







MOLECULES IN MOTIONMOLIM 2016WORKING GROUP 122.-24.8.2016ENERGY-RESOLVED METHODSHELSINKI

Book of Abstracts





Program

Monday 22.8.

08.45 - 09.00	Opening remarks
	Lauri Halonen and Attila Császár
	Invited talks - Session chair: Attila Császár
09.00 - 09.30	Alkali - Alkaline Earth Diatomics: Molecules for Ultracold Physics
	Wolfgang Ernst, Technische Universität Graz, Austria
09.30 - 10.00	Photoacoustic method in spectroscopy
	Jyrki Kauppinen, University of Turku, Finland
10.00 - 10.30	Molecular rotation of very floppy molecules: The case of CH ₅ ⁺
	Stephan Schlemmer , Universität zu Köln, Germany
10.30 - 11.00	Coffee/tea break
	Invited talks - Session chair: Lauri Halonen
11.00 - 11.30	New fragment methods for constructing vibrational coordinates and
	potential energy surfaces
	Ove Christiansen , Aarhus University, Denmark
11.30 - 12.00	On bridging high-resolution spectroscopy and thermochemistry
	Attila Csaszar, Eoivos Lorana University, Hungary
12.00 - 12.30	Molecular vibrations and rotations: Geometric algebra approach
10 20 14 00	Janne Tesonen, Oniversity of Heisinki, Fintana
12.30 - 14.00	Lunch
	Contributed talks - Session chair: Garold Murdachaew
14.00 - 14.25	Liquid Photoemission by Ab Initio Modelling
	Eva Muchova , University of Chemistry and Technology, Czech Republic
14.25 - 14.50	Theoretical investigation of the photo-induced intramolecular charge
	migration on gold nanoclusters passivated by a chromophore ligand Valérie Schwanen University of Liège Belgium
14 50 15 15	Computational Studies of Dispersion Interpotions in Coinage and Valatile
14.50 - 15.15	Metal Clusters
	Richard Hatz, Aalto University, Espoo, Finland
15.15 - 15.50	Coffee/tea break
15.50 - 17.30	Task group proposals and meetings
18.30 - 19.30	Welcome reception: Helsinki Old Town Hall

Tuesday 23.8.

	Invited talks - Session chair: Lauri Partanen
09.00 - 09.30	Investigations on the very few electronic states of monohaloacetylenes HC≡CX (X = F, Cl, Br)
	Gilberte Chambaud, Université Paris-Est Marne-la-Vallée, France
09.30 - 10.00	Computational study of the adsorption of rare-gas atoms on flat and
	nanostructured surfaces Sonja Grubišić, Center for Chemistry & IHTM, University of Belgrade, Serbia
10.00 - 10.30	On the interactions of monoatomic ions in charged organic and biomolecular systems: Insight from molecular dynamics simulations <i>Francesca Mocci, University of Cagliari, Italy</i>
10.30 - 11.00	Coffee/tea break
	Invited talks - Session chair: Stephan Schlemmer
11.00 - 11.30	High resolution spectroscopy and dynamics of 2OH-excited water containing molecular complexes Michel Herman, Université libre de Bruxelles, Belgium
11.30 - 12.00	Bimolecular complexes, thermodynamics and spectroscopy Henrik Kjaergaard , University of Copenhagen, Denmark
12.00 - 12.30	Intramolecular Quantum Dynamics and Electroweak Parity Violation in Chiral Molecules from High Resolution Spectroscopy <i>Martin Quack, ETH ZURICH, Switzerland</i>
12.30 - 14.00	Lunch
	Invited talks - Session chair: Hannes Jónsson
14.00 - 14.30	Quantitative infrared absorption intensities for HNO and HNNO: Beyond the double-harmonic approximation <i>Robert Hinde, University of Tennessee, USA</i>
14.30 - 15.00	Weak Intramolecular Interaction Effects on the Structure and Torsional Spectra of Ethylene Glycol, an Astrophysical Species <i>Maria Luisa Senent, Instituto de Estructura de la Materia - CSIC, Spain</i>
15.00 - 15.30	ExoSoft or how to compute molecular line lists for atmospheric characterizations of exoplanets <i>Sergey Yurchenko</i> , University College London, UK
15.30 - 16.00	Coffee/tea break
	Contributed talks - Session chair: Roberto Marquardt
16.00 - 16.25	Temperature and collision energy effects on dissociation of hydrochloric acid on water surfaces <i>Lauri Partanen, University of Helsinki, Finland</i>
16.25 - 16.50	Deprotonation of formic acid in collisions with a liquid water surface studied by molecular dynamics and metadynamics simulations <i>Garold Murdachaew</i> , University of Helsinki, Finland
19.00 -	Conference dinner: Ravintola Saaristo, Klippan Isle

Wednesday 24.8.

