

Transient 2D-IR Spectroscopy: Towards a Molecular Movie

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[§]Sofja Kovaleskaja Prize

Abstract: In NMR spectroscopy, multidimensional methods allow for fascinating insights into molecular structure and dynamics. With the introduction of ultrafast two-dimensional infrared spectroscopy, these concepts now enter the optical domain, measuring couplings and correlations between molecular vibrations with picosecond time resolution. The time resolution is sufficient to investigate transient species far away from equilibrium during fast photochemical reactions in real-time. Numerous applications of the method are found in chemistry and in biophysics.



Sofja Kovaleskaja Prize Goes to a Young Scientist at the University of Zurich

In his PhD work at the Institute of Physical Chemistry of the University of Zurich, the 31-year old Jens Bredenbeck investigated molecular processes in real time. Based on this work, the Alexander von Humboldt Foundation awarded him the Sofja Kovaleskaja Prize as one of the best young scientists. The prize money of 1.05 million Euros will allow Jens Bredenbeck to independently pursue his research interests.

Spectroscopic experiments investigate the properties of molecular systems by their interaction with electromagnetic radiation. In IR spectroscopy, light interacts with molecular vibrations, while high frequency magnetic field interacts with nuclear spins in NMR spectroscopy. However, from the perspective of chemistry, the object of interest often is not the spectroscopic transition itself, but rather the spectroscopic transition serves as a probe that provides insight into molecular structure and dynamics.

Multidimensional nonlinear spectroscopy allows one to extract information that by far exceeds that of conventional (1D) spectroscopy. It reveals observables that are difficult to obtain otherwise, uncovering couplings as well as static and dynamic correlations between states. This is demonstrated impressively already by basic two-dimensional NMR experiments such as COSY, NOESY or EXSY [1] where couplings and correlations of spins are used to determine molecular structures or to map the connectivities in kinetic networks of interconnecting chemical species. The transferability of the concepts of multidimensional NMR spectroscopy to IR spectroscopy has already been envisioned by Ernst and coworkers in their first publication on 2D-NMR spectroscopy [2]. However, it took more than two decades until the first 2D nonlinear IR (2D-IR) spectrum was measured [3]. The potential advantage of 2D-IR spectroscopy, as compared to 2D-NMR spectroscopy, is the intrinsic ultrafast time resolution of about 1 ps, sufficient to capture even very short-lived intermediates in fast chemical processes. Nevertheless, up to now, 2D-IR spectroscopy has been applied exclusively

to systems in equilibrium, for which also NMR spectroscopy can reach the picosecond regime, albeit indirectly through relaxation methods. We have recently introduced an extension of 2D-IR spectroscopy, termed transient 2D-IR (T2D-IR) spectroscopy, which investigates transient species in non-equilibrium processes and their evolution in real time, thereby taking full advantage of the high time resolution [4–8].

To explain the basic concept, Fig. 1 shows a 2D-IR spectrum of the asymmetric (2015 cm^{-1}) and symmetric (2084 cm^{-1}) C≡O stretching vibrations of dicarbonylacetylacetonato rhodium [9]. The 2D-IR spectrum can be explained with the level scheme in Fig. 1c that comprises the zero, one, and two quantum states of the C≡O vibrational manifold. Each allowed transition, depicted by an arrow in Fig. 1c, corresponds to one band in the 2D-IR spectrum (see numbers 1 to 8 in Fig. 1b and 1c). Bleach or stimulated emission (blue arrows, solid or dotted) yield negative (blue) bands while excited state absorption (red arrows) yields positive (red) bands in the 2D-IR spectrum. For each vibration we thus find a diagonal peak consisting of two bands, a negative one at the fundamental frequency and a positive one slightly red-shifted due to anharmonicity. Coupling between the vibrations gives rise to cross peaks, each also consisting of a positive and negative peak. If there was no coupling between the asymmetric and symmetric vibration, bands 1 and 2 as well as 7 and 8 would cancel exactly and no cross peak would remain. The separation of these bands is a measure of the coupling strength which, in turn, can be related to molecular structure.

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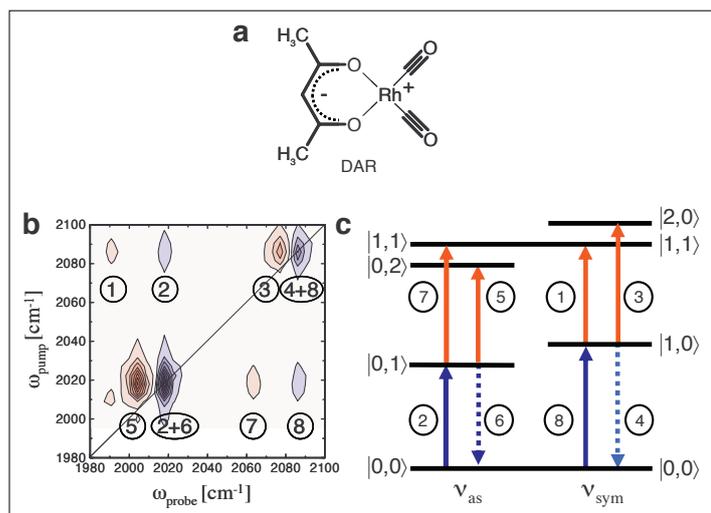


