Infrared Beamline Workshop Friday 10 April 2015
ETH Zurich, Hönggerberg Campus Building HCI, lecture Hall J7

Abstracts

Session 1	
Chairman Martin Quack (Physical Chemistry, ETHZ)	
08:30	Welcome
08:35 – 08:45	**Gabriel Aeppli** (Head of the Swiss Light Source) *Introduction, The Swiss Light Source*
08:45 – 09:15	**Sieghard Albert** (SLS, PSI and Physical Chemistry ETHZ) *Synchrotron-based high resolution FTIR and THz spectroscopy of chiral molecules and molecules of atmospheric and interstellar interest*
09:15 – 09:45	**Johannes Orphal** (KIT and University of Karlsruhe) *Remote-sensing of the Earth's atmosphere: needs and challenges for high-resolution infrared spectroscopy*
09:45 – 10:15	**Georg Mellau** (University of Giessen) *Unraveling the internal dynamics of small molecules using high-resolution spectroscopy*
10:15 – 10:45	Coffee Break
Session 2	
Chairman Alexander Wokaun (PSI and ETH Zurich)	
10:45 – 11:15	**Walter Caminati** (University of Bologna) *High accuracy vibrational energies of large amplitude motions as obtained from rotational studies*
11:15 – 11:45	**Marek Kreglewski** (University of Poznan) *Rovibrational structure of 5-methyltropolone*
11:45 – 12:15	**Stephan Schlemmer** (University of Köln) *Spectroscopy of molecular ions at highest resolution*
12:15 – 12:45	**Britta Redlich** (FELIX Laboratory, Nijmegen) *Opportunities for experiments in the infrared and THz using the FELIX Free Electron Lasers*
12:45 – 14:00	Lunch Break

Session 3	
Chairman Frithjof Nolting (Swiss Light Source, PSI**)**	
14:00 – 14:30	**Ben Murdin** (Advanced Technology Institute and SEPNet, University of Surrey, Guildford,UK), K.L. Litvinenko, E.T. Bowyer, P.T. Greenland, N. Stavrias, Juerong Li, R. Gwilliam, B. J. Villis, G. Matmon, M.L.Y. Pang, B. Redlich, A.F.G. van der Meer, C.R. Pidgeon, and G. Aeppli *Ramsey spectroscopy of silicon donors for quantum information applications*
14:30 – 15:00	**Hans Sigg** (SLS-PSI) *Ultra-broadband time resolved infrared pump-probe spectroscopy: from semiconductors devices to photo chemistry*
15:00 – 15:30	**Dirk van der Marel** (University Geneva) *Perspectives and opportunities for micro-spectroscopy at the Swiss Light Source*
15:30 – 15:45	**Ines Benmessaoud** and Laszlo Forro (EPF Lausanne) *Scanning Infrared Microscope Spectroscopy in neurodegenerative diseases*
15:45 – 16:00	**Axel Keens** (Bruker Optics Karlsruhe) *The High Resolution Challenge: How to build a FT Spectrometer with more than 11m Optical Path Difference*
16:00 – 16:30	Coffee Break
Session 4	
Chairman Martin Quack (Physical Chemistry, ETHZ)	
16:30 – 17:00	**Jérôme Faist** (Physics, ETH) *Quantum cascade laser frequency combs*
17:00 – 17:30	**Martin Suhm** (University of Göttingen) *Fighting against structural uncertainty in the gas phase: Insights into hydrogen bond docking preferences at low spectral resolution*
17:30 – 18:00	**Sonia Melandri** (University of Bologna) Accurate spectroscopy for astrophysical investigations: from the rotational spectrum of complex organic molecules in the millimeter and sub-millimeter wave regions to their infrared spectrum
18:00 – 18:30	**Sigurd Bauerecker** (University of Braunschweig) *IR spectroscopy of phase changes of freely suspended supercooled molecules, water particles and droplets*
18:30 – 19:00	**Peter Hamm** (University of Zurich) *THz Photon-Echoes in Water?*
19:00 – 20:00	*General Discussion*
ca. 20:00	Informal Dinner

Introduction

The Swiss Light Source

Gabriel Aeppli
Head of the Swiss Light Source
Swiss Light Source, Paul-Scherrer-Institute, CH-5232 Villigen, Switzerland,

Synchrotron-based high resolution FTIR and THz spectroscopy of chiral molecules and molecules of atmospheric and interstellar interest

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We present a detailed description of our high resolution FTIR setup at the infrared port of the Swiss Light Source described in Ref. [1-5] which is equipped with several external cells. One of them is a collisional cooling multireflection cell which makes it possible to record spectra down to 850 GHz (28 cm^{-1}) at low temperatures. Due to the high brightness of the synchrotron radiation the signal-to-noise ratio is effectively 5 to 50 times better than that of conventional thermal sources in the spectral region between 30 and 1000 cm^{-1}. Our resolution is on the order of 17 MHz. Using the collisional cooling method we are able to measure rotationally resolved spectra at T= 80 K and even 10 K. We present a THz spectrum of cooled CH_3D measured in the range 28 to100 cm^{-1} and 80 K [6].

