

## Ultrafast Structural Dynamics in Condensed Matter

Basic processes in Nature such as phase transitions or (bio)chemical reactions are connected with structural changes of matter. The spatial rearrangement of electrons and nuclei, the formation and breaking of chemical bonds, as well as atomic and molecular motions underlie those events. In liquids and solids, atoms and molecules couple through a variety of short- and long-range interactions, leading to structural changes on ultrafast time scales between  $10^{-15}$  s [1 femtosecond (fs)] and  $10^{-12}$  s [1 picosecond (ps)]. Nonlinear optical spectroscopy with femtosecond light pulses represents the only technique for inducing and probing such events in real-time, similar to recording a sequence of »snapshots« in photography on much slower time scales.

Experiments with a time resolution down to a few femtoseconds have provided detailed insight into ultrafast processes in physics, chemistry, and biology and have unravelled the underlying interaction mechanisms [1]. So far, structural dynamics have mainly been addressed by following the time evolution of absorption and emission bands assigned to a particular structural species. Though this indirect approach has been successful in numerous cases, a more direct observation and analysis of transient, in particular local structure is necessary for understanding structural dynamics in detail. Femtosecond multidimensional spectroscopy [2] representing the optical analogue of multidimensional nuclear magnetic resonance, and subpicosecond x-ray techniques [3] can grasp transient structures and – thus – have developed into fascinating new areas of ultrafast science. In the following, new results on hydrogen bonds in liquids and semiconductor nanostructures are presented.

### Ultraschnelle Strukturänderungen

Die Funktion physikalischer, chemischer und biologischer Systeme ist durch mikroskopische Vorgänge bestimmt, die extrem schnell im Zeitbereich zwischen 1 Femtosekunde ( $10^{-15}$  s, ein Milliardstel einer Millionstel Sekunde) und einigen Pikosekunden ( $1 \text{ ps} = 10^{-12}$  s, ein Millionstel einer Millionstel Sekunde) ablaufen. Dabei treten häufig Änderungen der atomaren oder molekularen Struktur auf. Mit neuen Methoden der Ultrakurzzeitspektroskopie lassen sich solch ultraschnelle Strukturänderungen sichtbar machen und in Echtzeit verfolgen. Die Arbeitsgruppe um Thomas Elsässer am Max-Born-Institut beschäftigt sich mit der Aufklärung ultraschneller Prozesse vorwiegend durch Femtosekunden-Infrarot- und Röntgenmethoden. Als Beispiele für diese in zahlreiche Kooperationen eingebundenen Arbeiten werden hier Untersuchungen zur Schwingungsdynamik von Wasserstoffbrücken und zur Gitterdynamik von Halbleiter-Nanostrukturen vorgestellt.

