



SCS

Division of
Chemical Research

Conference Report

Report on the Latsis Symposium 'Intramolecular Dynamics, Symmetry and Spectroscopy'

September 6–10, 2008, ETH Zürich, Switzerland

Carine Manca Tanner, Georg Seyfang, and Frédéric Merkt*

*Correspondence: Prof. Dr. F. Merkt, Laboratory of Physical Chemistry, ETH Zurich CH-8093 Zurich, E-mail: frederic.merkt@phys.chem.ethz.ch

Abstract: We provide here a short review of the Latsis symposium 'Intramolecular Dynamics, Symmetry and Spectroscopy' which took place at the ETH Zürich, Hönggerberg Campus, September 6–10, 2008. The goal of the meeting was to review recent progress in spectroscopy and intramolecular dynamics. A balanced mix of speakers covering theory, experiments and applications reviewed the latest developments and provided new impulses and ideas in this multidisciplinary field.

Keywords: Computational methods · Intramolecular dynamics · Spectroscopy · Symmetry

1. Introduction

The Fondation Latsis Internationale, Genève, provides each year generous support for the organization of a symposium at EPF Lausanne and ETH Zürich. We present here a brief overview of the symposium organized at ETH in 2008 on the theme 'Intramolecular Dynamics, Spectroscopy and Symmetry'. In the history of Latsis Symposia at ETH Zürich, this was the second symposium on a theme related to intramolecular dynamics. The previous one ('Intramolecular Kinetics and Reaction Dynamics') had been organized by Martin Quack in 1982. Since this first symposium, the development of the scientific field has been stimulated by considerable progress in experimental, theoretical and computational methods. To obtain an overview of this progress, it seemed the appropriate time to organize a second symposium on this topic, this all the more as 2008 coincided with Martin Quack's 60th birthday. As intramolecular dynamics and spectroscopy are closely related disciplines, but are usually reviewed separately in international conferences, we chose

to organize a symposium with both disciplines simultaneously at the focus in order to stimulate new interactions and ideas.

The more specific aims of the symposium were (i) to review the most recent theoretical and experimental developments in intramolecular dynamics and spectroscopy, (ii) to establish new directions for the future, in particular to address fundamental questions in chemistry and physics concerned with the reversibility of dynamical processes, the origin and the role of fundamental symmetries in nature, and (iii) to place fundamental studies in the context of a broad range of recent applications in astrophysics, atmospheric chemistry, analytical chemistry, physics and biology.

The scientific program was articulated around the four main themes 'Intramolecular Dynamics', 'Spectroscopy and Dynamics', 'Spectroscopy and Symmetry', and 'Applications of Spectroscopy and Intramolecular Dynamics'. The topics were covered by 33 invited lectures and about 96 contributed posters, which brought together about 200 participants.

The scientific program was complemented by an excursion to the medieval castle of Lenzburg where the conference dinner, held in honor of Martin Quack's 60th birthday, took place.



The full auditorium before a lecture.



The conference photograph taken on the Hönggerberg Campus of ETH Zürich.



Animated discussions during one of the evening poster sessions.



Marcel Snels, Martin Quack and Hans Hollenstein during the poster session.

2. Intramolecular Dynamics

The symposium started on Sunday morning with an opening address by ETH vice president *Peter Chen*, followed by the lecture ‘Adiabatic channel models in reaction dynamics’ from *Jürgen Troe*, University of Göttingen, who gave an overview of the statistical adiabatic channel model. Recent results on the recombination reaction $\text{H} + \text{O}_2 (+\text{M}) \rightarrow \text{HO}_2 (+\text{M})$ were presented which beautifully illustrated the power of this theory and its ability, with appropriate modifications, to describe high-pressure rate constants between 0 and 5000 K using a potential energy surface calculated by *ab initio* quantum chemistry.

William H. Miller, University of California (Berkeley), explained in his talk how to add quantum effects to classical molecular dynamics simulations. The talk reviewed the concepts of the semi-classical initial-value representation (SC-IVR) approach, gave a survey of recent applications to the treatment of reactions



Joshua Jortner and Jack Dunitz: lively exchanges and profound wisdom.

between atoms and molecules, including $\text{H}_2 + \text{F} \rightarrow \text{HF} + \text{H}$, and described how this approach can be extended to study reactions involving larger molecules.

