

## Ultrafast Two Dimensional-Infrared Spectroscopy of a Molecular Monolayer

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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 biochemistry.<sup>1</sup> Furthermore, coupling patterns of vibrational transitions contain information on molecular structure, a feature already explored in bulk experiments to measure structure parameters with femtosecond time resolution.<sup>2</sup> 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 subpicosecond timescales).<sup>3</sup>

For bulk studies, femtosecond two-dimensional infrared (2D-IR) spectroscopy, a vibrational analogue of 2D-NMR spectroscopy, has been shown to be ideally suited to reveal vibrational mode coupling.<sup>4</sup> In 2D-IR, one vibrational mode A is excited, and the effect of this excitation on a different mode B is probed. If the modes are uncoupled, mode B remains unaffected by excitation of mode A, and a spectral response is only observed for mode A at identical pump and probe frequencies, that is, on the diagonal of the 2D-IR spectrum. Inversely, the off-diagonal peaks between modes A and B 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 techniques like NOESY, COSY, and EXSY have been experimentally demonstrated.<sup>5</sup>

Here we introduce femtosecond sumfrequency generation 2D-IR spectroscopy (SFG-2D-IR) with submonolayer sensitivity and surface specificity. Closely related surface 2D vibrational techniques have been recently proposed theoretically.<sup>6</sup>

In bulk 2D-IR spectroscopy, a sequence of coherent interactions between the sample and the IR laser fields is designed such that an odd (generally third) order coherence is detected, which contains information about vibrational mode coupling.<sup>7</sup> 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. This upconversion process is beneficial in two ways. First, it ensures surface specificity for materials whose optical response is dominated by dipole contributions. Most materials are centrosymmetric, and the upconverted, even-order response can only originate from the surface molecules.<sup>8</sup> In combination with isotope labeling, bond specificity may be obtained.<sup>9</sup> Second, the upconverted signal is background free and lies in the visible spectral range, where CCD cameras with high quantum efficiencies are available, readily providing (sub)monolayer sensitivity.

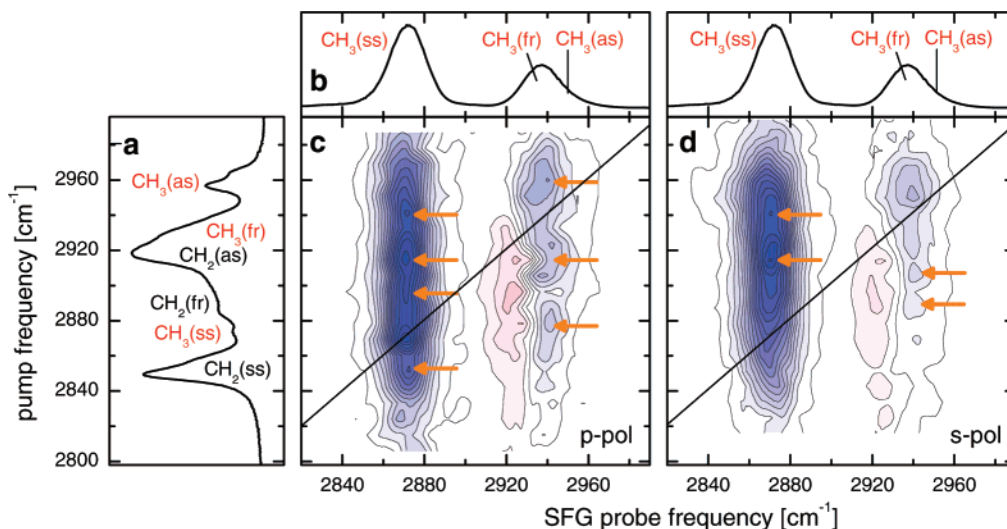
Specifically, in the experiments presented here we used a commercial Ti:Sapphire femtosecond amplified laser system to generate tunable, high-energy mid-IR pump and probe pulses.<sup>10</sup> The pump pulse was shaped using a computer controlled Fabry–Perot interferometer, resulting in a tunable narrowband  $\sim 15 \mu\text{J}$ ,  $20 \text{ cm}^{-1}$  pulse to excite specific vibrations. After a variable delay time, the surface was probed using simultaneous mid-IR and near-IR pulses. The  $\sim 10 \mu\text{J}$  IR probe pulse sustained a  $200 \text{ cm}^{-1}$  bandwidth to cover the whole spectral range of interest. To maintain a high spectral resolution in the upconversion step, a narrow-band ( $\sim 12 \text{ cm}^{-1}$ ) near-IR pulse (800 nm) was generated using a home-built pulse shaper. The resulting sum frequency generation (SFG) spectrum reveals the effect of the pump pulse on all resonances within the probe bandwidth.

