FUNDACJA ALEKSANDRA JABŁOŃSKIEGO

NICOLAUS COPERNICUS UNIVERSITY IN TORUŃ

cost EUROPEAN COOPERATION IN SCIENCE & TECHNOLOGY

COSY COST ACTION

FUNDAMENTAL INSIGHTS TO WEAK INTERACTIONS:

interplay of theory and spectroscopic experiments.

CONFINED ASTROCHEMICAL MICROENVIRONMENTS:

infrom gas to ice, dust and planetary soils.

Training School

Uniwersytet Wrocławski

Book of Abstracts

NICOLAUS COPERNICUS UNIVERSITY IN TORUŃ
FUNDACJA ALEKSANDRA JABŁOŃSKIEGO
UCZELNIA BADAWCZA INICJATYWA DOSKONAŁOŚCI
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Welcome!

COST COSY Training School "Fundamental Insights to Weak Interactions: Interplay of Theory and Spectroscopic Experiments"

Training school focuses on the analysis of intermolecular interactions in the wide range of molecular systems of astrochemical, biochemical or material science interest. The aim is to provide expert knowledge on modern theoretical tools and/or analysis of weak interactions from the experimental point of view.

The multidisciplinary program aims to provide participants with a structured introduction to the fundamentals and advanced aspects of theoretical, computational, and experimental approaches allowing for the detailed analysis and understanding of weak inter- and intra-molecular interactions. Covered topics will range from introductory to advanced, supplemented by hands-on tutorials, exercises, and computer simulations to encourage active learning and skill development.

The 2026 edition will focus on the evolution of spectral signatures of prebiotic molecules: from gas phase to confined astrochemical environments such as interstellar ices, grains, and planetary soils, by gradually increasing the size and complexity of studied molecular systems.

Highlights of the program:

- Fundamental aspects of weak interactions
- Analysis of weak interactions by means of symmetry-adapted perturbation theory (SAPT)
- Modeling of multi-dimensional potential energy surfaces (PES)
- Modern laser spectroscopy
- Analysis of fingerprints of weak interactions in the experimental Microwave and Infrared spectra
- Anharmonic effects in structures and spectroscopic properties by Vibrational Perturbation approaches (VPT2)

Program

Sunday, 14 June 2026

15:00 – Arrivals and hotel “Stary Tartak” check-in

Monday, 15 June 2026

09:00-09:15 – School Opening and Registration

9:15-11:00 – Fundamental aspects of weak interactions: introduction and recent advances – Lecture

Dr. Agnieszka Krzemińska

11:00-11:30 – Analysis of weak interactions by means of symmetry-adapted perturbation theory (SAPT) Lecture + Hands-on session 1

Prof. Piotr Żuchowski, Dr. Łukasz Rajchel

11:30-12:00 – Coffee break

12:00-13:30 – Analysis of weak interactions by means of symmetry-adapted perturbation theory (SAPT) Lecture + Hands-on session 2

Prof. Piotr Żuchowski, Dr. Łukasz Rajchel

13:30 -15:00 Lunch

15:00-15:45 – Analysis of weak interactions by means of symmetry-adapted perturbation theory (SAPT) Lecture + Hands-on session 3

Prof. Piotr Żuchowski, Dr. Łukasz Rajchel

15:45-16:30 – Modeling of multi-dimensional potential energy surfaces (PES) - Lecture

Dr. Dariusz Kędziera

16:30-17:00 – Coffee break

17:00-18:00 – Tails - Lecture

Prof. Konrad Patkowski

18:00-19.00 – Flash poster presentations

20:00 – Grill dinner

Tuesday, 16 June 2026

9:00-10:15 Weak interactions? Let's talk about He – Lecture

Dr. Tomás Gonzalez-Lezana

10:15-11.30 - Modern Laser Spectroscopy - Lecture

Prof. Lauri Halonen

11:30-12:00 – Coffee break

12:00-13:30 – The experimental Infrared spectra and fingerprints of weak interactions -Lecture

Dr. Justyna Krupa

13:30 -15:00 Lunch

15:00-16:00 - Anharmonic effects for structures and spectroscopy by Vibrational Perturbation approaches (VPT2) – from isolated molecules to weakly bonded systems – Lecture

Prof. Małgorzata Biczysko

16:00-16:30 – Spectroscopic fingerprints in astrochemistry, from isolated molecules to astrochemical ices and weak interactions – Hands on session 1

Dr. Silvia Alessandrini

16:30-17:00 – Coffee break

17:00-18:00 – Spectroscopic fingerprints in astrochemistry, from isolated molecules to astrochemical ices and weak interactions – Hands on session 2

Prof. Małgorzata Biczysko, Dr. Silvia Alessandrini

18:00-18:30 - Award for best flash presentation and Closing remarks

Wednesday, 17 June 2026

9:00- Departures

** The schedule is subject to change. For updates, please check the official conference website or contact the organizers.*

Lectures

&

Hands-on sessions

Fundamental Aspects of Weak Interactions: introduction and recent advances

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Weak inter- and intramolecular interactions are fundamental determinants of chemical structure, reactivity, and functionality across molecular, biological, and astrochemical systems. Although individually subtle, their collective effects, ranging from small molecular complexes through cooperative assemblies to nanoscale networks, govern phenomena such as molecular recognition, protein folding, supramolecular organization, and the formation of complex organic molecules in the interstellar medium (ISM). Accurate quantum-mechanical characterization of these interactions remains challenging because their interaction energies are extremely small compared with the total energies of the constituent monomers and dimers, requiring a delicate and highly balanced treatment of electrostatics, exchange, induction, dispersion, or even charge-transfer effects. Alongside supermolecular and Energy Decomposition Analysis (EDA) approaches, recent advances in Symmetry-Adapted Perturbation Theory (SAPT), including correlated and multiconfigurational variants, have enabled rigorous, physically transparent, and BSSE-free decomposition of interaction energies with near coupled-cluster accuracy [1]. These developments have opened new avenues for elucidating the microscopic mechanisms underlying molecular recognition, van der Waals cluster formation, and chemical evolution in the ISM.

Parallel to rigorous quantitative studies of non-covalent interactions (NCIs), there is a growing need for their spatial interpretation in three-dimensional molecular space [2]. A variety of visualization approaches have been developed for this purpose, including density-based methods such as electrostatic potential mapping, NCIPlots, deformation density analysis, and IGM/IGMH frameworks, as well as energy decomposition approaches based on SAPT. Each of these methods offers distinct advantages and limitations in describing the nature and spatial distribution of intermolecular interactions. Together, they provide complementary perspectives that contribute to a broader understanding of NCIs in molecular, supramolecular, and biomolecular systems.

1. Hapka, M., Patkowski, K., 2026, Symmetry-adapted perturbation theory, Handbook of Electronic Structure Theory, 245-262.
2. Lu, T., 2025. Visualization Analysis of Covalent and Noncovalent Interactions in Real Space. Angew. Chem. Int. Ed. 64, e202504895.

Analysis of Weak Interactions by Means of Symmetry-Adapted Perturbation Theory

Piotr Żuchowski[1] (pzuch@fizyka.umk.pl) and Łukasz Rajchel[2] (lrajchel@ukw.edu.pl)
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[2]*Faculty of Physics, Kazimierz Wielki University, Bydgoszcz, Poland*

The hands-on session introduces trainees to the quantum-mechanical description of non-covalent interactions (NCIs), a demanding field where results are very sensitive to computational details and depend heavily on systematic error cancellation.