We discuss the analyses of the rotationally resolved infrared spectra of naphthalene as a simple example of a polycyclic aromatic hydrocarbon with regard to the question of the unidentified infrared bands detected in space, the analysis of the spectra of chlorobenzene [7] as an atmospheric pollutant, the spectra of chiral molecules like dithiine and CDBrClF with regard to parity violation [8,9] and the tunneling switching in phenol and deuterated phenols [5].

Our synchrotron THz setup provides data which can be compared with the interstellar spectra taken by recent launched THz/FIR spectrometers operating in the upper atmosphere like SOFIA or in an earth orbit like HERSCHEL. As examples we discuss the THz spectra (0.8 - 3 THz) of methyl and cyano oxirane. Finally, we discuss the torsional fundamental of aniline located at 40.9 cm^{-1}. The potential use of coherent synchrotron radiation at the SLS will be also discussed.

[1] S. Albert and M. Quack, Trendbericht: Physik. Chem. 2013, *Nachr. aus der Chemie* **2014**, 62, 313.
[2] S. Albert, K. K. Albert, P. Lerch, M. Quack, *Faraday Discuss.* **2011**, *150*, 71-99.
[3] S. Albert, K. Keppler Albert, M. Quack, in *Handbook of High Resolution Spectroscopy, Vol. 2* (Eds.: M. Quack, F. Merkt), John Wiley & Sons, Ltd, Chichester, **2011**, pp. 965-1019.
[4] S. Albert, Ph. Lerch, M. Quack, *ChemPhysChem* **2013**, 14, 3204-3208.
[5] S. Albert, Ph. Lerch, R. Prentner, M. Quack, *Angew. Chem. Int. Ed.***2013**, *52*, 346.
[6] S. Albert, S. Bauerecker, I, Bolotova, Ph. Lerch, M. Quack and A. Wokaun, **2015**, *in preparation*.
[7] S. Albert, K Keppler, Ph. Lerch, M. Quack and A. Wokaun, *J. Mol. Spectrosc*. **2015** in press.
[8] M. Quack, *Fundamental Symmetries and Symmetry Violations from High Resolution Spectroscopy*, in *Handbook of High-Resolution Spectroscopy*, Vol. 1, (Eds. M Quack and F Merkt), Wiley, Chichester (**2011**), 659-722.
[9] M. Quack, J. Stohner, and M. Willeke, *Annu. Rev. Phys. Chem.*, **59**, 741 – 769 (2008).

Remote-sensing of the Earth’s atmosphere: needs and challenges for high-resolution infrared spectroscopy

Johannes Orphal

Institute for Meteorology and Climate Research (IMK)
Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

The Earth’s atmosphere is an essential element of the climate system. Infrared spectroscopy provides unique information on the horizontal and vertical distributions of the most important trace gases, day and night, and is therefore used by many instruments onboard satellites for weather forecast and atmospheric research.

In order to improve these methods, our institute at KIT has developed for many years new approaches concerning innovative instruments such as MIPAS, PREMIER, MACE, G3E and international networks like CoCCON, as well as different approaches for the analysis of available atmospheric measurements.

This talk will present an overview of our activities and highlight in particular the need for accurate spectroscopic measurements from the laboratory also in the future.

Unraveling the internal dynamics of small molecules using high-resolution spectroscopy

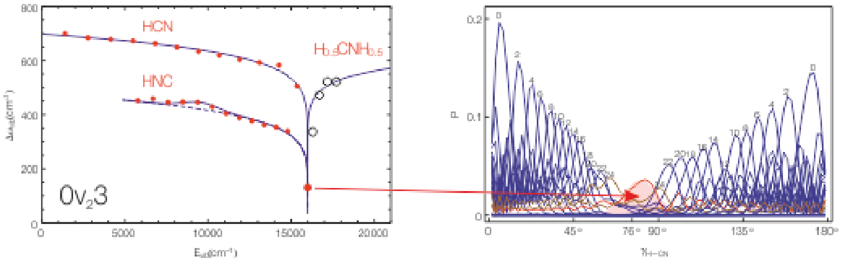
Georg Mellau

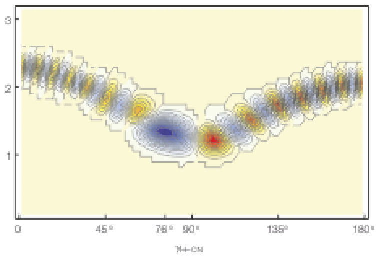
Physikalisch-Chemisches Institut, Justus-Liebig-Universität Gießen, Germany

