster prize (sponsored by TOPTICA Photonics AG)**

20:00 **DINNER (GRANDE BUFFET RESTAURANT)**

Thursday, June 9 Helsinki-Stockholm

Venue: Silja Line Symphony cruise ship
- Presentations in the *Starlight* arena (decks 7 and 8)
- The ship leaves the Stockholm harbor at 16:45 (**gate closes at 16:15**)
- Stockholm time zone: UTC + 2

07:00 – 09:30 **BREAKFAST IN GRANDE BUFFET RESTAURANT**

10:00 **THE CRUISE SHIP ARRIVES AT THE STOCKHOLM HARBOR**

10:00 – 14:30 **FREE TIME IN THE STOCKHOLM CITY CENTER**

14:30 – 15:00 **LIGHT LUNCH**

15:00 – 16:30 **TWO INVITED PRESENTATIONS**
Session chair: David Nesbitt

15:00 **Novel interaction and dynamics in a quantum degenerate gas of polar molecules**
Jun Ye, JILA, USA

15:45 **Combing molecules with light**
*Paolo **De Natale**, Istituto Nazionale di Ottica-CNR, Italy*

16:30 – 17:00 **COFFEE**

17:00 – 17:50 **TWO CONTRIBUTED PRESENTATIONS AND CONFERENCE SUMMARY**
Session chair: David Nesbitt

17:00 **Gas chromatography combined with broadband laser spectroscopy – road to comprehensive optical gas analysis**
*Markus **Metsälä**, University of Helsinki, Finland*

17:15 **Anharmonic partition functions using Monte Carlo integration and recursive stratified sampling**
*Gabriel **Rath**, RWTH Aachen University, Germany*

17:30 **Conference summary (B. Gerber)**

17:40 **Closing words (L. Halonen)**

Friday, June 10 Helsinki

Venue: Silja Line Symphony cruise ship and Kumpula Campus of the University of Helsinki
- NOTE Helsinki time zone: UTC + 3

07:00 – 09:30 **BREAKFAST IN GRANDE BUFFET RESTAURANT**

10:30 **THE CRUISE SHIP ARRIVES AT THE HELSINKI HARBOR**
NB: When making travel reservations, please note that there is some uncertainty in the cruise ship arrival time

11:30 – 14:00 **POSSIBILITY TO VISIT LASER LABS OF THE CHEMISTRY DEPARTMENT UNIVERSITY OF HELSINKI (REGISTRATION REQUIRED)**
Address: Kumpula Campus, Chemistry Department, A.I. Virtasen aukio 1, 00560 Helsinki.

Program

Oral sessions

Mechanisms and Dynamics of Atmospheric Reactions in Clusters and in Liquid Water

R. Benny Gerber[1,2], Natalia V. Karimova[2], Itai Zakai[1]

[1]*Institute of Chemistry, Hebrew University, Jerusalem, Israel*
[2]*University of California Irvine, California, USA*

The microscopic mechanisms and the dynamics in time of complex atmospheric chemical reactions in clusters and in bulk water are explored by Ab Initio Molecular Dynamics (AIMD) simulations. A major aspect of the approach are calculations of changes of electronic state and properties along the trajectories of the atomic motions. These provide important insights into the mechanisms.

HOX (X = halogen) are important atmospheric oxidants. Charge-exchange reactions of HOX with Y^- (halide anion) in water, the mechanisms of which are hitherto unknown, are unraveled by AIMD simulations. It is found that:

(1) The halogen-bonded complexes $(HOX)(Y^-)$ play a key role in the reaction. These complexes seem to play a more important role in water than in isolation.

(2) The charge-exchange reaction between Cl^- and HOI in water proceeds by a completely different mechanism than in the "dry" complex.

(3) The mechanism in water involves chemical participation of several water molecules. OH^- anions are formed as intermediates.

The findings may have important implications for mechanisms of other related reactions in water.

Intermediates and Adducts in Free Radical Kinetics

Mitchio Okumura[1]

[1]*Division of Chemistry and Chemical Engineering, California Institute of Technology, MC 127-72, Pasadena, CA 91125, USA*

The OH + CO reaction is a benchmark for experimental and theoretical studies of radical kinetics and dynamics. The reaction proceeds through the intermediate HOCO, which is readily stabilized by collisions with a third body. In previous work with the Ye group at Boulder, we had elucidated the kinetics of the deuterated analog of this reaction at room temperature using the JILA mid-IR frequency comb spectrometer, detecting both isomers of the DOCO intermediate.

In this work, we examine the influence of a pre-reactive complex – a weakly bound OH – CO adduct – on the low temperature kinetics. For reactions of OH with organic alcohols (e.g. methanol), hydrogen-bonded complexes in the entrance channel have been shown to accelerate reactions at low temperatures by orders of magnitude. Enhancement of the rate at astrophysical temperatures could resolve a long-standing puzzle, the anomalously large abundance of CO2 in the interstellar medium. The OH-CO complex, however, is relatively weak (approximately 6 kJ/mol). We have measured the overall reaction rate constant from 30 K to 294 K of OH + CO in a uniform supersonic flow (CRESU or Cinétique de Réaction en Ecoulement Supersonique Uniforme) with Pulsed Laser Photolysis. Disappearance of the OH is detected by Laser-Induced-Fluorescence. The results are compared to calculations using Semi-Classical Transition State Theory and Ring Polymer Molecular Dynamics; both calculations confirm the role of the pre-reactive well in enhancing the rate at lower temperatures. We discuss the impact of these rates on models of CO2 production in interstellar clouds.

Finally, we present the development of a chip-scale mid-infrared frequency comb based Interband Cascade Lasers (ICL). These lasers operate in the 3-4 micron region and are characterized by large comb tooth spacings (9-10 GHz) over a range of 20-60 cm-1. We have demonstrated the use of these lasers, coupled to an external cavity, using Vernier Spectroscopy. In this approach, the comb teeth are brought into resonance with the cavity modes, one at a time, by sweeping the cavity length. We have explored its feasibility for time-resolved detection of free radical intermediates and their kinetics in a pulsed-photolysis flow reactor. In addition, we have demonstrated Cavity-Ringdown Vernier Spectroscopy measuring ringdown decays of individual comb teeth as the cavity is swept.

Monday, June 6, 11:00 - 11:45

Symmetry Breaking and Chirality in Molecular Physics

Mats Larsson

Department of Physics, AlbaNova, Stockholm University, Stockholm, Sweden

Chirality, or handedness, goes back to the beginning of humanity and the realization that the left hand cannot be superimposed on the right hand. Molecular chirality was discovered by Louis Pasteur in 1848, but it would take a quarter of a century before the explanation- the tetrahedral asymmetric carbon atom – emerged. The fact that the molecules of life only occur in one chiral form (L form for amino acids, D form for sugars) remains unexplained.

In the talk I will briefly review symmetry breaking in physics and chemistry, and then explain a number of experiments I and my younger collaborators performed in Stockholm and Oslo with the aim to study the chiral-chiral interaction between molecules. I will also describe some future experiments that are being planned at an ion storage ring and Free Electron lasers.

Spectroscopy and dynamics of small molecular systems relevant for astrophysics, environment and biology

M. Hochlaf[1]

[1] *U. Gustave Eiffel, COSYS/LISIS, 5 Bd Descartes 77454, Champs-sur-Marne, France.*

The investigation of the structure, the spectroscopy and the dynamics of the neutral and cationic species of medium sized molecular systems is important to understand the physical chemistry of biological, atmospheric and astrophysical media. Such compounds correspond at least to DNA bases, amino acids, their analogues, combustion products and atmospheric species. They may possess numerous tautomers, rotamers and isomers that lie close in energy. The experimental characterization of a unique form is challenging. For this purpose, we apply single photon VUV synchrotron based experiments combined with state-of-the-art ab initio computations.

Experimentally, we use the VUV light emitted by the DESIRS beamline of synchrotron SOLEIL coupled to the double imaging photoelectron photoion coincidence (i2PEPICO) spectrometer DELICIOUS3. [1] The coincidence scheme allows the photoelectron images to be filtered as a function of mass and ion kinetic energy in a multiplex manner. Treatment of such photoelectron images as a function of the photon energy leads to the threshold / slow photo electron spectra of the selected masses [3,4]. Theoretically, the structures and the energetics of neutral and cationic molecular systems are determined using post Hartree-Fock-density functional theory composite schemes. We also treat these species in their electronic excited states using configuration interaction methods. [2] Afterwards, we use the theoretical results to disentangle the complex features observed experimentally.

Our combined theoretical and experimental approach can be applied to several medium sized molecular entities presenting a dense pattern of electronic and/or isomeric and/or tautomeric forms in their spectra. In sum, we established an equivocal way to characterize the neutral molecules prior to photoionization. Also, we derive a set of thermodynamical data of specific gas phase tautomers/isomers/rotamers produced in a molecular beam (e.g. adiabatic ionization energies, bond energies). Several examples will be presented. [3-8]

This work is a long term collaborative project involving colleagues from Synchrotron SOLEIL, CNRS, CEA, U. Paris Saclay, Sorbonne U., U. PE Créteil, U. Gustave Eiffel, U. Loraine, King Saud U., City U. Hong Kong, Chinese Academy of Sciences, and U. Tunis.

References:

[1] http://www.synchrotron-soleil.fr/portal/page/portal/Recherche/LignesLumiere/DESIRS
[2] M. Hochlaf. "Advances in spectroscopy and dynamics of small and medium sized molecules and clusters". *Phys. Chem. Chem. Phys.* **19**, 21236 (2017).
[3] J. C. Poully et al. *Phys. Chem. Chem. Phys.* **12**, 3566 (2010).
[4] Z. Chen et al. *J. Am. Chem. Soc.* **138**, 16596 (2016).
[5] I. Derbali et al. *Phys. Chem. Chem. Phys.* **21**, 14053 (2019).
[6] J. Bourgalais et al. *Phys. Chem. Chem. Phys.* **22**, 1222 (2020).
[7] X. Tang et al. *Chem. Commun.* **56**, 15525 (2020).
[8] M. Jarraya et al. *Faraday Discuss.*, (2022), in press.

Monday, June 6, 13:30 - 13:45

Ring opening and tunneling inversion in the cyclopropyl radical and cation

Nadav Genossar[1,2], P. Bryan Changala[3], Marie-Aline Martin-Drumel[4], Bérenger Gans[4], Jean-Chrisophe Loison[5] and Joshua H. Baraban[1*]

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[2]*IAEC, Tel Aviv, Israel*

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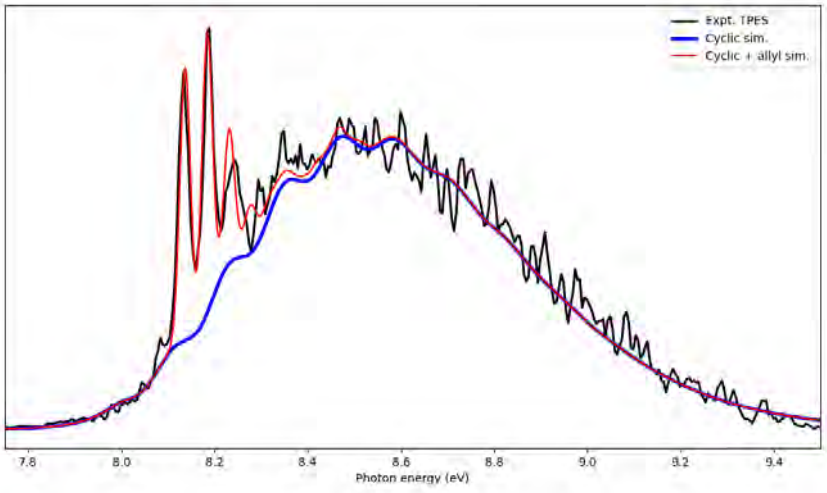
We report spectroscopic and theoretical studies of the cyclopropyl radical and cation (c-C_3H_5). The cation especially is unstable towards ring-opening to allylic geometries, and the radical exhibits inversion tunneling of the α-H atom through the C-C-C ring plane. These large amplitude motion phenomena complicate the photoionization spectra (among others) as well as the determination of properties that are of interest due to ring strain in this fundamental cyclic radical. Through multiscale reduced- and full-dimensional *ab initio* descriptions of the potential energy surfaces (PES) of both the radical and the cation, the ionization spectrum of the radical is simulated using advanced perturbative and variational rovibrational treatments.

Due to the large energy difference between the allylic equilibrium geometry and the unstable cyclic configuration on the cation PES, propagator-based methods that avoid the construction of cationic vibronic eigenstates were used to simulate the ionization spectrum. The results of our simulations, combined with high accuracy single-point *ab initio* calculations of the energy difference between the cation and the radical, compare well with both experimental photoionization data from the literature and new mass-selected threshold photoelectron measurements performed at the SOLEIL synchrotron. Further computational efforts are underway to improve the simulations.

Our results shed light on the most basic properties of the fundamental pericyclic reactions between allyl and cyclopropyl radical, and also between their respective cations. These were among the very first systems to be studied from the perspectives of Woodward-Hoffmann rules and correlation diagrams, but the predictions of these seminal methods were never directly explored experimentally in these archetypal systems. Additionally, we provide a qualitative explanation for the quantum mechanical effects that make the ionization transition favorable, despite accessing a portion of a potential energy surface with negative curvature.



Ozonolysis of α-pinene: Biradical route

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The atmospheric oxidation of organic molecules directly impacts global climate and human health, especially via the formation of fine particulate matter. Aerosol formed in the atmosphere by the oxidation of organic molecules make up between 20%-90% of the submicron aerosol mass.

For an organic molecule to contribute to atmospheric aerosol, it needs to have a very low volatility, which in practice implies multiple oxygen-containing polar functional groups. Precursor species, such as hydrocarbons emitted by vegetation and traffic, therefore need to be oxidized extensively before they can form aerosol. Recent studies [1,2] have demonstrated the existence of an extremely effective and fast mechanism for this oxidation, commonly denoted as autoxidation. Atmospheric autoxidation involves sequential steps of intra-molecular hydrogen migrations in peroxy radical intermediates, alternating with O_2 addition reactions. Due to the high atmospheric concentration of O_2, the process is essentially unimolecular, and thus forms the organic analogue to the effectively single-step formation of the key inorganic aerosol precursor sulfuric acid via SO_2 + OH.