Tilmann D. Märk, University of Innsbruck, gave a lecture on the topic ‘Low energy electron interaction with biomolecules: from gas to condensed phase – from room temperature to near absolute zero’. The lecture illustrated the role of dissociative electron attachment as trigger of chemical processes in biomolecules, *e.g.* nucleobases, and also showed how the chemical processes are influenced by phase or temperature changes. The use of labelled nucleobases has highlighted bond- and site-selective electron attachment, and studies of biomolecules embedded in large helium clusters revealed the astonishing properties of these clusters.

Molecules imbedded in large helium clusters were also a central theme in the lecture of *Marius Lewerenz*, University of Marne la Vallée, on ‘Doped helium clusters: Random walks in imaginary and real time’. The lecture demonstrated how the diffusion quantum Monte Carlo technique can be used to estimate static ground state properties of doped He clusters. The calculations showed that Ne as dopant in He clusters, ionized upon photoexcitation, fragments while Mg solvates and forms Mg_n clusters.

In a lecture of superlatives, *Joshua Jortner*, Tel Aviv University, reported on the ultra-fast dynamics in clusters exposed to ultra-intense laser fields. In larger clusters, the electron dynamics induced by the strong laser field triggers a nuclear dynamics which evolves into a Coulomb explosion of the clusters creating a large number of highly energetic multicharged ions. Results on the simulation of these ultra-fast dynamics were shown and a new model for nuclear fusion driven by Coulomb explosion was presented.

David Luckhaus, University of British Columbia, provided a theoretical approach on the topic ‘Hydrogen exchange tunneling: large curvature reaction path dynamics’. Hydrogen exchange tunneling typically exhibits large curved reaction paths, which was demonstrated to be the limitation of the Reaction Path Hamiltonian (RPH) approach. A solution to this problem was presented that relies on a non-orthogonal representation of the Hamiltonian with exact variational limit for all curvatures, offering the possibility to also treat bifurcating reaction paths.

Ioannis Thanopoulos, National Hellenic Research Foundation Athens, presented a method to control the pathway from an initial state to a selected final state by designed coherent external laser fields. The idea of coherent control is merged with the concept of adiabatic passage to calculate the complete population transfer from an initially populated bound state to a number of energetically degenerate continuum levels.

The talk of *Fleming F. Crim*, University of Wisconsin, was devoted to the theme ‘Vibrational control of dissociation and isomerization in gases and liquids’. Experiments on isolated molecules in the gas phase based on resonance-enhanced multiphoton ionization (REMPI) with short laser pulses are used to probe the influence of a pre-selected vibrational state on the reaction path followed in the electronically excited state. For ammonia, a conical intersection is reached when the molecule is pre-excited in the symmetric stretching vibrational state, but not if it is excited in the antisymmetric vibrational state. The spectroscopic experiments in the gas phase are then compared with measurements in the liquid phase to quantify the role of solvation on the intramolecular dynamics.

3. Spectroscopy and Dynamics

The first talk of this session was given by *Walter Thiel*, Max-Planck-Institut für Kohlenforschung (Mülheim), and was entitled ‘*Ab initio* vibration–rotation spectroscopy’. The lecture focussed

on recent developments of variational *ab initio* quantum chemical theories applied to the determination of accurate potential energy and dipole moment surfaces in order to compute spectra and predict isomerization reactions. The power of these theories was illustrated by a careful study of the six-dimensional potential energy surface of the electronic ground state of PH_3 , using the CCSD(T)/aug-cc-pV(Q+d)Z method which allowed the determination of vibrational energies in quantitatively excellent agreement with the available experimental data.

Wim Klopper, University of Karlsruhe, gave a talk on 'Slater-type geminals in molecular electronic-structure theory'. The focus of the lecture was on highly accurate *ab initio* quantum chemical methods and their use in the determination of thermodynamical properties of molecules. The CCSD-F12 method and its variants were shown to represent excellent methods to determine highly accurate thermodynamical data and potential energy surfaces at a reasonable computational cost. The talk also presented a set of highly accurate atomization energies at 0 K that can be used as reference for future computations and as a source of thermodynamical data.

