Ultrafast 2D-IR spectroscopy of a molecular monolayer

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***Abstract**. We report on ultrafast 2-dimensional vibrational surface spectroscopy, providing information on coupling and energy transfer between vibrations of surface molecules. As a 4th order technique, it is bulk-forbidden in centrosymmetric materials and hence surface specific.*

Coupling and energy flow through vibrational modes at surfaces and interfaces are important in areas as diverse as heterogeneous catalysis, electrochemistry, and membrane biophysics and –chemistry.[1] Furthermore, vibrational coupling patterns contain information on molecular structure, a feature already explored in bulk experiments to measure structure parameters with femtosecond time resolution.[2] However, measuring vibrational mode coupling at surfaces is challenging, because it requires both distinguishing the signal of a small number of surface molecules from a much larger bulk response and recording this signal within typical vibrational lifetimes (i.e. on sub-picosecond timescales).

For bulk studies, femtosecond two-dimensional infrared (2D-IR) spectroscopy has been shown to be ideally suited to reveal vibrational mode coupling, leading to off diagonal peaks in 2D spectra.[2] Off-diagonal peaks between modes are determined by the strength of their coupling and depend on their relative orientation and distance. As such, 2D-IR spectroscopy is increasingly useful in determining (sub)molecular structures and dynamics; 2D-IR analogues of NMR experiments like NOESY, COSY and EXSY have been demonstrated.[2-6] Here we introduce femtosecond sumfrequency generation 2D-IR spectroscopy (SFG-2D-IR) with submonolayer sensitivity and surface specifity.[7]

In bulk 2D-IR spectroscopy, a sequence of coherent interactions between the sample and the IR laser fields is designed such that an odd (typically third) order coherence is detected, which contains information about vibrational mode coupling. To apply 2D-IR spectroscopy to surfaces, we gain monolayer sensitivity and interface specificity through an additional interaction with a nonresonant near-IR laser pulse. This additional interaction upconverts the third-order coherence to an even (fourth) order coherence, which radiates a field in the visible, at the sum frequency of near-IR and IR. We expect this technique to be useful for a variety of applications, including the study of: the structure and reactivity of (mixed) molecular adsorbate layers in catalytic systems, the structures and interactions of membranes and membrane proteins as well as the structure and dynamics of interfacial water in various systems.

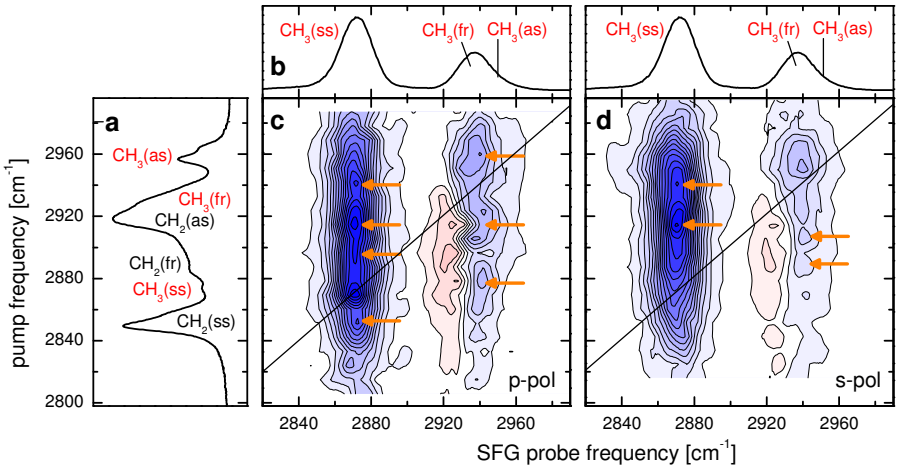

Fig. 1. *SFG-2D-IR spectra of a dodecanol monolayer on water. Blue (red) denotes a pump-induced decrease (increase) in SFG intensity. (a) IR spectrum of crystalline dodecanol at 150 K. (b) SFG spectrum of the monolayer, polarizations: SFG/VIS/IR: s/s/p. (c) SFG-2D-IR spectrum, p-polarized pump, t = 0.7 ps. (d) same, with s- polarized pump, for which the in-plane CH_2 modes are efficiently excited, leading to the dominance in the 2D spectrum of the cross-peak between the CH_2 (as) and CH_3 (ss) modes. Lines indicate the diagonal; arrows point to off-diagonal peaks indicative of vibrational coupling.*

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