The oxidation of the biogenic hydrocarbon α-pinene by ozone is a particularly efficient and globally significant source of SOA, and is therefore one of the most studied systems [3,4]. However, the initial ozone reaction step and the subsequent autoxidation mechanism are still not completely understood. In this work, we use quantum chemical modelling to resolve the biradical pathway of α-pinene + O_3. We show that the reaction can form a biradical intermediate that rapidly isomerizes to an endoperoxide. The formation of the endoperoxide is significantly exothermic, and the excess energy opens up reaction pathways to previously unreported fragmentation products and intermediates that can further autoxidize. These results advance our current understanding of the processes that precede the critical gas-to-particle conversion in the atmosphere.

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Monday, June 6, 14:00 - 14:45

In silico design of new Metal Organic Frameworks for gas adsorption

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The advances in using metal organic frameworks (MOFs) as adsorbent materials for gas capture and separation have been extensively investigated owing to their favorable properties such as large surface area, permanent porosity and tunable pore size/functionality. In search for low carbon future and good adsorbents for CO_2, capture, a nitrogen-rich triazole-type metal-organic framework, named ZTF, is proposed on the basis of rational design and theoretical molecular simulations. The structure of proposed MOF is constructed by modifying MAF-66, where the amine-organic linker is replaced by a triazole. We used grand-canonical Monte Carlo (GCMC) simulations based on generic classical force fields to predict correctly the adsorption isotherms of CO_2 at different temperatures. The influence of water on the CO_2 adsorption inside ZTF has been also observed. We show that the proposed porous material exhibits exceptional high CO_2 uptake capacity at low pressure, better than MAF-66. Computations show that the interactions occur at two different sites, which are Lewis acid - Lewis-base interactions and hydrogen bonding, together with obvious electrostatic interactions. More details can be found in Ref. 1.

In addition, we have studied by using GCMC simulations the capture of highly toxic gases as SO_2 and H_2S by ZTF and MAF-66 [2].Results show high capacity of investigated MOFs for SO_2 and H_2S adsorption. The nature of the interactions between H_2S /SO_2 with the pore surface cavities was examined at the microscopic level. SO_2 is adsorbed to the pore surface by two types of hydrogen bonds, either between O of SO_2 with the closest H of the triazole 5-membred ring or between O of SO_2 with the hydrogen of the amino group. Finally, the calculations demonstrated that the principal interactions between H_2S and pores were found at the nitrogens of material by a relatively strong hydrogen bonds.

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Monday, June 6, 14:45 - 15:30

Ultrafast dynamics in microsolvated biomolecules

Jochen Küpper

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Interactions between proteins and their solvent environment can be studied in a bottom-up approach using hydrogen-bonded chromophore-solvent clusters. The ultrafast dynamics following UV-light- induced electronic excitation of the chromophores, potential radiation-damage, and their dependence on solvation are important open questions. The microsolvation effect is challenging to study due to the inherent mix of the produced gas-phase aggregates. We used the deflector to spatially separate different molecular species in combination with pump-probe velocity-map-imaging experiments, including applications of 3D "cameras" based on Timepix3. We demonstrated that this powerful experimental approach reveals intimate details, e.g., on the radiation damage of pyrrole-water as well as on the UV-induced dynamics in the near-UV-absorbing prototypical biomolecular indole-water system. We determined the time-dependent appearance of the different reaction products and disentangled the occurring ultrafast processes. This novel approach ensures that the reactants are well-known and that detailed characteristics of the specific reaction products are accessible – paving the way for the complete chemical-reactivity experiment.

[1] https://www.controlled-molecule-imaging.org

Mixed metal clusters - core-shell structures, phase transitions, and nano alloying

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Through aggregation inside superfluid helium droplets, metal nanoparticles and core-shell clusters of different morphology are generated and deposited on solid carbon, h-BN, ITO, or SiN substrates. The created nanoparticles are characterized by temperature dependent electron microscopy, up to 1000 degrees C, energy-dispersive x-ray spectroscopy, electron energy loss spectroscopy, photoemission electron microscopy and optical absorption [1]. Recent investigations include the stability of a passivation of Ni [2], Fe [3], and Co cores of 2 to 3 nm diameter by a few layers of gold and the alloy formation at high temperature [4]. Ag@ZnO core@shell particles are studied by two-photon photoelectron spectroscopy. Upon excitation of the localized surface plasmon resonance in Ag at around 3 eV, plasmonic enhancement leads to a strong increase in electron emission when compared to pure ZnO clusters [5]. Vanadium oxides represent a prominent materials class for catalytic applications. On the way towards cluster catalytic experiments, we have shown that V2O5 nanoparticles can be generated by sublimation from the bulk [6] and deposited while keeping the original stoichiometry [7].

Nanoparticles in a core@shell@shell configuration are synthesized by sequential doping [8]. Rhodamine B molecules form complexes in helium droplets that give rise to a strong fluorescence upon laser excitation. In the presence of a Au core, the Rhodamine B fluorescence is quenched due to excitation transfer from excited shell molecules to the Au particle. The addition of an intermediate hexane layer inhibits the contact between Au core and RhB shell, which results in the recovery of the fluorescence.

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Monday, June 6, 16:45 - 17:30

Symmetries and time scales for molecular primary processes between yoctoseconds and days

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Symmetry and asymmetry are concepts, which are, indeed, used in a wide range of contexts, from the fundamental sciences, mathematics, physics, chemistry and biology to the arts, music and architecture [1]. We shall start with an introductory discussion of three fundamental questions on symmetry, relating physics to molecular quantum dynamics and stereochemistry.

(i) To what extent are the fundamental symmetries and conservation laws of physics and their violations reflected in molecular quantum dynamics and spectroscopy, in general, and how can approximate symmetries be used to understand the very different time scales for molecular primary processes between yoctoseconds, days, and even much longer times?
(ii) How important is parity violation –the violation of space inversion symmetry- for the quantum dynamics and spectroscopy of chiral molecules, in particular?
(iii) How important is parity violation for biomolecular homochirality, i.e. the quasi exclusive preference of L-amino acids and D-sugars in the biopolymers of life (proteins and DNA)?

The discovery of parity violation led to important developments of physics in the 20th century and is understood within the standard model of particle physics, SMPP. For molecular stereochemistry it leads to the surprising prediction of a small energy difference D (sub-feV, typically) of the ground state energies of the enantiomers of chiral molecules. For intramolecular dynamics this is related to the slow change of parity with time in isolated molecules[2-7]. We shall discuss the current status of theory and of our experiments including various primary processes such as intramolecular energy flow, nuclear spin symmetry violation and parity violation and, if time permits, the possible consequences for our understanding of molecular and biomolecular chirality. For background reading see [1-7]. (see also www.ir.ETHz.CH).

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Cold ion chemistry within the orbit of a highly excited Rydberg electron

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The study of ion-molecule reactions at low collision energies ($E_{\rm coll}$) below $E_{\rm coll}/k_{\rm B} = 10$ K, or low temperatures, is experimentally challenging because stray electric fields in the reaction volume heat up the ion samples. A potential difference of 1 mV across the reaction region accelerates the ions to 1 meV, which corresponds to heating them up to about 12 K. To overcome this problem and study ion-molecule reactions below 10 K, we have developed a new method, in which the ion-molecule reaction takes place within the orbit of a Rydberg electron at high values of the principal quantum number n. In high-n Rydberg states, the Rydberg electron only very weakly interacts with the ion core, so that it does not significantly influence the ion-molecule reaction taking place within its orbit but shields the ion from heating by stray electric fields. Instead of studying ion-molecule reactions of the type

$$\mathrm{I}_1^+ + \mathrm{M}_1 \rightarrow \mathrm{I}_2^+ + \mathrm{M}_2, \tag{1}$$

we study the reactions

$$\mathrm{I}_1^* + \mathrm{M}_1 \rightarrow \mathrm{I}_2^* + \mathrm{M}_2, \tag{2}$$

in which I_1^* and I_2^* represent atoms or molecules in high Rydberg states with ion cores I_1^+ and I_2^+, respectively.

To reach very low collision energies, we use chip-based Rydberg-Stark decelerators and deflectors [1,2] to merge cold supersonic beams of I_1^* and M_1 and to vary their relative velocities [3]. Monitoring the product yield as a function of the relative mean velocity of the two beams, we obtain the relative reaction cross sections as a function of the collision energy. At collision energies ($E_{\rm coll}/k_{\rm B}$) below 1 K, we find that the reaction rate coefficients deviate from those estimated with Langevin-type capture models [4-9], in accord with the predictions of adiabatic-channel models [5,6]. The deviations become particularly large when M_1 has a permanent dipole [7] or a quadrupole moment [8,9].

The talk will present general aspects of this new method as well as the results of studies of the reactions of H_2^+ and He^+ (I_1^+) with neutral molecules such as N_2, H_2, NO, CO, $\mathrm{CH_3F}$, $\mathrm{NH_3}$, $\mathrm{CH_4}$, and $\mathrm{C_2H_4}$ (M_1) at very low collision energies and will discuss the observed low-temperature behavior in terms of the electric dipole and quadrupole moments of M_1. Our latest detection of the theoretically predicted [10-13] factor-of-two quantum enhancement of rate coefficient of pure Langevin reactions at collision energies close to zero will be presented.

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Tuesday, June 7, 09:45 - 10:30

Observation of a periodic many-body system

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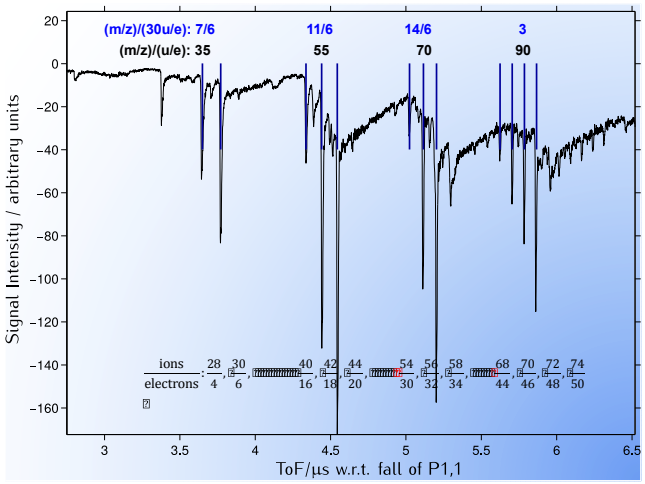
We report the experimental observation of a very striking periodicity in a many-body system--an ultra-cold plasma. A long life-time (>0.3 ms) *quantum degenerate* molecular Rydberg plasma is generated in the high-density region of a pulsed supersonic jet expansion by two-color resonant excitation of nitric oxide (10%) in neon (5bar) into the high-*n* Rydberg threshold region close to the ionization limit. For plasma densities of $> 10^{16}$ cm^{-3} reached in our experiments the electrons should become quantum degenerate, *i.e.* the electron *de Broglie* wavelength becomes larger than the Wigner-Seitz radius *a* relevant to describe the mean distance between the particles.

The time-of-flight (ToF) mass spectrometer used is depicted in the *r.h.s.* figure. Experimentally, two synchronous UV laser pulses produce the plasma a few mm away from the jet nozzle. After 170μs, when the plasma cloud is still *ca.* 130mm in front of aperture plate 1 (ap.1), two successive high-voltage (HV) pulses of 3.6 kV with a 0.2μs gap are applied to ap.1. The first HV pulse (P1,1; length 5.5μs) is followed by a gap of 0.2μs and a second pulse: P1,2. The observed ToF spectrum *w.r.t.* the falling slope of P1,1 is shown in the *l.h.s.* figure (positive particle detection on MCP). The observed sharp peaks ("*slices*") in the ToF spectrum follow a fully reproducible progression of (*m*/*z*) mass to charge ratios from 35 to 92.5 (blue: *w.r.t.* $m(NO^+) = 30$u). From the *m*/*z* one obtains the corresponding ion to electron ratios of the 12 slices (bottom of figure), from 7/1 to 37/25.



In conclusion, we observe a many-body system consisting of a series of objects that contain a magic number of ions and electrons for which the ion/electron ratio follows a periodicity. These objects are manipulated by fields in a ToF spectrometer without being destroyed, which shows that they behave as objects with a center of mass. The observation of such many-body states with periodic ion/electron ratios suggests a phase correlation and possibly quantum entanglement.

The path from *Structure* and *Phase* to *Quantum Entanglement* is of considerable interest in complex systems. Starting from the common textbook opinion that in many-electron atoms the electrons are entangled (a deeper reason for the periodic system of the elements), one can speculate that the observation of periodicity in the many-body system presented here might originate from quantum entanglement.

Tuesday, June 7, 11:00 - 11:45

Molecular dynamics in pristine and defective parahydrogen matrices

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Photolysis of formic acid molecules embedded in solid parahydrogen (pH_2) matrices produces OH radicals. These react with H_2 molecules in the matrix to produce H atoms and H_2O molecules which remain embedded in the matrix as substitutional impurities. Evidence for the production of H_2O comes from the observation of features in the system's infrared absorption spectrum that are associated with H_2O rovibrational transitions [1]. Some of these features are accompanied by weak satellite features, red- or blue-shifted from the main feature by approximately 1-2 cm^{-1}. The satellite features are believed to arise from rovibrational transitions of H_2O molecules in locally defective regions of the pH_2 matrix, such as "cages" where one of the H_2O molecule's 12 nearest neighbor pH_2 molecules is either missing or has been replaced by a hydrogen atom. To investigate this hypothesis, we study the rovibrational states of H_2O molecules in pristine and defective pH_2 matrices, employing high-accuracy H_2O-H [2] and H_2O-pH_2 potential energy surfaces computed using coupled cluster ab initio methods.