The lecture of **Roberto Marquardt**, University of Strasbourg, pertained to 'Molecular quantum dynamics and molecular kinetics: challenges and opportunities'. The lecturer pointed out how important the accuracy of a potential energy surface is in order to obtain reliable solutions for the time-dependent Schrödinger equation. This was illustrated with the photoinduced stereomutation reaction of ammonia.

Michael Hippler, University of Sheffield, talked about 'Quantum chemical studies and vibrational spectroscopy of hydrogen-bonded molecules in the gas phase'. The lecture presented stimulated Raman photoacoustic spectroscopy as a highly sensitive technique of high-resolution spectroscopy. The combination of this technique with *ab initio* calculations was used to investigate the structure of the molecular complex $\text{CHCl}_3 \cdot \text{SO}_2$ and the cyclic formic acid dimer.

Samuel Leutwyler, University of Bern, presented a lecture entitled 'Accurate structures of non-polar molecules by femtosecond rotational Raman coherence spectroscopy'. The lecture showed how molecular geometries can be determined by rotational coherence spectroscopy (RCS). The power of time-resolved RCS using femtosecond laser pulses was illustrated by application to non-polar cyclic alkanes and alkenes, and by measurements of highly accurate rotational and centrifugal distortion constants in isolated molecules.

Results on theoretical studies of the molecular structure and energetics of negatively charged DNA subunits were presented by **Henry F. Schäfer III**, University of Georgia. The lecture



Helmut Schwarz during his lecture on the metal-mediated activation of methane.

showed how broad and systematic searches of the multidimensional potential energy hypersurfaces enable the identification of key structures and reaction pathways in these molecules. It was argued that the accuracy of current state-of-the-art calculations on these systems can be used to decide which of two incompatible experimental results is the correct one.

The presentation by **Manfred Faubel**, Max Planck Institute for Dynamics and Self-Organization (Göttingen), was devoted to the investigation of chemical processes in aqueous solutions by photoelectron spectroscopy. The very elegant experiments introduce the aqueous solution in the high vacuum chamber of a photoelectron spectrometer by means of a liquid microjet. Experiments demonstrate that H_3O^+ is the prevailing cation of the hydrated proton in water. Studies by photoelectron spectroscopy of amino acids in aqueous solution further illustrated the power of this experimental approach.

Helmut Schwarz, Technical University of Berlin, talked about 'Ligand and cluster size effects in the metal-mediated activation of methane: a cold approach to a hot problem'. His lecture reviewed past and current approaches to a central problem of chemistry: how to catalytically activate methane and facilitate chemical reactions of this fundamental molecule without having to resort to high temperature conditions. The lecture very nicely illustrated how mass spectrometry can be used in systematic investigation of catalytic complexes and their reaction products and to provide insights in chemical reaction systems of fundamental importance.

In his talk entitled 'Determination of hydrocarbon cation structures in the gas phase', **Paul v. R. Schleyer**, University of Georgia, presented density functional theory calculations of the vibrational spectra of saturated and unsaturated hydrocarbon cations such as C_2H_3^+ or C_4H_5^+ with a number of added Ar-atoms. The results of the theoretical calculations agree with, and permit the interpretation of the experimental observations made in the group of M. A. Duncan (University of Georgia).

Gregory S. Tschumper, University of Mississippi, gave a talk entitled 'Generating benchmark interaction energies for weakly bound non-covalent clusters with the 2-body:many-body multi-centered QM:QM method' and described how to calculate accurately the energetics of weakly bound clusters with up to more than 20 molecular constituents.

4. Spectroscopy and Symmetry

A balanced combination of lectures covering theory and experiment was also offered in this session. The lecture of **Takeshi**



Takeshi Oka: H_3^+ and the origin of the universe.



Richard N. Zare during his lecture 'About molecular hydrogen' chaired by David M. Golden.

Oka, University of Chicago, was devoted to high-resolution spectroscopic studies of ro-vibrational spectra of small symmetrical protonated ions. The lecture beautifully illustrated how high-resolution molecular spectroscopy, combined with the elegant exploitation of symmetry selection rules can be used to address central questions of astrophysics. The laboratory spectra of H_3^+ in combination with spectra of this molecular ion observed from distant celestial objects namely represent the best sources of information to characterize such objects. The lecture showed how the recent analysis of spectra of H_3^+ located close to the galactic centre contributes to a better understanding of the processes leading to the formation of our universe. The IR spectrum of CH_5^+ was also presented as a challenge to molecular spectroscopy.