The [H,C,N] molecular system is an important prototypical double well system of molecular physics. The bending states at the H-CN respective CN-H sides of the isomerization barrier merge into the internal rotation states of the hydrogen atom around the CN core as the excitation is increased above the isomerization barrier. We use, for the analysis the [H,C,N] level set [1-3,..(11 papers)], the most extensive and complete rovibrational level set determined for any polyatomic molecule. As the experimental results reach only up to v_2=15 of the bending excitation, we combine the experimental results with calculated ab initio full dimensional rovibrational eigenenergies. The existence of an *ab initio* eigenenergy spectrum seems not to be helpful at first sight: the eigenenergies, labelled only by the rigorously good quantum numbers (*J* and parity), do not permit direct extraction of any physical insight from these data. To search for new classes of patterns in the spectra of vibrationally highly excited small polyatomic molecules and to investigate the validity of the vibrational model used at low internal excitation, the ab initio eigenenergy spectrum must be analyzed [1] in a way similar to how high resolution spectra are assigned and modelled. This is the first time that such a complete analysis of the rovibrational spectrum of a polyatomic molecule has been achieved. These data sets allow us to discover and interpret the internal dynamics of this molecular system [3,4].

As the vibrational excitation energy approaches the isomerization barrier, the spacing of the vibrational energies shows a vibrational angular momentum dependent Dixon-dip-like trend [1], which correlates with the semiclassical pattern of the level spacing [5]. Based on the level spacing we can determine the dynamical proximity of an eigenstate to the effective dynamical isomerization barrier. The barrier proximal "saddle point states" are found to be highly localized [6,7] in the bending coordinate at the saddle point as expected from a classical point of view. The localization takes place not only for pure bending states but also at all higher energies, exactly when the eigenenergies match the dynamical effective barrier height.

The central paradigm of the transition state theory is based on the highest point along the lowest energy path of the chemical reaction. Based on the vibrational spacing dip we can extract [5] chemically relevant *saddle point* energies from spectroscopically measured quantities. A simple vibrational analysis allows the determination of the energy and shape of the isomerization barrier and of the two minima of the isomers, it is possible to obtain up to 1% accurate saddle point energies using hot band spectroscopy. This method opens the possibility to use the hot gas molecular emission experiments to access the transition states of some fundamental chemical reactions directly.





[1] G. Ch. Mellau, J. Chem. Phys. **134**, 234303 (2011)
[2] G. Ch. Mellau, J. Chem. Phys. **133**, 164303 (2010)
[3] G. Ch. Mellau, J. Chem. Phys. **134**, 194302 (2011)
[4] G. Ch. Mellau, *in prep*. (2015).
[5] J. Baraban et al., *in prep*. (2015).
[6] G. Mellau, R. W. Field, O. L. Polyansky, A. Kyuberis, http://www.dpg-verhandlungen.de/year/2015/conference/Heidelberg/part/mo/session/20/contribution/4 (2015).
[7] G. Ch. Mellau et al., *in prep*. (2015).

High accuracy vibrational energies of large amplitude motions as obtained from rotational studies.

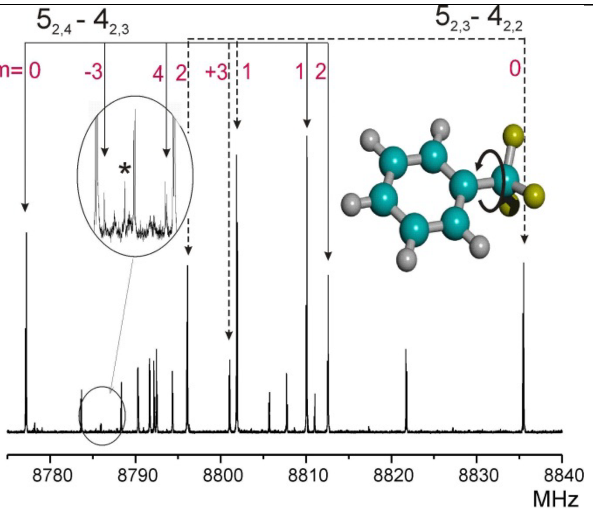
WALTHER CAMINATI

Dipartimento di Chimica "G. Ciamician" dell'Università, Via Selmi 2, I-40126~Bologna, Italy

I present below the information obtained by rotational spectroscopy on the vibrational energies of low lying vibrational levels of large amplitude (tensional) motions.