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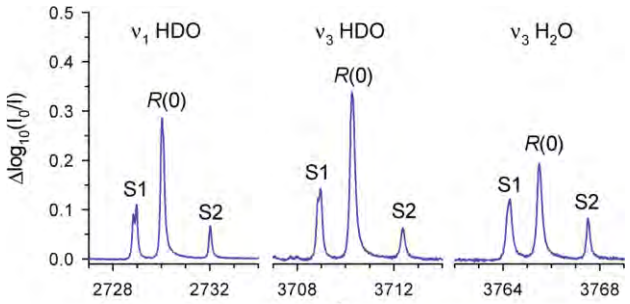

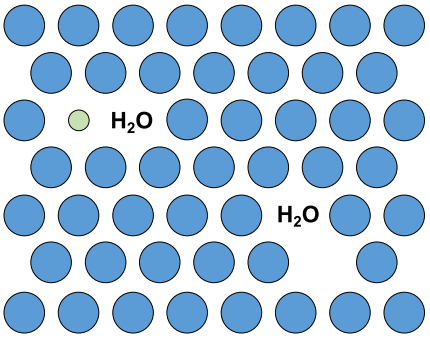

Atomistic modelling of the dynamics of soft liquid nano-droplets

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Helium nano-droplets are a chemical environment with the special property to be dense, liquid, and very cold (T < 1 K). The physics of pure droplets with sizes ranging from a few thousand atoms to millions of atoms and the experimental and theoretical study of species implanted into this special matrix has attracted a significant amount of interest over the last 25 years. The focus of attention has progressively shifted from collisional and spectroscopic studies to dynamical phenomena like multiple doping, nano-assembly, and chemical phenomena. Helium remains liquid at very low temperatures due to quantum effects which have to be accounted for in any theoretical treatment. In the past we have developed powerful quantum Monte Carlo techniques for the study of static properties. A full quantum dynamical treatment of thousands of particles is beyond current theoretical methodologies and the approximate approach used here combines classical trajectories with quantum effective potentials designed to account approximately for zero-point energy effects. Static properties derived from this approximate method can be checked against full quantum Monte Carlo results.

The photodissociation of a dopant molecule is strongly influenced by the possibility of energy transfer into the cold liquid environment. Studies in dense gases and conventional matrices have revealed the existence of the cage effect [1]. In a finite and very soft nano-droplet caging is expected to be less efficient and a new reaction channel is available: the exit of photofragments from the droplet with or without parts of the droplet which can be observed by modern techniques like velocity map imaging [2]. We present photofragment velocity and size distributions from calcularions for the photodissociation of iodine molecules inside droplets with 2500 – 9000 atoms [3]. For the real-time analysis of the time evolution of the fragment distribution and progressive atom evaporation we have implemented an efficient graph algorithm with linear scaling with the number of particles.

Most theoretical models of helium nano-droplets assume spherical droplets. The creation of the droplets in jet expansions or by fragmentation of a liquid jet implies that each droplet carries a significant angular momentum L which can lead to shape distortions as observed in recent ultrafast X-ray experiments. We have included an algorithm in our dynamics code which allows us to give a well defined L to our droplets and to study the resulting shape distortions and the droplet fragmentation scenarios at high L values.

We also present first results for the successive implantation of several dopants (xenon atoms) and the dynamics of their aggregation inside the nano-droplets leading to the eventual formation of small clusters occasionally passing through long-lived metastable structures.

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Detection of gaseous nerve agent simulants with photoacoustic Fourier transform spectroscopy

Tommi Mikkonen[1], Daniel Luoma[1], Hanna Hakulinen[2], Paula Vanninen[2], Juha Toivonen[1]

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Recent assassination attempts, deployments in the Syrian civil war and the ominous situation in Ukraine have demonstrated that nerve agents, among other chemical warfare agents (CWAs), continue to pose a threat in both military and civilian scenarios. Although most nerve agents are liquids at atmospheric conditions, gas phase detection of these volatile substances enables screening of a wider area and lower sample consumption when investigating potentially hazardous materials. Fourier transform infrared spectrometers (FTIRs) are conventionally used for fast and sensitive multi-component detection of CWAs [1], but the gas consumption of these systems is high, and the sensitivity cannot be easily improved. An alternative to the typical attenuation-based detection in FTIR is photoacoustic (PA) detection, where the intensity-modulated light from a scanning interferometer is converted to multi-frequency sounds via absorption and thermal relaxations. This so-called Fourier transform photoacoustic spectroscopy (FT-PAS) requires a small sample volume, and the sensitivity can be enhanced with novel microphones and light sources [2, 3].

Here, we demonstrate the detection of nerve agents using FT-PAS with a cantilever microphone and a mid-IR supercontinuum (SC) light source. A schematic of the experimental setup is shown in Fig. 1. We analyze the fundamental C–H stretch bands of four known nerve agent simulants at 4 cm^{-1} spectral resolution, and achieve detection limits of 60–500 ppb in one minute for the simulants with a gas consumption of 7 ml. This yields an estimated detection limit of 220 parts per billion for sarin, which is an order of magnitude worse compared with a high-performance FTIR [1], which however requires a 60 times larger sample volume. Moreover, we show our system's high selectivity and recovery times of a few minutes. Our results demonstrate the applicability of SC-based FT-PAS for accurate detection of nerve agents especially from field samples with limited availability.

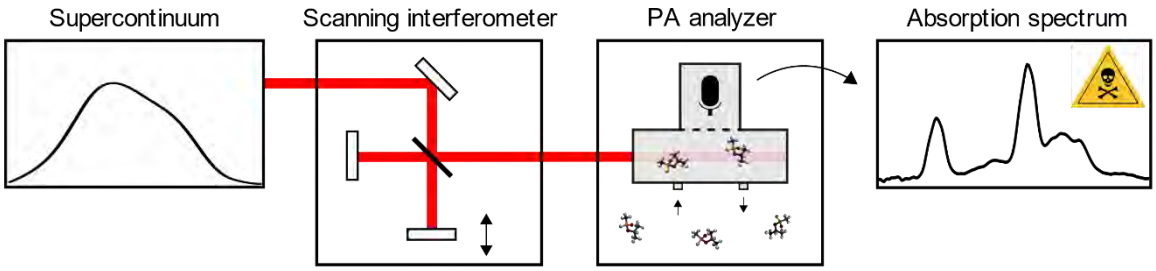

Fig. 1. A schematic experimental setup, containing a supercontinuum source, a scanning Michelson interferometer, an enclosed gas cell and a cantilever microphone.

References:
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Double-resonance spectroscopy of methane in the $3\nu_3 \leftarrow \nu_3$ region using a frequency comb probe

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Spectra of various astrophysical objects contain signatures of hot molecules. Methane in particular was the first organic molecule detected in a hot-Jupiter exoplanet [1]. Theoretical models of high-temperature molecular spectra are necessary to interpret these observations. These models, in turn, need to be validated by accurate laboratory measurements and assignments of hot-band transitions. Creating gas samples at high temperatures poses an experimental challenge, and the high-temperature spectra are congested and difficult to assign. Instead, hot-band transitions can be measured with high accuracy and selectivity using double-resonance techniques. However, the use of single-frequency lasers, required for accuracy, usually implies a limited spectral coverage. We developed optical-optical double-resonance spectroscopy with a frequency comb probe to measure previously unobserved sub-Doppler transitions in the $3\nu_3 \leftarrow \nu_3$ region of methane with line position accuracy of ~1.7 MHz [2, 3]. The methane sample was contained in a liquid-nitrogen cooled single-pass cell. The pump was the idler of a continuous-wave optical parametric oscillator stabilized to a Lamb dip in a selected CH_4 transition in the ν_3 band (~3.3 μm), and the probe was an Er:fiber frequency comb, shifted to 1.67 μm using a microstructured silica fiber. The comb spectrum was detected by a Fourier transform spectrometer with auto-balanced detection. Using the sub-nominal sampling-interleaving scheme [4], we measured probe spectra covering 6 THz with sampling point spacing of 2 MHz. The measured probe transition frequencies served as the first verification of theoretical predictions in this range, and agreed within 30 GHz with the data from the TheoReTS database [3, 5]. To increase the absorption sensitivity and line position accuracy, we recently implemented a room-temperature enhancement cavity for the comb probe. Compared to the initial demonstration, the absorption sensitivity is now increased by more than two orders of magnitude, which allows detection of weaker transitions with better signal-to-noise ratios, and the accuracy of the line positions is improved to <1 MHz. We assign the probe transitions by comparing line intensity ratios measured with parallel and perpendicular relative pump/probe polarizations, and by reaching the same final state with different pump/probe configurations. The cavity-enhanced system allows the detection and assignment of new hot-band transitions, and investigation of sub-Doppler probe transition line shapes.

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Intracavity 2-photon and double resonance spectroscopies

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Cantilever-enhanced photoacoustic spectroscopy (CEPAS) for highly sensitive detection of gas-phase molecules and light-absorbing aerosols

Markku Vainio[1, 2]

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[2]*Photonics Laboratory, Physics Unit, Tampere University, Tampere, Finland*

Photoacoustic detection is one of the most sensitive techniques developed for molecular spectroscopy and optical trace gas analysis. In photoacoustic spectroscopy (PAS), laser power absorbed by the sample leads to heating of the surrounding gas, generating a pressure change. If the absorption is made periodic by modulating the laser power or wavelength, also the pressure change is periodic. That is, we get an acoustic wave that can be detected with a sensitive microphone. Cantilever-enhanced photoacoustic spectroscopy (CEPAS) is a variant of PAS where the microphone is replaced by a few-micrometer-thin silicon cantilever [1]. The cantilever bends without stretching and its motion can be precisely tracked using a compact laser interferometer. This leads to substantial improvements in photo-acoustic detection sensitivity and dynamic range as compared to conventional PAS techniques.

This conference contribution focuses on the recent advances of CEPAS research in our laboratory at the University of Helsinki. The highlighted results include record-high sensitivities in trace gas detection, such as sub-parts-per-trillion detection limit for hydrogen fluoride [2] and 1.75×10^{-12} W cm^{-1} Hz$^{-1/2}$ normalized noise equivalent absorption with cavity-enhanced CEPAS [3]. The measurements require just a few milliliters of sample gas, which has motivated us to use CEPAS for spectroscopy of radioactive trace gases, such as $^{14}CH_4$ and $^{14}CO_2$. Owing to its wavelength-independent operating principle, CEPAS works from UV to THz [4] and can be combined with various light sources, including optical frequency combs [5].

As an example of an application beyond molecular spectroscopy, we are developing CEPAS for monitoring of black and brown carbon in the atmosphere [6]. In this case, the detection limit can be pushed down to a few light-absorbing particles in cm^3 – again a substantial improvement compared to established technologies.

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Tuesday, June 7, 16:00 - 16:45

High Resolution Spectroscopy of Molecular Transients: From Cosmochemistry to COVID

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The fundamental irony of chemistry is that what we often care most about are the chemical species that are the most reactive and therefore present in the smallest concentrations. As a result, one long standing challenge to physical chemistry has been about developing sufficiently sensitive spectroscopic methods with which to probe and report on such transient species, with diverse applications ranging from insights into atmospheric/combustion/interstellar chemistry to real time medical diagnosis of disease state. This talk will present results from our group that attempt to push these sensitivity limits in two quite different directions. The first is use of long path length slit supersonic discharges and quantum shot noise limited absorption sensitivities for study of exotic radicals and metastable oxyhydrocarbon species postulated to be present in star formation regions of the interstellar medium. The second topic reflects a collaboration between Ye/Nesbitt groups to use of broad-band, ultrastable infrared frequency comb light sources in the 3-5 and 5-10 μm IR fingerprint region with high finesse resonant cavities to probe small molecule content in exhaled human breath. These methods demonstrate > 100 million-fold enhancement in sensitivity x spectral throughput over conventional approaches, which in combination with machine learning algorithms have permitted encouraging first successes in real time identification of COVID disease state.

High-speed mid-infrared spectroscopy and microscopy

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Mid-infrared spectroscopy is an essential tool in molecular science, and Fourier-transform infrared (FT-IR) spectroscopy is the gold standard for measuring broadband vibrational spectra. Although FT-IR spectrometers have been widely used in various fields for decades, recent rapid advancements in mid-infrared optical technology have enabled the development of advanced spectroscopy and microscopy techniques.

Recently, extensive efforts have been made in developing dual-comb spectroscopy, a new modality of FT-IR spectroscopy with two mutually coherent laser frequency combs. A dual-comb system makes ultra-rapid delay scanning possible without a mechanical scanner, enabling high-speed spectroscopy at a rate of ~1 MSpectra/s, which is limited by the signal-to-noise ratio (SNR). To break the speed limit, we demonstrate time-stretch infrared (TS-IR) spectroscopy, which has higher SNR than FT-IR [1]. Time-stretch spectroscopy, also known as dispersive Fourier-transform spectroscopy, has been known for years as a single-pulse spectroscopy technique. It has been demonstrated in the near-infrared region, where low-loss telecom optical fibers and high-speed photodetectors are available. On the other hand, in the mid-infrared region, time-stretching with an existing mid-infrared optical fiber is not feasible because of a significant fiber loss. The bandwidth of mid-infrared detectors is also limited. We overcome the difficulties by using a time stretcher consisting of free space optics and a newly developed quantum cascade detector and demonstrate broadband mid-infrared spectroscopy at a record high spectral scan rate of 80 MSpectra/s.

Technology in mid-infrared microscopy has also been advanced. The spatial resolution of mid-infrared microscopy is limited by the diffraction limit of the long wavelength of the mid-infrared light. Therefore, it has rarely been used for single-cell imaging. To overcome the limitation, we have developed mid-infrared photothermal quantitative phase imaging (MIP-QPI), whose spatial resolution is determined by the diffraction limit of the visible light [2,3,4]. In this technique, wide-field illumination of mid-infrared light induces vibration-specific local heat hence refractive-index change via infrared absorption, which is probed by quantitative phase imaging with visible light. Our improved system enables high-speed single-cell imaging beyond the video rate.