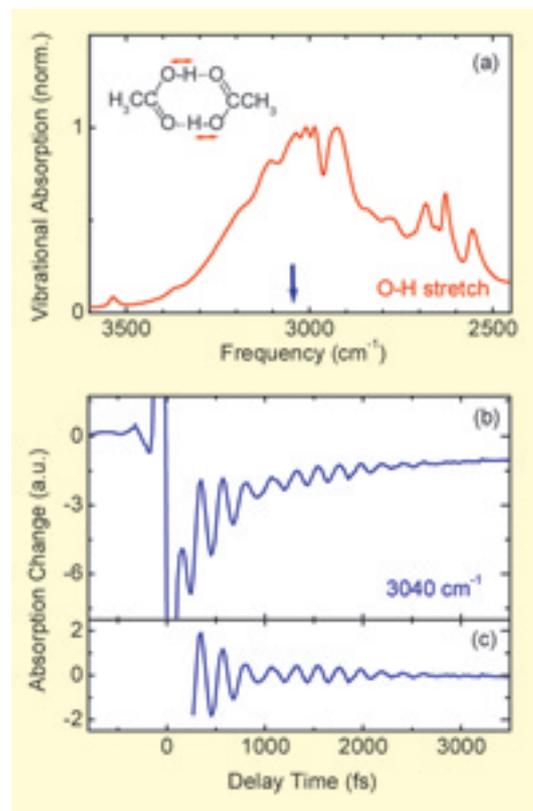


Fig. 1

(a) Absorption band of the O-H stretching vibration of cyclic acetic acid dimers (inset) dissolved in  $\text{CCl}_4$ . The absorption coefficient is plotted as a function of frequency. (b) Time resolved change of O-H stretching absorption measured at a frequency of  $3040 \text{ cm}^{-1}$  [blue arrow in Fig. (a)]. The change of absorption is plotted vs the delay time between pump and probe. The data display strong oscillations reflecting low-frequency vibrational motions of the dimer. (c) Oscillatory part of the time-resolved absorption change.

### Ultrafast vibrational motions of hydrogen bonds

Hydrogen bonding determines the structure of important molecular systems, among them crystalline ice, liquid water, and biomolecules like the DNA and numerous proteins. Hydrogen bonds are caused by an attractive interaction between a hydrogen donor group X-H [H: hydrogen, X: carbon (C), nitrogen (N), oxygen (O)] and a neighboring acceptor atom Y [N, O, S (sulphur)], resulting in a bond strength which is small compared to a covalent, e.g., the X-H bond. Nevertheless, this local interaction is strong enough to determine complex molecular structure. On the other hand, hydrogen bonds are weak enough to allow for structural flexibility, i.e., a making and breaking of bonds. The latter property is essential for the function of molecular systems and the related dynamics. Molecular functioning is connected with motions of the hydrogen bonded structure on time scales between 10 fs and several picoseconds [4]. Such motions are reflected in the steady-state and transient vibrational spectra of molecules, opening a direct window on hydrogen-bond dynamics [5].

As a model system, we studied carboxylic acid dimers which are held together by two intermolecular O-H...O hydrogen bonds [6–8], a structural motif also present in biomolecules. The geometry of cyclic dimers of ace-

tic acid is shown in Fig. 1 (a), together with the absorption band of the O-H stretching vibration of dimers dissolved in liquid  $\text{CCl}_4$ . In the experiments, the O-H stretching vibration is excited by a 100 fs infrared pulse and the resulting change of vibrational absorption is measured by a probe pulse of a variable time delay with respect to the pump. In Fig. 1 (b), the change of vibrational absorption at a frequency position of  $3040\text{ cm}^{-1}$  [arrow in Fig. 1 (a)] is plotted as function of the delay time between pump and probe pulses. The vibrational absorption displays a decrease upon femtosecond excitation and a fast partial recovery within the first 3 ps, followed by a slower complete recovery within 30 ps (not shown). The fast recovery is superimposed by strong oscillations which are plotted separately in Fig. 1 (c). The oscillatory absorption changes display a period of approximately 200 fs that is much longer than the O-H stretching period of 10 fs. The frequency spectrum of the oscillations as determined by Fourier analysis is shown in Fig. 2 (a) and consists of two major frequency components at 145 and  $170\text{ cm}^{-1}$ . The oscillations are due to low-frequency vibrations periodically changing the geometry of the dimer. Such vibrations are – anharmonically – coupled to the much faster O-H stretching mode. They are elongated upon O-H stretching excitation and start to oscillate with their intrinsic frequency. In a quantum mechanical picture, this nonstationary behavior is due to the superposition of several energy levels of the respective low-frequency oscillator, corresponding to the propagation of a wavepacket. Vice versa, the low-frequency motions modulate the O-H stretching absorption, in this way making the oscillatory changes of the dimer geometry directly visible. A theoretical analysis of the vibrational spectra and anharmonic couplings of acetic acid dimers shows that the underlying low-frequency modes are the in-plane dimer bending and stretching modes with the microscopic elongations shown in Figs. 2 (b) and (c) [7].

