Ultrafast Time-Resolved Vibrational Spectroscopy at University of Zurich

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Abstract: Vibrational spectroscopy uniquely combines ultrafast time-resolution with chemical selectivity and molecular structure resolution. A list of examples of experiments and applications pursued at University of Zurich highlights the wide-spread applicability of time-resolved vibrational spectroscopy for molecular sciences.

Keywords: 2D IR spectroscopy · Molecular dynamics · Multidimensional IR spectroscopy · Time-Resolved vibrational spectroscopy

Vibrational spectroscopy monitors the vibrations of atoms in a molecule upon resonant irradiation with IR light. Vibrational spectra are chemically selective; that is, certain molecular groups (such as a $-C=O$ group) give rise to characteristic bands in the IR spectrum (around 1650 cm^{-1} in this case). Chemical selectivity is obtained since the vibrational frequency depends on masses of the nuclei as well as the strength of the chemical bonds holding them together, whereas the band intensity reflects the polarity of a molecular group. Furthermore, vibrational bands often are quite sensitive probes of the environment around a molecule; for example, whether a group is exposed to a polar solvent or inside an apolar membrane, or whether it is hydrogen bonded. Vibrational spectra contain significantly more information about chemical structure than electronic spectra. Often, the assignments of vibrational spectra can be based on empirical rules with rather good accuracy (while in other cases, *ab initio* quantum chemistry calculations and/or isotope substitutions are required).

The chemical selectivity of vibrational spectra is the very reason why IR spectroscopy is used as a standard analytical tool during chemical synthesis.

However, vibrational spectroscopy has much more to offer for molecular sciences, as it is intrinsically a very fast spectroscopy. The intrinsic (maximal) time-resolution of a particular type of spectroscopy is dictated by the typical dephasing time of its spectroscopic transitions, which for vibrations in the solution phase is on the order of 1 ps (in some cases down to 100 fs). That is, to the extent vibrational spectroscopy tells about molecular structure, one can learn a lot about the dynamics of molecular systems with time-resolved vibrational spectroscopy. The time-resolution of vibrational spectroscopy is sufficient to resolve even the fastest chemical processes. Only with the development of reliable femtosecond laser-based IR light sources some 10–20 years ago, the time-resolution aspect of vibrational spectroscopy now starts to be fully explored by many research groups around the globe.

One important development in this regard (but certainly not the only one) is the advent of multidimensional IR spectroscopy.[1] Similar to 2D-NMR spectroscopy, a spectrum is spread into two or more dimensions, which enhances its resolution and at the same time allows one to correlate various transitions in the spectrum with each other. Such correlations may occur because two modes are coupled since they are spatially close in the molecular system, or because a molecule undergoes an ultrafast conformational transition that shifts the vibrational frequency of a particular group. 2D IR spectroscopy combines appreciable structural resolution with ultrafast time-resolutions in an unprecedented way. The research field has expanded tremendously since its first demonstration a little more than a decade ago,[1] and countless applications in physical, biophysical, chemical and material sciences are appearing. It is anticipated that 2D IR spectroscopy will soon develop into just a normal method for daily use, similar to current FTIR spectrometers.

The common denominator of the research performed in our group at University of Zurich is ultrafast time-resolved vibrational spectroscopy. We concentrate on instrument development for time-resolved vibrational spectroscopy and 2D IR spectroscopy,[2–7] the development of new spectroscopic approaches such as transient 2D IR spectroscopy[8–11] and 3D IR spectroscopy,[12–14] as well as the application of these techniques to solve problems of molecular sciences. In the following, I will briefly discuss some examples to illustrate the power of time-resolved vibrational spectroscopy. Review articles on our work appeared in refs. [15–18].

Ultrafast Protein Folding

The amide I band of peptides and proteins (mostly the $C=O$ vibration of the protein backbone) is known to be a sensitive probe of the protein secondary structure. The structure sensitivity of the amide I band results from the distance and angle-dependent coupling between various sites, as well as the characteristic frequency shift of a $C=O$ vibration upon hydrogen bonding. We have explored extensively the possibility to switch the conformation of a peptide with the help of covalently bound photo-switches (*i.e.* molecular moieties that undergo a rapid photochemical reaction and thus impose constraints onto the peptide backbone), and follow the refolding of the peptide through the response of the amide I band.[19–22] In particular in connection with isotope-labelling, which reveals site selective information, the folding process can be studied in unprecedented detail, allowing also for a direct link to all-atom molecular dynamics simulations.[23]