In the first part, we will compute interaction energies using supermolecular approach with the Hartree–Fock (HF) method and second-order Møller–Plesset perturbation theory (MP2), for simple noble gas dimer (He–Ne), noble gas-ion (He–Li^+), noble gas-water (Ar–H_2O) and water dimer, demonstrating sensitivity to various computational thresholds and basis sets. We will introduce practical remedies for the notorious basis set superposition error (BSSE).

Next, we will compute simple potential energy surfaces (PESs), for diatomic system (He_2) and atom-diatom (Ar–HF) introducing Jacobi coordinates.

The main part will focus on physical insight into results obtained so far. To this end, we will use symmetry-adapted perturbation theory (SAPT),[1,2] an established method for interaction energy decomposition into meaningful terms (electrostatic, induction and dispersion, together with their exchange counterparts). We will examine how these individual terms and total interaction energy depend on basis set. We will also introduce a neat method to visualize their respective contributions using ternary diagrams.

Finally, we will examine the flagship quantum chemistry method, density functional theory (DFT), in the context of NCIs, highlighting its common pitfalls and illustrating how corrections can be applied effectively using proper insights from quantum NCIs theory.

All computations will be performed with the Psi4 computational chemistry package.[3]

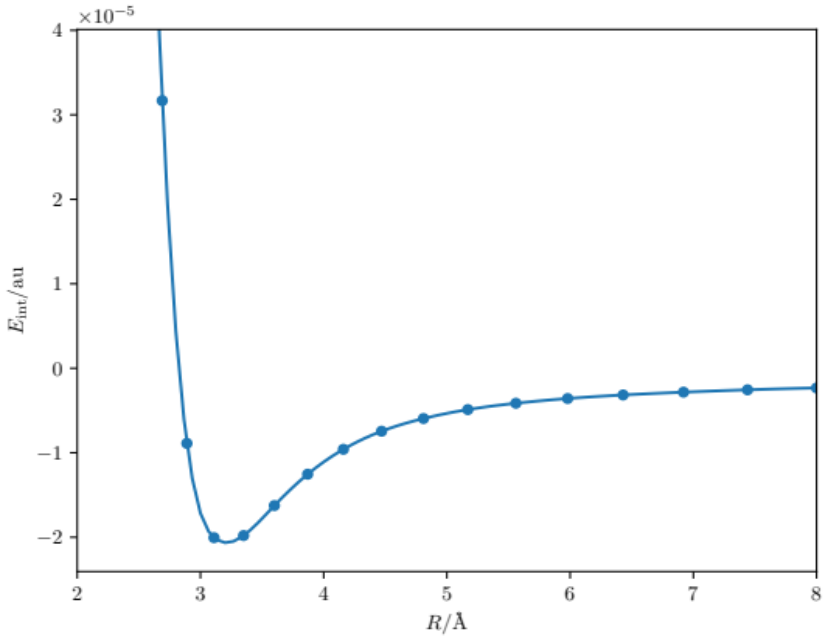

Figure 1:

Approximate He_2 interaction energy curve.

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Modelling of multi-dimensional potential energy surfaces (PES)

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Intermolecular potential energy surfaces (PESs) are essential for the theoretical description of weakly bound molecular complexes. In astrochemical applications, they provide the link between molecular-level interactions and quantities needed to interpret observations, such as collisional data used in non-LTE modelling. This provides the motivation for constructing accurate PESs, but the main focus of the lecture will be methodological: how multi-dimensional PESs are modelled in practice and how their reliability can be assessed.

Constructing reliable PESs is computationally demanding. Even within the rigid-monomer approximation, the dimensionality of the problem increases rapidly with the rotational degrees of freedom of the interacting partners. As a result, brute-force direct-product grids become impractical for many molecular systems, and efficient strategies are needed to reduce both the number of required ab initio points and the computational cost per point.

This lecture will discuss the practical modelling of multi-dimensional intermolecular PESs, with emphasis on SAPT(DFT)-based interaction energies and automated PES construction using the autoPES software package[1,2]. SAPT(DFT) will be presented as a physically motivated and computationally efficient method for describing intermolecular interactions, while autoPES will serve as an example of a workflow that combines electronic-structure calculations, physically guided sampling, analytic fitting, and long-range treatment based on molecular properties such as multipole moments and polarizabilities.

The main part of the lecture will describe the PES construction workflow from the user's perspective: preparation of monomer geometries, choice of electronic-structure method and basis set, definition of the analytic functional form, iterative generation of grid points, fitting of the surface, and assessment of the quality of the resulting representation. Practical fitting decisions, including the use of off-atomic sites and the analysis of different energy regions, will also be discussed. Selected applications will be used only as illustrative examples of typical choices, difficulties, and validation steps encountered in real calculations.

A major emphasis will be placed on validation. A small RMSE value is not sufficient to prove that a PES is physically reliable. The surface must also be checked through stationary points, selected one-dimensional cuts, asymptotic behaviour, and possible artefacts in the repulsive wall. In particular, I will discuss nonphysical "holes" in fitted potentials, their origin, and practical strategies for removing them

by targeted addition of ab initio points and refinement of the fit.

The aim of the lecture is to show that modelling multi-dimensional PESs requires more than automated fitting. Reliable surfaces require electronic-structure theory, physical intuition, numerical modelling, and systematic validation. Participants should leave with a clear understanding of the main steps and practical pitfalls involved in going from ab initio interaction energies to a usable analytic potential.

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Tails

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In computational chemistry, one often wants to find a simplified but sensible representation of some quantity. This could be, for example, a basis set representation for molecular orbitals, a model potential representing some physical interaction in a force field, or an analytical function approximating the potential energy surface for a molecule or an intermolecular complex. As we develop such simplified representations, we care about reproducing accurately the reference data, for example those from high-level calculations. However, we also don't want to mess up the performance of our representation away from the reference data, including its limiting behavior for very small or very large values of the distance/energy/... scale. This is where the *tails* come into play.

In this workshop, we will use simple Psi4 calculations and data visualization to interactively explore some of the questions related to the short- and long-range behavior of stuff. We will be covering some of the topics from this list:

1. Slater versus Gaussian basis functions: why do we prefer the latter?
2. Short-range correlation cusp and the explicitly correlated F12 theory: Do the commonly used F12 algorithms, with the Slater correlation factor expanded in Gaussians, reproduce the cusp? Does F12 improve basis set convergence?
3. Long-range interaction energy on the example of two rare gas atoms: How do long-range results depend on the cardinality of the basis set? Does F12 (a method designed to fix the short range) improve the long range? Does the addition of midbond functions improve the large-R results? Does it improve the asymptotic constant?
4. Density tails and their role in intermolecular interactions: How do electron densities and their overlap decay at large R? How does the basis set influence this decay? How does density overlap relate to first-order exchange energy? What is charge penetration and why should we care?

Weak Interactions? Let's talk about He

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Helium is usually seen as a paradigm for weak interactions. Superfluidity behavior of helium nanodroplets is currently used in spectroscopy given their capability as an ultracold environment where embedded species can move almost freely. We will review the current understanding of solvation in this quantum medium [1-4] and practical exercises to visualize and distinguish well ordered geometrical structures formed by He atoms surrounding atomic ions will be proposed.