1) Intertorsional interactions revealing absolute configurations: The V_6 internal rotation heavy-top case of benzotrifluoride (in collaboration with V.V. Ilyushin, L.B. Favero, J.-U. Grabow)

The rotational lines of several torsional states of the internal rotation of the CF$_3$ group are labeled in the Figure below, while symmetries and vibrational energies are listed in the nearby Table.



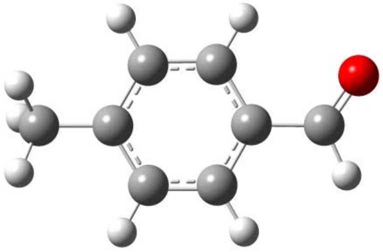
Energy of the lowest torsional levels of BTF.

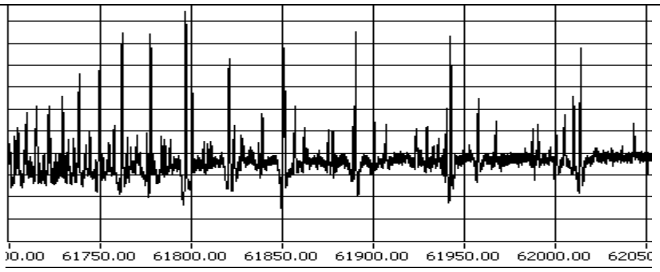
m	Symmetry[a]	Energy/MHz
0	A1	0.0[b]
±1[c]	E1	10956.3369(24)[d]
±2[c]	E2	43048.3119(79)
3	B2	79711.039(24)
-3	B1	128083.983(76)
±4[c]	E2	187317.202(69)
±5[c]	E1	287103.87(12)
-6	A2	409399.93(22)
6	A1	412261.63(23)

[a] Symmetry species of the G_{12} group. [b] The torsional zero point energy of the $0_{0,0}$ $m=0$ state, 1.52 cm^{-1}, has been subtracted from all energy levels. [c] Doubly degenerate levels. [d] Error in parentheses in units of the last digits.

2) Information Transfer along Conjugated π-Electron Systems: Remote Governance of the Internal Motion in Paratolualdehyde (in collaboration with H. Saal, J.-U. Grabow, A. R. Hight Walker, J. T. Hougen, I. Kleiner.)

Pure rotational measurements up to $v = 3$ have allowed the determination of the V_3 and V_6 terms of the potential energy surface of the internal rotation of the methyl group in *p*-tolualdehyde (*p*TA). The observed $J = 34 \leftarrow 33$ μ_a-*R*-band of *p*TA, recorded in a steady free-jet expansion with T ≈ 50 K, is shown in the right Figure below..





Rovibrational structure of 5-methyltropolone

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In 5-methyltropolone as proton moves from one oxygen atom to another, the equilibrium positions of all heavy atoms of the seven-membered ring shift, the single and double CC bonds exchange their positions, and methyl group, attached to the ring in the position 5, rotates by 60°. The G_{12} symmetry group of the molecule is isomorphic to the C_{6v} point group and the rovibronic states belong to one of the allowed species A_1, A_2, B_1, B_2 , E_1 or E_2. Since the dipole moment belongs to the irreducible representation A_2, the spectra of 5-methyltropolone should contain four series of allowed transitions: $A_1 \leftrightarrow A_2$, $B_1 \leftrightarrow B_2$, $E_1 \leftrightarrow E_1$ and $E_2 \leftrightarrow E_2$.

The fluorescence excitation and hole burning spectra in the $S_1 - S_0$ region of 5-methyltropolone were studied and proved that the spectra are split into four subsystems [1], in agreement with the group theory predictions of four series of transitions. However, the resolution of electronic spectra is too low to allow for the determination of the rovibrational structure of the S_0 electronic state.

Ilyushin *et al* reported a very accurate microwave study of 5-methyl tropolone which provided information about rotational structure and tunneling splittings in the ground vibrational state in the S_0 electronic state..

So far, no infrared spectra for 5-methyltropolone have been reported. Due to the intensity of the source and very high resolution, the SLS creates a unique opportunity to record FTIR spectra at low frequencies. That would allowed for systematic study of energy transfer from the methyl group to the intramolecular proton bond through the π-electron system of the ring.

