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PICOSECOND INFRARED SPECTROSCOPY AS  
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REACTIONS IN SOLID MATRICES

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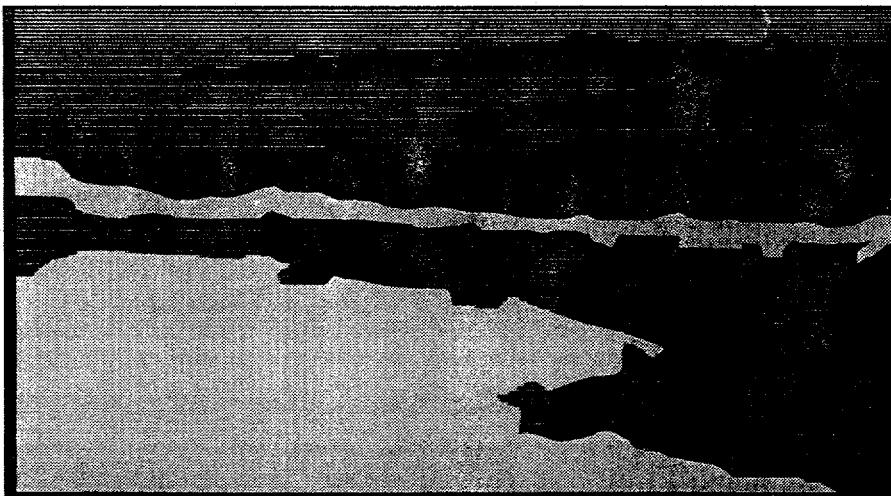
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# PICOSECOND INFRARED SPECTROSCOPY AS PROBE FOR PHOTOCHEMICAL OR THERMAL REACTIONS IN SOLID MATRICES

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## Abstract

Spectroscopy in the mid-IR on timescales from pico to milliseconds has been developed for the study of laser-material interactions over broad timescales. To reach these timescales we have employed two configurations: (1) for the ps to ns timescale a one and a two stage difference frequency mixing setup is employed, (2) for the longer timescale, CW mid-IR laser diodes have been used. In general, we excite the sample with one pulse at 1064/ 266/355 nm and probe some time later in the mid IR (2900 - 800 cm<sup>-1</sup>). In the case of photochemical reactions, we excite the sample directly in the UV. Alternatively, we initiate thermal reactions by pumping a "heater" dye at 1.064  $\mu$ m, which quickly converts the photon energy into heat. The potential of this technique to study reactions in the solid state was demonstrated for a photochemically induced (266 nm) reaction (Wolff rearrangement of a  $\alpha$ -diazo-ketone to  $\alpha$ -keto-ketene) in a polymer matrix. Thermal initiation resulted in a similar reaction. The position, amplitude and width of the product bands changed, we believe due to additional side reactions and temperature effects.

## Introduction

In the course of chemical reaction, reactants are converted through various transition states and intermediates that occur on the reaction pathway. The properties of these reactive intermediates and/or transition-state species are central to determining the reaction rate and selectivity. Recent developments in laser techniques have made pico and femtosecond timescales available (on a routine basis) for the observation of short lived intermediates and even the transition state<sup>1</sup>. The study of reactions on ultrafast timescales helps in understanding the details of the reaction pathway and reaction coordinates. In addition, ultrafast measurements are necessary for determining the kinetics of fast reactions. For example, to perform detailed computer modeling of the detonation of plastic bond explosives (PBX) many kinetic and mechanistic parameter must be included, but because of a lack of experimental data, many parameters will have to be estimated. In the investigation of a complex system, such as a PBX, detailed molecular interpretations are very difficult. For example, most investigations of ultrafast dynamics have been performed by observation of the changes in the visible region of the spectra. Unfortunately, for larger and more complex systems, the visible absorption spectrum consists typically of broad, overlapping features from which one can extract little structural information. This difficulty has led to the development of structurally sensitive, ultrafast vibrational spectroscopies that now allow one to gather correlated structural and temporal information on these large and complex systems. Use of time resolved Raman techniques, such as CARS<sup>2</sup>, also gives detailed structural information, but CARS measurements are restricted to only a few strong Raman bands. In this article, we describe our experimental set-up, which was developed to study the thermal decomposition of crystalline energetic materials embedded in polymer matrices using time resolved infrared absorption spectroscopy, which allows the observation of far more bands than Raman techniques. We will discuss first results for a model compound in a polymer matrix.

## Experimental

The experimental set-up is shown in Fig. 1. Laser pulses are derived from a mode-locked Nd:YAG laser (Coherent Corporation, Antares 76-S) which produces about 22 W at 1064 nm at 76 MHz with a pulse length of 100 ps. The 1064 nm pump pulse is frequency doubled in a temperature tuned LBO crystal resulting in a doubled output power of around 2 W, with a pulse length of 70 ps. The resulting 532 nm beam is actively position and power stabilized (Coherent 7670 AAS) and used to synchronously pump a dye jet laser (Rhodamine 6G in ethylene-glycol,  $\approx$ 540 -625 nm). The dye laser cavity is a four mirror design with a cavity length matched to the mode-locking frequency of the Nd:YAG laser. To shorten the dye laser pulse length (and additional passive mode locking) a saturable absorber jet (DQOCl) is installed, but not used in our preliminary experiments. The dye wavelength is tuned with a birefringent filter. Both the dye laser and Nd:YAG cavities are mounted on low thermal expansion plates (Invar) to

reduce cavity length fluctuations due to typical laboratory temperature variations. An autocorrelator is used to monitor the dye pulses, which have typical lengths of 3-6 ps.