	Invited talks - Session chair: Vesa Hänninen
09.00 - 09.30	Molecular clustering in the atmosphere Hanna Vehkamäki, University of Helsinki, Finland
09.30 - 10.00	Calculation of tunneling splittings with variational and path-integral methods <i>Edit Matyus, Eötvös Loránd University, Hungary</i>
10.00 - 10.30	An Extended Jahn-Teller Hamiltonian for Large-Amplitude Motion in Molecules and Clusters: Applications to $E \otimes e$ and $T_2 \otimes e$ Systems David Perry, University of Akron, USA
10.30 - 10.45	Coffee/tea break
	Invited talks - Session chair: Martin Quack
10.45 - 11.15	Atoms moving in a strongly anharmonic potential: Small and large amplitude atomic motion in the bifluoride anion <i>Roberto Marquardt, Institut de Chimie - Université de Strasbourg, France</i>
11.15 - 11.45	Self-interaction corrected functional calculations of loosely bound, Rydberg excited and localized electrons Hannes Jónsson, University of Iceland, Reykjavík
11.45 - 12.00	Closing remarks Martin Quack
12.00 -	Lunch

Abstracts of Talks

(In Order of Presentation)

Alkali – Alkaline Earth Diatomics: Molecules for Ultracold Physics

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The cooling and controlled manipulation of molecules that possess both magnetic and electric dipole moments has been a long-time goal in the physics of ultracold quantum gases. One of the promising concepts for the creation of ultracold molecules makes use of the laser-assisted formation of molecules from ultracold atoms in a trap. Mixed alkali – alkaline earth diatomics have a $^{2}\Sigma$ ground state with a single unpaired electron, have a significant electric dipole moment, and first realization of a combined quantum degenerate mixture of Rb and Sr was demonstrated in a magneto-optical trap [1]. The association of molecules and subsequent coherent population transfer into their ground state is based on a profound knowledge of their electronic structure and the related spectroscopy.

In our investigation of this interesting group of diatomics, the unique experimental conditions provided by helium nanodroplets (He_N) [2] are utilized to form diatomic molecules from one alkali (Ak) and one alkaline earth (Ake) metal atom, both heliophobic dopants that reside on the droplet surface. We recorded laser excitation spectra of LiCa [3], RbSr [4,5], and RbCa [6] on helium droplets, with RbSr appearing to be the most interesting candidate for laser associated formation. Our own quantum chemistry calculations allowed the assignment of the electronic band systems in the wavenumber range between 11,500 and 23,000 cm⁻¹ [3,6,7]. The permanent electric dipole moment turns out to point in different directions for states of doublet and quartet multiplicity and changes the sign in some cases as a function of bond length which can be explained by molecular orbital theory [8]. We currently work on the prediction of a suitable laser-optical population transfer of formed molecules into their lowest energy state. First results will be reported.

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Photoacoustic method in spectroscopy

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Photoacoustic spectroscopy (PAS) has many applications in various fields of research and industry. It has been used in biology, medicine, and in controlling industrial processes and monitoring indoor air quality as well as pollutants or toxic gases. The improvements of lasers and detection techniques have increased the significance of the photoacoustic method. Some demands for a gas analyzer include stability, sensitivity, and selectivity. A possibility to perform real time measurements and size and robustness of the analyzer are also desirable features. These demands can be fulfilled with photoacoustic spectroscopy.

The photoacoustic method is based on the absorption of light by gas molecules that are enclosed in the photoacoustic cell. The gas absorbs some of the radiation and excites to a higher energy level. This energy level can relax back to the ground level by a non-radiative process. This process will increase the temperature and further on the pressure of the gas. When radiation is chopped with a proper frequency, the pressure variations can be detected with a microphone at the chopping frequency. Also liquids and solids absorb radiation heating the surrounding gas, where the increase of the pressure takes place.

The sensitivity of the photoacoustic method has been restricted by the detector of the pressure signal, i.e., the microphone. The recently developed cantilever-enhanced photoacoustic spectroscopy has proven to be a very sensitive method [1,2]. The high sensitivity is achieved with a micromechanical cantilever, whose displacement is measured with a laser interferometer. The high sensitivity allows the measurements of the photoacoustic signal with non-resonant modes of the cell and cantilever. The cantilever has a broadband frequency response and therefore it is possible to exploit its sensitivity also in Fourier transform infrared (FTIR) spectroscopy. The cantilever-enhanced detection has also been used in the selective differential method for trace gas analysis [3]. With the tunable diode laser and the cantilever sensor we have achieved to our knowledge the best result so far for the normalized noise-equivalent absorption. The ultimate sensitivity is limited by the Brownian noise.

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Molecular rotation of very floppy molecules: The case of CH₅⁺

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Light-Induced Reactions (LIR) in cryogenic traps are used to record action spectra of electronic, vibrational, and pure rotational transitions of many molecular ions. One example concerns the enigmatic CH_5^+ molecule, protonated methane. This molecule exhibits large amplitude motions in almost all degrees of freedom and therefore the rovibrational spectrum in the range of C-H stretching vibrations contains thousands of lines even at T = 10 K. The challenge of these complex spectra is to understand the rotational motion in this very fluxional molecule, whose large amplitude motions cannot be frozen at even lower temperatures.

In our infrared experiments the line centers of the measured transitions are determined with an accuracy of better than 1 MHz in most cases by calibration against a frequency-comb. Based on these very high-precision measurements we started to reconstruct the low energy term diagram based on ground state combination differences [1]. These term diagrams are related to the lowest energy rotational and vibrational modes of the molecule. We present a model of collective molecular rotation which combines the end-over-end rotation with the internal rotation in this very fluxional molecule. The zeroth order model leads to a very simple, algebraic energy relation. The corresponding energy levels agree very well with the experimentally found values. In conclusion, there is strong evidence for collective rotational motions, i.e. rotations in higher dimensions, in very floppy molecules like CH_5^+ .