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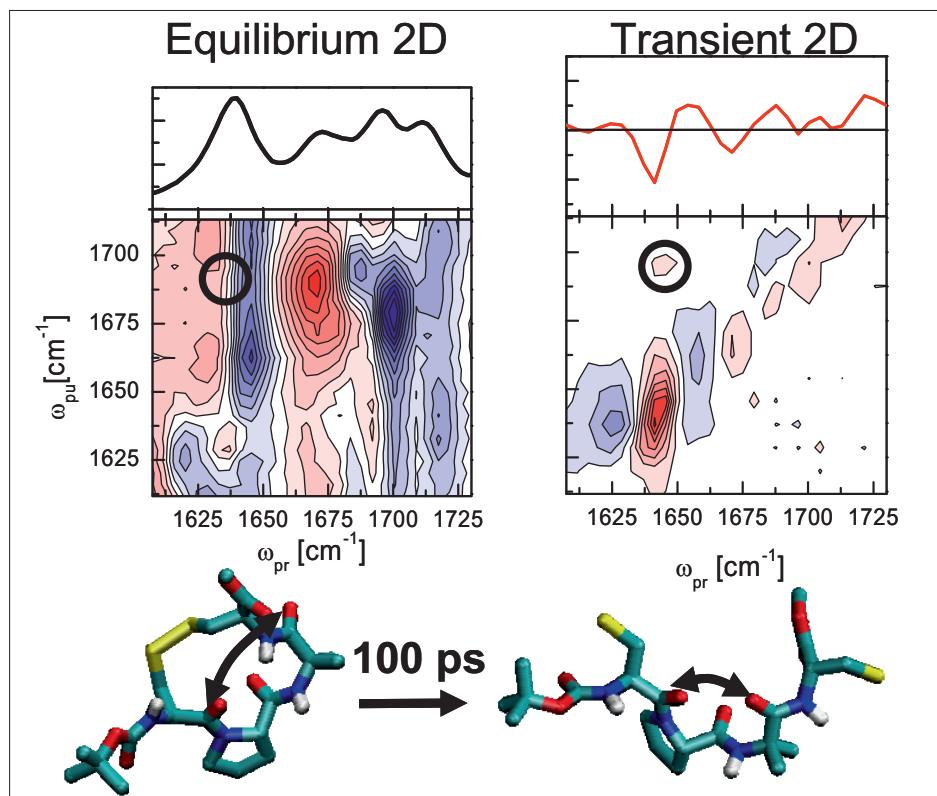Fax: +41 44 635 68 38
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Fig. 1. Equilibrium and transient non-equilibrium 2D-IR spectra of a small disulfide-bridged peptide, cyclo-(Boc-Cys-Pro-Aib-Cys-OMe) together with example structures obtained from a MD simulation. The crosspeak marked by circles in either spectrum relates to the coupling across the hydrogen bond in the β-turn structure. Adapted from ref. [9].
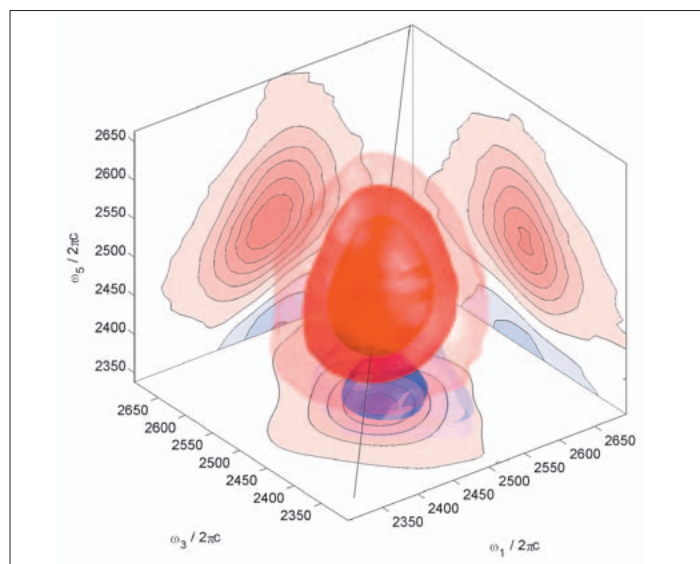

Fig. 2. 3D IR spectrum of the OD vibration of HOD in H_2O. See ref. [25] for details.