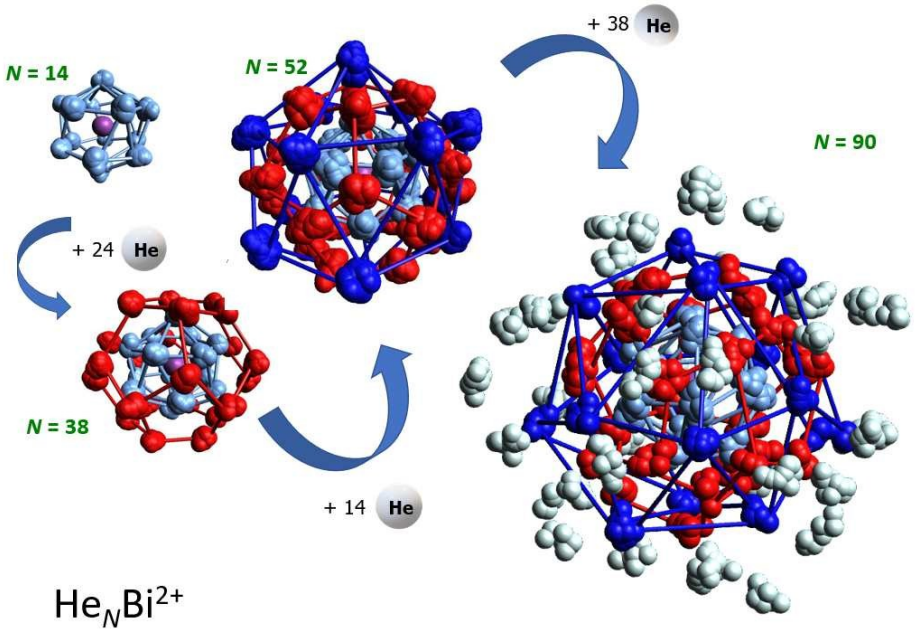

Figure 1. Mozartkugel-like structure observed for solvation shells of He around Bi^{2+}

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Modern Laser Spectroscopy

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Laser spectroscopy has become an important tool in many applications, which include, for example, analytical, atmospheric, and interstellar chemistry. Consequently, it is natural that this field develops all the time, i.e., new laser spectroscopic experiments constantly appear. This presentation starts with a short review of laser properties. These include laser beam divergence, monochromaticity, brightness, and coherence. Frequency tuning, mode locking, and harmonic generation are also discussed. Appropriate examples of lasers and laser type devices would be helium-neon laser, diode laser, titanium-sapphire ring laser, optical parametric oscillators, and optical frequency combs.

The most natural starting point for spectroscopic experiments is an ordinary laser absorption experiment with its weaknesses and improvements. Unlike in standard absorption, photoacoustic and cavity ring-down experiments provide methods where strong undesirable signals are not masking the signal of interest. The first of these methods is applied to unstable and radioactive species[1-4] and the second one to human breath samples.[5] The development of the high repetition rate cavity ring-down method provides speeds which will be useful in dynamics studies.[6]

Fluorescence in electronic spectroscopy is a commonly used sensitive method that is widely employed particularly in chemical kinetics and dynamics. The much less usual and somewhat demanding vibrational fluorescence is discussed to observe states that are forbidden by one-photon absorption from the ground state.[7] The famous stimulated emission pumping is shown to work in the infrared region.[8]

Cold temperatures obtained with molecular jets make congested spectra, for example, of hydrocarbons simple[9] and make it feasible to observe new molecular complexes.[10] Collisional cooling is another method to obtain reduced temperatures as is seen in observing a fully resolved rotational structure in the infrared spectrum of the largest molecule so far.[11]

Optical frequency combs provide rulers to fix frequency scales for observed transitions. They are also excellent light sources for spectroscopy. Dual comb spectrometers can give large time and frequency resolution which, in addition, allow to record spectra over large frequency ranges.[12] Recent spectra of some small molecules will be presented.

Raman spectroscopy has become an important tool particularly in material science and medical applications due to higher order effects such as stimulated Raman effect[13] and the use of Raman spectroscopy with microscopy. Unlike in infrared spectroscopy, samples containing water can be investigated easily. These aspects will be discussed.

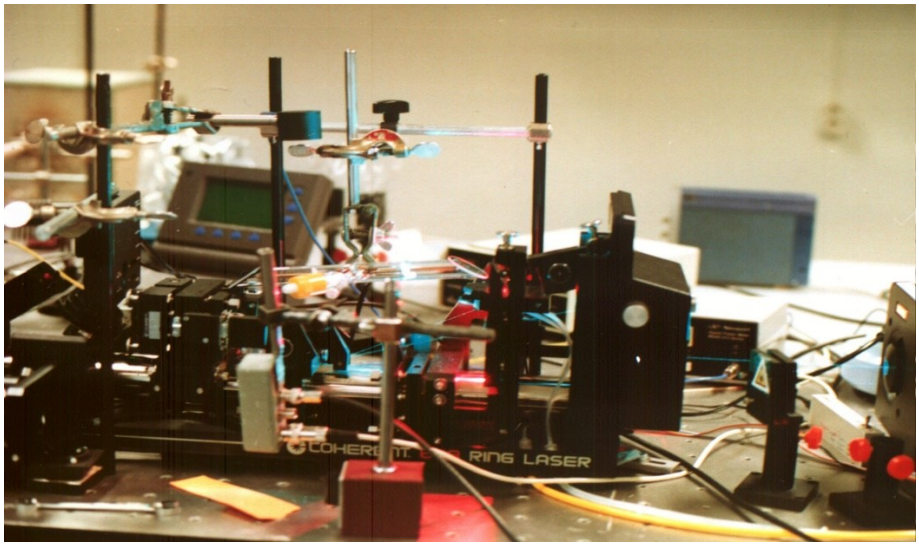

Figure 1. Intracavity photoacoustic experiment with a titanium-sapphire ring laser.

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Matrix Isolation FTIR Spectroscopy as a Tool to Investigate Weak Intermolecular Interactions and Photochemical Reactivity

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Matrix isolation technique (MI) involves the rapid condensation of a mixture of studied molecules and an excess of an inert gas at low temperature to form a rigid solid matrix. The method was originally developed for the study of unstable species. Since then, its value for studying the structural and photochemical properties of stable molecules and molecular complexes has been demonstrated. Matrix isolation is joined very often with FTIR spectroscopy. The recent development of the laser techniques allowed for a combination of the MI-FTIR with in situ narrow band irradiation of matrices using either UV/visible or NIR ranges.

The equipment necessary to obtain matrices using this technique will be discussed. As well as the main difficulties that may be encountered when using this method will be presented.

Here, several examples of matrix isolation studies performed in our group will be also shown. They include both conformational and photochemical studies of various types of organic molecules as well as studies of molecular complexes formed between species of atmospheric or interstellar relevance. Analysis of all presented results was supported by extensive quantum chemical calculations.

First, the structures of HNCO dimers[1] and HNCS-SO_2 complexes[2] of the important interstellar /atmospheric species will be discussed based on both MI-FTIR experiments and calculations to check which interaction: hydrogen bonding or van der Waals is the most important binding force in these systems. Next, it is shown that weak molecular complexes can also be formed upon UV irradiation due to the reaction of the H_2O_2 photolysis products with the nitrogen matrix[3].

In the second part of the presentation, UV- and NIR-induced photochemical studies will be discussed. Five examples of UV-induced photochemical reactions of larger organic molecules will be shown: isoeugenol (IE–IZ), safrole (SF), 3-amino-1,2,4-triazole (AT), 3-mercapto-1,2,4-triazole with N_2 (ST), and anisole (AN). In the first four cases, several different transformations are observed upon UV irradiation, including *trans–cis* isomerization in isoeugenol[4], photo-rotamerization of the *allyl* group in safrole[5], and tautomerization in triazole derivatives[6,7]. The last compound, anisole[8], serves as a simple example of how photochemical decomposition reactions can be monitored in matrices using a selective UV radiation source.

For NIR-induced phototransformations, two examples will be presented: structural changes in glycolic acid[9] conformers, and OH photo-rotamerization in indazole-3-carboxylic acid (HIC)[10].