Reference:

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New fragment methods for constructing vibrational coordinates and potential energy surfaces

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Accurate calculations of vibrational spectra and vibrational wave function techniques require accurate representations of multi-dimensional potential energy surfaces (PESs). However, the construction of a full-dimensional PES is a tremendous computational task governed by both the (i) number of required electronic energy calculations (EECs) and (ii) the cost per EEC. By approximating the PES in an incremental, so-called *n*-mode expansion, polynomial scaling in the number of EECs is obtained [1]. The computational scaling of each EEC can be reduced to linear scaling when using incremental (many-body) fragmentation approaches [2]. We present a combination of these ideas in the so-called double incremental expansion. This approach works most efficiently when the vibrational coordinates are semi-local. For this we employ our recently introduced FALCON (Flexible Adaptation of Local COordinates of Nuclei) coordinates [3]. With some additional tricks we can thereby achieve linear scaling of the *accumulated* cost of the EECs required in the PES generation. I will describe the perspectives and the theoretical backgrounds for these algorithms. Numerical examples of these double incremental approaches for oligo-phenyls show fast convergence with respect to the maximum number of simultaneously-treated fragments. The approach, presented here, represents a major step towards the construction of PESs of sizable, covalently bound systems with hundreds of degrees of freedom, which are prerequisites for the applicability of vibrational wave function methods to these systems [4].

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High-accuracy high-temperature thermochemical functions

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High-resolution molecular spectroscopy is able to yield a large number, in fact tens of thousands, of bound as well as unbound rovibronic energy levels. Most of these energy levels are highly accurate, with an accuracy usually exceeding 10^{-2} cm⁻¹ even in the worst cases (corresponding to emission spectroscopy), usually perhaps by several orders of magnitude. This experimental energy level and uncertainty information can be obtained via the Measured Active Rotational-Vibrational Energy Levels (MARVEL) approach [1].

Since even the simplest and smallest tightly-bound polyatomic molecules possess a few hundred thousand if not a few million rovibrational states within their ground electronic state, the experimental energy level information must be supplemented by reasonably accurate first-principles results when used for thermochemistry. In the fourth age of quantum chemistry [2] determination of a few million rovibronic energy levels can be achieved by sophisticated techniques of nuclear motion theory for di- and triatomic molecules. Determining all the rovibrational energy levels below the dissociation limit for tetratomic molecules and beyond is still a considerable challenge.

At high temperatures the information about bound states must be supplemented by that corresponding to unbound, including resonance, states. It is less straightforward how this information can be obtained *ab initio* for polyatomic molecular systems but certain possibilities are sketched during the talk.

When the bound and unbound energy levels are available one needs to consider how to treat them during the determination of high-accuracy high-temperature partition functions. In particular, novel ways are suggested how to include unbound states in the direct "partition sum" by changing to an integral formulation.

The molecular examples treated include different isotopologues of MgH [3] and $H_2^{16}O$ [4]. The temperature ranges covered are 0 – 3000 and 0 – 6000 K, respectively. The ideal gas isobaric heat capacity turns out to be especially sensitive to details of the treatment employed.

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Molecular vibrations and rotations: Geometric algebra approach

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The molecular Hamiltonian is needed when the vibration-rotation energy spectrum of a polyatomic molecule is modeled. While it is fairly straightforward to obtain the potential energy part of the Hamiltonian in the framework of the Born-Oppenheimer approximation (at least in in principle), obtaining the respective kinetic energy operator, in contrast, is not. Luckily, the recently developed geometric (Clifford) algebra approach allows one to overcome this difficulty, and formulate the kinetic energy operator with surprising ease [1,2,3]. It does not matter which body-frame or which shape coordinates are used. Unfortunately, this methodology is still not as widely known as it should be.

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Liquid Photoemission by Ab Initio Modelling

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Photoemission spectroscopy is a straightforward approach which allows study of electronic structure of molecules and solid state materials. However, theoretical modelling of photoemission is a complex and difficult case. The main reasons are long-range interactions and a large number of nearly degenerate states present in liquids. In my talk, I will present a novel computational protocol for modelling photoemission spectra of liquids. For this purpose, we use *ab initio* based path-integral molecular dynamics simulations greatly accelerated with the so-called colored noise thermostat (PI+GLE) method [1]. To effectively calculate the valence ionization energies we employed the DFT version of the Koopmans' theorem *via* the optimally-tuned range-separated hybrid functionals (OT-RSH) [2]. I will show that this approach can not only describe quantitatively the valence photoemission spectrum of liquid water, i.e. the position, shapes and widths of the photoemission peaks, but also captures the subtle isotope effects, e.g. we can account for nuclear quantum effects. The present approach seems to be a promising route to modelling photoemission spectra of liquids and of liquid/vapor interfaces. This is important mainly because of the possibility to reveal also the electronic structure of solute molecules which can facilitate understanding of chemical reactions taking place both in bulk and on interfaces.



