Highly sensitive multichannel spectrometer for subpicosecond spectroscopy in the midinfrared

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A spectrometer system is presented for time-resolved probing in the midinfrared between 5 and 11 μm with a temporal resolution of better than 400 fs. Multichannel detection with HgCdTe detector arrays consisting of ten elements in combination with a high repetition rate permits one to record weak absorbance changes with an accuracy of 0.1 mOD.

Time-resolved excitation and probe measurements with probing pulses in the mid-IR spectral region yield important new information on fast reactional and relaxational processes. The condensed phase, in which electronic excitation processes trigger fast reactions that can be followed in the IR, e.g., by means of phonon populations or band shifts of vibrational modes, is of special interest. Important questions on the microscopic details of fast reactions can be answered in this way. Whereas conventional systems addressed mainly the shorter-wavelength range (3–5 μm) or the picosecond domain,[1–5] we focus here on a subpicosecond time resolution in the mid-IR between 5 and 11 μm. In a previous study we described the generation of tunable subpicosecond IR pulses in this spectral range,[6] which is the most important region for experiments in molecular physics since here many characteristic absorbance bands from $C = 0$, $C = C$, and $C - N$ stretching and $C - H$ bending modes are found (fingerprint domain). Since the absorption cross section of vibrational modes is much weaker than the absorption cross section of typical electronic transitions of dye molecules, one can expect only a weak absorption change in IR probe experiments. As a consequence, the highest sensitivity is necessary for those experiments. In this Letter we present an experimental setup that permits the measurement of transient absorption spectra with an accuracy (< 0.1 mOD) and time resolution (< 400 fs) that, to our knowledge, have not yet been achieved in this spectral range. To obtain the experimental data necessary for the interpretation of the spectra in a reasonable measurement time, we introduce multichannel detection, and we demonstrate the ability of the system in the following experiment.

A schematic of the experimental setup is shown in Fig. 1. The optical system is based on a femtosecond Ti:sapphire laser combined with a regenerative amplifier as the master light source. The amplifier is pumped with a Q-switched intracavity-frequency-doubled Nd:YLF laser operating at a repetition rate of 1 kHz. The amplifier supplies pulses at a wavelength of 815 nm with a pulse duration of 120 fs and a pulse energy of 500 μJ. The IR pulses are generated

by the difference-frequency mixing of the Ti:sapphire pulse and a synchronized red-shifted tunable light pulse in a AgGaS$_2$ crystal. Collinear type I phase matching with parallel light beams is used. The second light pulse is generated in a tunable two-stage traveling-wave dye laser, delivering a spectrally narrow output with an energy of several microjoules. To cover the IR region of interest, we use two different laser dyes (IR 140 and IR 143) in the traveling-wave dye laser. The system delivers subpicosecond pulses between 5 and 11 μm.

In contrast to our recent study of pulse generation, we use here a AgGaS$_2$ crystal with a smaller thickness of 0.5 mm to reduce group-velocity dispersion. By this means, mid-IR pulses as short as 300 fs (at 1500 cm^{-1}) with a pulse energy of 10 nJ can be obtained. At 1000 cm^{-1} the pulse length increases to 400 fs. The spectral bandwidth ($\Delta\nu = 65$ cm^{-1} FWHM) is significantly smaller than the bandwidth of the Ti:sapphire laser. The bandwidth is limited mainly by the phase-matching condition and is nearly independent of the center wavelength. The IR pulses are nearly transform limited, with a time–bandwidth product of $\Delta\nu t_p = 0.6$ at 1500 cm^{-1}. So far, we have made no efforts to increase the band-
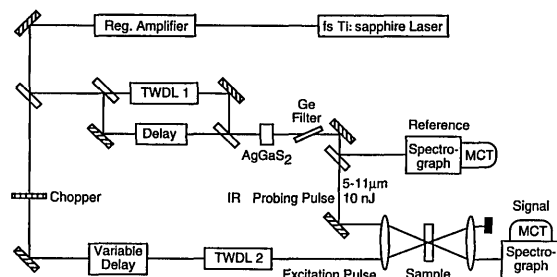

Fig. 1. Experimental setup. Tunable subpicosecond pulses in the mid-IR are generated by difference-frequency mixing the output of a Ti:sapphire laser regenerative (Reg.) amplifier system with pulses from a traveling-wave dye laser (TWDL 1) in a AgGaS$_2$ crystal. Excitation pulses at an independent wavelength are generated in a second traveling-wave dye laser (TWDL 2). Broadband transmission spectra of the sample for the IR probing pulses are recorded by spectrograph–MCT-detector combinations.

width of the IR pulses by producing a range of phase-matching angles by focusing the near-IR light beams into the crystal.

