Theoretical and experimental advances in atmospheric photochemistry

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1. Description

At first glance, the Earth's atmosphere appears to be mainly composed of simple, inert gases like O_2, N_2, or the infamous CO_2. However, the reality is somewhat different, and our atmosphere behaves more like a massive chemical reactor due to the presence of reactive molecules like CH_4, halocarbons, O_3, N_2O, NO, or volatile organic compounds (VOCs). The degradation of biogenic and anthropogenic VOCs takes place via a highly complex network of chemical processes and is intimately connected to the concentration of OH, ozone, and secondary organic aerosol (SOA) precursors in the troposphere. The result of this is VOCs are strong contributors to both global warming and air pollution, and a great deal of effort has been devoted to understanding and predicting their atmospheric concentrations using detailed chemical models. As environmental policy decisions are driven by such atmospheric models, it is essential they accurately reflect the different chemical reactions in the atmosphere.

Historically, these chemical mechanisms have mostly neglected reactions involving the interaction of VOC intermediates with sunlight, and the resulting photochemical reactions. Hence, a complete family of chemical reactions is missing in current atmospheric models, and the influence of these reactions on the composition of our atmosphere is largely unknown, partly as photochemical experiments on (transient) VOCs are highly complex to realize.

How can theoretical and computational chemistry help? Simulating the photochemistry of a molecule requires the inclusion of nonadiabatic effects, i.e., the coupling between electronic states and nuclear motion, which is not straightforward as it challenges several approximations commonly used in theoretical chemistry. For example, nonadiabatic effects lead to a breakdown of the Born-Oppenheimer approximation, classical approximations for the nuclear degrees of freedom may be inadequate, and out-of-equilibrium processes can challenge established reaction rate theories.

While numerous methods have been devised to tackle these issues – e.g., MCTDH, trajectory surface hopping, ab initio multiple spawning – their application to study the photochemistry of atmospheric molecules faces numerous challenges. Examples are: the complexity in simulating observables of interest for spectroscopists and atmospheric modelers; the challenging electronic structure of multichromophoric VOCs; the types of excited-state dynamics created by sunlight excitation; the long-time excited-state dynamics associated with VOCs; the importance of intersystem crossings or collisional processes; and the effect of an aqueous environment, such as in atmospheric aerosols and clouds.

Over the last decades, atmospheric chemistry has stimulated the development of new theoretical methods to investigate complex *ground-state* chemical reactions and their mechanisms. Such a connection between theory and experiment *does not currently exist in atmospheric photochemistry* involving electronically excited states, despite the importance for current atmospheric models and a strong push from the experimental side to obtain reliable data for modeling the composition of the atmosphere. With this CECAM workshop, we wish to create a bridge between the worlds of computational photochemistry and atmospheric chemistry to bolster a synergistic discussion between these two groups aiming to (i) connect theory with experiment, (ii) define key targets for theory, and (iii) identify current theoretical challenges and their possible solutions.

Key References

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2. Program

Day 1 - Tuesday March 26th 2024

- 08:30 to 09:00 - Registration
- 09:00 to 09:15 - Welcome & Introduction

Talk Session I – Chair: Daniel Hollas

- 09:15 to 09:55 - **Joseph S. Francisco**
  Heterogeneous chlorine activation reactions in the stratosphere revisited
- 09:55 to 10:35 - **Ruth Signorell**
  Accelerated and unexpected aerosol photochemistry
- 10:35 to 11:05 - Coffee break

Talk Session II – Chair: Jack Taylor

- 11:05 to 11:45 - **Petr Slavíček**
  Electronic spectra in Wigner perspective: How far we can get?
- 11:45 to 12:25 - **Veronica Vaida**
  Multiphase organic chemistry in the natural environment: A closer look at water-air interfaces at water-air interfaces
- 12:25 to 14:30 - Lunch and coffee discussion

Contributed Talks I

- 14:30 to 14:50 - **Krispin Dettlaff**
  Spatial modulation spectroscopy of single optically-trapped aerosol particles
- 14:50 to 15:10 - **Javier Carmona-García**
  Shedding light on the atmospheric cycle of mercury through computational photochemistry
- 15:10 to 15:30 - **Daniel Hollas**
  ATMOSPEC: Automated workflow for ab initio photoabsorption cross-sections
- 15:30 to 15:50 - **Jiří Janoš**
  Wavelength-dependent photodynamics of the atmospheric molecule CF3COCl
- 15:50 to 16:10 - **Svetlana Tsizin**
  Valence photoelectron imaging of molecular oxybenzone
- 16:10 to 16:40 - Coffee break

Contributed Talk II

- 16:40 to 17:00 - **Jack Taylor**
  On the description of conical intersections between excited electronic states with LR-TDDFT and ADC(2)

- 17:00 to 17:20 - **Leon Cigrang**
  Photochemical simulations: The simple and the strenuous

- 17:20 to 17:40 - **Jiří Suchan**
  Exploring long-lived coherences of molecular excited states