In addition to the anharmonic coupling to low-frequency modes, the O-H stretching mode couples to combination and overtones of other vibrations. Coherent nonlinear experiments in which a sequence of 3 femtosecond infrared pulses interacts with the molecular sample, allow to determine such couplings and visualize them in so-called two-dimensional vibrational spectra. In Fig. 3, a two-dimensional spectrum of cyclic acetic acid dimers is shown as contour plot for a measurement time  $T=0$ .  $T$  is the time interval between pulse 2 and 3, the so-called population time. The nonlinear signal is plotted as a function of the excitation frequency  $\nu_1$  and the detection frequency  $\nu_3$ . There are essentially 2 peaks on the diagonal of the plot

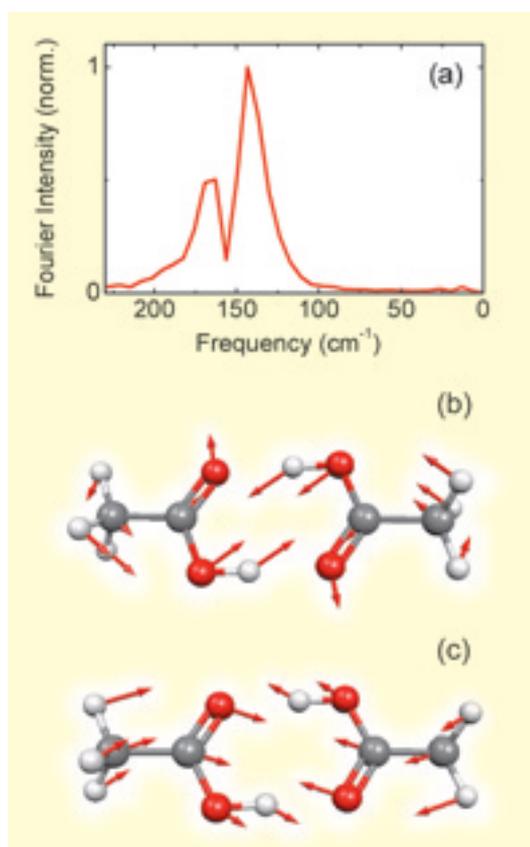


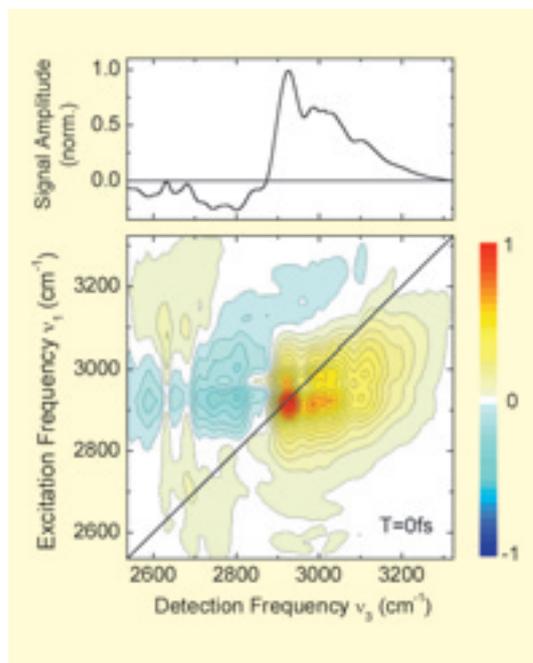
Fig. 2

(a) Frequency spectrum of the low-frequency oscillations in Fig. 1 (c) showing two major components with maxima at 145 and  $170\text{ cm}^{-1}$ .

(b) Microscopic elongations of the  $145\text{ cm}^{-1}$  in-plane bending mode of the dimer.