From the theoretical point of view the problem of coupling between proton tunneling, torsion and rotation is well understood and the method of the effective Hamiltonian can be used to analyze the spectrum in terms of rotational constants and tunneling splittings. In our group we are working on the alternative approach which should directly provide the shape of the large amplitude potential surface.

[1] K. Nishi, H. Sekiya, H. Kawakami, A. Mori, Y. Nishimura, *J. Chem. Phys.*, **109** (1998) 1589 –1592; *J. Chem. Phys.*, **111** (1999) 3961 –3969.

[2] V.V. Ilyushin, E.A. Cloessner, Y.-C. Chou, L.B. Picraux, J.T. Hougen, R. Lavrich, *J. Chem. Phys.* **133** (2010) 184307

Spectroscopy of Cold Molecular Ions

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Cryogenic multipole ion traps have become very popular devices in the development of sensitive action-spectroscopic techniques, including Laser Induced Reaction (LIR) spectroscopy, IR predissociation spectroscopy of Van-der Waals-clusters, and more recently, Laser Induced Inhibition of Cluster growth (LIICG). The low ion temperature leads to enhanced spectral resolution, and less congested spectra.

In the LIR method a chemical reaction between stored ions and neutral collision partners is promoted by the excitation of the trapped ion. The spectrum is detected by recording the number of reaction products as a function of wavelength. Recently the resolution of ro-vibrational spectroscopy of CH_2D^+ and CD_2H^+ [1] was pushed to predict rotational spectra in the THz regime helping to identify these molecules in astrophysical observations. Employing a frequency comb in combination with cw-OPOs, transition frequencies of ro-vibrational lines of CH_5^+ have been determined with sub-MHz resolution [2]. This development paves the road to pinpoint combination differences (CDs) of complex spectra where thousands of lines lead to an enormous number of CDs. Pure rotational transitions of several molecular ions have been detected by using the state-dependent association rate with He at 4 K. Such laboratory spectra led to the identification of l-C_3H^+ in space [3]. IR-THz two photon double resonance spectroscopy has been used to record the J=1-0 rotational transition of OH^- [4]. Also spectra of complexes such as He-H_3^+ and He-D_3^+ have been measured very recently.

References

1. S. Gärtner, J. Krieg, A. Klemann, O. Asvany, S. Brünken, S. Schlemmer, *High-Resolution Spectroscopy of CH_2D+ in a Cold 22-Pole Ion Trap,* J. Phys. Chem. A, **117** (2013) 9975–9984

2. O. Asvany, J. Krieg, and S. Schlemmer, *Frequency comb assisted mid-infrared spectroscopy of cold molecular ions,* Review of Scientific Instruments, **83** (2012), 076102. http://dx.doi.org/10.1063/1.4753930.

3. S. Brünken, L. Kluge, A. Stoffels, O. Asvany, and S. Schlemmer, *Laboratory Rotational Spectrum of l-C3H+ and Conformation of its Astronomical Detection*, ApJ **783** (2014) L4

4. P. Jusko, O. Asvany, A.-C. Wallerstein, S. Brünken, S. Schlemmer, *Two photon rotational action spectroscopy of cold OH^- at 1 ppb accuracy*, Phys.Rev.Lett. **112** (2014) 253005

Opportunities for experiments in the infrared and THz using the FELIX Free Electron Lasers

Britta Redlich

on behalf of the FELIX team

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The status of the infrared and THz user facility FELIX at the Radboud University Nijmegen, comprising two free electron lasers – FLARE, the recently commissioned THz laser as well as the FELIX and FELICE laser beam lines - will be reviewed. The FELIX (Free Electron Lasers for Infrared eXperiments) Laboratory offers the international user community a unique wavelength range covering the mid- and far-infrared as well as the THz range from 3 μm to 1500 μ (3300 – 6 cm^{-1} or 100 THz – 0.2 THz) with continuous tuning and picosecond laser pulses.

The layout of the facility including the user laboratories as well as some of the special features offered to the users will be presented. Unique experimental possibilities are created by the combination of the infrared and THz free electron lasers with the high magnetic fields of up to 38T (increased to 45 T in 2017) of High Field Magnet Laboratory. Different fields of applications of IR and THz radiation will be reviewed. A number of selected examples of user experiments demonstrating the versatility of the FELs and of the scientific applications will be discussed.