The research was supported by the National Science Centre Project no. 2013/11/B/ST4/00500 and project no.2025/56/Q/ST4/00207 (SHENG 4 call), as well as the Academy of Finland, grant number 332023. Allocation of computer time from the Wrocław Centre for Networking and Supercomputing (Wrocław, Poland) is gratefully acknowledged. The support of the COST Action CA21101 (COSY) is highly appreciated.

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Anharmonic effects for structures and spectroscopy by Vibrational Perturbation approaches (VPT2) – from isolated molecules to weakly bonded systems

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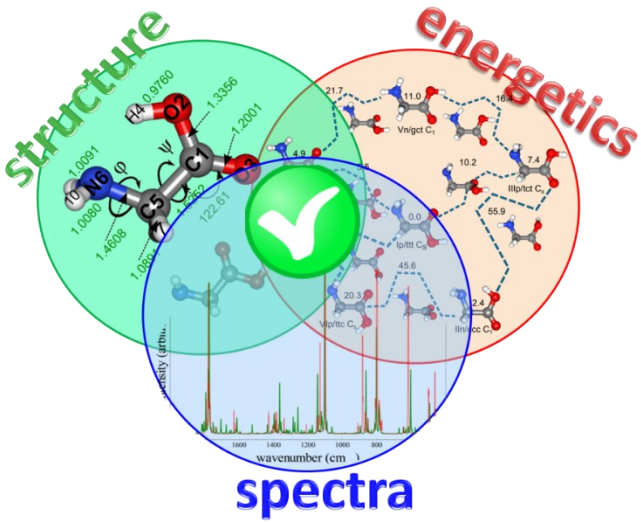
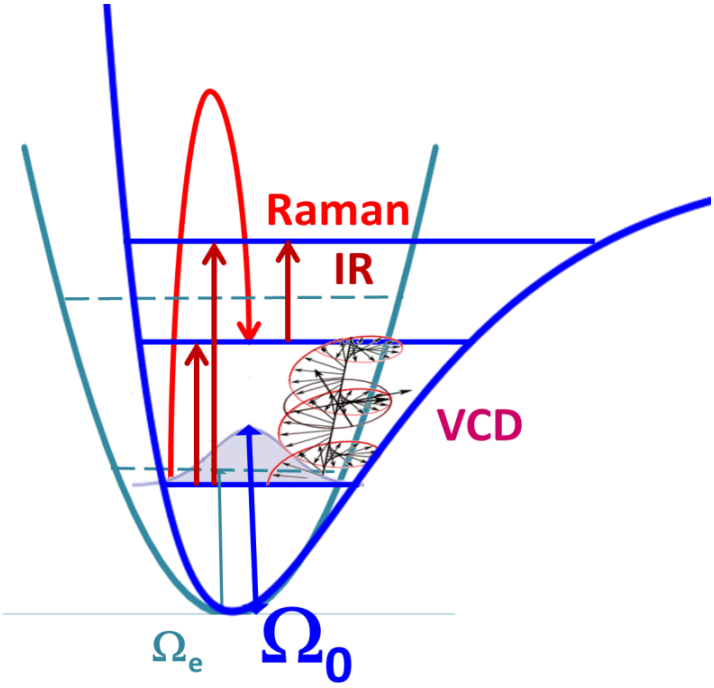
Analysis of the experimental spectroscopic data for molecular systems of increasing size and complexity can be strongly facilitated by the direct comparison with realistic spectra line-shapes, simulated taking fully into account the information connected to both position and shape of spectral bands. The information required for predicting and/or analyzing spectra starts from (i) accurate equilibrium molecular structures, (ii) accurate free energies of different conformers for specific experimental conditions, (iii) accurate rotational and vibrational parameters to predict the corresponding spectra for all conformers and isotopologues possibly present in the experimental mixture. Since the molecules are never "frozen" to obtain data directly corresponding to experimental observables requires to include vibrational effects, at best at anharmonic level. Indeed, harmonic approximation assumes fully symmetric potential energy surface (PES), while in reality it is not – bonds are broken at larger distances and at closer distances strong repulsion prevents atoms collapsing. From the computational perspective harmonic approximation is simpler, but for instance it will predict that structure and properties are the same as the equilibrium ((Ω_e - it would be simple!), while in reality their correspond to the vibrationally average structure (Ω_0).



For quantitative structural and spectroscopic characterizations, the basic requirements are spectroscopic parameters/energy levels and corresponding intensities. In the field of vibrational spectroscopy the former, vibrational wavenumbers are univocally defined, but the definition of the latter depends on the technique considered (infrared (IR), vibrational circular dichroism, Raman). These data, along with the

thermodynamic properties, allow to simulate vibrational spectra of single molecules or mixtures of several species or conformers, which can be directly compared with experimental counterparts.



Till now vibrational effects for all but the smallest molecules are still mainly performed within the double harmonic approximation, possibly employing simple or more sophisticated scaling factors to improve the agreement with anharmonic fundamental transitions. These approaches are often not satisfactory, and in order to fulfil the accuracy (for wavenumbers) and interpretability (for intensities) requirements, it is mandatory to go beyond the double-harmonic approximation. Indeed, only computations which take into account anharmonic effects on the transition moments provide information about the intensities of overtones and combination bands, which might be necessary to correctly analyze experimental outcomes. Suitable examples are spectral ranges where only non-fundamental transitions are present, either in mid-IR range or in the near-infrared (NIR) region, and experimental mixtures where low-intensity features related to non-fundamental transitions of the most populated species and fundamental transitions of the less abundant ones are concomitantly present.

The lecture will discuss underlying theoretical background and examples of fully anharmonic computations of vibrational effects on structures and properties, in particular on IR spectra line-shapes, including overtones and combination bands, through second order perturbation theory, based on a normal mode representation and a polynomial approximation of the potential energy surface (PES, to the fourth order) and property surface (PS, to the third order). The vibrational corrections to molecular properties or thermodynamic functions are then obtained from the same anharmonic force fields as employed in the determination of vibrational properties. These data are used to simulate IR spectra for medium-sized isolated molecules and complex molecular mixtures relevant for simulation of interstellar ice environments which usually depend on the synergistic combination of specific and nonspecific interactions, including the inter- and intramolecular hydrogen bonding and van der Walls/dispersion. Spectroscopic experiments allow analyzing in detail specific interactions in isolated molecular systems, as well as gradually including the perturbations due to the environment, for example by micro-solvation.

But, accurate computations of the spectroscopic properties for molecular systems governed by week interactions pose further challenges related to the accurate description of the underlying potential energy surfaces and the treatment of nuclear motion. I will discuss the status and perspective of the project based on the second-order perturbation theory (VPT2) in conjunction with PES description by QM methods ranging from density functional theory (DFT) to coupled-cluster (CC). Problems related to the description of large-amplitude motion (LAM) will be in a first approximation treated by ad hoc reduced dimensionality models. This allow for the improved treatment of weak interactions and accounting for the anharmonicity of both wave function and properties, resulting in a correct description of the intensity of non-fundamental transitions and more accurate band-shapes. The accuracy of such obtained results will be tested against the available experimental data for systems of increasing size and complexity.

Acknowledgements

This work has been supported by the National Science Centre under the SHENG 4 call, project no.2025/56/Q/ST4/00207 and the COSY COST Action CA21101 "COSY - Confined molecular systems: from a new generation of materials to the stars". Computations have been performed at the Wroclaw Centre for Supercomputing (wcss.pl).

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Spectroscopic fingerprints in astrochemistry, from isolated molecules to astrochemical ices and weak interactions – Hands on session

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Intermolecular interactions between two or more molecules can lead to the formation of different conformers stabilized by distinct non-covalent interactions.