In the present study, we investigated a dodecanol monolayer on water—a model system for biological membranes<sup>11</sup>—in the region of the C–H stretching modes of the alkyl chains. The sample was prepared by putting a small crystal of 1-dodecanol (Sigma Aldrich) in contact with water ( $\text{D}_2\text{O}$ , to suppress interferences with the O–H stretch vibration of  $\text{H}_2\text{O}$ ), resulting in a self-assembled monolayer at the water–air interface. Figure 1a and b show the IR absorption spectrum of bulk dodecanol and the static 1D SFG spectrum of the monolayer. The C–H stretching region (Figure 1a) features a series of vibrational modes assigned to symmetric and antisymmetric  $\text{CH}_2$  and  $\text{CH}_3$  stretching (ss and as) perturbed by Fermi resonances (fr) with bending modes.<sup>12</sup> For symmetry reasons, only some of these modes are SFG active and appear in the static SFG spectrum in Figure 1b.

Figure 1 panels c and d show the SFG-2D-IR spectra of the self-assembled monolayer. In addition to the diagonal peaks, several off-diagonal peaks appear (indicated by yellow arrows) that indicate mode coupling. As SFG selection rules apply for the probe process, off-diagonal peaks reporting on vibrational coupling appear at the two frequencies corresponding to the two peaks in the static SFG spectrum. The collective molecular alignment present at the interface (as opposed to the bulk) allows us to enhance or diminish the sensitivity to specific modes and their coupling, by controlling the polarization of the IR pump pulse relative to their vibrational transition dipole moments (and relative to the subsequent pulses), as evident from a comparison of Figure 1 panels c and d. Further polarization selectivity may be explored in future by selecting different polarizations of the IR probe and near IR pulse as well as of the fourth order SFG signal.

In addition to the expected coupling between the  $\text{CH}_3(\text{ss})$  and  $\text{CH}_3(\text{as})$  modes (being two modes of the same functional group), a remarkably strong coupling between  $\text{CH}_2(\text{as})$  and  $\text{CH}_3(\text{ss})$  is observed. As the transition dipole coupling for the weak CH modes is anticipated to be small, this observation suggests an important role of mechanical coupling, potentially relevant for lipid membranes as well. Because the spectra are recorded at 0.7 ps delay between the IR pump and probe pulse, some of the off-diagonal

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**Figure 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.<sup>13</sup> (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 as in panel c, with s-polarized pump, for which the in-plane  $\text{CH}_2$  modes are efficiently excited, leading to the dominance in the 2D spectrum of the cross-peak between the  $\text{CH}_2$  as and  $\text{CH}_3$  ss modes. Lines indicate the diagonal; arrows point to off-diagonal peaks indicative of vibrational coupling.

intensity might result from energy transfer, in addition to direct anharmonic coupling. A detailed analysis of the different contributions to these 2D-IR spectra is underway.

When comparing the surface 2D-IR technique to bulk 2D-IR spectroscopy,<sup>4</sup> a few striking characteristics of the new technique are apparent from the data: First of all, the different selection rules for pump interactions (IR activity) and probe interactions (SFG activity requiring IR and Raman activity as well as suitable symmetry) make off-diagonal peaks appear that report on vibrational coupling between SFG inactive modes that are visible only in the IR absorption spectrum (shown along the pump axis) and SFG active modes (shown along the probe axis) that are visible in both the absorption and the SFG spectrum. Second, there is remarkably little increase in SFG-2D-IR intensity (positive red features in Figure 1 panels c and d). In third-order bulk 2D-IR spectroscopy, an individual 2D-IR spectral response consists of a positive and a negative feature owing to ground-state depletion and excited-state absorption. These paired features are suppressed in SFG-2D-IR spectra owing to the relative insensitivity of SFG to excited-state transitions (the homodyne SFG signal is proportional to the square of the population difference between vibrational levels; heterodyne detection will allow the detection of excited-state dynamics as well).<sup>13</sup> Third, coherent interferences between the different modes play a role in determining the SFG-2D-IR spectrum. These coherent interferences (intrinsic to the surface specificity of the approach) result from collective molecular alignment at the interface and can be straightforwardly quantified using the static SFG spectrum. In fact, the increase in SFG intensity at  $2920\text{ cm}^{-1}$  can largely be accounted for by these interferences. Interestingly, the sign of off-diagonal peaks resulting from interference depends on relative orientation of interfering oscillators, directly revealing structural information.

In summary, we have demonstrated the successful implementation of ultrafast surface 2D-IR spectroscopy. 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 and the structures and interactions of membranes and membrane proteins as well as the structure and dynamics of interfacial water in various systems.

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**Supporting Information Available:** Details on coherent interferences, cut through the 2D spectrum. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (14) In Figure 1a the absorption spectrum of crystalline dodecanol at 150 K is shown along with the SFG-2D-IR spectra of the monolayer, because in the crystalline phase the ordered conformation of the alkyl chain resembles the highly ordered chain structure in the monolayer at room temperature.

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