- 17:40 to 20:00 - Poster session & aperitif

Day 2 - Wednesday March 27th 2024

Talk Session III – Chair: Leon Cigrang

- 09:00 to 09:40 - **Scott Kable**
  Atmospheric photochemistry: The forgotten role of the ground state

- 09:40 to 10:20 - **Antonio Prlj**
  Investigating sunlight-triggered excited-state dynamics of transient atmospheric molecules

- 10:20 to 10:50 - Coffee break

Talk Session IV – Chair: Jiří Suchan

- 10:50 to 11:30 - **Christopher Hansen**
  Fluoroform (CHF3) production from CF3CHO photolysis and implications for the decomposition of hydrofluoroolefins in the atmosphere

- 11:30 to 12:10 - **Daniel Roca-Sanjuán**
  Multiconfigurational quantum chemistry approach to address atmospheric chemistry phenomena with strong electron correlation

- 12:10 to 12:50 - **Eva Muchova**
  Auger spectroscopies - what for?

- 12:50 to 14:30 - Lunch and coffee discussion

Experimentally-driven round-table

- 14:30 to 16:00 - Discussion

- 16:00 to 16:30 - Coffee break

- 16:30 to 19:30 - Informal discussions and free time

- 19:30 to 22:30 - Social dinner

Day 3 - Thursday March 28th 2024

Talk Session V – Chair: Javier Carmona Garcia

- 09:00 to 09:40 - **Robert Benny Gerber**
  Reactions of HOCl with ions in seawater

- 09:40 to 10:20 - **Todd Martinez**
  Photochemistry of Nitrophenol

- 10:20 to 10:50 - Coffee break

Talk Session VI

- 10:50 to 11:30 - **Ivan Kassal**
  Simulating photochemistry on quantum computers

- 11:30 to 12:10 - **Zhenggang Lan**
  Nonadiabatic dynamics and atmospheric photochemistry

- 12:10 to 12:50 - **Graham Worth**
  Simulating photo-dissociation using wavepacket dynamics

- 12:50 to 14:30 - Lunch and coffee discussion

Theoretically-driven round-table

- 14:30 to 16:00 - Discussion

- 16:00 to 16:30 - Coffee break

- 16:30 to 17:15 - Closing Word

- 17:15 to 19:00 - Aperitif

3. Abstracts

Accelerated and unexpected aerosol photochemistry

Ruth Signorell

ETH Zurich, Switzerland

Photochemical processes have been identified as the main causes of degradation and oxidation of matter in atmospheric aerosol particles. When light interacts with an aerosol particle, the light intensity can be greatly amplified inside the particle as the latter acts as a light-amplifying cavity. These optical confinement effects result in an acceleration of photochemical reactions in aerosol particles compared with reactions in the extended condensed matter. The second part of the talk will address specific examples of unexpected chemical reactions in droplets, which were recently observed in our laboratory. A final understanding of the causes and the involved mechanisms behind the observed processes is still missing. Nevertheless, we suggest preliminary explanations that are in agreement with the observed phenomena.

ATMOSPEC: Automated workflow for ab initio photoabsorption cross-sections

Daniel Hollas, Basile Curchod

University of Bristol, United Kingdom

UV/Vis spectrum of a molecule is a basic observable that determines it’s photophysical and photochemical properties. While conceptually simple, it’s accurate experimental determination for gas phase molecules is non-trivial, especially for short-lived intermediates. Accurate ab initio modelling of absorption cross-section is thus highly valuable.

We have recently shown that the Nuclear Ensemble Approach (NEA) offers a pragmatic route for UV spectra of Volatile Organic Compounds.[1] Here, I will present an initial prototype of ATMOSPEC (available under MIT license at https://github.com/ispg-group/aiidalab-ispg), a user-friendly software package that implements a robust and automated protocol to determine actinic cross sections. The package utilizes automatic conformer sampling and ab initio calculations to generate NEA spectrum on top of a harmonic Wigner distribution. The graphical interface is provided via a Jupyter notebook rendered as a webpage. We hope the tool is sufficiently user friendly to be used an exploratory tool by the atmospheric modelling community.

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Atmospheric photochemistry: The forgotten role of the ground state

Scott Kable

University of New South Wales, Australia

Absorption of sunlight drives atmospheric chemistry. Consequently, photochemical products and quantum yields of atmospherically-relevant species have been investigated, experimentally and theoretically, for more than half a century. Almost all atmospheric photochemical mechanisms are attributed to reaction on an excited singlet or triplet state of a molecule. However, notable exceptions exist, for example HCHO produces H_2 + CO on the ground electronic state following excitation to the S_1 state in the near-ultraviolet. The S_0 potential energy surface, at energies relevant to photolysis, is complex. Many chemical pathways are available, including formation of radicals and closed shell molecules, and photoisomerization. In addition, the vibrationally-excited S_0 molecule has sufficient internal energy to open up new “activated”, bimolecular chemical reactions.