Computationally, one can explore these different conformations and characterize them in order to establish their relative stability, identify the dominant intermolecular interaction, and derive accurate spectroscopic parameters. These computational findings have to be validated against experimental data and the experimental reference for gas-phase environments is rotational spectroscopy.[1]

In fact, rotational spectroscopy provides fingerprints of molecules in the gas-phase, allowing discrimination among them. The technique is so sensitive that one can distinguish between isotopically-substituted species of the same molecule. This sensitivity arises because the rotational spectrum is determined by the rotational constants, that in turn are obtained from the analysis of rotational transitions measured in the laboratory and are inversely related to the molecular moments of inertia. Since different conformers are often characterized by rotational constants that differ by only a few percent, their analysis requires a combined approach based on theoretical predictions and laboratory measurements.

This practical session aims to provide an overview of the interplay between quantum chemistry and rotational spectroscopy and how this interplay can be employed to analyze the impact of non-covalent interactions on molecular structures. In this context, we will briefly highlight the relevance of this interplay in astrochemical environments.

The first part of the session will focus on the interplay of theory and experiment. I will provide you with computed spectroscopic parameters for two conformers of the OCS-H_2O complex and using these values you will analyze a portion of the rotational spectrum of the complex. In this manner, you will derive the experimental rotational constants of the complex and determine which of the proposed conformers is observed experimentally.

In the second part of this handout, you will focus on the derivation of the vibrationally averaged structure for the OCS-H_2O complex. Vibrationally averaged structures correspond to the vibrational ground state level. They can be obtained directly from a least-squares fit of experimentally determined rotational constants. The least-squares fit will combine the rotational constants derived during this exercise (main

isotopic species) with literature data for several isotopologues, which will be provided in the input file. To analyze the effect of non-covalent bonding on the structure, I will also provide the vibrationally averaged structures of the isolated OCS and H_2O molecules together with the complete input file for the structural fit.

To carry out this practical session you will need two programs that are available for all the different operating systems (Windows, Linux, and MacOS). The first program is called PGOPHER[2] and will be used to analyze the rotational spectrum of the complex. The second one is STRFIT from Kisiel[3] and it will be used to derive a vibrationally averaged structure of the complex. PGOPHER can be downloaded from: https://pgopher.chm.bris.ac.uk/, while STRFIT from this other webpage: http://info.ifpan.edu.pl/~kisiel/struct/struct.htm#strfit

By the end of this practical session, you will have performed a spectroscopic analysis, from conformer identification to the determination of the vibrationally-averaged molecular structure of the complex.

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"Flash" presentations

Characterising the Influence of Non-Covalent Interactions on Reactivity: Application to the Reaction of Acetic Acid Aggregates with Methylamine

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Non-covalent interactions locally modify the electron density of the species. This redistribution of electron density can affect, either directly or indirectly, the reactivity of the species [1]. The use of electron density as a quantitative descriptor of this modification is therefore relevant. Thus, the Quantum Theory of Atoms in Molecules (QTAIM) allows these modifications in electron density to be quantified and the weakening of a bond to be assessed from the topological analysis of the electron density. Furthermore, the Electron Localisation Function (ELF) makes it possible to determine the formation and disappearance of electron-density basins [2]. With these tools, we aim to investigate the reaction leading to the formation of a peptide bond between acetic acid and methylamine, and to assess the influence of non-covalent interactions between the molecules involved in this reaction.

From an experimental perspective, aggregates of acetic acid are formed in a molecular beam, then ionised by VUV photons on the DESIRS beamline of the SOLEIL synchrotron. Under these conditions, protonated acetic acid aggregates are produced. The CERISES [3] set-up then enables these aggregates to be identified and mass-selected in a quadrupole. Methylamine is subsequently introduced into an octopole, and the reaction products are analysed using a second quadrupole.

The complementarity between experiment and theory enables the reaction products to be identified and the influence of aggregate size on reactivity to be understood in terms of perturbations of the local electron density within the aggregates.

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Surveying the ground electronic state potential energy surface of the 'mysterious' CO dimer

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Eleven feasible stationary points have been located on the potential energy surface of the ground electronic state of $(CO)_2$ with shapes H, I, T, V, X, and Z. The global minimum has a planar, slipped, antiparallel arrangement of the atoms with CC contact. There is a secondary minimum with OO contact. The first-order transition state connecting the two minima has CO contact. The remaining feasible stationary points are higher-order transition states. At intermediate levels of electronic structure theory, one can easily become lost in the web of polytopism. [1] The relative energies of the most important stationary points were determined with the help of the focal-point analysis scheme. The relative energies are based on calculations up to the CCSDT(Q) level of electronic structure theory, basis sets up to aug-cc-pV6Z, and the inclusion of so-called 'small' corrections due to core-core and core-valence correlation, relativistic effects, and the diagonal Born–Oppenheimer correction. [2] The electronic interaction energy of the global minimum is $-(hc)136.8(15)$ cm^{-1}, while the electronic energy difference between the global and local minima is $(hc)17.1(25)$ cm^{-1}. A detailed interaction energy analysis via symmetry-adapted perturbation theory suggests that the bonding in the dimer arises primarily from dispersion rather than electrostatics. [3]

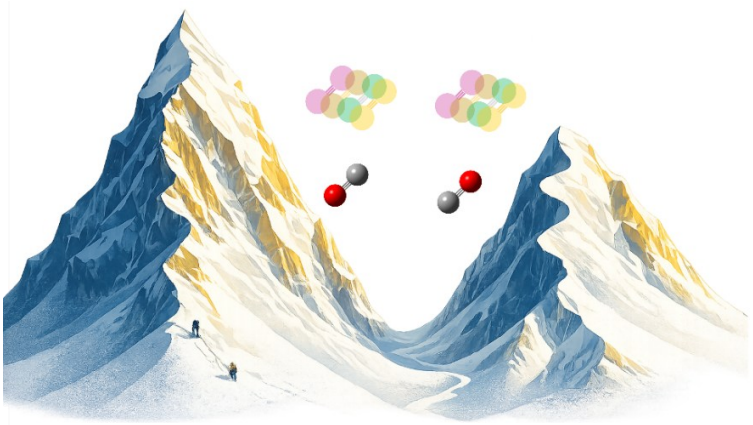

Figure 1. Two rugged mountains illustrate the complexity of the potential energy surface (PES) of the CO dimer, where locating the global minimum is akin to finding a hidden basin. Above it, aurora-like features depict the symmetry-adapted perturbation theory (SAPT) energy decomposition.

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What is the nature of inter-radical interactions in K_2TCNE_2 dimer?

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Tetracyanoethylene ($TCNE^-$) radicals together with counterions (e. g. K^+) can form dimers (see Fig. 1) interacting by a mixture of covalent and van der Waals interactions.[1] These interactions keep the monomers at an equilibrium distance of 2.735 Å, which is larger than the longest covalent bond observed, but shorter than the sum of van der Waals radii.[1] The goal of this study is to describe this two-electron, four-center bond-like interaction using different multireference computational approaches accounting for dynamic correlation. These approaches are quantum Monte Carlo[2] and complete active space adiabatic connection method with short-range density functional correction.[3]

Resulting interaction energies at equilibrium distance align with the experimental values.[4,5] Moreover, a comparison between methods that account for dynamic electron correlation and those that do not provides insight into the nature of this unusual bond.