The same ion, CH_5^+ , was at the heart of the lecture of *Tucker Carrington Jr.*, Queen's University Kingston, who reported on very recent progress in the calculation of the vibrational spectrum of this ion. Such calculations are extremely challenging because the Schrödinger equation for the nuclear motion on a 12-dimensional potential energy surface has to be calculated to 'spectroscopic' precision if such calculations are to be helpful in the assignment of the extremely complex IR spectrum of CH_5^+ . A new method exploiting contracted basis functions in conjunction with the Lanczos algorithm was presented to determine the vibrational levels with high accuracy.

Robert Berger, Frankfurt Institute of Advanced Studies, reviewed the current status of quantum chemical predictions of molecular parity violation, and of combined efforts using high resolution spectroscopy and highly accurate quantum chemical calculations to quantify the role of the electroweak force in chemistry. He also outlined the potential of studies of parity violation in chiral molecules to detect new physics beyond the standard model.

Richard N. Zare, Stanford University, gave a lecture 'About molecular hydrogen'. A combined study involving full quantum calculations and Stimulated Raman Pumping (SRP) experiments was presented which over the past years has led to an almost complete understanding of the reactive scattering process $\text{H} + \text{D}_2 (\nu = 0, j = 0, 1, 2) \rightarrow \text{D} + \text{HD} (\nu' = 3, j')$. The lecture highlighted the importance of achieving and exploiting angular momentum alignment and orientation to unravel the details of bimolecular reactions.

The lecture of *Martin Suhm*, University of Göttingen, was entitled 'Playing with transient chirality in the gas phase'. Techniques like laser-induced fluorescence, resonance-enhanced multiphoton ionization or Raman scattering in jet expansions can be used to investigate chirality discrimination effects in the formation of complexes involving two molecules in the gas phase. The talk focussed on the chirality synchronization aspect, *i.e.* on the mechanism by which two achiral molecules (for example,

an ethanol and a water molecule) assemble to form a molecular complex of defined chirality.

The lecture 'Single conformation spectroscopy of synthetic foldamers and alkylbenzene' by *Timothy S. Zwier*, Purdue University, presented the use of multiple resonant spectroscopic methods such as Stimulated Emission Pumping-Population Transfer Spectroscopy (SEP-PTS) to identify the different conformers of large molecules present in a gas phase sample and to experimentally determine the isomerization barriers between the stable conformers.

5. Applications of Spectroscopy and Intramolecular Dynamics

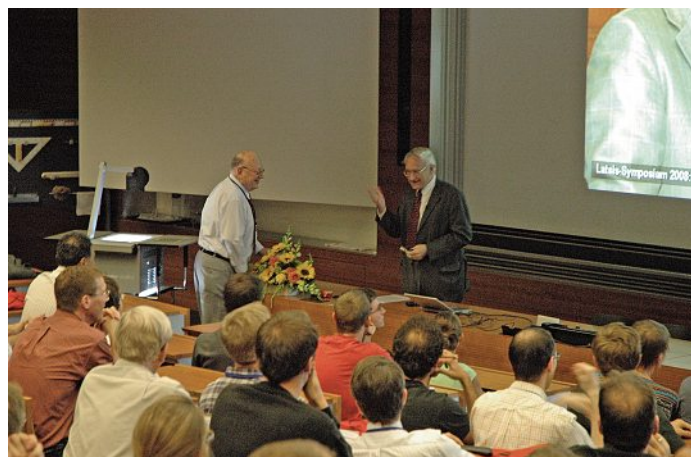
Several lectures were devoted to applications of spectroscopy and dynamics in a broad range of scientific fields. *Jean-Marie Flaud*, University of Paris-Est, gave a lecture on 'Infrared laboratory spectroscopy and satellite remote sensing measurements'. The use of spectroscopy to monitor the concentrations of molecules and their evolution in the atmosphere is an essential aspect of atmospheric chemistry and of studies of climatic change. To illustrate this, the lecture presented data recorded with the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) in the middle and upper atmosphere and showed how this data helped in quantifying the concentration of species like ethylene, formaldehyde and isotopomers of nitric acid (H^{14}NO_3 and H^{15}NO_3), and in some cases, even contributed new information on the spectroscopic properties of these molecules.