(c) Microscopic elongations of the  $170\text{ cm}^{-1}$  in-plane stretching mode of the dimer.

corresponding to identical excitation and detection frequencies. Such peaks reflect the behavior of a particular vibrational transition which is excited and later probed at the same frequency. More interesting are the off-diagonal peaks: after excitation of a particular transition, a nonlinear response is found on a different transition, demonstrating a coupling between such two excitations. A cross section through the two-dimensional spectrum (upper panel of Fig. 3) reveals couplings between a number of transitions within the very broad O-H stretching band of the acetic acid dimer. Taking two-dimensional spectra for different population times  $T$  allows to dissect the highly complex behavior of the coupled system into different contributions. The couplings evident from Fig. 3 are due to (Fermi) resonances of the O-H stretching mode with the O-H bending, C=O stretching and other modes at



**Fig. 3**  
Two-dimensional vibrational spectrum of cyclic acetic acid dimers in  $\text{CCl}_4$ . The nonlinear signal is plotted as a function of the excitation and the detection frequency. Upper panel: Cross section through the two-dimensional spectrum at an excitation frequency  $\nu_1=2920\text{ cm}^{-1}$ .

lower frequencies. In addition to intra-dimer vibrational couplings, the interaction with the liquid environment plays an important role for the ultrafast vibrational dynamics [8,9].

#### Femtosecond x-ray diffraction: Coherent atomic motions in a semiconductor nanostructure

X-ray diffraction represents a standard technique to determine the equilibrium structure of crystalline materials. In the simplest picture, the superposition of waves elastically reflected from different planes in the crystal lattice leads to the formation of an x-ray beam in a direction determined by the constructive interference of the reflected waves. So far, x-ray diffraction has mainly been applied to analyze time-independent structure of a large variety of systems including large biomolecules. In principle, diffraction of ultrashort x-ray pulses allows to take sequences of diffraction patterns and in this way analyze time-dependent structure, i.e., follow atomic motions in real-time. Currently, there is substantial effort worldwide to implement such ultrafast x-ray diffraction schemes and apply them to investigate structural changes. In the following, very recent results on coherent atomic motions in a semiconductor superlattice are presented [10].

The experiments are based on a pump-probe scheme where an ultrashort excitation pulse induces atomic motions in a crystal lattice and a delayed x-ray probe pulse is diffracted from the excited sample. Measuring the diffraction pattern as a function of the time delay between pump and probe gives insight into the lattice dynamics. Pump pulses of 50 fs duration are derived from the output of an amplified Ti: sapphire laser working at a 1 kHz repetition rate. The major part of the laser output generates a plasma on a copper target emitting subpicosecond hard x-ray pulses ( $\text{K}_\alpha$  radiation) which are synchronized with the laser. Such pulses are diffracted from the excited sample.

As a prototype system characteristic for a larger class of nanostructures, a GaAs/AlGaAs superlattice is studied which consists of a sequence of 8 nm thick GaAs quantum well layers separated by 8 nm thick AlGaAs barrier layers [Fig. 4 (a)]. The static diffraction pattern of this sample around the (002) peak is displayed in Fig. 4 (b). It shows a strong central maximum with a position determined by the average lattice constant of the entire crystal of approximately 0.56 nm and two first-order satellite peaks. The satellites are due to the »artificial« periodicity of the superlattice and are determined by the superlattice period of 16 nm, much longer than the lattice constant. The satellites originate from the AlGaAs barrier layers as the GaAs structure factor and – thus – the intensity diffracted from the quantum wells are negligibly small.

Excitation of this sample by the 800 nm pulse promotes electrons from the valence band into the (anti-binding) conduction band of the quantum wells and weakens interatomic covalent bonds in the GaAs crystal lattice. This excitation is periodic in space as the 800 nm pulse is absorbed in the quantum well layers exclusively. As a result of excitation, the strength of the superlattice peaks exhibit pronounced oscillations as a function of delay time. This is shown in Fig. 4 (c) for the -1st order peak. The oscillation period is 3.5 ps corresponding to a frequency of 0.29 THz. The angular position of the satellite peaks remains unchanged during the oscillations, demonstrating that changes of the average superlattice period, i.e., changes of the crystal volume, are negligible on this time scale.