In this talk, I will show experimental and theoretical evidence of multiple competing pathways on the ground electronic state of selected carbonyl compounds. In addition to the well-known Norrish Types I and II reactions, we have identified the following active pathways:

- Production of H_2 from all carbonyls via a 4-centre elimination;
- Concerted triple fragmentation into CO, H_2 plus an alkene;

- Dissociation into ketenoids (ketene, methylketene, dimethylketene, etc);
- Photoisomerization to enols; and
- Activated bimolecular reaction with O_2 molecules.

Bulb experiments are used to provide end-products and quantum yields. These are complemented by molecular beam experiments, which provide mechanistic information on the primary processes. Theory and modelling include *ab initio* calculations of critical energies, Master Equation models of kinetics, and box and global transport models of atmospheric chemistry. Our conclusion is that the ground state photochemistry of carbonyls is a rich source of airborne radicals and molecules. These mechanisms are mostly not present in current atmospheric models and their impact on atmospheric chemistry is not well-known.

I acknowledge the work of many research students, post-doctoral research fellows and senior collaborators in this work, who will be named throughout the talk.

Auger spectroscopies – what for?

Eva Muchova[1], Rebecca Ann Ingle[2]
[1]University of Chemistry and Technology, Czech Republic
[2]UCL, United Kingdom

X-ray spectroscopies are useful techniques because of site and element specifically which is extremely useful in probing local chemical environment. Especially information-rich is resonant Auger spectroscopy based on tuning the incident X-ray photon energy to match core-valence excitations and monitoring the Auger electrons. In this case, the spectra contain information on core, valence and virtual orbitals of molecules at the same time and provide an experimental approach to the deconvolution of heavily congested absorption spectra and to the recovery of information on the electronic and vibrational structure of the molecule, e.g. resonant Auger spectroscopy can be viewed as a 'projection' of the complex absorption process. I will show a few cases of resonant Auger spectroscopy for small organic molecules and will discuss theoretical approaches how to interpret the spectral fingerprints [1,2]. I will discuss metastable states, description of outgoing electron as a plane or Coulomb wave function and description of singly and doubly ionized states. I will also show how the core-hole-clock method in resonant Auger spectroscopy can be used for studying charge-transfer processes on subfemtosecond timescale and how these timescales can be inferred from energy-resolved experiments.

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Electronic spectra in Wigner perspective: How far we can get?

Petr Slavíček
University of Chemistry and Technlogy, Prague, Czech Republic

Accurate determination of absorption cross sections is paramount for understanding atmospheric photochemistry modelling. The data are often difficult to achieve experimentally. While molecular quantum mechanics-based techniques are prevalent, their applicability is often questioned due to uncertainties. The quality of data hinges on electronic structure methods, which can be systematically refined. The shape of the spectrum is controlled by nuclear dynamics in the excited state. Although highly accurate results for absorption cross sections can be achieved for small molecules, challenges persist in modeling solvated chromophores, interfaces, aerosols, and complex molecules. Conventional semiclassical methods, like the nuclear ensemble method based on reflection principle, offer simplicity but falter in capturing critical aspects, notably in modeling distribution tails vital for atmospheric chemistry. In this presentation, I will explore potential enhancements to these models while maintaining manageable complexity. I will also focus on capturing non-Condon effects, showing failure of ensemble-based techniques in some cases. Additionally, I will delineate “best practices” for simulations with molecular ensembles.

The talk will cover some discussions I had with my (former and present) Ph.D. students Štěpán Sršeň, Jiří Suchan and Tomáš Jíra.

Exploring long-lived coherences of molecular excited states

Jiří Suchan, Benjamin G. Levine
Stony Brook University, United States

Quantum coherence between excited electronic states is a fundamental phenomenon with practical implications for light-initiated processes. Initially excited system can exist in a superposition of multiple states which introduces interference effects. Present photoionization experiments are able to directly probe such effects. Moreover, for some molecules, multiphoton absorption can be used to prepare electronic coherences that can persist for several hundreds of femtoseconds.
In this work, we use mixed quantum-classical dynamics to explore long-lived coherences in thiophene. We combine the time-dependent configuration interaction method (TDCI) for propagation of the electrons and decoherence-corrected Ehrenfest molecular dynamics to describe the nuclear motion. With these recently developed tools we aim to reconstruct the experiment by modeling excitation and subsequent dynamics on an ensemble of molecules. Initial results indicate the involvement of low-lying Rydberg states that maintain coherence throughout extensive vibrational motion.

Fluoroform (CHF3) production from CF3CHO photolysis and implications for the decomposition of hydrofluoroolefins in the atmosphere

Christopher Hansen
UNSW Sydney, Australia

Hydrofluoroolefins (HFOs) are the leading synthetic replacements for compounds successively banned by the Montreal Protocol and amendments. HFOs readily decompose in the atmosphere to form fluorinated carbonyls, including CF_3CHO in yields up to 100%, which is then photolyzed. A longstanding issue, critical for the transition to safe industrial gases, is whether atmospheric decomposition of CF_3CHO yields any quantity of CHF_3 (HFC-23), which is one of the most environmentally hazardous greenhouse gases. This talk will describe the outcomes of a comprehensive, and largely unpublished, experimental investigation that combined velocity-mapped ion imaging (VMI), a new technique (purpose built) for determining relative photolysis quantum yields in a molecular beam, synchrotron multiplexed photoionization mass spectrometry, Fourier-transform Infrared (FTIR) spectroscopy with *in situ* photolysis, chirped-pulse Fourier-transform microwave spectroscopy, and sophisticated atmospheric modelling to confirm that this reaction occurs under atmospheric conditions and provide pressure-dependent quantum and molar yields.