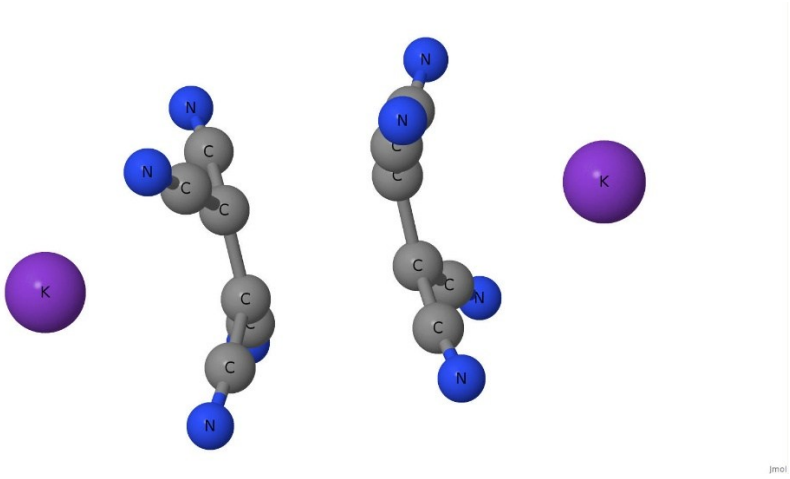

Figure 1. K_2TCNE_2 *dimer at equilibrium distance between monomers.*

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Molecule-surface interactions and the role of dispersion correlation in the adsorption of polycyclic aromatic hydrocarbons on the epsomite [010] surface

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Epsomite ($MgSO_4 \cdot 7H_2O$) is a hydrated magnesium sulphate of astrobiological interest, as Mg-rich sulphate deposits explored by the Mars2020 Perseverance mission at Jezero crater represent targets for preservation and detectability of molecular biosignatures[1]. In this work, a slab model of the [010] epsomite surface has been worked out by means of periodic Density Functional Theory (DFT) calculations using the CRYSTAL software[2]. The model surface has been subsequently applied to study the adsorption mechanism of hydroxylated polycyclic aromatic hydrocarbons (PAHs) of interest in the context of the Perseverance rover measurements performed within the Mars 2020 mission[3]. Adsorption has been simulated by considering configurations driven by either interaction with under-coordinated Mg^{2+} cations or hydrogen bonding (HB) involving exposed water molecules or sulfate groups. Different orientations of the PAHs have been considered, according to the electrostatic features of the interacting moieties. Efforts have been devoted to understanding the character of the Mg-O bond and to elucidate the role of dispersion forces in driving the adsorption process and their interplay with more directional H-bond interactions. Electron density difference and charge displacement[4] analyses have revealed that the Mg-O interaction exhibits a closed-shell character, as also confirmed by a topological Bader analysis[5]. Molecule-surface interactions involving Mg^{2+} coordination with molecular oxygen atoms appear to be energetically favoured when dispersion is included. Dispersion interactions significantly affect the adsorption mechanism and their role has been estimated by considering the adsorption behaviour of molecules of 1,3-dihydroxynaphthalene and naphthalene as case studies. For 1,3-dihydroxynaphthalene, the average molecule-surface HB energy, estimated from local electronic kinetic energy density, has been found to be inversely correlated with the relative amount of dispersions to the interaction energy, highlighting the competitive interplay between these contributions.

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Hydrogen Motion, Anharmonicity and Structural Dynamics in Barium Hydride: A Neutron Spectroscopic Study

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Barium hydride, BaH_2, is a remarkable high-temperature hydride-ion conductor and a well-defined inorganic system in which the motion of a light hydride sublattice can be studied within a much heavier barium framework. It undergoes a reversible high-temperature transition from the orthorhombic *Pnma* phase to the hexagonal $P6_3/mmc$ phase, accompanied by a sharp increase in hydride-ion conductivity and by reorganisation of the hydrogen sublattice.[1] Recent neutron studies further indicate that the high-temperature behaviour is governed by a frustrated hydride sublattice, correlated migration and a distinct hydride-ion diffusion pathway.[2,3]

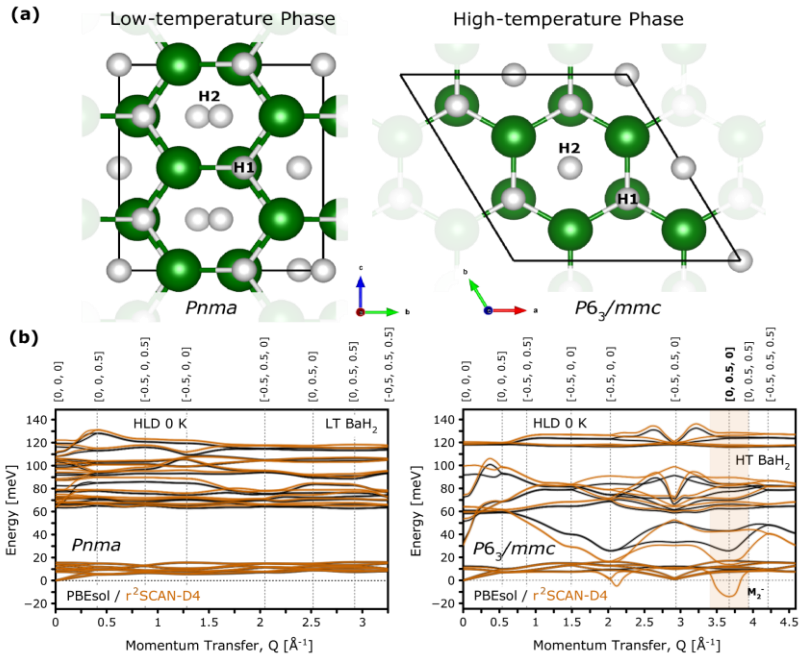

Figure 1. (a) Crystal structures and (b) phonon band structures of low- and high-temperature BaH_2 obtained from GGA and meta-GGA calculations. The comparison highlights the Pnma → $P6_3/mmc$ transformation and the associated hydrogen-dominated phonon instability.

Here, neutron spectroscopy is combined with first-principles modelling to examine hydrogen motion and structural dynamics in BaH_2.[4] Inelastic neutron scattering (INS) is used to benchmark the calculated

hydrogen-weighted vibrational response, while neutron Compton scattering (NCS) provides access to isotope-specific nuclear kinetic energies. The data are interpreted using harmonic lattice dynamics (HLD), the quasi-harmonic approximation (QHA), and finite-temperature *ab initio* molecular dynamics (AIMD). The low-temperature *Pnma* phase is found to be a stable harmonic reference structure. In contrast, the high-temperature $P6_3/mmc$ phase lies close to the edge of dynamical stability and contains a hydrogen-dominated zone-boundary instability. The corresponding double-well potential-energy landscape is sensitive to volume and exchange-correlation functional, indicating that the transition cannot be described as a simple crossing of harmonic free-energy surfaces. Instead, the high-temperature phase is better considered as an anharmonically and entropically stabilised average structure. Within the broader efforts of the STARSHIP project, this study uses BaH_2 as a model system to assess how far neutron spectroscopy and first-principles modelling can distinguish site-specific and sublattice-specific dynamical contributions in functional materials.[4,5]

Acknowledgements: This work was supported by the National Science Centre, Poland, through the STARSHIP project: *Structural Transformations Across Chemical Routes of Stabilization in Hybrid Intercalated Perovskites* (grant no. UMO-2024/54/E/ST3/00298). We acknowledge PLGrid and the ACK Cyfronet AGH HPC Centre for computational resources on Helios under grant no. PLG/2025/019086 (ID: plgstarship2026), ARCHER2 access through the UKCP consortium funded by EPSRC grant EP/X035891/1, and access to the ISIS Neutron and Muon Source under beamtime award RB1820194.