References:
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Wednesday, June 8, 11:00 - 11:45

Quantum Solvation of Fluxional molecules: From Tagging to Superfluid Helium

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Helium nanodroplet or para-hydrogen matrix approaches to cryochemistry require the theoretical treatment of reactive molecular aggregates that are embedded in a superfluid quantum solvent subject to Bose-Einstein statistics. I will outline our recent advances that allow us to perform converged reactive path integral simulations at temperatures on the order of 1 Kelvin, taking into account the bosonic nature of these quantum solvents, at essentially converged coupled cluster accuracy. The latter is achieved in an automated way by building upon high-dimensional neural network potentials to accurately describe all interactions. Some applications will be presented, including protonated methane interacting with helium from the tagging limit to superfluid helium.

Methodological Review:
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Ab initio molecular dynamical simulations of electrochemical reactions – Hydrogen reactions on Pt(111) surface

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[1]*Aalto University, Department of Chemistry and Materials Science, POB 16100, 00076 Aalto, Finland*

Hydrogen evolution reaction (HER) on Pt is one of the key reactions in electrochemistry. It has been studied extensively and here we present a state-of-the-art study on this reaction using ab initio molecular dynamics (AIMD) [1]. In this work, we assess the importance of explicit solvent dynamics on the free energy profile of the Volmer–Tafel hydrogen evolution mechanism on Pt(111) through constrained AIMD simulations and the thermodynamic integration method. Simulations are conducted at two hydrogen coverages to gauge the coverage dependence from a fully dynamic perspective. We found that during the electrochemical Volmer step the electric potentials changes significantly and we used a capacitive model of the electrified interface to correct this effect [2]. The uncertainty in the highly non-trivial treatment of the electrode potential is carefully examined and we provide a quantitative estimation of the error associated with dynamically simulated electrochemical barriers. Interestingly by increasing the hydrogen coverage from 2/3 to a full monolayer results in a change in the rate determining step from the Tafel reaction to the Volmer reaction.

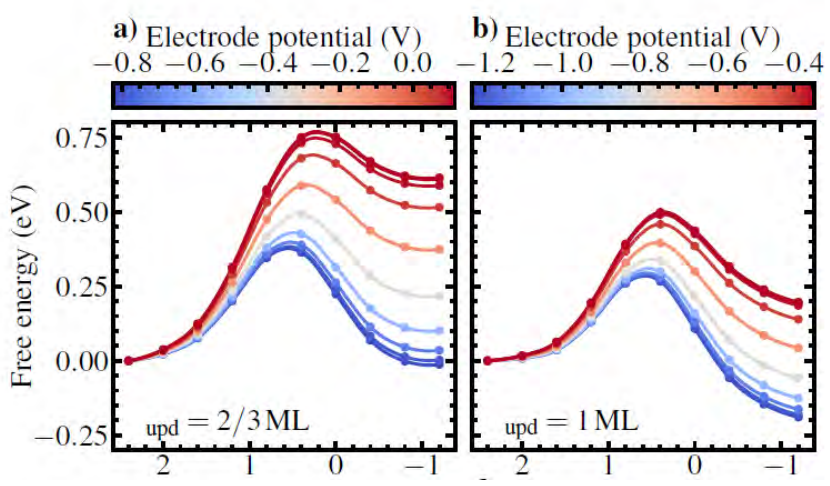

Figure: Electrode potential dependence of the Volmer free energy surfaces at a) 2/3ML and b) 1ML hydrogen coverages.

References:
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Interaction and reactivity of molecules on activated surfaces

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Structure and reactivity of adsorbed molecules on metallic or activated surfaces have been investigated in relation with catalysis, sequestration or development of novel functional materials for optical, photovoltaic and electrode applications. We develop and use high level theoretical approaches to explore the electronic structures of small molecular systems interacting with various surfaces. In these studies, transition and particularly coinage metals are of major importance either as metallic surfaces or clusters or as metallic atoms dispersed on various supports.

Nanocatalysis represents a novel and rapidly expanding field of research for industrial chemistry particularly to improve reaction yields and selectivities, as well as the durability of the catalysts. Many examples of applications of nanostructured materials in both homogeneous and heterogeneous catalysis have been developped with nanoparticles as oxides, metals and semiconductors for the synthesis of important chemical products or intermediates or for the degradation of contaminants and pollutants. We present here theoretical investigations of the potential catalytic activity of transition metal atoms (TM) trapped by defects on graphene or on monovacancies of hexagonal boron nitride (h-BN)[1]. Such activated surface has been used to study the oxidative degradation of formaldehyde, a major indoor air pollutant, where it was demonstrated that formaldehyde oxidation on a substrate consisting in Fe on graphene proceeds through low-energy barriers and thus can be efficiently realized under mild conditions. We performed several studies on the oxidation of CO on Pt/h-BN, or Au/h-BN and we could show that the reaction proceeds through rather low energy barriers, and that the chemical bonding between the B/N atoms around the vacancies and the TM atom is effective not only in trapping the metal atoms, but also in changing the composition and energetic distribution of the electronic states of the composites. Recently we have also studied the evolution of the catalytic surface under reaction conditions.

Another field of investigation concerns the behaviour of imidazole units, an important model molecule, interacting with Au (surface or clusters) for the sequestration of CO_2, or in zeolitic imidazolate frameworks[2]. Such studies apply to the sequestration of gas in zeolitic structures or to the adsorption of ionic liquids at electrode.

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Spectroscopy and Gibbs Energy of Bimolecular Complexes

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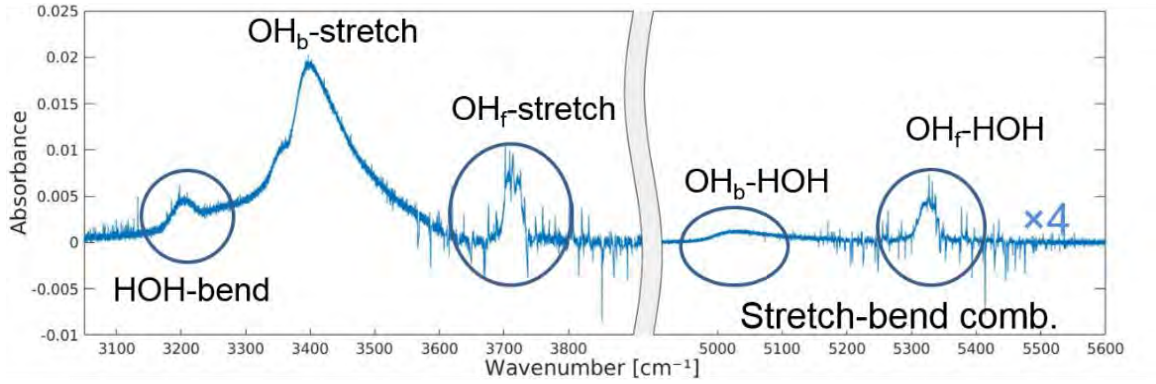
In atmospheric research, the formation of complexes affects among other radiative transfer, reaction mechanisms and nucleation. The formation of a molecular complex relies on the Gibbs energy of formation, ΔG, which is difficult to obtain accurately, from pure experimental or theoretical methods. We have developed a combined experimental and theoretical approach with which ΔG of bimolecular complex formation can be determined with an accuracy better than 1 kJ/mol.[1] This requires accurate calculation of the oscillator strengths of vibrational transitions associated the observable vibrational bands.

We have developed a reduced dimensionality vibrational model within the local mode framework, which can be combined with *ab initio* methods to calculated oscillator strengths. In bimolecular complexes, it is important to consider the effect of the six intermolecular modes. For hydrated complexes (H_2O-X), our model includes the three intramolecular high frequency modes of the water molecule (OH-stretch & HOH bend) as well as selected low frequency intermolecular modes. For the water-trimethyl amine complex, we use this approach for several observed vibrational transitions (see figure) to improve the ΔG determination.[2] We are currently extending our approach to the weaker bound water-dimethyl ether complex. The OH-O hydrogen bond of this complex is similar to that in water dimer (H_2O-H_2O), which is a key compound to the radiative transfer in our atmosphere. We continue our efforts to improve the calculation of water dimer spectra,[3] and have found that frequencies of OH stretching transitions can be well described from reduced dimensional models.



Gas phase spectrum of the water-trimethyl amine complex.[2]

References:
[1] A.S. Hansen, E. Vogt, H.G. Kjaergaard, *Int. Rev. Phys. Chem.* **38**, 115 (2019).
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Wednesday, June 8, 15:30 - 15:45

Variational calculation of molecular vibrational states using neural networks

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Modern computer algorithms for solving the Schrödinger equation for molecular vibrations, such as, for example, TROVE, GENIUSH, MULTIMODE, describe wave functions as linear combinations of products of optimised and contracted basis functions. The linear expansion coefficients solution is framed as an eigenvalue problem with an N3 cost scale with respect to the number of expansion terms N. The desired energy spectrum and the quality of the basis set functions dictate the number of expansion terms and hence the computational cost of N3. Typically, the basis functions are optimised to satisfy solutions to specific reduced-mode problems and then kept fixed. An intriguing question is whether optimising the basis functions in conjunction with the linear expansion coefficients results in a considerable reduction in the number of linear expansion coefficients, hence speeding up variational convergence. Here we present a methodology that paves the way for constructing and optimising more flexible wave functions by composing standard basis sets with invertible neural networks [1]. The variational solution entails optimising both the linear expansion coefficients and the parameters of the neural network. We apply the approach to computing the vibrational energy levels of the water molecule and demonstrate a significant speed up of variational convergence as compared to the standard linear expansion approach.

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Vibrational Band Shapes in Hydrogen Bound Complexes: From Jet-Cooled to Room Temperature

Emil Vogt[1], Henrik G. Kjaergaard[1]

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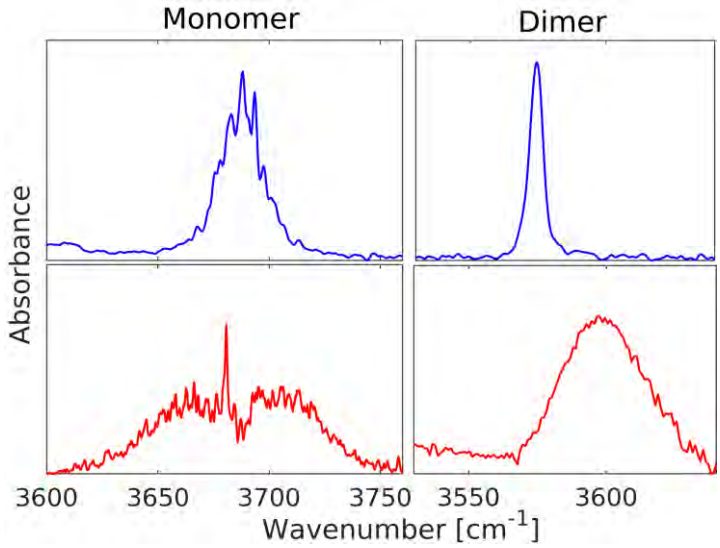
The infrared spectra of molecules vary continuously with temperature, from sharp individual transitions under cold conditions to broader bands at room temperature. In isolated molecules (figure, left), the broader bands observed at elevated temperatures are typically centered around the transitions observed under cold conditions. This variation with temperature is a consequence of the large number of thermally accessible rotational states. In addition, thermally populated excited vibrational states of low-frequency modes can also contribute to the observed spectra (i.e. hot bands).

In bimolecular complexes, six low-frequency intermolecular vibrations arise upon complex formation. For weakly bound complexes like the methanol dimer (figure, right), many excited states of the low-frequency intermolecular modes are thermally accessible. As a consequence, the population of the vibrational ground state quickly diminishes relative to the population of all the excited vibrational states [1,2]. This leads to a very different spectral temperature dependence for weakly bound complexes, compared with that of isolated molecules, with clear shifts in band maxima of certain bands. A physical picture of the temperature dependent vibrational band shapes in hydrogen bound complexes will be presented.



Jet-cooled (blue lines) and room temperature (red lines) spectra of the OH-stretching fundamental band of methanol (left) and the bound OH-stretching fundamental band of the methanol dimer (right). For methanol, the elevated temperature results in a broadening of the band due to transitions from excited rotational states. For the methanol dimer, the elevated temperature results in a blueshift of the band maximum due to transitions from excited vibrational states

References:

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Wednesday, June 8, 16:00 - 16:45

Clusters in Motion

Attila G. Császár[1], Tamás Szidarovszky,[1] Irén Simkó,[1] Roland Tóbiás,[1] Csaba Fábri,[1] Oskar Asvany,[2] Stephan Schlemmer[2]

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[2] *I. Physikalisches Institut, Universität zu Köln, Germany*

The first members of the $(H/D)_nRg_m^+$ complexes (with rare-gas atoms Rg = He, Ne, Ar) are the rare-gas-solvated proton (n = 1), H_2^+ (n = 2), and H_3^+ (n = 3). Due to different bonding arrangements these complexes exhibit interesting and diverse structures, unusual nuclear motions, and complex rovibrational spectra.

The molecular structures, the (ro)vibrational energy levels, and the spectroscopic fingerprints of the complexes $(H/D)He_n^+$, corresponding to He-solvated proton, have been investigated experimentally (via mass and low- and high-resolution molecular spectroscopy) [1-3] and at high levels of electronic-structure theory [3-6]. The MS measurements reveal interesting trends about the stability of the starting members of the HHe_n^+ family. The computations and the low- and high-resolution rovibrational spectroscopy experiments [1,2] establish that the basically linear, strongly bound, symmetric triatomic molecular ion $He(H^+)He$, with an experimentally determined equilibrium H–He distance of 0.924 Å, is the molecular core of all of the $n \geq 3$ complexes. Definitive quantum-chemical results are obtained for a number of these complexes. A useful notation, $[k–l–m]$-HHe_n^+, is introduced to characterise qualitatively the three possible belts around the $He–H^+–He$ core in HHe_n^+ ($n \geq 3$), where l denotes the number of He atoms in the central belt and $k \geq m$ denote the number of He atoms in the top and bottom belts. Capping He atoms attached to the belts can be indicated by sub- and superscripts.