Heterogeneous chlorine activation reactions in the stratosphere revisited

Joseph S. Francisco
University of Pennsylvania, United States

Polar stratospheric clouds (PSCs) play important roles in stratospheric ozone depletion during winter and spring at high latitudes (e.g., the Antarctic ozone hole). PSC particles provide sites for heterogeneous reactions that convert stable chlorine reservoir species to radicals that destroy ozone catalytically. Heterogeneous chlorine activation appears to be well understood from an experimental perspective. It is generally accepted that under most conditions' chlorine activation occurs on/in liquid cloud droplets. However, uncertainties remain for the molecular details describing the underlying chemistry. Since the discovery of heterogenous chlorine activation on polar stratospheric cloud interfaces, there have been notable advances in theoretical methods and models that can help facilitate further molecular insight into PSC processes. This talk will review ab initio, small cluster models and molecular dynamics approaches that have helped evolve our understanding of polar ozone depletion and the interplay of chlorine chemistry at the interface of cloud surfaces.

Investigating sunlight-triggered excited-state dynamics of transient atmospheric molecules

Antonio Prlj
Rudjer Boskovic Institute, Croatia

Volatile organic compounds (VOC) are ubiquitous atmospheric molecules which generate a complex network of chemical reactions in the troposphere, often triggered by absorption of sunlight. Since the short lifetime of some transient VOCs poses significant challenges for accurate experimental and spectroscopic measurements, there is an urgent need for predictive computational approaches to study photochemistry and photophysics of VOCs.

We show how recent advances in computational photochemistry allow us to calculate in silico photolysis rate constants.[1] Such rate constants are utilized in general atmospheric models used to predict the accurate composition of atmosphere but are often not experimentally available for transient VOCs. Photolysis rate constants depend on three key pieces of information: the flux of the radiation source (sun/laser), the photoabsorption cross-section of the molecule and the wavelength-dependent photolysis quantum yield. We show how one can evaluate the sought-for ingredients – and consequently the corresponding photolysis rate constants – by combining state-of-the-art electronic structure and nonadiabatic molecular dynamics methods.

Furthermore, we provide a detailed analysis of how initial conditions may influence the calculation of experimental observables by focusing on the photochemistry of methylhydroperoxide. We investigate the outcomes of trajectory surface hopping simulations for distinct sets of initial conditions sampled from different approximate quantum distributions: harmonic Wigner distribution and ab initio molecular dynamics using a quantum thermostat. We show how the choice of initial conditions critically affects photoabsorption cross-sections, photolysis quantum yields, and translational kinetic energy maps, in particular when low-frequency normal modes are coupled to the photophysics of a molecule. [2,3]

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Multiconfigurational quantum chemistry approach to address atmospheric chemistry phenomena with strong electron correlation

Daniel Roca-Sanjuán
Universitat de València, Spain

In atmospheric chemistry research employing computational tools, we frequently encounter complex physicochemical phenomena characterized by significant electron correlation effects. Examples include sunlight-induced chemistry involving electronic excited states with similar energies, as well as singlet-triplet or doublet-quadruplet states with strong couplings, and various radical configurations. In such scenarios, the CASSCF/CASPT2 method emerges as a practical choice for achieving accurate and quantitative determinations, supported by benchmarks from higher-level MRCI methodologies. Over the past five years, we have utilized these methods to improve current climate chemical models, particularly focusing on adding rates associated with challenging thermally and photo-induced phenomena. Moreover, we have devised computational strategies based on CASSCF/CASPT2 to attain higher accuracy in determining cross-sections under distinct conditions, notably in the gas phase, within bulk water, and at the air-water interface [1-3]. Additionally, we have employed surface-hopping dynamics, considering couplings between states of different multiplicities and incorporating relativistic effects when necessary, to predict the quantum yields of various photoinduced reaction pathways. Further developments based on machine learning have been addressed to extend the simulation times in photodynamics.

In this contribution, we will exemplify the characterization of strong electron-correlation problems through studies we have conducted to deepen our understanding of atmospheric mercury speciation (involving conversions between Hg(0), Hg(I), and Hg(II)) [4,5], the significance of intermediates in stratospheric sulfur chemistry relevant to geoengineering proposals addressing global warming [6,7], the involvement of OSSO in the chemistry of Venus' atmosphere [8], and the quantification of ClOOCl's contribution to ozone depletion mechanisms.