Ramsey spectroscopy of silicon donors for quantum information applications

BN Murdin (1), K.L. Litvinenko (1), E.T. Bowyer (1), P.T. Greenland (2), N. Stavrias (3), Juerong Li (1), R. Gwilliam (1), B. J. Villis (2), G. Matmon (2), M.L.Y. Pang (1), B. Redlich (3), A.F.G. van der Meer (3), C.R. Pidgeon (4), and G. Aeppli (5)

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Shallow Group V donors in silicon, such as Si:P, once frozen out at low temperature, share many properties in common with free hydrogen atoms [1]. The Group IV host is tetrahedrally bonded, and the Group V impurity has an extra valence electron that orbits around the singly positively charged ion in much the same way. The primary difference is that the host is a dielectric, with electrons that screen the Coulomb force, (a smaller secondary effect is that the host is a crystal with bands that have an “effective mass” that is less than the free mass).
The energy scale that defines the Lyman series absorption lines is in the UV for hydrogen, whereas for silicon donors they are in the far-IR or THz. The Bohr radius is similarly affected, and is correspondingly larger – the ground state radius is 3nm, and the first excited state is 20nm, which puts them on the scale of CMOS devices in commercial use.

Coherent control of free atoms and impurities in solids is important for quantum technologies. This requires time-resolved experiments with short THz pulses. We have developed THz Ramsey spectroscopy for this, which is essentially a time-resolved version of FTIR. This spectroscopy relies on coherence left in the atoms by a short coherent pulse, and a second pulse interferes with the oscillation left in the matter. The interference amplitude dies with increasing time delay between the pulses on a scale determined by the inverse of the line-width. The pulse sequence is crucial for some quantum information processing gating schemes. We show that the coherence lives for many tens of picoseconds, and that it may be read out either optically or electrically [1].

[1] K.L. Litvinenko et al, "Coherent creation and destruction of orbital wavepackets in Si:P with electrical and terahertz read-out" Nature Communications, (2015) DOI: 10.1038/ncomms7549

Ultra-broadband time resolved infrared pump-probe spectroscopy

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Synchrotron infrared sources are popular mainly because of their excellent broadband brilliance, which enables spatial-mapping of stationary objects at the diffraction limit over a large wavelength band with spectral high resolution. Here, we focus on a further advantage of such sources – their unique time structure – to bring time resolved FTIR broadband spectroscopy down to the 100ps limit for studying dynamic phenomenon on a long to medium time scale.

An overview of experiments is given to demonstrate that infrared Pump-Probe experiments at synchrotrons are particularly attractive for condensed matter and chemical reaction experiments to identify state populations and intermediate reaction species, respectively.

Perspectives and opportunities for micro-spectroscopy at the Swiss Light Source

Dirk van der Marel
Université de Genève

Infrared optical spectroscopy is one of the most versatile experimental probes of the electronic structure of materials. It can be used to study materials under conditions of high pressure, high magnetic fields, low or high temperatures, and can provide access to buried interfaces. In certain cases these conditions can only be reached for relatively small samples, in which case a high brilliance broadband source of infrared radiation is required to do spectroscopy with sufficient signal to noise. The best known solution to date is the use of synchrotron radiation. In this talk examples are shown of successful high pressure studies of metal insulator transition in BiTeI [1] and dimensional cross-over in purple bronze [2] using the SLS infrared beamline. Furthermore novel opportunities of synchrotron infrared light source are discussed for magneto-infrared microscopy and for scanning probe local- and non-local infrared spectroscopy.

[1] M. K. Tran et al., Physical Review Letters 112, 047402 (2014)
[2] M. K. Tran, Ph D thesis, Univ. de Genève (2014)

“Scanning Infrared Micro-Spectroscopy in neurodegenerative diseases”

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Laboratory of Physics of Complex Matter
Ecole Polytechnique Fédérale de Lausanne

Several human diseases, ranging from Alzheimer's to prion disease, have now been identified to be caused by proteins; which auto-assemble into high molecular weight aggregates. There is a subgroup of ten such diseases that are related to abnormal polyglutamine (polyQ) repeats, one of which is Huntington's Disease (HD). Its symptoms are progressive deterioration of cognitive and motor functions, along with extensive loss of neurons primarily in the striatum. We used a rat model of HD to examine the chemical makeup of the brain slices. Traditional histochemical staining, shows sequential appearance of htt aggregates and the beginning of cell death on the timescale of over 3 months. We have investigated the striatum with synchrotron-assisted Fourier transform infrared microspectroscopy (SIRMS). One brain hemisphere was infected with HD while keeping the second one as a control. The two types of matter in the striatum are affected in different manners: in neuron-rich gray matter exposed to the disease, a higher content of aggregated protein is detected as early as 6 weeks after infection, but no signs of cell death up to 8 weeks. In contrast, myelin-rich white matter does not show any aggregates, but surprisingly shows a significant increase in phosphorylation. We interpret this as the activation of the cellular response to stress which leads in the end to cell death.