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Theoretical investigation of the photo-induced intramolecular charge migration on gold nanoclusters passivated by a chromophore ligand

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Stoichiometric gold nanoclusters functionalized by a ligand shell are the subject of intensive research efforts, both experimentally and theoretically [1-2]. Inspired by the work of Devadas et al. [3], we designed model systems based on the experimentally accessible gold nanoclusters $Au_{11}(PR_3)_7Cl_3$ [4], $Au_{20}(SR)_{16}$ [5] and $Au_{25}(SR)_{18}$ [6] that we functionalized by a methyl viologen moiety through substitution of one ligand in their passivation shell. We theoretically investigated the ultrafast charge migration triggered by the excitation of these model systems by an ultrashort strong optical pulse. We show that a significant amount of charge is transferred from the viologen chromophore to the metallic core after photoexcitation on the three models, accompanied by the beating of the electron density between the two subunits of the cluster [7]. We highlight that the superatomic [8] character of the nanocluster influences the amplitude of charge migration through the nature of their stationary electronic excited states. Preliminary results suggest that the nuclei of the viologen moiety specifically rearrange to the non-equilibrium electron density depending on the nature of the stationary states populated by the optical pulse.



Figure 1: Illustration of a purely electronic dynamic experiment on $Au_{11}(PH_3)_7Cl_2S$ -bipy-CH₃ (bipy=bipyridine). (a) The 350nm pulse (σ =1.4fs, f=0.01a.u.) polarization direction in the molecular frame of the cluster. (b) Evolution of the time-dependent dipole moment, which is an observable of the electron density, along the x, y, and z axes for this exciting pulse (note that the field strength of the pulse is not to scale). (c) Stationary fraction of the charge depletion on the viologen moiety (black line) and time evolution of the electron density difference with respect to the initial density on the viologen (red line).

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Computational Studies of Dispersion Interactions in Coinage and Volatile Metal Clusters

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London dispersion forces are a ubiquitous part of intermolecular interactions, but they can be difficult to model accurately due to their entirely quantum mechanical nature and the high-level electronic structure methods required. A simple but effective method to calculate the total dispersion energy based on atomic, orientation dependent C_6 coefficients has been developed [1, 2] and successfully applied to small clusters of coinage (Cu, Ag, and Au) [1, 2] and volatile (Zn, Cd, and Hg) metals [3, 4]. Novel theoretical results [5] allow for a more straightforward vector-based description of the interaction tensor governing the orientation and distance dependence of all long-range intermolecular forces.



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Investigations on the very few electronic states of monohaloacetylenes HC≡CX (X = F, Cl, Br)

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Highly correlated electronic wavefunctions within the Multi Reference Configuration Interaction (MRCI) approach are used to study the stability and the formation processes of the monohaloacetylenes HCCX and monohalovinylidenes C_2HX (X = F, Cl, Br). These tetraatomics can be formed through the reaction of triatomic fragments C₂F, C₂Cl and C₂Br with a hydrogen atom or of C₂H with halogen atoms via barrierless reactions whereas the reactions between the diatomics $[C_2 + HX]$ need to overcome barriers of 1.70, 0.89 and 0.58 eV for X = F, Cl and Br, respectively [1]. It is found that the linear HCCX isomers, in singlet symmetry, are more stable than the singlet C₂HX iso-forms by 46.0, 48.0 and 45.2 kcal/mol for X = F, Cl and Br, respectively. The spectroscopy of these haloacetylenes has been investigated by the variational approach. The very small isomerization barriers from iso to linear forms are calculated to be 1.54, 1.01 and 2.30 kcal/mol for F, Cl and Br systems, respectively. The dissociation energies of the HCCX systems (without ZPE corrections), resulting from the breaking of the CX bond, are calculated to be 130.24, 108.17 and 95.23 kcal/mol for X = F, Cl and Br, respectively. At the equilibrium geometry of the $X^{1}\Sigma^{+}$ state of HCCX, the vertical excitation energies in singlet and triplet symmetries are all larger than the dissociation energies. Stable excited states are found only as ${}^{3}A'$, ${}^{3}A''$ and ${}^{1}A''$ monohalovinylidene structures [2].



Figure 1. Energy diagram of the [C₂HF] system

References:

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Computational study of the adsorption of rare-gas atoms on flat and nanostructured surfaces

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The DFT/vdW-WF method, recently developed to include the van der Waals interactions in Density Functional Theory (DFT) using the Maximally Localized Wannier functions, is applied to the study of the adsorption of rare-gas atoms (Ne, Ar, Kr, and Xe) on the Al(100), Cu(111), and Pb(111) surfaces, at three high-symmetry sites [1, 2]. The role of the chosen reference DFT functional and of different van der Waals corrections, and their dependence on different rare-gas adatoms, has been investigated.

The accurate physisorption potential for a planar surface (Ar on Al(100)) have been used as the basic input to derive the corresponding three-dimensional adsorption potential for the nanostructured substrate, using a well-established thoretical tool described in the literature. The adsorption properties of argon on model nanostructured Al substrate at 85 K and 128 K have been studied, too. Two types of nanopores have been analyzed: (a) cylindrical pores of nanoscopic cross section open at both ends and (b) cylindrical pores with a closed bottom.