Fig. 1: Features of 2D-IR spectra: (a) Dicarbonylacetylacetonato rhodium (DAR), (b) 2D-IR spectrum of the CO stretching vibrations of DAR, (c) level scheme rationalizing the various contributions to the 2D-IR spectrum. The numbered transitions correspond to the bands in (b). Adapted from Ref. [9].

The capability of 2D-IR spectroscopy to elucidate equilibrium structures and fluctuations has been demonstrated in our group for small peptides [10][11]. First steps into the nonequilibrium regime have been achieved by the implementation of T2D-IR spectroscopy. In this experiment an additional UV_{pump} pulse precedes the 2D-IR pulse sequence and prepares the system in a non-equilibrium state, *e.g.* by triggering a photo-chemical reaction. After the trigger pulse, 2D-IR snapshot spectra are taken while the molecular system undergoes a transition. This is the basic implementation of T2D-IR, with which we recently succeeded to literally make a ‘molecular movie’ of the unfolding of a photo-switchable peptide [5]. T2D-IR spectroscopy uniquely combines ultrafast time resolution with appreciable structure resolution power.

Furthermore, the addition of a new pulse greatly enhances the flexibility of the experiment [6–8]. For example, if the UV_{pump} is sandwiched by the 2D-IR pulse sequence, a new method termed T2D-IR Exchange Spectroscopy (T2D-IR-EXSY) is realized: A first IR pulse labels a particular molecular group, the intermediate UV_{pump}-pulse initiates a photochemical reaction, and the final IR pulse correlates the labelled group between reactant and product state. As an example, Fig. 2 shows the metal-to-ligand charge transfer of [Re(CO)₃(dmpby)Cl] [6]. Upon charge transfer, the various C≡O groups change their vibrational frequencies, but from conventional 1D spectroscopy one could not decide which band in the product state (Fig. 2b, positive bands) originates from which in the reactant state (Fig. 2b, negative bands). T2D-IR-EXSY provides exactly this information and reveals an un-

ambiguous assignment (Fig. 2c). With the help of T2D-IR-EXSY, we recently unravelled the migration of a CO molecule to different binding sites in myoglobin after dissociation from the heme group [8].

The sum of this work [4][6–9][11], performed to a large extent by Jens Bredenbeck, has led to a distinction of his PhD thesis [12]. Furthermore, Jens Bredenbeck was awarded the Sofja Kovaleskaja prize from the Alexander von Humboldt Foundation. The prize money of 1.05 Mio Euro gives him scientific independence for four years. He will continue to develop the technique of 2D-IR spectroscopy at the University of Frankfurt.

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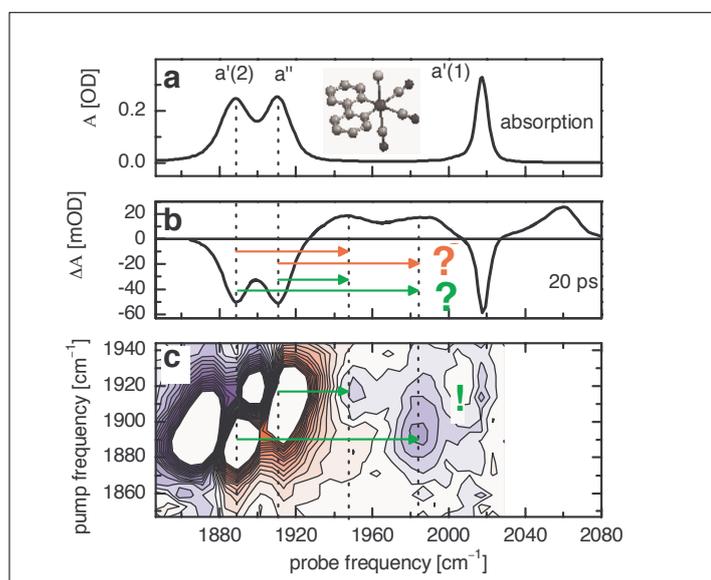


Fig. 2: (a) FTIR absorption spectrum of the CO stretching modes of [Re(CO)₃(dmpby)Cl]. (b) Time resolved absorption spectrum 20 ps after UV excitation, from which one cannot deduce whether the bands shift according to the red or the green ones. (c) The T2D-IR-EXSY spectrum proves a shift according to the green arrows. Adapted from Ref. [6].

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