The drastic changes in the white matter were detected in the case of multiple sclerosis. We have studied its animal model, the experimental autoimmune encephalomyelitis (EAE). It is characterized by heavy loss of the insulating lipid-layer, the myelin around axons. This has been clearly confirmed by SIRMS and FTIR. Analysis of spatially-resolved maps by both unsupervised principal component analysis and chemical signatures show additional features of this disease.

Both studies indicate that SIRMS is a powerful tool of detecting complex chemical processes in biological tissue in a relatively easy way.

Acknowledgment: This work is performed in collaboration with Markus Bonda, Sylvia Jeney, Ruth Luthi-Carter, Lisa Miller, Bertrand Vileno.

The High Resolution Challenge:
How to build a FT Spectrometer with more than 11m Optical Path Difference

Dr. Axel Keens, Bruker Optik GmbH, 76275 Ettlingen, Germany

After a short review of the original request for a FT spectrometer with maximum optical path difference (MOPD) of at least 15m, the important considerations to design such an instrument are discussed. Numerical values for the acceptable misalignment of the mechanical versus optical axis are presented. Arguments are given to limit the MOPD to 11.7m for the actually built instrument.

The adaptation to the synchrotron light source at the Paul-Scherrer-Institute is briefly discussed.

Finally it is shown how the alignment of the instrument can be checked by observation of Haidinger fringes.

Mid-infrared and THz Quantum cascade laser frequency combs

Jérôme Faist[1]

1. QOE, Institut for Quantum Electronics, ETH Zürich

The quantum cascade laser has demonstrated the ability to provide gain over a very broad wavelength range. Recently, we have shown that such broadband devices, when operated in continuous wave, emit as a coherent optical comb[1] in which the phase relation between the comb modes corresponds approximately to a FM modulated laser. By combining a Maxwell-Bloch equations and a modal decomposition, the nature of this mode-locking has been elucidated[2] . We have also recently shown that these combs can also be produced in the THz region of the spectrum, with the gain bandwidth covering a full octave[4].

These new comb lasers enables the fabrication of a dual comb spectrometer based on a quantum cascade laser that offers a broadband, all solid-state spectrometer with no moving parts and a ultrafast acquisition time. We demonstrate a spectrometer and its first proof-of-principle applications.

Finally, by using a high-finesse Fabry-Perot cavity as an optical discriminator, we are able to show that the linewidth of a QCL comb is limited by the Schawlow-Townes formula as it is for a single frequency laser. A linewidth of 300Hz is measured for an optical power of 25mW[5].

1. A. Hugi, G. Villares, S. Blaser, H. C. Liu and J. Faist, Nature **492** (7428), 229-233 (2012).
2. J. B. Khurgin, Y. Dikmelik, A. Hugi and J. Faist, Applied Physics Letters **104** (8), 081118 (2014).
3 A. Hugi, S. Blaser, G. Villares, and J. Faist, *Nature Communications*, vol. 5, pp. 1–9, Oct. 2014.
4. M. Rösch, G. Scalari, M. Beck, and J. Faist, *Nature Photonics*, vol. 9, no. 1, pp. 42–47, 2015.
5. F. Cappelli, G. Villares, et al, unpublished.

Fighting against structural uncertainty in the gas phase: Insights into hydrogen bond docking preferences at low spectral resolution

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The spectroscopic characterization of hydrogen bonded complexes profits from low effective temperatures realized in supersonic jets. This is often the only experimental source for the preferred structure of such assemblies, because matrix embedding interferes with the feeble intermolecular interactions within the complex. Ultimate structural proof in the gas phase usually requires some kind of high resolution spectroscopy, either spectral (MW, IR, UV) or temporal (fs rotational coherence). However, these techniques and their spectral interpretation tend to be rather time-consuming when screening for interesting qualitative effects as a function of molecular shape and size. Furthermore, they are limited in molecule size for practical and also fundamental reasons. We offer an efficient pre-screening tool by synchronizing intense supersonic gas pulses (containing the cluster constituents in a large excess of a carrier gas) to short FTIR spectrometer scans and repeating the process at low duty cycle until the desired signal-to-noise ratio is achieved [1]. The spectral resolution is pragmatically set to 0.5-4 cm^{-1}, depending on the expected spectral structure and available signal strength. Applications between 200 [2] and 8000 cm^{-1} [3] have been demonstrated, but most of our work concentrates on the hydride stretching region, because its structural sensitivity offers a way out of the limited cluster size specificity.

Examples which are small enough to be confirmed/challenged by high resolution spectroscopy and others where this confirmation may be more challenging [4] will be presented and discussed briefly. By focusing on binary decisions and by including auxiliaries like isotope substitution, overtone spectroscopy, and quantum chemical predictions, the low resolution evidence can sometimes be turned into high certainty.