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Quantum Dynamics of Electron Transfer in C_3H_2,NS3: C7, Photovoltaic Complexes

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Photo-induced electron transfer (ET) is the foundational mechanism governing the efficiency of organic photovoltaic (OPV) materials based on bulk heterojunctions (BHJs) 12. Because these donor-acceptor (D-A) complexes are aggregated primarily via weak van der Waals interactions, their specific geometric configurations and relative orientations dictate the resulting charge separation efficiency.This work investigates the time-dependent quantum dynamics of ET within a novel organic solar cell complex consisting of a star-shaped Tris[4-(2-thienyl)phenylJamine (CH,NS) donor and an enhanced-absorption C,, fullerene acceptor. Using a time-dependent quantum mechanical framework based on the Cayley propagator[3] combined with static DFT calculations, we simulate the ET process induced by external Gaussian electromagnetic pulses across five representative geometric configurations. Crucially, the varying ET efficiencies are directly correlated with the fundamental aspects of the weak directly intermolecular interactions stabilizing each distinct spatial arrangement. By mapping how the underlying multi- dimensional potential energy surfaces (PES) and non-covalent D-A alignments influence electron dynamics, this study bridges the gap between weak interaction landscapes and macro-level device optimization. Our findings suggest optimal structural setups and pulse parameters for practical, high-efficiency OPV realizations.

Acknowledgements: This work was supported through the project no. 61TE, code PN-IV-P2-2.1-TE-2023-0300 and project no. 27N/03.01.2023, code PN 23 24 01 02, carried out with the support of MEC, and COST Action CA21101 - COSY COST Action.

Comprehensive *ab initio* characterization of CO electronic states for astrophysical spectroscopy

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Carbon monoxide (CO) is a fundamental molecule in molecular spectroscopy and astrochemistry, where accurate electronic-structure data are required for interpreting laboratory and astrophysical spectra. In this work, we present a comprehensive ab initio characterization of the complete set of eighteen adiabatic electronic states of CO correlating with the first dissociation limit, C(³P) + O(³P). The investigated states include singlet, triplet, and quintet manifolds of Σ±, Π, and Δ symmetries. Potential-energy curves were computed using state-averaged CASSCF followed by MRCI with Davidson correction, together with large augmented correlation consistent basis sets. Basis-set convergence was assessed through complete-basis-set extrapolation, providing an estimate of the remaining uncertainty in the calculated electronic energies.[1,2]

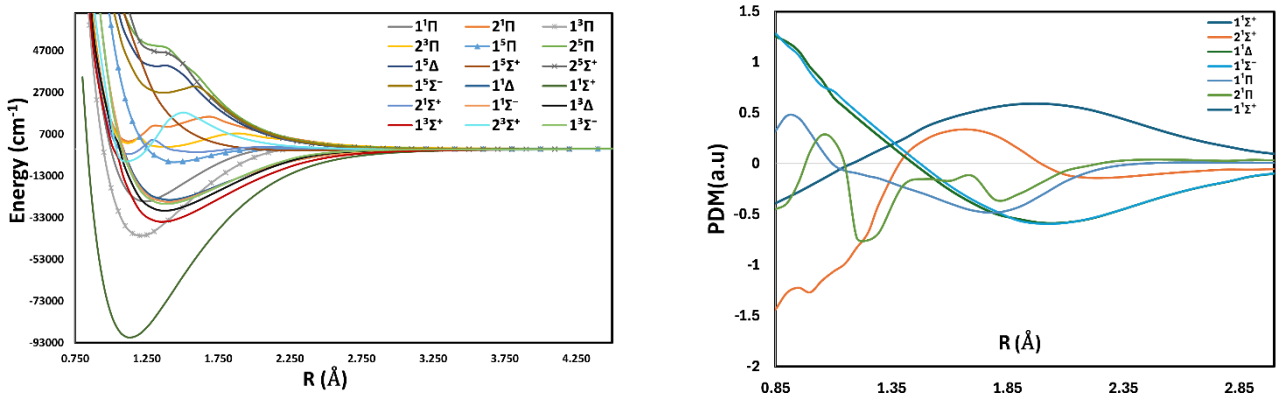

Figure 1. (left panel) The selected PECs of the CO molecule. (right panel) Permanent dipole moment for the singlet states of CO

From the calculated potential energy curves, spectroscopic constants were derived for the bound and weakly bound states and compared with available experimental and theoretical values. The results show good agreement for the well-characterized low-lying states and provide additional predictions for higher-lying and less studied electronic states, including quintet states that are often omitted in earlier studies. Permanent dipole-moment functions were also computed along the internuclear distance for all eighteen states, giving complementary information on the evolution of the electronic charge distribution[1,2]

The resulting dataset provides a consistent theoretical reference for CO electronic states associated with the first dissociation asymptote.

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σ-Aromaticity of $(LiH)_n$ Clusters (n = 1-6): A CCS(D) study

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Lithium chemistry originated in the early universe during the post-recombination epoch, when neutral atoms and the first molecules began to form from a cooling primordial gas. Among these species, lithium hydride (LiH) stands out as one of the simplest heteronuclear diatomic molecules which has been studied extensively both theoretically and spectroscopically.[1] In astrophysics, LiH and LiH^+ are of interest as two of the earliest predicted heteronuclear molecules after HeH^+ that likely formed in trace amounts in the early universe. Experimentally, Broyer and co-workers characterized $(LiH)_n$ clusters using photoionization, absorption cross section measurements, and time-of-flight mass spectrometry (TOF-MS).[2] On the theoretical side, most studies on $(LiH)_n$ clusters have investigated their equilibrium geometries, energetics, and spectroscopic properties employing semiempirical methods, density functional theory (DFT), and low-level wavefunction methods.[3] However, comparatively fewer studies have employed high-level wavefunction methods, such as coupled cluster (CC) theory, on these systems. In light of the continuing interest in lithium chemistry and the feasibility of high-level electronic structure calculations on larger systems, the energetics of small and medium-sized $(LiH)_n$ clusters (n = 2–6) at the CCSD(T)/CBS limit have beem investigated. To the best of our knowledge, the dissociation and total atomization energies (TAE) of these $(LiH)_n$ clusters at their global minima have not yet been examined with sub-kcal/mol accuracy. In this work, we characterize the electronic structure of the cyclic species through nucleus-independent chemical shift (NICS) analysis to provide a better understanding of the cooperative effects that dictate the cluster stability via σ-aromaticity. At the ring centers, the isotropic NICS(0) values are small and only weakly negative (from −0.5 ppm to −0.2 ppm) for all cluster sizes considered, indicating that any ring-current effects are modest. This suggests that σ-aromatic stabilization is not driven by a strongly delocalized, collective ring current. In contrast, NICS(0) values at the midpoint of the Li–H bonds are substantially more negative and decrease further with increasing cluster size, pointing to pronounced local σ-electron delocalization along the Li–H bonds. This distinction is also supported by the $NICS(0)_{ijmax}$ values, which are negligible at the ring centers for $(LiH)_3$, $(LiH)_4$ and $(LiH)_5$ clusters but reach large negative values at the bond midpoints, consistent with strong anisotropic magnetic shielding associated with σ-bonding. The systematic increase in the magnitude of NICS(0) and $NICS(0)_{ijmax}$ from $(LiH)_2$ to $(LiH)_5$ indicates a cooperative enhancement of σ-electron delocalization as the clusters grow. An apparent exception to the general trend is observed

for the $(LiH)_2$ dimer, where the $NICS(0)_{ijmax}$ value at the ring center takes the most negative value (−9.93 ppm). In the case of $(LiH)_2$, the "ring center" is ambiguous as the system does not form a conventional cyclic framework but rather a small and highly constrained motif. Consequently, the probe position may lie near the Li–H bonds, capturing local σ-bonding shielding rather than a global ring current. As the size increases, the ring interior becomes more spatially defined and is "magnetically decoupled" from σ bonds, causing these values to diminish. Overall, the NICS results show only weakly negative values at the ring centers but significantly more negative values at the Li–H bond midpoints, indicating that the delocalization is predominantly local and bond-centered.