Experimental as well as computational results have also been obtained for the $(H/D)_2He^+$ system [3,4]. The band origins obtained experimentally are fully explained by accurate variational computations of the bound and resonance [6] rovibrational states of H_2He^+ and D_2He^+ based on the three-dimensional potential energy surface.

Similar results obtained for rare-gas atoms other than He are also discussed in the talk. The structures of the HRg_2^+·Rg' complexes are characterized by significant nuclear delocalization. Large shifts of the in-plane and out-of-plane bends, as well as of the symmetric and antisymmetric stretches of the chromophores of these complexes are observed.

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Accurate molecular line list for studies of hot atmospheres

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The ExoMol project aims to provide molecular data for spectroscopic analysis and modeling of exoplanetary atmospheres and the atmospheres of other hot bodies. Work initially focused on computing comprehensive line lists of key molecules; see for example our latest (2020) data release [1]. Currently the ExoMol database holds upwards of 700 billion transitions and provides data on 85 molecules (including 6 molecular ions). For most species the line lists are available for several isotopologues.

In the second phase of the project, ExoMolHD, new objectives are (a) the provision of high accuracy line lists for high resolution studies, (b) creating high accuracy line list for isotopologues, (c) providing temperature-dependent photodissociation cross sections and rates, and (d) calculating temperature-dependent line-broadening parameters, as well as, of course, maintaining and extending the ExoMol database.

The requirement for high accuracy spectroscopic data is driven by the use of high resolution cross correlation spectroscopy to identify novel species in exoplanets. This has motivated the development of a procedure to treat fully hyperfine-resolved spectra with the variational diatomic nuclear-motion code Duo [2]. At the same time, we make extensive use of experimental data via the MARVEL (measured active vibration-rotation energy levels) procedure (see [3] and references therein) to provide high accuracy, empirical energy levels. This methodology can increase the number of transitions predicted to experimental accuracy by a factor of more than 20 compared to the original transition list (eg [4]).

A new method of treating photoabsorption spectra, including photodissociation, using bound state nuclear-motion codes and a discretized representation of the continuum which is then smoothed has been developed [5]. This methodology allows cross sections and rates to be computed as a function of the temperature of the target in a straightforward manner. This temperature dependence can lead to increases in photodissociation rates by one to two orders-of-magnitude in radiation fields typical of those displayed by cool stars.

Progress on these projects will be summarized at the meeting.

I thank the members of the ExoMol team for their collaboration and the European Research Council for support under Advance Investigator grants 267219 and 883830.

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Novel interaction and dynamics in a quantum degenerate gas of polar molecules

Jun Ye[1]

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The advent of a degenerate Fermi gas of polar molecules [1] sets the stage to explore novel molecular dynamics. We apply a precisely controlled electric field to tune the elastic dipolar interaction by orders of magnitude while suppressing reactive losses. Efficient dipolar evaporation leads to the onset of quantum degeneracy in two-dimensional optical traps [2]. The electric field tuning of the rotational energy also produces sharp collision resonances, giving rise to three orders-of-magnitude modulation of the chemical reaction rate [3].

The precise control of electric field has also allowed us to prepare and address isolated, individual two-dimensional layers of molecules with arbitrary choices of rotational state. We study exchanges of rotational angular momenta between molecules of neighboring layers through long-range dipolar interactions, demonstrating fully quantum-state engineered stereo chemical reaction [4]. Meanwhile, when protected, these interacting molecules in 2D are used to realize a tunable spin Hamiltonian for quantum magnetism.

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Combing Molecules with Light

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The frequency comb synthesizer (FCS) emblematically appeared at the dawn of the new millennium, promising a revolution in metrology [1]. Indeed, this appeared to be the case since the first few years from its demonstration. However, it was atomic metrology to be affected at the beginning, the spectral coverage of the first Ti-Sa based combs being from around 500-1000 nm. Once triggered, revolutions do not easily stop, and soon after, in parallel with more compact FCSs, covering more and more the Infrared (IR) range, molecules started to benefit from the new photonic tools. In the last few years, also very compact sources, like Quantum and Interband Cascade Lasers (ICLs and QCLs) have proved to be not only comb emitters, but truly metrological-grade FCSs [2,3]. Interestingly, thanks to the spectral coverage of QCLs, also the THz range has become an active research area for FCSs [4]. This enormous progress is opening brand new routes to manipulate and interrogate molecules with light, with unprecedented precision and sensitivity levels [5], also in cold or ultracold samples [6]. Ultimately, classical noise can limit this renewal of molecules-light interaction and looking out into Quantum Technologies can point to new, ambitious science [7].

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Gas chromatography combined with broadband laser spectroscopy – road to comprehensive optical gas analysis

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We have recently demonstrated a combination of gas chromatography (GC) with cantilever-enhanced photoacoustic spectroscopy (CEPAS) using an external-cavity quantum cascade laser (EC-QCL) working in the 10 μm infrared (IR) wavelength region (900 to 1200 cm^{-1}) [1]. This allowed us to analyze a gas mixture of seven alcohols in a quasi-online manner. The intrinsic noise limit of the spectrometer gives a single-digit ppb limit for the sensitivity of the setup. Instrumental noise currently increases the limit of detection by approximately one order of magnitude. Sensitive multi-species analysis of such slightly larger molecules (up to 130 atomic mass units) is not currently feasible optically without the chemical separation provided by the GC column. Analysis of the even larger molecules with higher boiling points was mostly limited by the current temperature upper limit (50 °C) of the CEPAS cell.

We believe that the hyphenation of GC with broadband laser spectroscopy holds great promise for the development of optical trace gas analyzers. By adding the chemical separation stage in front of the IR spectrometer allows one to drastically simplify the spectra and analyze even larger molecules which exhibit broad and overlapping spectral features. The drawback is a longer analysis time since the GC separation inherently takes time. Using so-called fast gas chromatography (fast-GC) principles, the separation can be reduced to a time scale of minutes or less. The additional chemical speciation provided by the IR spectra also means that perfect separation is not needed, and even co-eluting peaks can be analyzed [1].

The main challenge in combining GC with laser spectroscopy is the small volume of gas packets eluting from the GC column. The volume of the effluent is normally sub-mL whereas standard optical gas cells are >100 mL in volume. This limits the attainable sensitivity significantly. The CEPAS technique benefits from a very small sample cell, 11 mL and amenable to further miniaturization. However, other types of optical gas cells can also be miniaturized. We have calculated that it should be possible to manufacture a 10 cm optical cavity of < 500 μL volume without diffractive losses limiting the sensitivity. A combination of such small volume high-finesse optical cavity and a mid-IR optical frequency comb (OFC) would serve as an excellent broadband GC detector. The advantage of cavity-enhanced (CE) techniques over CEPAS is that analysis can be performed online. The photoacoustic technique is sensitive to acoustic noise generated by a continuous gas flow. The GC-CE-OFC combination should provide unprecedented chemical speciation in optical gas analysis and significantly expand the currently rather limited horizons of optical trace gas sensing.

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Anharmonic Partition Functions using Monte Carlo Integration and Recursive Stratified Sampling

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Accurate thermochemical data are needed to model atmospheric, industrial, and combustion processes. Due to their influence on energy balances and reaction equilibria, significant scientific effort has been invested in their prediction, with contributions focusing on either electronic energies or energies arising from the motion of nuclei [1].

Most state-of-the-art models for nuclear motion rely on the same, core process of approximations to tackle the common set of challenges posed when dealing with the potential energy surface (PES) of a sufficiently accurate *ab initio* electronic structure method. First, the high-dimensional system is split up into a series of uncoupled, low-/one-dimensional model systems. Then, a model PES made up of a combination of those model systems is built using few data points as possible from the *ab initio* PES. The choice of which models to use and what *ab initio* data points to take varies between different methods like RRHO, VPT2 [2], MSTor [3], *et al.*, but the process itself remains the same.

However, using a different approach opens up a new way to deal with nuclear motion that can more easily capture certain, coupled behaviors that those methods rooted in the standard approach struggle with. Rather than create bespoke, localized approximations on-the-fly, one can use a PES that is known to be approximate to begin with but that is fast enough to be sampled broadly, *e.g.* UFF [4], DFTB [5], or machine learning potentials. One can numerically integrate it over thermally accessible regions and correct for quantum effects with the Pitzer-Gwinn correction [6]. This allows one to calculate fully-coupled anharmonic correction factors that can be applied to the RRHO results of an *ab initio* PES.

Configuration Integral Monte Carlo Integration (CIMCI) [7] is a new method taking this approach. It uses Monte Carlo integration and an enhanced version of MISER [8] recursive stratified sampling to perform the necessary high-dimensional integration. Improvements to MISER that allow it to reuse pre-sampling data when calculating final results remedy shortcomings in it that have been known since its inception. While accurate-enough reference data have turned out to be surprisingly rare, the few systems that do have this data show CIMCI performing very well. *E.g.*, UFF with CIMCI gives standard molar entropy correction factors for H_2O_2 that are better than M06-2X [9] with VPT2 and on par with M06-2X with explicit 1D hindered rotor handling; absolute standard molar entropies with UFF with CIMCI are also better than CCSD coupled cluster with RRHO.

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Poster presentations

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P. 10	Luis Duarte	Interaction of Formic Acid with Carbon Monoxide and its effect on the Tunneling Dynamics
P. 11	Galib Hasan	Quantum Chemical Investigation of the Reaction Routes for $^3(RO\cdots OR')$ Intermediates Formed in Peroxy Radical Self- and Cross-Reactions
P. 12	Teemu Järvinen	Using Molecular Dynamics to Determine Site Structures of Molecules Embedded in Noble Gas Matrices
P. 13	Juho Karhu	Cantilever-enhanced photoacoustic spectroscopy for high-sensitivity detection of benzene at 14.8 μm
P. 14	Jochen Küpper	Selection and control of (bio)nanoparticles with electric fields
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P. 18	Jari Peltola	Time-resolved, broadband UV-absorption spectrometry measurements of unimolecular reaction kinetics of dimethyl-substituted Criegee Intermediate $(CH_3)_2COO$
P. 29	Matti Rissanen	Gas-phase benzene oxidation: Semi-empirical model building with experimental and theoretical constraints
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P. 21	Ville Ulvila	Advancing optical isotope ratio spectroscopy for carbon dioxide

Disentangling the relationship between S_N2 and E2 reactions in ethyl halides

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The bimolecular nucleophilic substitution reaction (SN2) and bimolecular elimination reaction (E2) are two essential reaction types in organic chemistry [1]. As both reactions lead to the same ionic product, it is inherently difficult to distinguish between them solely with experimental approaches. In an attempt to overcome this experimental deficiency, we measured the reaction of fluoride with iodoethane and its fully β-carbon-fluorinated counterpart. The latter leads to the complete suppression of the E2 pathway. Here, we report the results of the reactions in the gas phase at four collision energies between 0.4 and 2 eV. For these measurements, we employed a crossed molecular beam setup combined with a velocity map imaging spectrometer. The obtained energy and angle differential cross-sections can reveal a mechanistic understanding of reaction dynamics on an atomic level [2], especially in cooperation with state-of-the-art theory [3]. In the reaction with CF3CH2I, we observe an increased signal in the proton transfer channel, which is negligible in the reaction with CH3CH2I. Furthermore, at higher collision energies, the formation of $CF2CI^-$ becomes the dominant channel, while no similar product is observed in the unfluorinated case. In Figure 1 the differential cross-sections for iodide stemming from the reaction of F^- with CH3CH2I and CF3CH2I are depicted. In the first case the product ions can stem from both the SN2 and the E2 pathway while in the latter the source is solely SN2.

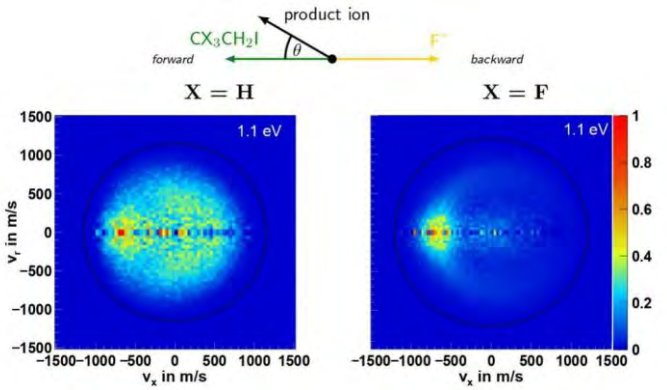

Figure 1: Three dimensional velocity distributions for I^- stemming from the reactions F^- + CH3CH2I (left panel) and F^- + CF3CH2I (right panel) in the center of mass frame.

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Spectroscopy of the radioactive molecule $H^{36}Cl$

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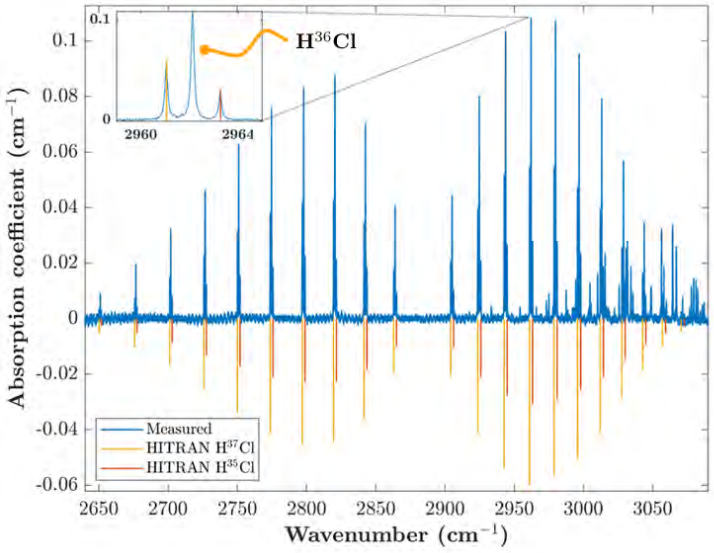
Hydrogen chloride is an important molecule for atmospheric chemistry, astrochemistry and volcanic activity research, to name just a few applications. In contrast to the well known stable isotopologues $H^{35}Cl$ and $H^{37}Cl$ and their deuterated forms, the radioactive isotopologue $H^{36}Cl$ has not been previously studied optically. The radioactive chlorine isotope ^{36}Cl can be found in nuclear reactor materials due to neutron activation of ^{35}Cl [1]. Some of ^{36}Cl might be released in the form of $H^{36}Cl$ providing one possible application for measuring this species. Laser spectroscopy has shown great promise for the detection of radioactive compounds [2–4]. They offer portable, affordable, and possibly less laborious sample preparation requiring alternatives for the contemporary techniques Accelerator Mass Spectrometry and Liquid Scintillation Counting.