[1] M. A. Suhm, F. Kollipost **Femtisecond single-mole infrared spectroscopy of molecular clusters** Phys. Chem. Chem. Phys. 15 (2013) 10702-10721, doi:10.1039/c3cp51515j

[2] F. Kollipost, R. Wugt Larsen, A. V. Domanskaya, M. Nörenberg, M. A. Suhm **Communication: The highest frequency hydrogen bond vibration and an experimental value for the dissociation energy of formic acid dimer** J. Chem. Phys. 136 (2012) 151101, doi:10.1063/1.4704827

[3] Franz Kollipost, Kim Papendorf, Yu-Fang Lee, Yuan-Pern Lee and Martin A. Suhm **Alcohol dimers - how much diagonal OH anharmonicity?** Phys. Chem. Chem. Phys. 16 (2014) 15948-15956, doi:10.1039/c4cp01418a

[4] Robert Medel, Matthias Heger, and Martin A. Suhm **Molecular Docking via Olefinic OH...π Interactions: A Bulky Alkene Model System and its Cooperativity** J. Phys. Chem. A 119 (2015) 1723-1730, doi:10.1021/jp508424p

ACCURATE SPECTROSCOPY FOR ASTROPHYSICAL INVESTIGATIONS: FROM THE ROTATIONAL SPECTRUM OF COMPLEX ORGANIC MOLECULES IN THE MILLIMETER AND SUB-MILLIMETER WAVE REGIONS TO THEIR INFRARED SPECTRUM

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ABSTRACT

The investigation of phenomena related to the chemistry of the Cosmos is strongly based on the identification and quantification of molecules by spectroscopic methods, thus laboratory work is essential to provide the community with the spectral features needed to analyze the cosmological surveys.

Many of the molecular systems which are searched for in space, include complex organic molecules which can show some degree of molecular flexibility. The presence of several low energy conformations and the presence of large amplitude motions on shallow potential energy surfaces are peculiar to this kind of systems giving rise to complex rotational spectra, which represent a challenge for spectroscopic and computational methods.

Our spectroscopic strategies for the rotational study of flexible organic molecules include the use of the cold and isolated conditions of a free jet expansion and heated sources for the non volatile systems. The experimental work is strongly supported and complemented by theoretical modeling and calculations with the aim of assigning the observed spectra and to obtain information on the molecular dynamics which involve, for example, conformational rearrangements, tautomeric equilibria, large amplitude motions, vibro-rotational coupling and the prediction of vibrational spectra.

We will give examples of the spectroscopy of molecules and molecular complexes studied in the microwave and millimeter ranges (6-18 and 52-74.4 GHz).

IR spectroscopy of phase changes of freely suspended supercooled molecules, water particles and droplets

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The talk was cancelled due to illness of the speaker.

THz Photon-Echoes in Water?

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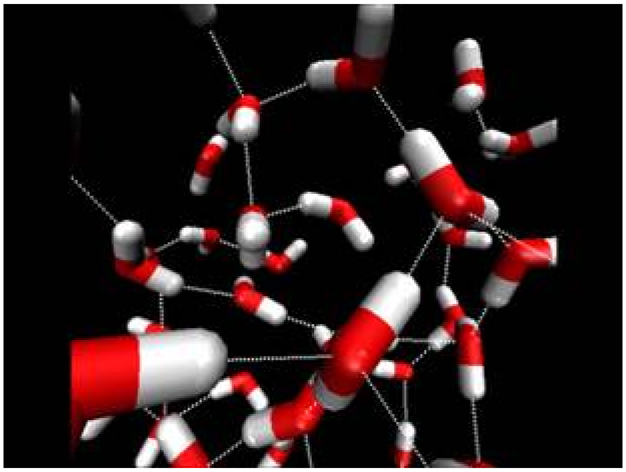
Water is a complex liquid due to the hydrogen-bond network that it forms and that is responsible for the many peculiarities of water. The associated low-frequency spectrum of water in the THz regime reports directly on its thermally excited intermolecular degrees of freedom, i.e., the vibrations of the hydrogen bond network. However, that spectrum is essentially featureless. In order to extract the information, a multidimensional spectroscopy directly in that frequency range has been developed. The results [1] provide evidence for very short-lived echoes, which indicate a heterogeneous distribution of hydrogen-bond structures.



References

[1] J. Savolainen, S. Ahmed and P. Hamm, "2D-Raman-THz Spectroscopy of Water" Proc. Natl. Acad. Sci. USA, 110 (2013) 20402