The excitation pulses for the pump–probe experiment are also supplied from the amplified Ti:sapphire pulses at 815 nm. Since enough energy (>200 μJ) remains after IR generation, nonlinear techniques such as frequency doubling, optical parametrical generation, white-light continuum generation, and the use of a traveling-wave dye laser can be used to obtain tunable excitation pulses. A second single-stage traveling-wave dye laser is used to cover the spectral range between 860 and 1100 nm with different laser dyes.

Since the bandwidth of the IR pulse of ~ 65 cm^{-1} is broader than the bandwidth of typical molecular IR absorption lines, multichannel detection becomes reasonable; after passing through the sample the probing pulses are dispersed by a flat-field grating sprectrograph (focal length, 250 mm; two sets of 60- and 150-line/mm gratings) and are measured with two ten-element HgCdTe detector arrays (MCT's) (Grasbey Infrared USA, $D^* = 4 \times 10^{10}$ cmH$^{1/2}$/W). Each element of the array has a size of 1 mm $\times$ 2 mm. The gap between two elements is 0.2 mm, yielding a total array size of 12 mm $\times$ 2 mm. The spectral resolution (in units of inverse centimeters) of the system depends on the grating and on the wavelength used and varies between 3 and 10 cm^{-1}. The output signals of the HgCdTe detector elements are handled in parallel; they are preamplified (Le Croy Type 2724), digitized in a 12-bit analog-to-digital converter (Le Croy Type 1885F), and finally transferred to a personal computer.

The shot-to-shot fluctuations of the output of each detector element are approximately 30% rms. Since this number is not sufficient for the sensitive detection of weak transmission changes, additional improvements are required. First, a dual-beam setup is realized as follows (see Fig. 1): In front of the sample, part of the IR pulse is split off by a wedged ZnSe plate with a reflectivity of approximately 15%. This reference pulse is analyzed in a first spectrograph–detector pair. The main part of the IR pulse is passed through the sample and is measured in a second spectrograph–detector pair. The ratio of the outputs of corresponding signal and reference detector elements is directly proportional to the transmission of the sample. Since the fluctuations of the signal and the reference detector are highly correlated, dual-beam detection enhances the precision of the transmission data by a factor of 5–7. Second, the excitation beam is chopped at 500 Hz (half the repetition rate of the laser system), and thus the sample is excited only every second laser pulse. The changes in transmission spectrum are calculated from experiments with and without the pump pulse. In this way, long-term drifts of the system are essentially eliminated.

Under standard operating conditions the setup yields a single-pulse-pair standard derivation of the normalized signal of 20–30 mOD rms. We can improve this value by averaging over a sufficient

number of experiments. To resolve an absorbance change of 0.1 mOD at one delay-time position, one requires an averaging time of less than 5 min.

In the spectral range of interest there exist numerous strong absorption lines corresponding to rotational–vibrational transitions of H_2O vapor in air. As a result of their very small widths, these absorption lines leave the energy transmission of the broad IR pulses practically unchanged. However, the coherent interaction of the short IR pulses with the absorption lines modifies the pulse shape of the transmitted subpicosecond IR pulses; i.e., a single IR pulse transmitted through 1 m of atmospheric air with a relative humidity of 70% is changed to a sequence of IR pulses. The intensity of the trailing pulses decays according to the dephasing time T_2 of the H_2O transition, which is ~ 50 ps.[7] To avoid the disturbance from the H_2O bands, we enclose the entire experimental setup in a case purged with dry air.

As a first demonstration of the possibilities of the spectrometer system we present data on light-induced IR transmission changes of the laser dye IR 26 (Lambda Physik) dissolved in 1-1-dichloroethane. Highly concentrated solutions in cuvettes with 10–50-μm path lengths are used. To prevent heating and dye degradation, we exchanged the irradiated volume between two laser shots by rotating and translating the sample cuvette. Excitation of the dye molecules was performed at 870 nm in the high-frequency wing of the S_1 absorption band, i.e., at ~ 2200 cm^{-1} above the 0–0 transition. The lifetime of the electronically excited S_1 state is measured to be ≈ 20 ps.[8]

The application of the experimental system as a transient spectrometer is demonstrated in Figs. 2(c) and 2(d). Here transient absorbance changes recorded 1 ps after excitation are plotted as a function of IR frequency. The spectra are composed of a series of ten-channel measurements performed at different settings of the IR light source. The accuracy within one single ten-channel experiment is better than 0.1 mOD. The inevitable changes that
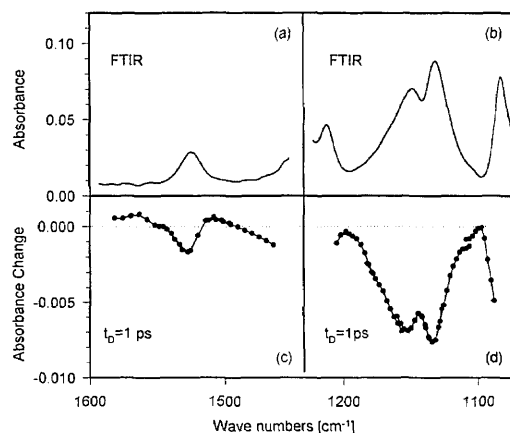