In order to apply laser spectroscopy for detection of any gas phase compound knowledge on the absorption spectrum of the species of interest is required. To this end we reported for the first time on the absorption spectrum of $H^{36}Cl$ in our recent publication [5]. We were able to determine using Fourier Transform Infrared Spectroscopy the wavenumbers of the fundamental P(10)–R(10) and the first overtone P(1)–R(7) rovibrational lines with respective 1σ uncertainties of less than 0.002 cm^{-1} and 0.007 cm^{-1}. A simple spectroscopic model was applied to extract the molecular constants of the lower and upper states. Our conference contribution presents our results on the above-mentioned $H^{36}Cl$ measurements.



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First-principles numerical model for irreversible dissociation of alkoxy radical dimers

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Organic peroxyl radicals are formed in the atmosphere as a product of O_2 addition to carbon centered radicals. This means that they are an abundant class of compounds in the atmosphere, and their gas-phase chemistry is thus of great interest, not in the least because it is quite complex. [1] One of the more significant reactions of these compounds is recombination of two peroxyl radicals, which eventually produces an O_2 molecule and a triplet-coupled dimer of two alkoxy radicals. There are three documented reaction pathways this radical dimer can undergo, of which one is dissociation of the dimer into two free alkoxy radicals.

Experiments show that the dissociation is a significant pathway for many simple alkoxy dimers, [2] but computational studies have thus far been unable to reconcile experimental branching ratios with computationally determined rate coefficients, [3] mostly due to compromises made when calculating the dissociation rate.

This study aims to remedy this problem by introducing a simple first-principles model for calculating the dissociation rate: By solving the equations of motion for the reduced two-particle system $V(\vec{r}_{rel})$ on a potential energy surface parametrized on quantum chemical scans of the O-O distance and numerically determining a rate of escape from the dimer potential well (k_{esc}) as a function of relative velocity of the two radicals. The dissociation rate is then determined by integrating over the Maxwell-Boltzmann distribution in relative velocity coordinates:

$$k_d = \int_{-\infty}^{\infty} k_{esc}(\vec{v}_{rel}) f(\vec{v}_{rel}) \mathrm{d}\vec{v}_{rel}$$

A comparison of our alkoxy dimer dissociation rates with computational reaction rates of the two competing reactions from reference [3] and experimental branching ratios from reference [2] show reasonable agreement, especially considering we have neglected the non-equilibrium thermal effects present in the formation of the dimers in question. This was seen as indication that the model accurately describes what it is meant to describe, and that the same approach can be repeated for similar chemical systems. For the alkoxy dimer system in particular, the results finally confirm that the efforts in determining computational reaction rates have at least not been far off.

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Versatile frequency combs for spectroscopy applications

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In our conference contribution, we present a simple and versatile mid-infrared Optical Frequency Comb (OFC) source that is promising for applications in molecular spectroscopy. The OFC light source is based on seeded Optical Parametric Generation (OPG) supported by pulse trapping effect (see Fig. 1a) [1], which can boost the photon conversion efficiency to over 70 % [2-4]. The seeding plays a crucial role in the OPG process making it possible to adjust repetition rate (f_r), Carrier-Envelope Offset (CEO) frequency (f_{CEO}) and common phase (φ) of the generated signal and idler combs. All the parameters contribute to the OFC electric field [3]:

$$E(t) = \sum_{n=N_i}^{N_f} A_n \; e^{i2\pi n f_r t} e^{i2\pi f_{CEO} t} e^{i\varphi}. \qquad (1)$$

Here, A_n is the electric field amplitude and n is an integer mode number that takes values from N_i to N_f,. By driving the OPG process with an amplitude modulated CW seed laser, one can divide the repetition rate by any arbitrarily large integer fraction [3], which translates into a high spectral resolution in frequency-comb spectroscopy. An example of such a division can be seen in Fig. 1b, where the timing between the OPG output pulses is altered by the seed repetition rate. The spectra of the signal and idler combs become denser as can be seen in Fig. 1c for the division factor of 2. The CEO and the common phase of the generated combs can be precisely adjusted simply by tuning the frequency or phase of the seed laser, respectively [2-4].

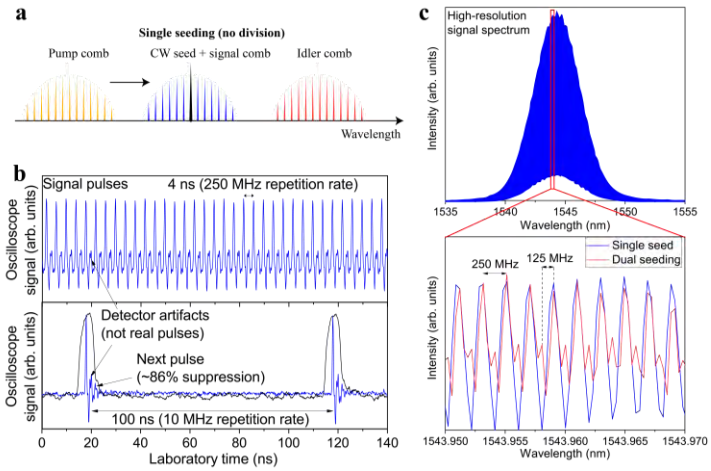

Fig. 1. (a) OPG schematic in the case of CW-seeding; (b) Time domain trace of the signal comb when seeded with amplitude modulated seed; (c) High-resolution spectrum of the signal comb when repetition rate is divided by a factor of 2.

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Fragmentation of peroxides in PTR-based mass spectrometers

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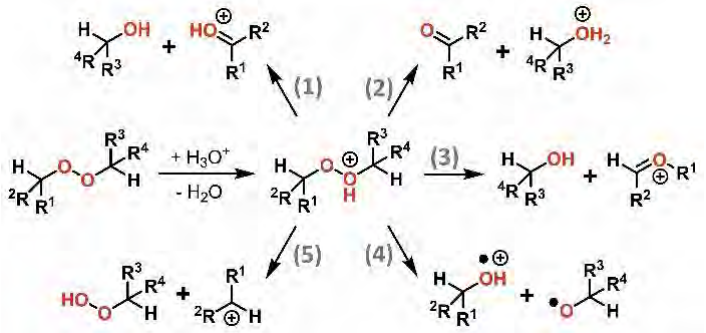
Experiments conducted with Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) have largely failed to detect ROOR accretion products [1], peroxides derived from atmospheric oxidation of volatile organic compounds. Formed from self- and cross-reactions of peroxyl radicals (RO_2) [2], these compounds were shown to be among the most important agents in atmospheric aerosol formation and growth, especially when highly oxygenated [3]. Chemical ionization mass spectrometers employing other reagent ions such as I^-, NO_3^- and aminium are successful at detecting ROOR species [1], possibly implying that rapid fragmentation of the protonated peroxides may be behind their lack of detectability in PTR-based techniques. Quantum chemical calculations and a master equation solver were used to estimate how fast a series of ROOR compounds would fragment following protonation by H_3O^+ in the gas-phase. The selection included simple model compounds, as well as peroxides derived from cyclohexene oxidation by OH and O_3. The detection of ROOR formed from α-pinene + O_3 and cyclohexene + O_3 was also studied with a Vocus-PTR mass spectrometer, without OH radical scavenging agents. Several fragmentation channels are possible for $(ROOR)H^+$, most of which have previously been described by Schalley et al. (1997) [4]. The computational results indicate that most of the studied $(ROOR)H^+$ species undergo significant fragmentation within 100 µs, the average residence time of an ion in the spectrometer. No α-pinene derived ROOR was detected in the experiments, while only small signals corresponding to cyclohexene ROOR were observed, the largest of these being $C_{12}H_{20}O_4$. This signal potentially corresponds to ROOR formed from OH oxidation, which the calculations predict to be less prone to fragmentation than its O_3 oxidation counterpart.



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Machine learning representations of the three lowest $^2A'$ adiabatic electronic potential energy surfaces for the ArH_2^+ reactive system

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The argonium molecular cation, ArH^+, can be formed through the exothermic reactions, Ar (^1S) + H_2^+ $(X^2\Sigma_g^+)$ → ArH^+ $(X^1\Sigma^+)$ + H (^2S), and Ar^+ (^2P) + H_2 $(X^1\Sigma_g^+)$ → ArH^+ $(X^1\Sigma^+)$ + H (^2S). The adiabatic electronic potential energy surface (PES) for the first reaction is the only reactive one, while the second reaction relies on the strong electronic coupling in the entrance arrangement, giving rise to non-adiabatic transitions. Non-adiabatic reaction dynamics studies of these reactions have been reported over the past decades, usually based on DIMZO (diatomics in molecule with zero overlap) PESs [1]-[6]. Here, we present, to the best of our knowledge, the first accurate full-dimensional representations of the lowest coupled ^{2}A' adiabatic PESs, obtained by means of machine learning (ML) methods. In particular, the technique of gaussian process (GP) regression was used, assuming the functional form of the kernels, $k(\boldsymbol{x}_i, \boldsymbol{x}_j)$, in the covariance matrix to be of the form, $k(\boldsymbol{x}_i, \boldsymbol{x}_j) = D(\boldsymbol{x}_i, \boldsymbol{x}_j, \sigma)\mathcal{M}_v(\boldsymbol{x}_i, \boldsymbol{x}_j, \boldsymbol{l}) + W(\boldsymbol{x}_i, \boldsymbol{x}_j, n)$ [7], where $\boldsymbol{x}_i, \boldsymbol{x}_j$ are two geometries of ArH_2^+, and D, $\mathcal{M}_v$ and W are the dot product, Matérn and white noise kernels, respectively. The necessary *ab initio* computations were performed at the ic-MRCI+Q/aug-cc-pVQZ level of theory. Preliminary results show the root mean square error (RMSE) to be ~0.0055 meV for the ground state PES (see Fig. 1). The RMSEs of the excited states are similar.

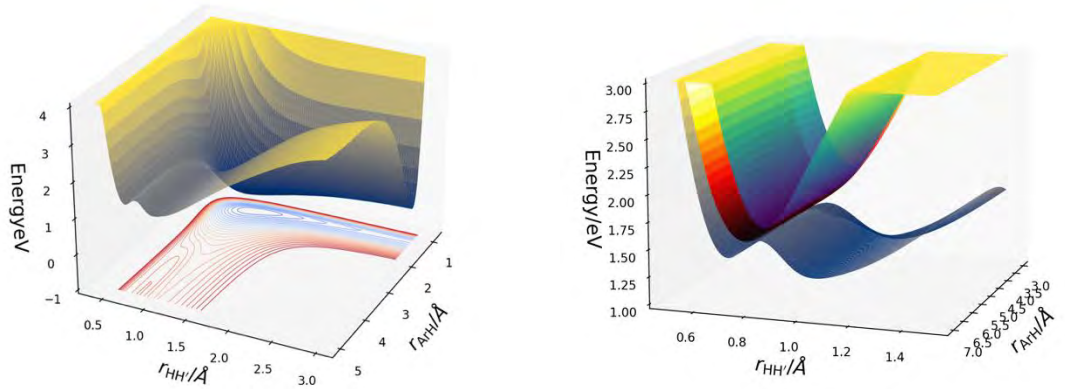

Figure 1: Surface and projected contour plot for the ground state PES (left), as well as a surface plot showing the ML models of all three PESs in the entrance arrangement (right).

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A statistical adiabatic channel model for competing inelastic and reactive processes involving molecules of astrophysical interest

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The computation of state-to-state rate coefficients for complex-forming collisional processes using fully quantum mechanical approaches (close-coupling (CC) or time-dependent wave packet (TDWP)), is challenging. Due to the statistical nature of said collisions, we may resort to much simpler statistical models, such as the statistical adiabatic channel model (SACM) [1]-[2]. The state-to-state integral scattering cross sections (ICSs) can be obtained via, $\sigma_{i\to f}(E) = \frac{\pi}{(2j+1)k_i^2}\sum_{J=0}^{+\infty}(2J+1)\left|S_{if}^J(E)\right|^2$, where for a sufficiently long-lived complex [3], $\left|S_{if}^J(E)\right|^2 \approx p_i^J(E)p_f^J(E)/\sum_{f'} p_{f'}^J(E)$. The capture and decomposition probabilities are determined by counting the open channels using adiabatic channel potentials, which are computed by diagonalization of $\frac{(\hat{J}-\hat{j})^2}{2\mu_R R^2} + \hat{h} + V(R,\theta;r)$ [4]. The method has been benchmarked for several systems of astrophysical interest (Fig. 1), for which the potential energy surfaces (PESs) and the high-level-of-theory state-resolved rate coefficients were available, showing rather good agreement (typically better than factor 2, which meets the astrochemistry accuracy requirements) [4]-[7]. Currently, efforts are directed towards the application to systems for which CC or TDWP calculations are prohibitive, if not impossible.