State-of-the-art computational methods have been used to obtain (i) accurate threedimensional adsorption potentials for the nanostructured substrate starting from the corresponding ab initio physisorption potential for a planar surface, and (ii) the adsorption and desorption isotherms by means of Grand Canonical Monte Carlo simulations [3]. The effect of pore shapes upon argon adsorption in the case of a substrate characterized by a periodic arrangement of identical cylindrical nanopores, open at both ends or with one end closed, has been studied. The occurrence of hysteresis loops between adsorption and desorption cycles in open-end pores has been observed, in accordance with recent experiments and previous theoretical approaches. At variance with the prediction of the empirical Cohan's law, we have also observed hysteresis in pores with one closed end. Typical problems related to the influence of confinement on the phase behavior of the confined fluid have been analyzed. It has been shown that the mechanism of the adsorption/desorption process depends on the shape of the pore walls and on the temperature.

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On the interactions of monoatomic ions in charged organic and biomolecular systems: Insight from molecular dynamics simulations

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Interactions between organic and bioorganic molecules with monoatomic ions are of great relevance in determining structural and dynamical parameters. This is particularly true for charged compounds such as ionic liquids or charged biopolymers, such as nucleic acids. The experimental and modeling studies of these organic-inorganic structures are complicated due to a multitude of interactions, ranging from weak van der Waals to strong Coulombic forces. On the other hand, properly modeling the interactions between the organic moiety and the inorganic cations or anions is of fundamental importance to characterize their behavior and function [1-2].

In this talk, I will describe our latest studies in this field, discussing our approach to simulate and verify the results concerning the interactions between DNA and some of its monovalent biological counter ions, and those between the organic moieties of ionic liquids of the imidazolium class having a halogen anion as the counter ion [2-4]. To obtain information of the structure and dynamics of these classes of molecules, it is very important to have a proper coupling with experimental data, and I will highlight in particular the role of the use of the NMR signal of quadrupolar ions in the validation of the simulation [5].



Figure: Variation of the spatial (left) and radial (right) distribution function of potassium around the averaged DNA quadruplex structure using three different sets of force field parameters.

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High resolution spectroscopy and dynamics of 2OH-excited water containing molecular complexes

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We have developed the Fantasio+ set-up combining a cavity ring-down spectrometer and a supersonic expansion to investigate overtone excited molecular complexes [1]. We recently investigated H₂O-Ar [2], H₂O-Kr [3] and (H₂O)₂ [4]. The set-up and the main results will be presented, including upper state vibrational predissociation lifetimes. The focus will be set on the latest, unpublished results concerning 2OH-excited H₂O-Ar.

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Bimolecular complexes, thermodynamics and spectroscopy

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The interest in complex formation is multifold in atmospheric research with examples like radiative transfer, reaction mechanisms and nucleation all affected by complex formation. Central is the formation of a molecular complex which relies on the Gibbs free energy of formation, ΔG .

We have detected a series of bimolecular complexes that all contain an X-H---Y hydrogen bond, where X is O, N, or Cl and Y is O, S, N or P. Using infrared spectroscopy, we have measured the fundamental XH-stretching transition for these complexes. By combining the measured room temperature gas phase intensity of this transition with calculated intensities of the relevant vibrational transitions, we determine the abundance of the complex and thereby the equilibrium constant (K) and ΔG for the complex formation [1-3]. To improve the accuracy of the calculated intensities, we have developed a local mode perturbation theory (LMPT) approach that includes the XH-stretching mode and perturbation from the intermolecular modes [4]. In all examples, we find that ΔG of the hydrogen bond formation to O, S and P are surprisingly similar and significantly weaker than that to N [5].

More recently, we have recorded spectra in a temperature range from room temperature to 100°C, to determine ΔH values and by combination with the determined ΔG values we also obtain ΔS . For the methanol-dimethylamine complex with obtain accurate thermodynamic parameters ($\Delta H = -29.5 \pm 2 \text{ kJ/mol}$; $\Delta G = 3.9 \pm 0.3 \text{ kJ/mol}$; and $\Delta S = -111 \pm 10 \text{ J/(mol K)}$) such that benchmarking of theoretical methods is possible [6].



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Intramolecular Quantum Dynamics and Electroweak Parity Violation in Chiral Molecules from High Resolution Spectroscopy

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The time dependent quantum dynamics of molecules in motion is the fundamental primary process in all of molecular kinetics and chemical reactions [1-15]. New considerations have arisen from the recent experimental developments in high resolution spectroscopy on the one hand and the theoretical developments in the treatment of multidimensional quantum dynamics in relation to spectra and motion of polyatomic molecules on the other hand. In the lecture we shall start with a discussion of the fundamental importance of symmetries and symmetry violations in relation to molecular quantum dynamics. We shall then present recent results from the work of our group on intramolecular vibrational energy flow, tunneling processes and the current status of the study of parity violation in chiral molecules by means of the new process of the time evolution of parity in isolated molecules, leading to a highly energy resolved parity violating energy difference between enantiomers of chiral molecules predicted by our recent theory in the sub femto eV range. If time permits we shall also address the question of the homochirality in the evolution of life [11] and possible spectroscopic studies of CPT violation [6, 11].