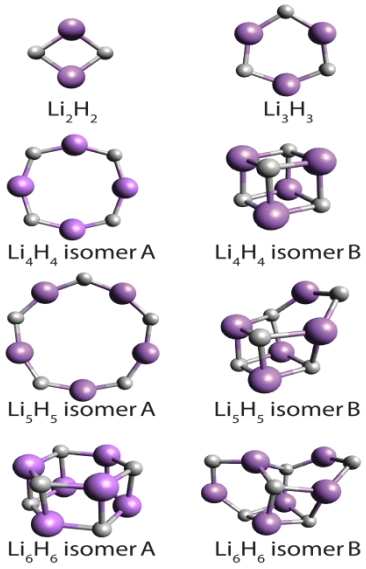

Figure 1. Optimized structures of the studied $(LiH)_n$ species in this work..

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From Electronic Structure to Ultrafast Dynamics: A Multiscale Investigation of Macular Xanthophylls in Lipid Bilayers.

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Macular xanthophylls, principally lutein and zeaxanthin, are essential photoprotective pigments in the human retina that safeguard photoreceptor cells from light-induced oxidative damage. Their remarkable efficiency originates from ultrafast nonradiative relaxation processes that dissipate excess electronic excitation before harmful photochemical reactions can occur. Despite extensive spectroscopic investigations, the molecular mechanisms underlying these relaxation pathways remain incompletely understood, particularly in the heterogeneous and dynamically fluctuating environment of biological membranes. The influence of lipid confinement, chromophore orientation, and local membrane organization on the excited-state energy landscape presents a challenging multiscale problem that requires the integration of electronic structure theory, molecular simulations, and nonadiabatic dynamics.

In this work, we investigate the excited-state properties and relaxation mechanisms of macular xanthophylls embedded in lipid bilayers using a hierarchical computational framework. Classical molecular dynamics simulations are employed to characterize the structural organization and orientational preferences of lutein and zeaxanthin within model membrane environments. To establish a reliable electronic-structure description, we first analyze reduced polyene models representing the conjugated backbone of xanthophylls. These simplified systems enable a detailed characterization of the low-lying excited states, molecular orbital interactions, and multiconfigurational character using CASSCF calculations. Benchmark calculations employing high-level wavefunction-based approaches, including EOM-CCSD, are performed on representative model systems to validate the energetic ordering and nature of the relevant excited states. The resulting electronic-structure insights provide the foundation for the development and assessment of computationally efficient methodologies suitable for larger carotenoid systems.

Building upon this understanding, we employ semiempirical FOMO-CI-based excited-state dynamics simulations to explore nonadiabatic relaxation pathways and the role of membrane confinement in modulating ultrafast photophysical processes. Particular attention is devoted to identifying the structural distortions and electronic-state couplings that facilitate rapid internal conversion through conical

intersections. By connecting molecular-level electronic structure with membrane-scale organization, this study aims to establish a mechanistic framework for understanding retinal photoprotection and to provide general insights into the photophysics of carotenoids in complex biological environments.

Threshold Photoelectron Spectroscopic Study of the *N*-Carbazolyl π-Radical and Its Antiaromatic Nitrenium Ion

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One of the most challenging aspects of chemistry is understanding and characterizing reactive intermediates. Radicals and cations, fundamental yet highly demanding species, have garnered widespread attention. However, the study of nitrogen-centered radicals (NCRs) and their corresponding nitrenium ions remains limited compared to their carbon counterparts, with their synthetic potential largely unappreciated and unexplored.[1]

This work describes the VUV photoionization of the *N*-carbazolyl radical, using a combination of synchrotron radiation, photoelectron photoion coincidence spectroscopy, and supporting ab initio calculations. Through these methods, the adiabatic ionization energy of the *N*-carbazolyl radical to both the singlet and triplet state of its corresponding nitrenium ion is directly determined using photoion mass-selected threshold photoelectron spectroscopy. The *N*-carbazolyl radical is characterized as a highly delocalized π-radical, which leads to the generation of an extremely unstable antiaromatic nitrenium ion.[2]

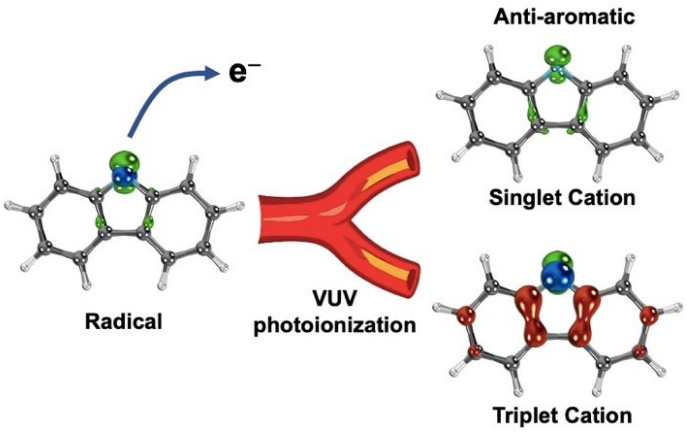

Figure 1. Photoionization of N-carbazolyl radical.

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Electron density changes induced by noncovalent interactions within the SAPT framework

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When two molecules are in proximity, their electronic densities fluctuate and deform due to the presence of the partner. These changes, although small in magnitude, constitute a driving force in many physical, chemical, and biological phenomena such as collision-induced absorptions in molecular spectra, formation of molecular crystals, and ligand – protein binding. In this work, we investigate the behavior of electron density changes for selected model systems upon different types of van der Waals interactions, including hydrogen bond, σ-bond, atom…atom, and dispersive stacking interactions. To this end, we employ an innovative approach capable of calculating the changes of electron density as a series of perturbation corrections in orders of the interaction operator. The method dubbed propSAPT is a variant of symmetry-adapted perturbation theory (SAPT) designed for calculations of molecular properties. It has been developed by our group and has already been used to study interaction-induced properties, such as dipole moments.[1] In the propSAPT method, the interaction-induced corrections to electron density (or one-electron properties) naturally decompose into polarization, exchange, and dispersion contributions, analogously to the decomposition of interaction energy known from SAPT. This decomposition opens a new avenue for studying noncovalent interactions by analyzing and visualizing physically well-defined contributions to the electron density shifts. We compare our differential densities to those obtained from the supermolecular coupled-cluster method. Moreover, we compare dispersion-driven changes from propSAPT to those of a recently developed variant of the empirical many-body dispersion model (MBD@FCO) based on quantum Drude oscillators.[2]

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The complex potential energy surface of the diaminoethane cation as a challenge for density functional theory.

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Accurately describing the potential energy surfaces (PES) of radical diamine cations is a well-known challenge for both density functional theory (DFT) and wave-function methods due to the competing effects of electron correlation and self-interaction error [1-10]. While previous research on the larger N,N'-dimethylpiperazine (DMP) cation revealed a delicate balance between localized and delocalized minima[1-10], this study demonstrates that the smaller diaminoethane cation exhibits a significantly more intricate PES. Using the nudged elastic band (NEB) method [11], we systematically mapped this landscape and identified four distinct minima (one localized and three delocalized) along with their connecting transition states. These structures were systematically evaluated across a broad spectrum of DFT approximations, spanning GGA, hybrid GGA, meta-GGA, hybrid meta-GGA, and double-hybrid functionals. Our benchmark reveals a strong functional dependence: several widely used functionals fail to reproduce both the localized state and its corresponding transition state. These results underscore the necessity of reliable electronic-structure methods for accurately describing mixed-valence radical systems.

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