Fig. 2. (a), (b) IR absorbance spectra of the laser dye IR 26 measured with a Fourier-transform IR (FTIR) spectrometer. (c), (d) Time-resolved difference spectra recorded at a delay time of $t_D = 1$ ps. Each time-resolved spectrum is obtained from a series of ten-channel measurements connected by the solid curves.
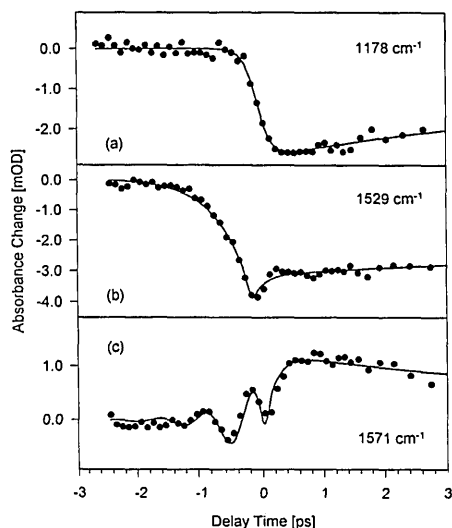
Fig. 3. Absorbance changes of the dye IR 26 induced by subpicosecond light pulses at 870 nm recorded at the three probing wavelengths of (a) 1178, (b) 1529, and (c) 1571 cm^{-1}.

occur when the IR source is tuned, together with long-term drifts of the experimental system, cause a relative inaccuracy among different ten-channel experiments of 0.3 mOD, which can be reduced when the experiments are performed with a certain spectral overlap.

In the investigated spectral range the stationary IR spectrum measured by a Fourier-transform IR spectrometer [Figs. 2(a) and 2(b)] shows only one distinct band at 1527 cm^{-1} [Fig. 2(a)] and a series of bands at 1210, 1143, and 1130 cm^{-1} [Fig. 2(b)]. The transient spectrum at $t_D = 1$ ps follows the absorption spectrum in the 1080–1205-cm^{-1} range [Fig. 2(d)]. There is a predominant bleaching of the vibrational bands on formation of S_1 state. In the 1500-cm^{-1} range there is also bleaching of the vibrational band of the ground-state molecule, and a broad induced absorption appears.

In a second type of application the time dependence of IR transmission is required at certain wavelengths. Three typical traces are recorded in Fig. 3. An investigation of the relatively broad spectral feature near 1178 cm^{-1} yields an instantaneous absorption decrease appearing within the $\approx$350-fs time resolution of the system. When narrow bands are bleached by the electronic excitation, coherent coupling between the oscillating polarization induced by the probing light pulse and the excitation process leads to apparent absorption changes at a negative delay time t_D.[9] At resonance [$\nu = 1527$ cm^{-1}; Fig. 3(b)] the decay of ΔA proceeds with $-\exp(t_D/T_2)$, $t_D < 0$, where T_2 is the dephasing time. An analysis of Fig. 3(b) yields a dephasing time of $\approx$600 fs, in agreement with the bandwidth of the observed transition of $\Delta\nu \approx 18$ cm^{-1}. When probing off resonance, we see

that pronounced modulations of ΔA occur at $t_D < 0$. These oscillations are evident from Fig. 3(c) and are reproduced by a simulation of the coherent process (solid curve). The frequency equals the detuning of the probing wavelength with respect to the resonance frequency. Another fast kinetic component (decay time 100–300 fs) is seen in Fig. 3(b) superimposed upon the bleaching of the ground-state vibrational mode at 1529 cm^{-1} and the coherent artifact around this mode. This signal becomes more apparent when the coherent artifact is averaged out by integration over a bandwidth of 50 cm^{-1} (data not shown). The amplitude of this kinetic component is negative above $\approx$1500 cm^{-1} and becomes positive at a frequency below 1500 cm^{-1}. This finding may be explained by a fast thermalization in the electronic S_1 state; because of the large excess energy of the pump pulse, higher vibrational states are excited. In this nonequilibrium state, absorption from hot vibrational levels occurs (because of the anharmonicity of the potential surface) that is at lower energies ($<$1500 cm^{-1}) than that of the vibrational ground state. After thermalization (after 200–400 fs) the fast bleaching has disappeared, and the induced absorption that is due to the vibrational ground state in S_1 remains.

In conclusion, we have presented a dual-beam spectrometer system that permits the sensitive detection of weak absorbance changes with subpicosecond ($<$400-fs) time resolution in the mid-IR between 5 and 11 μm. In a first experimental application we demonstrated the potential of the system for the study of fast processes in organic molecules.

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