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Quantitative infrared absorption intensities for HNO and HNNO: Beyond the double-harmonic approximation

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Ultraviolet irradiation of solid parahydrogen (pH₂) matrices doped with suitable H atom precursor molecules generates H atoms in situ through a series of photoinitiated chemical reactions. These H atoms move through the matrix via a quantum diffusion process that involves the tunneling-mediated reaction $H + H_2 \rightarrow H_2 + H$. The mobile H atoms may react chemically with other species that are also embedded in the pH₂ matrix; an investigation of the kinetics of these H atom reactions provides us with information about reaction dynamics in the pH₂ matrix environment.

In pH₂ matrices doped with NO or N₂O impurities, reactions of mobile H atoms with NO or N₂O dopants produce HNO or HNNO species that can be detected using infrared absorption spectroscopy [1, 2]. In the solid pH₂ environment, the H + NO \rightarrow HNO reaction exhibits Arrhenius-type kinetic behavior, and proceeds more quickly at higher temperatures. However, the H + N₂O \rightarrow HNNO reaction exhibits non-Arrhenius behavior, and slows down dramatically once the pH₂ matrix is heated above T = 2.4 K.

A detailed investigation of the kinetics and mechanisms of these two reactions in solid pH_2 requires accurate infrared absorption coefficients for the HNO and HNNO product species, so that concentrations of the products can be inferred from their absorption spectra. Here we present initial work aimed at determining these absorption coefficients. We also assess the reliability of the VPT2 method for computing anharmonic vibrational fundamentals for these two molecules.

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Weak Intramolecular Interaction Effects on the Structure and Torsional Spectra of Ethylene Glycol, an Astrophysical Species

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A variational procedure of reduced dimensionality based on CCSD(T)-F12 calculations is applied to understand the far infrared spectrum of ethylene glycol. This molecule can be classified in the double molecular symmetry group G_8 and displays nine stable conformers, *gauche* and *trans*. In the gauche region, the effect of the potential energy surface anisotropy due to the formation of intramolecular hydrogen bonds is relevant. For the primary conformer, the ground vibrational state rotational constants are computed at 6.3, 7.2 and 3.5 MHz from the experimental parameters.



gauche

trans

Ethylene glycol displays very low torsional energy levels whose classification is not straightforward. Given the anisotropy, tunneling splittings are significant and unpredictable. The ground vibrational state splits into 16 sublevels separated by ~142 cm⁻¹. Transitions corresponding to the three internal rotational modes allow assignment of previously observed Q branches. Band patterns, calculated between 362.3 and 375.2 cm⁻¹, between 504 and 517 cm⁻¹ and between 223.3 and 224.1 cm⁻¹, that correspond to the tunnelling components of the v₂₁ fundamental (v₂₁ = OH-torsional mode), are assigned to the prominent experimental Q branches.

ExoSoft or how to compute molecular line lists for atmospheric characterizations of exoplanets

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The use of variational nuclear motion programs to compute line lists of transition frequencies and intensities is now a standard procedure. The ExoMol project [1] has used this technique to generate line lists for studies of hot bodies such as the atmospheres of exoplanets and cool stars. The resulting line lists can be huge: many contain 10 billion or more transitions. Computing these line lists has led us to develop or improve specialist programs designed to study the nuclear motion problem of the various molecules under consideration.

A common theme of all these programs is the direct solution of the nuclear motion Schrödinger equation using a variational treatment. For diatomic systems we use our program especially developed for the project, Duo [2]. For triatomic systems the exact kinetic energy nuclear motion code DVR3D [3] has been employed. For tetratomic systems calculations have largely been performed with TROVE [4]. Finally a new hybrid methodology based on the combined use of the variational principle and perturbation theory has been developed for larger systems [5]. The main challenge is that very high rotational and vibrational excitations are needed for accurate descriptions of hightemperature molecular spectra. This in turn requires larger basis sets and therefore larger Hamiltonian matrices, with associated increase of the calculation costs in terms of memory (both RAM and storage) and time. In order to tackle these and other challenges a number of critical modifications to the methodological approach adopted by ExoMol were required. These software and algorithmic developments will be presented.

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Temperature and collision energy effects on dissociation of hydrochloric acid on water surfaces

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Collisions of HCl at the air-water interface modelled by a 72 molecule water slab are studied for a range of various impact energies and temperatures using ab initio molecular dynamics with density functional theory. A range of short-timescale events can follow the collision, from direct scattering to nondissociative trapping on the surface. In most cases, HCl dissociation occurs within a few picoseconds, followed by the formation of a solvent-separated ion pair, or rarely, the reformation of HCl [1]. With increasing impact energy and/or system temperature, dissociation occurs more rapidly, with Cl⁻ tending to diffuse deeper into the slab. At temperatures corresponding to the frozen water regime, dissociation is seen only once out of the five thermal collisions, but with the addition of a total of 4kT or more of kinetic energy to HCl, it occurs in all our trajectories within a few ps.