The oscillations in the diffracted intensity are caused by coherent acoustic phonon oscillations in the superlattice. Upon excitation of electrons into the conduction band, the weakening of the covalent bonds in the GaAs layers leads to an expansion of the quantum wells in space and a compression of the AlGaAs barriers [Fig. 4 (a), bottom], in this way impulsively launch-

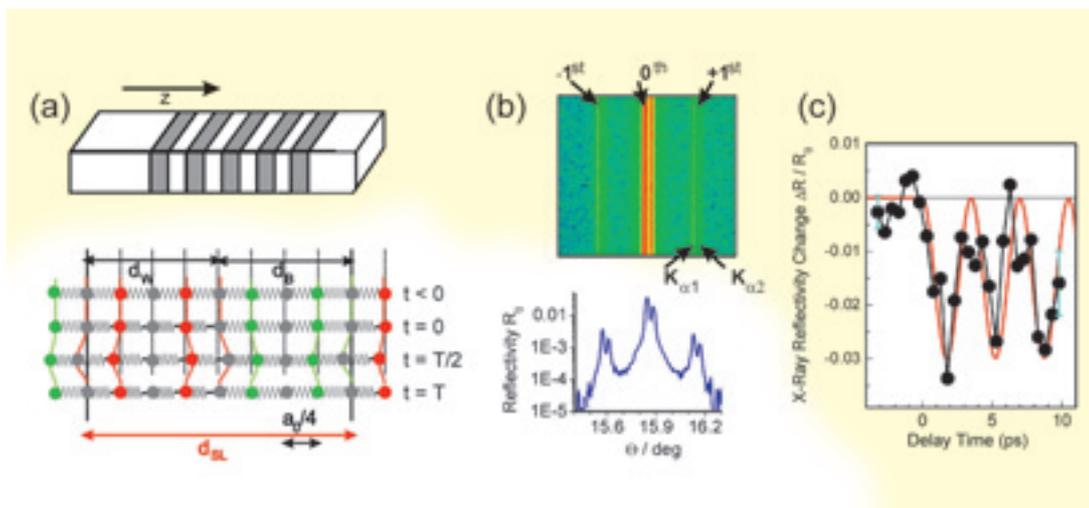


Fig. 4

(a) Top: Schematic of the semiconductor superlattice consisting of GaAs quantum wells (white) and AlGaAs barriers (grey). Bottom: Schematic linear chain model of the phonon dynamics as a function of time  $t$  after excitation. The circles represent atoms linked to each other by covalent bonds (springs). Excitation at  $t=0$  leads to an instantaneous stress in the quantum wells and a compression of the springs. At later times, one observes the acoustic phonon oscillation with a period of  $T$ .

(b) X-ray diffraction pattern of the superlattice and cross section through it.

(c) Intensity modulation of the  $-1^{\text{st}}$  diffraction peak after ultrafast excitation of the superlattice. The relative x-ray reflectivity change is plotted as a function of delay time between the pump pulse and the diffracted x-ray pulse. The oscillations directly reflect the phonon oscillations. Red solid line: calculated response.

ing acoustic phonon oscillations in the superlattice. The wavevector of the phonons created is determined by the spatial periodicity of the optical excitation. Such phonon oscillations are equivalent to a periodic modulation of the lattice constant of the AlGaAs layers, i.e., the atomic motions of this part of the crystal lattice are directly monitored.

A theoretical analysis of the experimental results confirms this qualitative picture [red solid line in Fig. 4 (c): calculated response] and gives a very small oscillation amplitude of  $10^{-4}$  of the average lattice constant. This underlines the very high sensitivity of the experiment and demonstrates the potential of this technique to observe fully reversible structural changes in real-time. Future studies will concentrate on reversible phase transitions in materials with correlated electron systems like, e.g., superconductors and ferromagnets.

#### Literature

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