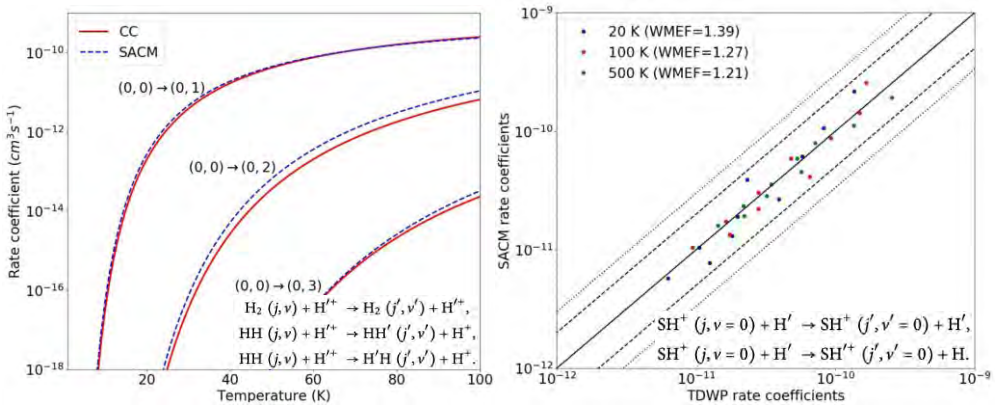

Figure 1: Direct comparison of the SACM and high-level-of-theory state-to-state rate coefficients for the $H_2 + H^+$ (left panel) and $SH^+ + H$ (right panel) systems [7].

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TamkinTools – Improved one-dimensional hindered rotor treatments to include single- and zero-point energy effects

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Intermolecular interactions in dimers include the hindered rotation of the two partners. This may involve several conformations of shallow energy differences. The Goebench challenge put attention to methanol-furan dimers, which are potential renewable fuels and solvents producible from biomass and CO2. Special attention by experimentalists and theoreticians put on the various π- and OH-bonded conformations, which differ by energies in the order of only 1 kJ/mol [1]. Only demanding high-level electronic structure methods can determine the correct energetic order of the conformations.

In our study, we present further minima and transition states for furan-, 2-methylfuran-, and 2,5-dimethylfuran-methanol complexes. Energies are computed with DLPNO-approximated coupled cluster and several basis sets for comparison.

In addition to single-point energies, anharmonicity critically influences zero-point energies of these structures and changes the energetic conformational order at 0 K. Modeling of torsional anharmonicity is possible by solving Schrödinger's equation for the corresponding one-dimensional potential, which is readily implemented in the python package TamKin [2]. We used double-hybrid DFT methods to optimize the conformers and calculate their frequencies. We compare harmonic oscillator (HO) and hindered rotor (HR) results and note that at 0K, the conformational orders of complexes change in HO and HR calculations compared to the order inferred from potential energies alone.

To improve anharmonicity corrections in the HR model, we present the TamkinTools package that extends the state-of-the-art one-dimensional treatment for the following important points: (a) Include high-level single-point energies and optimized stationary points into the Fourier fit. (b) Avoid oscillations occurring at jumps frequently present in one-dimensional potentials (due to coupling to other degrees of freedom) by minimizing, along with the quadratic error, the curvature of the potential. (c) Compute energy-resolved probabilities for the different conformations present in the one-dimensional potential by integrating the probability density from the wave function within each minimum. By this, we can determine the preferred conformation at 0 K and at finite temperature.

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Pre-Reactive Complex Formation and Recombination Reactions Between Peroxy Radicals

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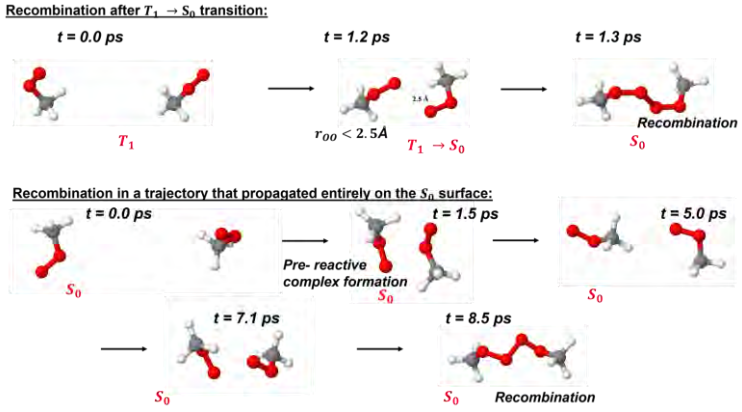
Peroxy radicals (RO_2) are an important class of reactive intermediates in the atmosphere[1]. Studying reactions between these radicals is challenging, owing to the multiple spin states (singlet and triplet) which must be considered. In recent work, our research group studied the energetics of these reactions[2]. However, the dynamics of the reactions were not explicitly considered. Here, we present the extension of our work to the reaction dynamics, focusing mainly on the formation of pre-reactive complexes during initial gas-phase collisions and the subsequent reaction to form a tetroxide intermediate (RO_4R). We use three complementary molecular dynamics (MD) approaches: 1) Multi-reference perturbation theory (XMC-QDPT2), very expensive but accurate, 2) Semi-empirical ODM2, less expensive and more flexible, but also perhaps less accurate, and 3) Empirical OPLS-based force fields, unable to include reactions, but computationally cheapest and able to be easily extended to larger molecules.

Our main findings are: 1) XMC-QDPT2 trajectories confirm our previous results, showing that the RO_4R formation from the pre-reactive complex is rapid and effectively barrier-less. 2) Semi-empirical trajectories of the full collision (including a simplified model for surface hopping) (Figure 1) predict reaction rates in good agreement with the experimental data, and 3) Empirical force fields can predict formation of pre-reactive complexes in good agreement with experimental data for a wide range of different peroxy radicals. Our results have been recently published[3].



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Interaction of Formic Acid with Carbon Monoxide and its effect on the Tunneling Dynamics

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Quantum mechanical tunneling (QMT) is a universally occurring event with implications for biochemistry, combustion chemistry, chemical catalysis, and interstellar chemistry [1]. QMT can affect the reactivity and selectivity of chemical reactions and tunneling control has emerged as a new reactivity paradigm in chemistry [2]. One of the main challenges regarding QMT is how the phenomenon can be exploited in chemical synthesis and other applications. One possible route for tuning or affecting the outcome of QMT is through molecular interactions. In this work, complexes of formic acid (FA) with carbon monoxide (CO) were studied experimentally and computationally. The structure, energetics, and vibrational properties of the complexes were calculated at different levels of theory (DFT and Ab initio). Several structures of the *trans*-FA···CO complexes were identified by infrared spectroscopy in inert cryogenic matrices. Higher energy *cis*-FA···CO complexes structures were prepared by selective narrowband infrared light excitation of the *trans*-FA conformer in the *trans*-FA···CO complexes [3-4]. The *cis*-FA···CO complex structures decay back to the *trans*-FA···CO structures by H atom tunneling. The effect of complexation on the tunneling dynamics of *cis*-FA is discussed and compared with the decay of *cis*-FA isolated in carbon monoxide matrices.

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Quantum Chemical Investigation of the Reaction Routes for ^{3}(RO···OR′) Intermediates Formed in Peroxy Radical Self- and Cross-Reactions

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Gas phase dimer (accretion product) formation is regarded as a significant reaction in the atmosphere because it can lead to the formation of very-low volatility highly oxygenated organic molecules (HOMs), which later form aerosol particles [1]. On the other hand, organic peroxy radical (RO_2) are the key intermediates in the chemistry of the atmosphere. One of the main sink reactions of RO_2 is the recombination reaction RO_2 + R'O_2 [2]. This reaction goes through an intermediate complex (RO…$^3O_2$…OR'). The $^3O_2$ is very weakly bound, and evaporates from the system, giving a ^{3}(RO…R'O) dimer cluster. This dimer has three major reaction channels: 1) R_{-H}=O + R'OH 2) ROOR', and 3) RO_2+ R'O_2.

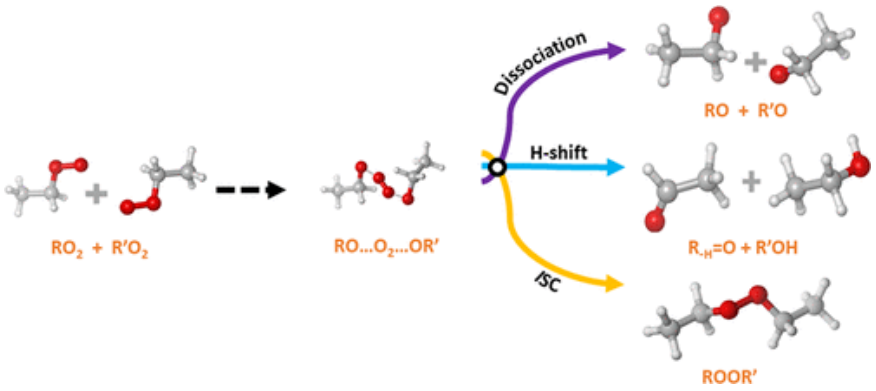

Figure 1: Reaction between two peroxyl radicals (RO_2) and their fates.

In our study, we have performed a systematic conformation search on the ^{3}(RO…R'O) dimer cluster on the triplet potential energy surface using a state-of-the-art quantum chemical approach [3-5]. Then we tried to estimate the kinetics of the three channels: evaporation or dissociation to RO + R'O, a hydrogen shift reaction forming R_{-H}=O + R'OH, and a "spin-flip" (intersystem crossing) leading to the formation of ROOR' "dimer" accretion products. We have found that all these channels are indeed competitive (with typical rates of at least greater than 10^6 s^{-1}, and many have rates exceeding 10^{10} s^{-1}) in the atmosphere. This suggests that the computationally proposed novel RO_2 + RO_2 reaction mechanism is qualitatively compatible with experimental results on accretion product formation and may thus play a key role in the formation of organic aerosols.

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Using Molecular Dynamics to Determine Site Structures of Molecules Embedded in Noble Gas Matrices

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We present a molecular dynamics based method to calculate site structures for molecules embedded in noble gas matrices. The method, based on QM-MM formulation, allows calculation of IR spectra, which can be compared to experimental spectra to identify site structures. We present several identified site structures and show how well the calculated IR spectra corresponds to experimental measurements.

Cantilever-enhanced photoacoustic spectroscopy for high-sensitivity detection of benzene at 14.8 µm

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There has been significant interest in development of spectroscopic methods for trace-gas detection of benzene. Many previous methods target the benzene absorption band at 3 µm region, where high sensitivity has been demonstrated. However, spectroscopic detection in this region is constrained by overlapping absorption bands of common interferents; so-called BTEX (benzene, toluene, ethylbenzene, and xylene) compounds are especially challenging [1]. The proper treatment of this interference negatively affects the achievable detection limits. Furthermore, selective detection of benzene is of importance since it is toxic at significantly lower concentrations compared to the other BTEX compounds. The strongest benzene absorption band is around the wavelength 15 µm, but the detection limits reached in measurements in the past have been limited by the lack of available light sources and limited sensitivity of detectors available at that wavelength region.

Here, we present a simple benzene trace-gas detector based on photoacoustic spectroscopy [2]. The light source is a continuous-wave quantum cascade laser emitting at the wavelength 14.8 µm [3]. Since it is relatively independent of the excitation wavelength, photoacoustic spectroscopy allows reaching high sensitivity in the long wavelength infrared region, where sensitive photodetectors are not widely available. Our setup uses a cantilever microphone, which leads to orders of magnitude improvement in sensitivity compared to traditional photoacoustic spectroscopy. We reach a noise level (one standard deviation) below parts-per-billion (ppb) level with 2 min averaging time. The target wavelength region has no significant overlap with absorption bands of other BTEX compounds, and the main interference is from a nearby CO_2 line. We have further improved the detection limit and selectivity towards benzene with modest sorption enrichment [4]. The sample gas is collected on Tenax TA sorbent for 30 s and the enriched sample is measured with the photoacoustic spectroscopy setup. We reach a noise level of 0.05 ppb over a single measurement cycle of 90 s, with good immunity against BTEX interferents.

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Selection and control of (bio)nanoparticles with electric fields

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Single-particle imaging (SPI) experiments at free-electron lasers (FELs) promise high-resolution-imaging of the structure and dynamics of nanoparticles and macromolecules. Guiding sampleparticles into the focus of an FEL, diff raction patterns of individual particles can be collected. Sufficient amounts of patterns of identical nanoparticles are needed to overcome the inherently small signal-to-noise ratio and reconstruct the underlying 3D structure. Size-optimized delivery of identical nanoparticles is key to efficient and successful SPI experiments. Here, we present approaches for the production of purified high-density beams of a broad variety of biological nanoparticles. We establish control through electric fields, aiming at charge state or conformational state selectivity.

This is especially relevant for soft biological samples, such as proteins or protein complexes, which in uncontrolled environment are prone to structural instability.

Accurate equilibrium structures of linear triatomic molecules from a combined theoretical-experimental method: The protonated nitrogen molecule, HN_2^+

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The determination of the equilibrium structure of molecules is one of the key goals of spectroscopy. Geometric parameters can be unambiguously deduced only from equilibrium rotational constants B_e, which are unfortunately not directly accessible experimentally. Theoretical models have to be used to account for the effect of vibration-rotation coupling and to provide corrections to the effective rotational constants B_v for a vibrational state v, with a special interest in the zero-point correction, $\Delta B_0 = B_e - B_0$.

The concept of the equilibrium molecular structure is theoretically well defined. Within the Born-Oppenheimer approximation, a molecule is described by a mass independent potential energy surface (PES). The minimum of the PES uniquely defines the equilibrium structure. Numerically exact quantum-mechanical calculations with exact kinetic energy operators are then needed to establish a direct link between a given PES and spectroscopic observables. The connection to experimental spectroscopic parameters can be established by fitting the computed rovibrational energies to effective spectroscopic Hamiltonians.

We examine several strategies which can be used to derive molecular equilibrium structures from experimental data and extend our previously suggested method [1,2] to HN_2^+. Full-dimensional rovibrational calculations are carried out for eight isotopologues of HN_2^+ using two *ab initio* potential energy representations [3]. Rovibrational energies computed for rotational angular momenta up to J=15 in both parities are used to derive theoretical vibration-rotation corrections to ground state rotation constants B_0. These results are combined with B_0 values derived from experiments to determine the r_0, r_α, and r_e structures of the ion. Higher-order corrections beyond the commonly used vibration-rotation α constants are found to be essential for the structure determination. Our analysis is supported by graphical representations, illustrating the anticorrelation of the structural parameters. The r_0 structure is rationalized in terms of a structure projected onto the principal *a* axis and examined for the isoelectronic series of linear triatomic molecules HCO^+, HCN, HN_2^+, HNC, and HOC^+.