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Multiphase organic chemistry in the natural environment: A closer look at water-air interfaces at water-air interfaces

Veronica Vaida
University of Colorado, United States

Inspired by atmospheric measurements, which have established that atmospheric chemistry occurs in many phases and at interfaces, my group explored the unique reaction environments presented by aqueous environments including water-air interfaces. Surface reflection spectroscopies (IRRAS and UVRES) developed to study interfacial chemistry are described along with results for organic chemical and photochemical studies at the water surface. The special morphological and chemical properties of organic films on aqueous solutions will be discussed with reference to atmospheric aerosols, sea surface microlayers, cloud and fog droplets. The surface of water on aqueous drops and at the sea surface provides a special and unique reaction environment with qualitatively different thermodynamic and kinetic properties from bulk aqueous solutions. Examples will be presented of surface reflection studies to follow chemistry initiated at the water surface leading to increase in the chemical complexity of the system. Solar radiation is the largest source of energy on both the contemporary and early Earth. Multiphase photochemical mechanisms will be discussed by which a-keto acids react in aqueous environments to form organic radicals, which then recombine to form larger, more complex lipids. The relevance of this chemistry to reactions in the contemporary atmosphere as well as chemistry that may have occurred prebiotically, in the absence of enzymes on ancient Earth, will be discussed.

Nonadiabatic dynamics and atmospheric photochemistry

Zhenggang Lan
South China Normal University, China

Nonadiabatic dynamics widely exist in photophysics, photochemistry and photobiology. Particularly, many important photoinduced reactions in atmospheric photochemistry are governed by the nonadiabatic dynamics. Here we tried to develop theoretical approaches to study the photoinduced nonadiabatic dynamics.

We employed the on-the-fly nonadiabatic dynamics simulation to study the photolysis of volatile organic compounds (VOC). Here the CH3ONO2 compound was chosen as a typical example to explore its photolysis mechanism. The wavelength-dependent photolysis procedures were clarified. The impact of mode-specific excitations on the nonadiabatic dynamics were examined.

We combined the doorway-window representation of the nonlinear response theories and ab initio nonadiabatic dynamics to simulate the time-resolved pump-probe spectra, including both transient absorption spectra and time-resolved fluorescence spectra. Two interesting examples, including photoinduced energy transfer and photoisomerization, are discussed.

On the description of conical intersections between excited electronic states with LR-TDDFT and ADC(2)

Jack Taylor[1], David Tozer[1], Basile Curchod[2]
[1]Durham University, United Kingdom
[2]University of Bristol, United Kingdom

Regions of nuclear-configuration space away from the Frank-Condon geometry often prove problematic for conventional electronic structure methods, given the propensity of such regions to possess (highly connected) points of degeneracy between electronic states - i.e., conical intersections. Conical intersections (CXs) play a critical mechanistic role in our theoretical framework in understanding the rapid, nonradiative processes exhibited by the plethora of exotic molecular species within the Earth's atmosphere. With the likelihood (perhaps even inevitability) for nonadiabatic dynamics simulations to explore molecular geometries in close proximity to CXs, it is therefore vital that the individual performances of standard electronic structure methods are routinely (re-)examined in this context.

In our recent work, [1] the (in)ability of linear-response time-dependent density functional theory within the adiabatic approximation (AA LR-TDDFT) to provide a proper description of minimum energy CXs (MECXs) - in terms of their topology and topography - was revisited, with particular attention being paid to MECXs between two excited electronic states. The behavior of the equally computationally cheap wavefunction-based method, ADC (2), was similarly probed.

Here, we first present a summary of this investigation for two prototypical molecules, protonated formaldimine and pyrazine, then secondly, we expand upon this work [2] by considering whether AA LR-TDDFT can correctly reproduce the topological phase accumulated by the electronic wavefunction upon traversing a closed path around a given excited-to-excited-state MECX, despite not using the appropriate (quadratic-response) nonadiabatic coupling vectors. Likewise, we explore the ability of the ground-to-excited-state intersection ring exhibited by AA LR-TDDFT in protonated formaldimine to give rise to a similar topological phase in spite of its "defective" dimensionality. [3] Such an intersection ring can be recognized as tying together two supposedly different observations - that of sometimes, a linear seam of intersection [4] and other times, two interpenetrating cones. [5]

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Photochemical simulations: The simple and the strenuous

Leon Cigrang
University College London, United Kingdom

This talk will discuss different aspects of simulating photodissociation processes and emphasize which parts of the problem are difficult to get right and which parts are more straightforward. Within this context, results of Quantum Dynamical (QD) simulations (using the D-vMCG method [1]) of small organic molecules (relevant in the atmosphere as well as outer space) will be presented and discussed. It will be evident that once a successful QD calculation is run, a collection of analysis tools makes the determination of key properties simple (e.g. branching ratios, electronic state populations, time constants). On the other hand, the main bottlenecks of achieving successful simulations will be described (i.e. electronic structure methods and scaling). Some possible solutions to these bottlenecks will be suggested with an outlook to future/ongoing work within the group.

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Photochemistry of nitrophenol

Todd Martinez
Stanford University, United States

We discuss recent simulations of the photochemistry of *o*-nitrophenol, using multiple electronic structure methods. Comparisons to ultrafast electron diffraction data are provided. We find that the inclusion of dynamic electron correlation can change the ordering of the low-lying excited states and that a dark $n\pi^*$ state may exist below the optically bright $\pi\pi^*$ state.