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Deprotonation of formic acid in collisions with a liquid water surface studied by molecular dynamics and metadynamics simulations

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Our previous studies have examined deprotonation of mineral acids at aqueous and icy interfaces [1-2]. Organic acids also play important roles in atmospheric chemistry and other disciplines. This article explores interactions of formic acid (FA), including ionization, in collisions at the air-water interface. Ab intio molecular dynamics simulation with dispersion-corrected density functional theory was used. Within up to 50 ps, all trajectories resulted in adsorption of the acid at the interface. Despite the known acidic weakness of FA, spontaneous deprotonation was observed at the interface in 4% of the trajectories. It occurred on a wide picosecond timescale, ranging from a few picoseconds typical for stronger acids, to tens of picoseconds, and it was followed by ultrafast Grotthuss proton migration through adjacent water molecules. To better understand the deprotonation mechanisms at the interface compared with the process in bulk water, we used welltempered metadynamics to obtain deprotonation free energy profiles. While in bulk water FA deprotonation has a free energy barrier of 14.6 kJ/mol, in fair agreement with earlier work, the barrier at the interface is only 7.5 kJ/mol. Thus, at the air-water interface, FA may dissociate more rapidly than in the bulk. This finding can be understood by reference to the dissimilar aqueous solvation and hydrogen-bonding environments in the interface compared to those in bulk liquid water.



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Molecular clustering in the atmosphere

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Atmospheric aerosol particles affect human health, visibility and climate. Cloud formation in our atmosphere always involves particles as cloud condensation nuclei. The direct scattering effect together with the influence via clouds constitute the largest uncertainty in predicting future climate. Not all the particles are emitted in the air in solid or liquid form: it is estimated that approximately half of modern-day cloud condensation nuclei originate from atmospheric nucleation born in the air from condensable vapours. In many atmospheric locations, the strongest candidate for a particle forming vapour is sulphuric acid, but other vapours are needed to assist the process. The molecular mechanisms for formation of molecular clusters and their growth to atmospheric aerosol particles has not been uncovered yet.

We have developed an Atmospheric Cluster Dynamics Code (ACDC) to simulate the time evolution of cluster size distributions in multicomponent systems. ACDC generates the birth-death equations governing the formation and loss processes of the clusters, and solves them numerically to find cluster concentrations as a function of time. The kinetic processes include all possible collisions and evaporations within the studied set of clusters, as well as external cluster sinks, and possible ionization and recombination processes in the case that the simulation includes also charged clusters. ACDC can be used to study the cluster concentrations, formation rates and growth pathways in the presence of different realistic atmospheric compounds [1].

As input, the rate constants of all the kinetic processes are required. Quantum chemical thermodynamic data can be used in the ACDC framework by converting the cluster formation free energies into evaporation rates [2], but we can also use cluster properties derived from thermodynamics or hypothetical model substances for model and approximation testing purposes. So far, kinetic gas theory has been used to model the collisions between clusters and clusters and vapour molecules.

We have demonstrated that ACDC with quantum chemistry based evaporation rates can reproduce formation rates observed in the atmospherically relevant CLOUD chamber particle formation experiments performed at CERN using a mixture of sulphuric acid, ammonia, dimethylamine and water. Detailed comparison of modelled and observed cluster concentrations suggests that fragmentation occurs inside the mass spectrometer used to detect the clusters [3,4].

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Calculation of tunneling splittings with variational and pathintegral methods

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I shall speak about the tunneling splitting pattern, rovibrational energy levels and transitions of the methane-water dimer to exemplify the beauty and power of the direct variational solution of the rovibrational Schrödinger equation [1]. Excellent agreement is obtained [2] with far-infrared high-resolution measurements of this dimer [3], which also justifies the good quality of the potential energy surface underlying our computations [4]. Certainly, this direct approach provides us with the most detailed information about the dynamical properties of molecular systems but it quickly runs out of steam when it comes to trimers and smaller clusters. However, smaller clusters have been studied by high-resolution spectroscopic techniques, so in this respect theory lags behind experiment. In the second part of the talk, which focuses on recent developments rather than applications, I shall propose an alternative approach which relies on a symmetrized path-integral formalism [5] and has very favorable scaling with the system size. Due to the proper symmetrization, the computed energy splittings correspond to exact quantum numbers and thereby, they can be directly compared with spectroscopic measurements.

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An Extended Jahn-Teller Hamiltonian for Large-Amplitude Motion in Molecules and Clusters: Applications to $E \otimes e$ and $T_2 \otimes e$ Systems

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The Jahn-Teller effect [1] was formulated to address the spontaneous distortion in the degenerate electronic states of symmetrical molecules. It is now recognized that the Jahn-Teller concept provides a generally applicable formalism for interaction of degenerate and quasi-degenerate levels in molecules and clusters and in the solid state. In this paper, we consider the case of large-amplitude nuclear motion (LAM) that extends far from the symmetric reference geometry (SRG).