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Theoretical predictions of the activity of noble-metal single-atom catalysts for CO oxidation

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Noble metals are widely used in industrial catalysis because of their unique properties and high catalytic efficiency and versatility. Indeed, important industrial processes involving noble metal catalysts include CO and hydrocarbons oxidation, NOx reduction, methane steam reforming, water oxidation electrocatalysis, olefins epoxidation, asymmetric hydrogenation and others. Due to their high cost, special care must be taken in the design and manufacturing of noble-metal-based catalysts in order to boost their performance, stability and reliability under severe reaction conditions. Recent advances in nanotechnology allow for maximizing the exploitation of the noble metal atoms, by tuning both the morphology of the catalyst surface and the electronic properties of the metal nanoparticles/atoms, making them suitable for the large-scale production. As an example of a potential application of such systems in heterogeneous catalysis, we present the results of a theoretical investigation of the catalytic activity of Pd atoms mono-dispersed on graphene (PdGr) as promising catalysts for CO oxidation. By using density functional theory computations, based on the Perdew−Burke−Ernzerhof functional within the generalized gradient approximation and density functional semicore pseudopotentials, we show that the Pd atoms trapped on graphene monovacancies can bind strongly to O2, acting as the major species responsible for the CO oxidation. The high catalytic activity is due to the specific electronic structure of the partially positively charged metal atoms trapped on monovacancies. Furthermore, we show that the oxidation proceeds through a revised Langmuir−Hinshelwood pathway, where the dissociation of the peroxide intermediate (O−O−C=O) is the rate-limiting step.

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Study of the effect of higher-order dispersions on photoionization induced by ultrafast laser pulses applying a classical theoretical method

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We investigated the effect of higher order dispersion on ultrafast photoionisation with Classical Trajectory Monte Carlo (CTMC) method for hydrogen and krypton atoms. In our calculations we used linearly polarised ultrashort 7 fs laser pulses, 6.5×10^{14}W/cm^2 intensity, and a central wavelength of 800 nm. Our results show that electrons with the highest kinetic energies are obtained with transform limited (TL) pulses. The shaping of the pulses with negative second- third- or fourth- order dispersion results in higher ionisation yield and electron energies compared to pulses shaped with positive dispersion values. This phenomenon can be quantitatively characterised by the asymmetry parameter defined as

$$A(D) = \frac{N(D) - N(-D)}{N(D) + N(-D)}$$

where *N(D)* is the number of photoelectrons at a given value of dispersion. We have also investigated how the Carrier Envelope Phase (CEP) dependence of the ionisation is influenced by dispersion. We calculated the left-right asymmetry defined as

$$A(E, \varphi_{CEP}) = \frac{N^+(E, \varphi_{CEP}) - N^-(E, \varphi_{CEP})}{N^+(E, \varphi_{CEP}) + N^-(E, \varphi_{CEP})}$$

where $N+$ and $N-$ mean the number of electrons having positive and negative momentum along the polarization axis respectively. We carried out the calculations for sodium atoms employing pulses of 4.5 fs, 800 nm central wavelength, and 4×10^{12}W/cm^2 intensity. We found that the left-right asymmetry is more pronounced for pulses shaped with positive Group Delay Dispersion (GDD).

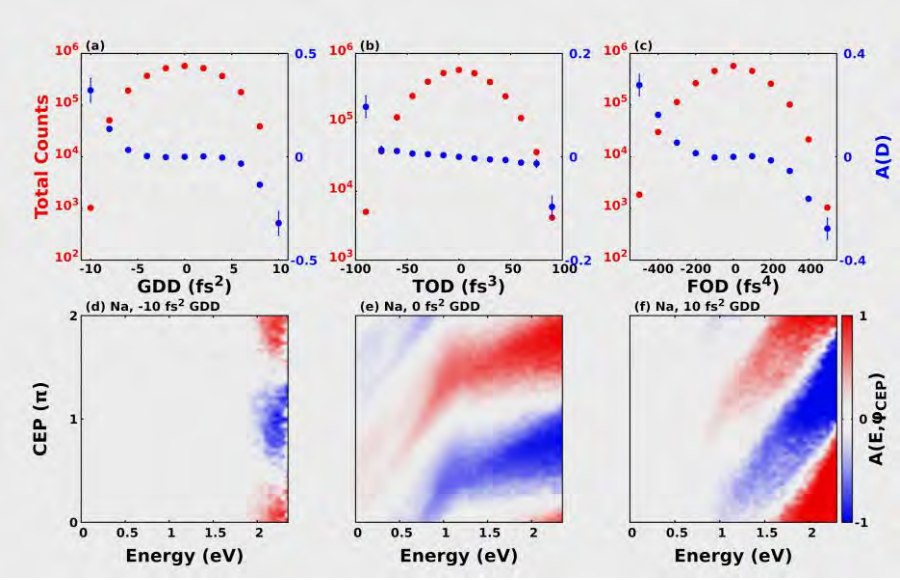

FIG. 1. Number of electron counts and asymmetry parameters for hydrogen calculated with different GDD (a), TOD (b) and FOD (c). Calculated maps of the asymmetry defined by Eq. (2) for Na at 4×10^{12}W/cm^2 intensity with different values of GDD (d)-(f).

Time-resolved, broadband UV-absorption spectrometry measurements of unimolecular reaction kinetics of dimethyl-substituted Criegee Intermediate $(CH_3)_2COO$

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Very recently, we introduced a new time-resolved, broadband cavity-enhanced UV-absorption spectrometer apparatus (see Fig. 1) that we have constructed and utilized for temperature- and pressure-dependent measurements of stabilized Criegee Intermediate (sCI) kinetics [1]. In that study, we showed the capability of the new set-up for unimolecular reaction kinetic measurements of formaldehyde oxide (CH_2OO) and its bimolecular reaction with formic acid over wide pressure and temperature ranges. We also introduced a new photolytic precursor for CH_2OO, bromoiodomethane (CH_2IBr), which photolysis at 213 nm in presence of O_2 produces CH_2OO. This new precursor was found to be free from secondary reactions that may regenerate CH_2OO in kinetic experiments.

Here, we present our latest results of unimolecular decomposition kinetic study of acetone oxide ($(CH_3)_2COO$) using 2-bromo-2-iodopropane ($(CH_3)_2CIBr$) as a new precursor for $(CH_3)_2COO$ [2]. The unimolecular decomposition rate coefficient of $(CH_3)_2COO$ has been measured over wide pressure (5–350 Torr) and temperature (243–340 K) ranges. The results show that the thermal unimolecular reaction is even more important main loss process of $(CH_3)_2COO$ in the atmosphere than direct kinetic studies have suggested hitherto. In addition, the current measurements bring the direct and relative-rate measurements of thermal unimolecular reaction kinetics of $(CH_3)_2COO$ into the quantitative agreement.

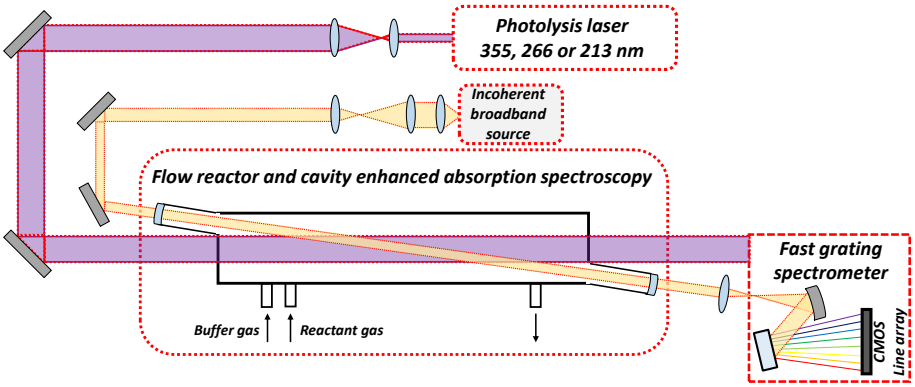

Figure 1: The schematic picture of the time-resolved, broadband cavity-enhanced absorption spectrometer. The sCI is produced along a heated (or cooled) flow tube reactor by a single-pass photolysis laser pulse. The formed sCI is probed by overlapping incoherent broadband beam. The sensitivity of the detection is enhanced using an optical cavity formed by two highly reflecting concave mirrors. The time-dependent broadband absorption spectrum of sCI is measured by a grating spectrometer combined with a fast CMOS line array camera.

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Gas-phase benzene oxidation: Semi-empirical model building with experimental and theoretical constraints

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Benzene is a common petrochemical emission released by various anthropogenic activities. It is the most prototypical aromatic compound, and its detailed formation pathways during combustion have puzzled researchers for decades. Reflecting this, also its gas-phase oxidation mechanism has attracted considerable interest (*e.g.*, References 1 and 2). Recently, benzene was shown to yield highly oxygenated organic molecules (HOM [3-5]) by autoxidation, but also by sequential OH oxidation [4], representing the first steps of ambient secondary organic aerosol (SOA) from aromatic compounds. While the formation of bicyclic peroxy radicals (BPR) in this system have been well-documented [1], the next steps up to HOM products have not been reported previously. Importantly, the abundant BPR seem as a dead-end to the autoxidation propagating by unimolecular H-shifts, and thus call for alternative explanations.

In lack of unambiguous oxidation pathways up to HOM products, our model building retorts to a semi-empirical approach. We devise a model in which the benzene HOM spectrum is reproduced with the help of a near-explicit mechanism augmented by prototypical reaction steps known from the literature (*e.g.*, alkoxy mediated ring breaking). The goal of this procedure is to reproduce the experimental observations obtained from a set of flow tube studies providing the experimental constraints. At the same time, we are assessing the likelihood of several other potential reactions, which are far more uncertain, and thus often overlooked. These include further reactions of the abundant BPR with, for example, O_3 and OH. The ultimate aim here is to provide a benzene oxidation model that can account for the condensable product formation (*i.e.*, mainly HOM), to use in atmospheric models detailing SOA formation and the related nanoparticle dynamics.

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A systematic study on the kinetics of H-shift reactions in pristine acyl peroxy radicals

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Studies on the acyl peroxy radicals or $RCH_2C(=O)OO\cdot$ gained importance due to the fact that these radicals are crucial for the understanding of atmospheric NO_x. Acyl peroxy radicals are produced from aldehydes primarily via reactions with OH radical and photolysis [1]. Owing to the low bond strength and being highly labile, the H atom of the –CHO group can easily be cleaved by the OH radical to form acyl radical. This is followed by either the elimination of CO to give alkyl radicals with one less carbon atom or concomitant addition of molecular O_2, which leads to the formation of acyl peroxy radical. It can then undergo an intramolecular H-shift via several pathways depending on the chain length as presented in

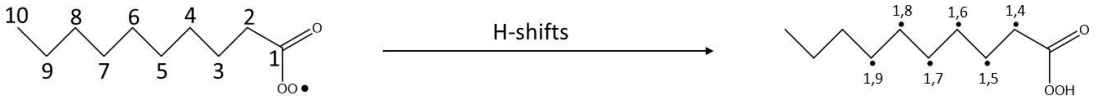

Figure 1. Schematics of H-shifts in acyl peroxy radicals

Figure 1 to yield peroxy acids with the radical centered at different Cs of the aldehydic chain. Investigations have previously been reported for the H-shift reactions in substituted acyl peroxy radicals of varying chain length [1], however, there are no such results on H-shift reactions for the pristine species, i.e., radicals without any functionalities on the C chain as shown in the figure. This H-shift reaction is quite an important step in the autoxidation of aldehydes that can lead to the formation of highly oxygenated organic molecules (HOMs). The present work is an attempt to fill this gap.

Here, we performed a systematic study of [*n*,*m*] H-shifts ranging from 1,4 to 1,9 on aldehydes starting from ethanal up to decanal covering primary as well as secondary C radical centers. Density functional theory (DFT) was used as the prime investigating tool to obtain the optimized geometries of the species involved using Gaussian suite of programs [2]. We have done conformational sampling of each species in SPARTAN'20 with Merck Molecular Force Field (MMFF) method [3,4]. Further refinement of the energies of the involved systems were done at coupled cluster level of theory to get reliable and accurate barriers. The H-shift reaction rate coefficients were then estimated using MESMER [5] and also MC-TST equation [4]. Our study reveals an increase in the rate coefficients as one increases the aldehydic chain length for a particular [*n*,*m*] H-shift. On the other hand, for a particular parental aldehyde, we found maxima in the rate coefficients at a certain [*n*,*m*] H-shift. This trend is attributed to the barrier heights and tunneling corrections involved.

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Advancing optical isotope ratio spectroscopy for carbon dioxide

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Carbon dioxide and methane levels in atmosphere have become higher than ever before. It is therefore of utmost importance to reduce emission of these greenhouse gases. In order to help this action, one has to be able to distinguish between anthropogenic and natural emission sources. Stable isotopes of carbon dioxide can be used in this task since different sources can have unique isotopic fingerprint in their emissions [1].

Optical spectrometers are relatively low-cost and can be used in field measurements to provide near real-time data on isotopic composition of CO_2. In our work, we have developed optical isotope ratio spectrometer (OIRS) to meet the strict requirements of global greenhouse gas monitoring communities.

OIRS-instrument is based on laser absorption spectroscopy (LAS) and quality of the laser will have big influence on the precision of the instrument itself. In order to improve the precision, we have tested low-noise current drivers for the laser in the analyzer. In our conference contribution, we present results from these experiments. In addition, we have tested and characterized different multipass cells, which is one of the crucial part in LAS-method and in OIRS-instrument. We will also discuss performance of these cells and our OIRS-instrument in our contribution.

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