The lecture of *Vincent Boudon*, Dijon University, provided information on the 'Present status and future prospects of methane spectroscopy for planetary applications'. Methane being one of the main greenhouse gases, particular efforts need to be invested to understand all details of its spectrum in the IR. The STDS software developed in the Dijon group is aimed at studying rovibrational spectra of spherical top molecules. In particular, the line-by-line analysis of the IR spectrum of methane has resulted in a quantitatively correct description of the methane spectrum in the 0–4800 cm^{-1} range. The next goal, the extension of the current model to the region up to 6300 cm^{-1} was discussed in the light of current developments and spectroscopic measurement campaigns in the atmosphere.

John P. Maier, University of Basel, talked about 'Electronic spectra of carbon chains and rings: astrophysical relevance?'. The lecture summarized recent spectroscopic work carried out in Basel on the electronic spectra of carbon chains in various charge states and with various substituents. This effort has not only led to a detailed understanding of the electronic structure and spectra of these species but also to a body of data with which astronomical data can be compared to identify molecules in the interstellar space.

Thomas R. Rizzo, EPF Lausanne, gave a lecture entitled 'Multiple-laser photofragment spectroscopy: from triatomics to helical peptides'. The lecture described a new experimental technique with which samples of protonated amino acids and small peptides can be prepared at low temperature (~ 10 K) in ion traps. IR spectra of these molecules recorded by infrared laser-assisted photofragment spectroscopy provide rich information on their structural and dynamical properties.

Hubert van den Bergh, EPF Lausanne, discussed the application of photonics to medical problems, especially to the early detection and minimally invasive diagnostics and therapies of diseases. The lecture presented an overview of the collaborations with medical doctors and hospitals that enabled the development of attractive methods for the early detection of bladder cancer and for the therapy of age-related macular degeneration of the retina.



Urs Wild and Richard R. Ernst at the beginning of a memorable evening lecture bridging Fourier transformation and Tibetan art.

The lecture of **Joachim Sauer**, Humboldt University (Berlin), entitled 'Structure and reactivity of metal oxides: gas-phase clusters compared to solid catalysts' showed how the combination of multiphoton dissociation experiments using the far infrared free electron laser FELIX and B3LYP density functional theory calculations makes it possible to identify the structure of the different isomers of the $(V_2O_5)_n^-$ clusters. The lecture then provided a discussion of relationship between the structural and catalytic properties of these clusters.

Marcel Snels, University of Rome, talked about 'Cavity ring-down spectroscopy on explosives'. The lecture presented a cavity ring-down spectrometer designed to measure traces of explosive compounds at frequencies in the IR and telecommunication ranges. NIR spectra of 2,4-DNT, 2,6-DNT as well as TNT were presented and discussed in the context of the detection of explosives in 'sensitive' environments such as airports.

After a general introduction to the broad subject of energy resources, **Oliver Monti**, University of Arizona, described in his presentation the interfacial structure and dynamics of organic and hybrid organic/inorganic photovoltaic cells. To reduce the complexity resulting from the heterogeneity of the bulk, the mechanism of charge transfer in the cells was deduced from single molecule fluorescence spectroscopic studies carried out under highly defined conditions.

6. Evening Lecture

Following the tradition of Latsis Symposia, an evening lecture for a broader audience was organized on Monday evening. This lecture was held by Nobel Prize Laureate **Richard R. Ernst**, ETH



The sponsors of the symposium.

Zürich, on the topic 'Fourier transformation and spectroscopy, a symbiotic pair'. The first part of the lecture was devoted to the Fourier transformation in science and more specifically in spectroscopy. After a fascinating historical introduction, the lecturer reviewed the main scientific applications of Fourier transformations ranging from IR spectroscopy to medical imaging experiments using X-rays and magnetic resonance. In a second part of the lecture, Richard Ernst introduced the audience to his second scientific passion: the study of pigments in Tibetan art using Raman spectroscopy.

Acknowledgements

The organizing committee is deeply indebted to the Fondation Internationale Latsis, Genève, for the generous financial support. Further financial support was provided by the Swiss Chemical Society, the Swiss National Science Foundation and by industry sponsors as listed in the figure above. Most of the photographs were taken by Alexander Kushnarenko.

Received: June 24, 2009