Transient 2D IR Spectroscopy

2D IR spectroscopy combines in a unique manner ultrafast time resolution with appreciable structure resolution power. To explore this combination, we introduced the method of transient 2D IR spectroscopy;[8–11,16,17,23,24] that is, we initiate a photochemical reaction by an ultrafast visible or UV pulse, and probe the subsequent structural transition of the molecule with an IR pulse sequence to measure a transient 2D IR spectrum. As an example, we could observe the 'unfolding' of a small β-turn peptide upon photo-cleavage of a stabilizing disulfide bridge (see Fig. 1).[9]

3D IR Spectroscopy and the Dynamics of Hydrogen Bond Networks

The true breakthrough of NMR spectroscopy came about only with the development of sophisticated pulse sequences containing hundreds of pulses. The same will probably not be possible for vibrational spectroscopy, nevertheless, with the addition of two more pulses leading to 3D IR spectroscopy,[14] the possibilities to control the selectivity of the spectroscopy is tremendously enhanced.[15] For the time being, we concentrate on the complicated rearrangements of the hydrogen bond network in liquid water by 3D IR spectroscopy (see Fig. 2),[12,13,25] but as the technology becomes more reliable, many more applications will appear. One idea is to use the first excitation frequency to label a specific site in a protein, then transfer the coherence to water in the vicinity of that probe and thus measure the dynamics of protein water directly.

Energy Transport in Macromolecules

Biomolecules deal with energy in an extremely efficient way; as such a microscopic understanding of vibrational energy transport and energy loss mechanisms is desired. It has been speculated based on molecular dynamics simulations that the two sites in allosteric proteins (*i.e.* the allosteric and the active site) communicate with each other through exchange of vibrational energy. Femtosecond IR-spectroscopy is very well suited to study vibrational energy transport mechanism in peptides and proteins. To this end, we covalently attach a local heater to a peptide or a protein, and use certain vibrational modes as local thermometers at various distances from the heater so we can observe the transport through a protein in unprecedented detail. We have tested various heaters (an ultrafast photochemical reaction after UV pumping,[26] direct IR excitation of vibrational modes,[27] or through the plasmon resonance of gold-nano particles[28]), all revealing very similar heat transport times, suggesting that vibrational energy is randomized fairly quickly.

IR-Induced Proton Transfer

Electronically driven photochemistry often is ultrafast, a discovery for which Ahmed Zewail received the Nobel prize in 1999. However, most (not all) chemistry is thermally driven and is happening on electronic ground state potential energy surfaces rather than through electronically excited states. We investigate IR-driven photochemical reactions in rare gas matrix environment, acting as a weakly interacting 'solvent', with the help of femtosecond IR spectroscopy to obtain a fundamental understanding of this important class of chemical reactions. The prototype example is the IR induced *cis-trans* isomerization of

HONO,[29–31] which features an exceptionally high isomerization quantum yield of close to 100%. This high quantum could be explained through a funnel-like energy pathway.[31]

Vibrational Polarons

The peculiarity of the hydrogen bonds which stabilize protein secondary structures may lead to unconventional vibrational states such as vibrational solitons, self-trapped states and polarons. We investigate vibrational self-trapping peptide models and model peptides. Crystalline acetanilide (ACN) has been widely used as a simple model system to study these phenomena. The crystal consists of quasi-one-dimensional chains of hydrogen bonded peptide groups with structural properties that are comparable to those of α-helices. With the help of IR-pump-IR-probe spectroscopy, IR-quantum beat spectroscopy and 2D IR spectroscopy we could provide compelling evidence that such nonlinear excitations do indeed exist.[32,33] We have furthermore shown that real α-helices may exhibit vibrational self-trapping as well, even in the disordered environment of the solution phase and at room temperature.[34]

Artificial Photosynthetic Systems

Photocatalytic systems aim to mimic natural photosynthesis, producing molecular hydrogen from water after absorption of light in a photosensitizer. Photocatalytic systems are discussed as a possible source of renewable and sustainable energy. They contain kinetically coupled redox compounds through which an electron is relayed from a photosensitizer to a hydrogen evolution catalyst to eventually reduce water to molecular H_2. With the help of time-resolved vibrational spectroscopy, the redox states of the various compounds as well as the formation of certain chemical bonds (*e.g.* the Co–H bond in the hydrogen evolution catalyst) can be investigated with unprecedented detail, providing feedback to synthetic groups to optimize the performance of the overall system.[35,36]

These examples demonstrate the widespread applicability of time-resolved vibrational spectroscopy for molecular sciences. This is just a small selection of applications performed in our group, and many other research groups worldwide use time-resolved vibrational spectroscopy for a much wider range of tasks. A good overview of the field is given by the Time Resolved Vibrational Spectroscopy (TRVS) series of conferences, the XV'th edition of which will take place in Ascona/Switzerland in summer 2011 (see *www.trvs.info*).

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