Reactions of HOCl with ions in seawater

Robert Benny Gerber, I. Mandal, N. V. Karimova, I. Zakai
The Hebrew University of Jerusalem, Israel

Reactions between ions at water surfaces and incoming atmospheric molecules are of fundamental interest in the chemistry of seawater. Extensive experimental studies were reported, but so far microscopic understanding of the mechanisms is not available.

In this paper, we unravel the molecular level mechanism of the reaction of HOCl with anions such as Cl^- and I^- at the water surface region. Our approach is based on Ab Initio Molecular Dynamics (AIMD) simulations. In addition to exploring the nuclear motions, we also analyze the changes in the electronic states along the reaction pathways.

Results are presented for the halogen exchange reaction: $HOCl + I^- \rightarrow HOI + Cl^-$ and on the production of Cl_2 from HOCl and Cl^-. The main findings include:

1. Halogen-bonded complexes between HOCl and anions play a key role in the processes.
2. Water molecules participate chemically in the halogen exchange reaction. The water catalyzes the process.
3. Low pH greatly enhances Cl_2 formation.
4. Photochemistry of $(HOCl)\ldots(Cl^-)$ is predicted to take place at atmospheric conditions, due to organic photosensitizers such as 4BBA.

Shedding light on the atmospheric cycle of mercury through computational photochemistry

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Mercury (Hg) is a hazardous pollutant of global concern that is mainly released into the atmosphere in its gaseous elemental form Hg(0). The long atmospheric lifetime of this species allows for the long-range transport of this neurotoxin far away from its emission sources. Then, it can be deposited onto terrestrial and marine environments, a process that is enhanced following the oxidation of Hg(0) to divalent Hg(II) in the atmosphere. Thus, understanding the physical processes and redox mechanisms that govern the chemical cycling between Hg(0) and Hg(II) is crucial to evaluate the dispersion and accumulation of the metal in our planet.

Over the last few years, we have explored the impact of light-induced reactivity on the conversion between oxidized and reduced Hg species in the atmosphere. By means of computational photochemistry, we have studied the photochemical properties of major oxidized Hg compounds, assessing the impact of their photochemistry in the global cycling of this pollutant through atmospheric modelling simulations. In this contribution, we will give a brief overview of the main results obtained, starting with our current understanding of Hg photochemistry in the troposphere. Our studies have shown that Hg(I) and Hg(II) compounds can undergo fast gas-phase photolytic reduction in this atmospheric region, leading directly, or indirectly, to Hg(0) [1,2]. This process competes with the deposition of the pollutant, increasing in such manner the atmospheric mercury lifetime. Then, we will focus on Hg cycling in the stratosphere, an atmospheric region in which most aspects of Hg chemistry remain unknown. Taking that into account, we have proposed a novel chemical mechanism for Hg oxidation in this region initiated by photosensitized reactions, followed by second-step chlorine chemistry [3]. The results obtained indicate that stratospheric Hg oxidation is faster than what was initially thought, although it is moderated by light-induced reduction of the resulting oxidized Hg compounds. Finally, initial results concerning the absorption properties in aqueous solution of a selected group of mercuric bromides ($HgBr_2$, $HgBr_3^-$ and $HgBr_4^{2-}$) will be presented. These latest studies will allow deciphering their role in the observed Hg reemissions from the snowpack in the Arctic region, a process that is suggested to occur through light-induced reduction of the deposited oxidized Hg in the snow and subsequent reemission of Hg(0) [4].

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Simulating photo-dissociation using wavepacket dynamics

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Photodissociation is a key process in atmospheric chemistry. It is, however, a non-trivial process for accurate simulations if the molecule has more than 3-4 stoms. The reason for this is that in many systems of interest the manifold of excited-states involves non-adiabatic coupling, meaning that quantum dynamics (or at least semi-classical dynamics) are required to follow the state evolution which will involve crossings between the states. For accurate simulations, full quantum (wavepacket) dynamics are needed to model the nucelar coherence. However, calculating good potential energy surfaces and couplings is very hard. In this talk, an overview of the direct-dynamics variational multi-configurational Gaussian (DD-vMCG) method will be given, showing how it copes with many coupled bound and dissociative states, as found in many molecules of atmospheric importance [1,2].

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Simulating photochemistry on quantum computers

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The computational resources required for the most accurate dynamical calculations in photochemistry grow rapidly with the size of the system being simulated because of the difficulty of representing the full quantum-mechanical motion of electrons and nuclei. In this talk, I will explain the power of quantum computers to solve this problem, allowing chemical simulations that are exponentially faster than what is possible currently. I will argue that special features of photochemical problems make them especially suitable for quantum-computer treatment.

I will discuss my group's recent results on using analog quantum simulators to bring forward useful quantum computing for chemistry through an order-of-magnitude reduction in required quantum resources [1]. We have shown how to perform fully non-adiabatic simulations of chemical dynamics using trapped-ion quantum computers by exploiting the motion of the trapped ions to represent the motion of the nuclei. Our experimental demonstrations have led to the best quantum simulation of spectroscopy to date [2] and the first direct observation of geometric-phase interference in dynamics around a conical intersection in any system [3].