Although the development is general, the specific application here is to the vibrational Jahn-Teller effect, in which the high-frequency (fast) degenerate degrees of freedom are CH stretches (*E* or T_2) that are taken to be adiabatic functions of the large-amplitude coordinates (*e*). The example cases are CH₃SH ($E \otimes e$) and the CH₄ complexes with either the F⁻ or Na⁺ ions ($T_2 \otimes e$). In the former case, the LAM is motion of the sulfide proton; in the latter, it is rotation of CH₄ within the complex. In both cases, the LAM may be described approximately as motion on a sphere, with the spherical polar coordinates, (ρ , γ). The Jahn-Teller Hamiltonian is expanded in symmetrized combinations of the spherical harmonics. In the $T_2 \otimes e$ case, the Hamiltonian for the fast degrees of freedom is

$$H_{f}(\rho,\gamma) = \begin{bmatrix} H^{a_{1}} - \frac{1}{2}H_{\vartheta}^{e} + \frac{\sqrt{3}}{2}H_{\varepsilon}^{e} & H_{z}^{t_{2}} & H_{y}^{t_{2}} \\ H_{z}^{t_{2}} & H^{a_{1}} - \frac{1}{2}H_{\vartheta}^{e} - \frac{\sqrt{3}}{2}H_{\varepsilon}^{e} & H_{z}^{t_{2}} \\ H_{y}^{t_{2}} & H_{z}^{t_{2}} & H^{a_{1}} + H_{\vartheta}^{e} \end{bmatrix}$$

The terms with $\Gamma = a_1$, *e* and t_2 are expanded as $H_k^{\Gamma}(\rho,\gamma) = \sum_i c_i f_{i,k}^{\Gamma}(\rho,\gamma)$ where the c_i are expansion coefficients and the $f_{i,k}^{\Gamma}(\rho,\gamma)$ are the tetrahedral harmonics with $k = \varepsilon, \vartheta$ or x, y, z. Whereas previous extended Jahn-Teller Hamiltonians have used power series in the displacement from the SRG [2, 3], the present expansion treats all locations on the sphere in an even-handed way. The 2x2 $E \otimes e$ case is similarly expanded.

These Hamiltonians are used to fit *ab initio* data on the example systems. The $T_2 \otimes e$ systems each have 8 C_{3v} geometries, at which there are symmetry-required conical intersections (CIs). In addition in C_s geometries, there are numerous symmetry-allowed CIs and also narrowly avoided intersections between the different adiabatic surfaces. CH₃SH also has both kinds of CIs, but the pattern of the CIs is different from the CIs previously reported [3] for CH₃OH. Alternative diabatization schemes for these systems highlight expected differences in the large-amplitude vibrational dynamics.

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Atoms moving in a strongly anharmonic potential: Small and large amplitude atomic motion in the bifluoride anion

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The bifluoride anion (FHF⁻), a prototype example of a three-center four- electron bond [1], has been challenging theoreticians and experimentalists for almost a century because of its linear equilibrium configuration, the rather low dissociation energy of nearly 2 eV leading to HF + F- [2], and the strong anharmonicity of its potential energy surface. In this paper we describe a new, recently developed global potential energy surface for the FHF⁻ system that is based on analytical formulae for both covalent and pure long range electrostatic interactions [3]. The analytical representation was fit to energy data from *ab initio* calculations carried out at the coupled cluster CCSD(T) level of theory and explicitly correlated atomic bases. The vibrational structure was calculated from a discrete variable representation of an exact Hamiltonian expressed in Radau coordinates, and the importance of the strong anharmonic and Coriolis coupling is underlined. The potential proves to be an excellent playground to explore small and large amplitude atomic motion in the complex and the underlying quantum effects. Results from full quantum dynamical scattering calculations using the Heidelberg Multi-Configuration Time Dependent Hartree program will be presented.

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Self-interaction corrected functional calculations of loosely bound, Rydberg excited and localized electrons

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Practical implementations of Kohn-Sham density functional theory such as GGA, meta-GGA and hybrid functionals have various shortcomings in describing, for example, localized electronic states and weakly bound electrons extending far from atomic nuclei. A fully variational and self-consistent implementation of the Perdew-Zunger self-interaction correction (PZ-SIC) using complex optimal orbitals [1] has been found to give excellent results for several systems, including dipole bound anion [2], Rydberg excited states of molecules and molecular clusters [3], and the localized charge state in a diamine cation [4]. The results of these calculations are found to be in excellent agreement with experimental measurements and/or high level quantum chemistry calculations. The computational effort of the PZ-SIC calculations scales with system size in the same way as DFT/GGA calculations but the prefactor is large since an effective potential needs to be evaluated for each orbital - calculations that could well be carried out in parallel. PZ-SIC is an example of an extended functional form where the energy depends explicitly on the orbital densities, not just the total electron density. While significant improvements are obtained with PZ-SIC compared with regular DFT, as listed above, problems can also be introduced such as incorrect symmetry breaking [5]. The orbital density dependent functional form could, however, be exploited more generally to develop a self-interaction free functional rather than as a correction to Kohn-Sham functionals, thereby providing a mean field theory for optimal orbitals and orbital energies.



Figure. Left: Orbital density of the highest occupied molecular orbital of CH_3CN^- showing the distribution of the dipole bound electron calculated using PZ-SIC [2]. Isosurface corresponding to electron density of 0.0005 e/Å³. Right: Minimum energy path between localized (left) and delocalized (right) state of DMP⁺ [4]. Red dots show PZ-SIC calculations where a barrier of 0.2 eV separates the metastable, localized state from the delocalized state. Green dots show calculations using the M06-HF functional where MP2 optimized structures were used for endpoints. No energy barrier is produced and a structure optimization starting from the localized state converges on the delocalized state. Similar results were obtained for all other commonly used DFT functionals [4].

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