Our work indicates that chemistry on quantum computers will be fundamentally different from chemistry on conventional computers. For example, on quantum computers, full dynamics simulations will be easier than calculating single-point energies and simulating open quantum systems (such as reactions in solution) could be easier than simulating the same molecules in vacuum. This indicates a useful complementarity between problems best solved classically and those better left to quantum computers and bolsters the claim that chemistry—hopefully *photo*chemistry—will be the first real-world problem at which quantum computers outperform conventional ones.

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Spatial modulation spectroscopy of single optically-trapped aerosol particles

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Absorption of light by aerosol particles is of key importance in photochemical processes and for the assessment of their direct effect on radiative forcing, which remains very uncertain. However, it is intrinsically difficult to measure light absorption by aerosol particles as distinct from their light scattering, the other contribution to light extinction. This is the reason why quantitative absorption measurements on single aerosol particles are still missing. Here we are developing spatial modulation spectroscopy (SMS) further into a new spectroscopic tool for the precise quantitative determination of the light absorption by single optically-trapped aerosol particles as distinct from light scattering. Conventional SMS is a state-of-the-art technique for measuring the extinction of single particles supported by a substrate. The proposed technical developments extend SMS to aerosol particles isolated in air and to absorption measurements. This new experiment enables fast measurements in the UV or visible spectral range with the capability to retrieve quantitative data on the light absorption, scattering and extinction by trapped aerosol particles. The study of trapped aerosol particles allows to study aerosol processes such as their photochemistry over extended periods of time (several days if necessary) with a time resolution of a few seconds in a well-controlled environment (gas composition, relative humidity, temperature). Such time resolved measurements of particle absorption will help improve our understanding of the photochemistry of aerosol particles.

Valence photoelectron imaging of molecular oxybenzone

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Oxybenzone (OB, $C_{14}H_{12}O_3$) is a common UV filter in sunscreens [1], but poses environmental concerns particularly in marine ecosystems. Recent studies [2], [3] indicate that aqueous OB in the presence of 290–370 nm light activates a toxic metabolic pathway in sea organisms and is a cause of reef bleaching. While extensively studied in solution, its behavior in isolated or small cluster form remains less explored [4], [5] (and references therein). A detailed understanding of the properties of isolated OB in both its ground and excited electronic states is still missing and was the focus of this work.

We characterized the gas-phase OB molecule using mass spectrometry and angle-resolved photoelectron spectroscopy, employing both multiphoton and single ionization techniques (photon energies up to 35.7 eV, generated in a tabletop high harmonic source [6]). Vertical ionization energies, appearance energies, and energy-dependent anisotropy parameters were determined and compared with DFT calculations. Two-photon ionization with 4.7 eV light exhibited a higher appearance energy compared to extreme ultraviolet ionization, suggesting the population of an intermediate state in the multiphoton process. Mass spectra showed no significant differences in single-photon ionization between 17.2 and 35.7 eV. However, multiphoton ionization by 4.7 eV (2 photons) and 3.1 eV (3 photons) light was sensitive to both the laser intensity and ionization order. Two-photon ionization with 4.7 eV light was found to be the “softest” method and led to no measurable fragmentation up to an incident light intensity of $5\cdot10^{12}$ W/cm^2.

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Wavelength-dependent photodynamics of the atmospheric molecule CF3COCl

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Understanding the photodecomposition mechanism of transient volatile organic compounds and quantifying their photoproduct quantum yields is essential for modelling atmospheric processes such as ozone depletion or global warming. However, providing such information is often cumbersome and requires a combination of computational and experimental methods. In this contribution, we investigate the atmospherically relevant molecule CF_3COCl, which exhibits complex wavelength-dependent photochemistry governed not only by populating different electronic states but also by the amount of internal energy deposited in a single state. To reveal the mechanism behind the photon-energy dependence, we combine nonadiabatic *ab initio* molecular dynamics techniques with the velocity map imaging (VMI) experiment. We describe a consecutive mechanism of photodissociation where an immediate release of Cl in an excited electronic state is followed by a slower ground-state dissociation of the CO fragment. The CO release is subject to an activation barrier in the ground-electronic state and controlled by the excess internal energy injected in the molecule by the excitation wavelength. Therefore, a selective release of CO along with Cl can be achieved. The mechanism is fully supported by the measured kinetic energy distributions in the VMI experiment. Finally, we will comment on the influence of the electronic structure methods and nonadiabatic dynamics techniques for the simulation of dissociative photodynamics processes.

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4. Posters

A quantum dynamics study of tetraphenylpyrazine molecular crystals

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Photodynamic therapy (PDT) for cancer treatment is based on the interaction between photosensitizers, light, and molecular oxygen. Traditional photosensitizers face limitations in their aggregation state, lowering emission efficiency. To overcome this, Aggregation-induced emission luminogens (AIEgens), like tetraphenylpyrazine (TPP), have been introduced[1]. AIEgens increase their quantum yield when aggregated, improving PDT efficiency.

This study delves into the excited state quantum dynamics of the TPP molecule in gas phase. For this purpose, a Linear Vibronic Coupling (LVC) method was used to approximate the potential energy surfaces (PESs) and the nuclear dynamics was carried out using the ML-MCTDH method as provided by the QUANTICS package[2].This approach allowed to calculate the non-adiabatic dynamics for TPP across 144 vibrational normal modes. Future research aims to expand the system size to further elucidate mechanisms of aggregation-induced emission in AIEgens.

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Formation of chlorine in the atmosphere by the reaction of hypochlorous acid with seawater

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The highly reactive dihalogens and radicals play a significant role in the oxidative chemistry of the troposphere and stratosphere. One of the main reservoirs of these halogens in the atmosphere is hypohalous acids, HOX, which produce dihalogens in the presence of halides (Y^-), where X,Y=Cl, Br, I. These reactions occur in and on aerosol particles and seawater surfaces and have been studied experimentally and by field observations. Also, gas-phase (HOX)...(Y^-) complexes were explored spectroscopically by our collaborators [1]. However, the mechanisms for these atmospheric reactions are still unknown. Here, we establish the atomistic mechanism of $HOCl+Cl^- \rightarrow Cl_2+OH^-$ at the surface of the water slab by performing ab initio molecular dynamics (AIMD) simulations. Main findings are: 1) This reaction proceeds by halogen-bonded complexes of (HOCl)…$(Cl^-)_{aq}$ surrounded with the neighboring water molecules. 2) The halogen bonded (HOCl)…$(Cl^-)_{aq}$ complexes undergo charge transfer from Cl^- to OH^- to form transient Cl_2 at neutral pH. 3) The addition of a proton to one proximal water greatly facilitates the Cl_2 formation, which explains the enhanced rate at low pH. Relation of these reactions to halogen exchange process in water would be discussed also.

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Quantum computing applications for photochemistry

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Simulating chemical reactions that are beyond the capabilities of classical computers is expected to be one of the earliest applications of quantum computing and promises to revolutionize our understanding of many import chemical processes. However, the majority of research into chemical applications of quantum computing has been dedicated to solving problems in electronic structure with little attention given to the potential for quantum computers to solve problems in chemical dynamics. To that end, we have developed several quantum algorithms to simulate chemical dynamics with an eye toward simulating photodynamics. Our methods allow us to measure several quantities that are important for studying photodynamics including quantum yields and photolytic reaction rates. The photodynamics involved in atmospheric chemistry offer ideal early use cases of our methods because here the relevant molecules tend to be small, i.e., contain relatively few nuclei and electrons, and the interesting dynamics occurs on short timescales. Both of these facts mean that the quantum computing resources necessary to run simulations are kept low. Taken together, solving photodynamics problems in atmospheric chemistry could be one of the first applications in quantum computing to achieve a practical advantage over classical computing.

Revisiting sulfine and its athermal ground-state chemistry

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Thioformaldehyde s-oxide (sulfine) is a small organic molecule exhibiting surprisingly rich photochemistry. When excited by light with a wavelength of 254 nm, sulfine has been shown to form methylidyne-λ^4-sulfanol, which contains a carbon-sulfur triple bond. [1] Upon irradiation of sulfine at 313 nm, it can rearrange to the three-membered heterocycle oxathiirane, from which a plethora of photoproducts can be created. [2] In contrast to standard photochemistry, where photoproducts are formed in electronically excited states, the actual chemistry of sulfine has been shown to take place in a hot ground state. [3] Recently, sulfine has been reexamined experimentally, employing the state-of-the-art FERMI light source. As the pump pulse was centered around 266 nm, the experiment predominantly excited into the second excited state of sulfine. The involvement of this bright pipi* state calls for revisiting the nonadiabatic dynamics of sulfine from a theoretical point of view. In this work, we meet this calling by characterizing the deexcitation pathway of sulfine and performing nonadiabatic molecular dynamics simulations to calculate the experimental observables.

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Triggering non-adiabatic dynamics in PAHs: Using coronene as model

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Polycyclic aromatic hydrocarbons (PAHs) are crucial for the understanding of atmospheric photochemistry due to their involvement in several processes. These compounds undergo photochemical reactions in the atmosphere, influencing environmental dynamics. Additionally, PAHs play a role in parallel transformations within atmospheric chemistry and toxicology, showcasing their impact on environmental and human health. They are ubiquitous atmospheric pollutants with toxic properties, emphasizing the importance of studying their chemistry and behavior in the environment.

This work [1] is focused on coronene, the smallest unit of a graphene nanoflake and the smallest PAHs with benzene symmetry. Several studies have found that coronene shows fluorescence and phosphorescence in the visible range of the light spectrum. As a starting point, the excited state deactivation pathways of a single unit of coronene are unraveled using the ML-MCTDH method and approximating the electronic Hamiltonian using a linear vibronic coupling model, including singlet and triplet states.

Moreover, this study has been extended to circumcoronene in the direction towards graphene, where promising results have been found.

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