The dye pulses are amplified as follows: The output of the Nd:YAG laser is passed through a doubling crystal and the remaining fundamental is separated from the second harmonic by a dichroic mirror and used to seed a regenerative amplifier. The regenerative amplifier (home built, close to the design of a Continuum RGA60) is Q-switched and frequency doubled in a KDP crystal producing about 2 W of 532 nm with a repetition rate of 50 Hz and a pulse length of 70 ps. The fundamental (100 ps, 6 W) is again separated by a dichroic and used as pump beam for our experiments (or the harmonics are used). Since the amplifier pulses have been derived from the Nd:YAG oscillator, they are accurately timed to the dye laser pulses. The doubled output of the regenerative amplifier is passed through a delay line which is used to optimize the timing, and then split in order to pump the three stage dye amplifier. Each stage consists of a flowing cell of a dye (Kiton Red for the one crystal stage set-up and Rhodamine 6G for the two stage set-up) in methanol. Before each cell the pump beam is split and then overlapped with the dye beam. The first stage has a gain of about 1000, the second stage has about 100 and the third about 10. After the last amplifier stage a small piece ( $\approx 5\%$ ) of the amplified dye is focused together with the output of a Ne lamp into a monochromator and monitored with a CCD camera for accurate determination of the wavelength.

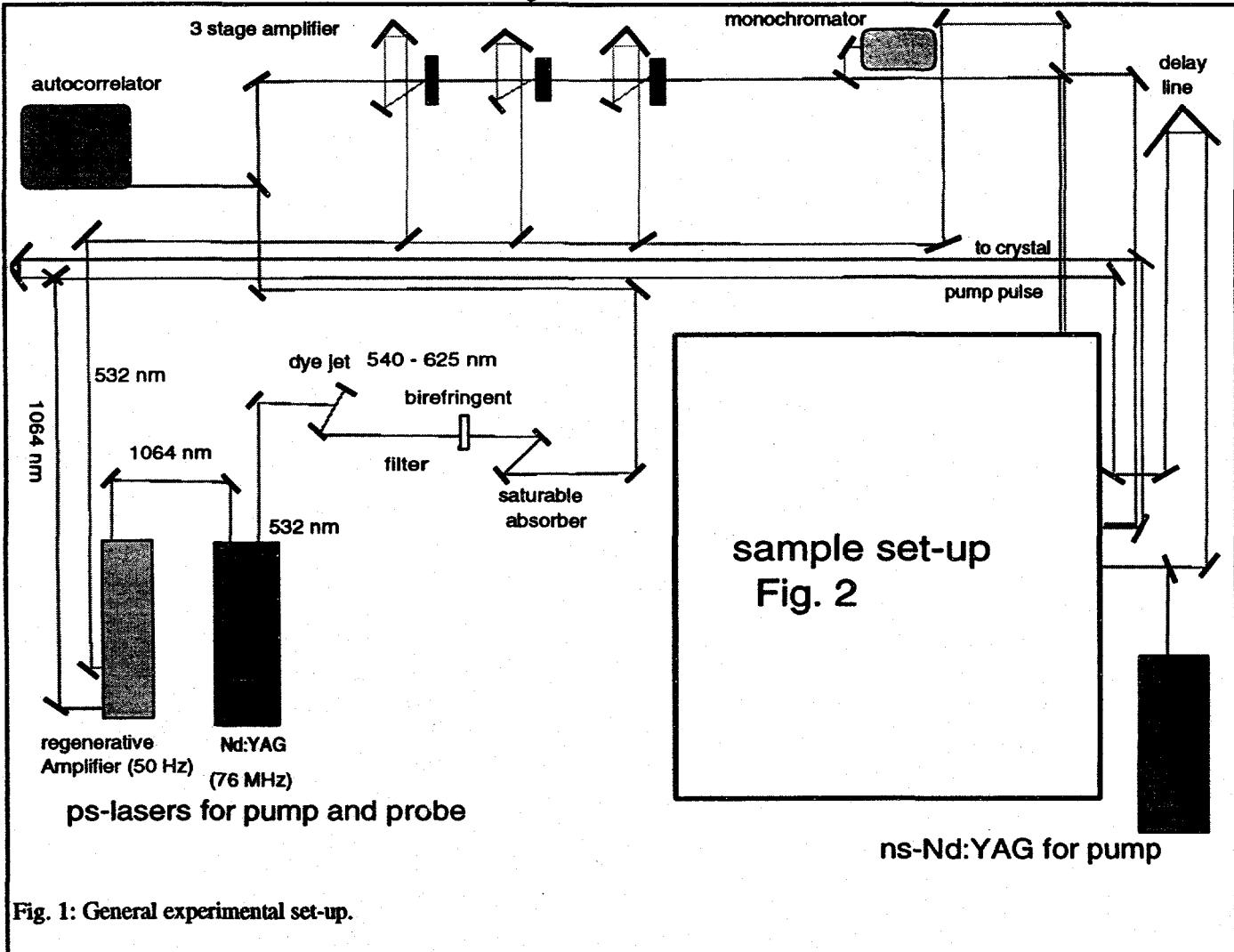


Fig. 1: General experimental set-up.

Short pulse mid-IR was generated using two different setups. For IR generation between 1800 and 2900  $\text{cm}^{-1}$ , the outputs of the amplified dye laser and the frequency doubled regenerative amplifier are overlapped in time (by using a delay line for the 532 nm) and then passed through a LiIO<sub>3</sub> crystal (InRad, 10x10x10 mm,  $\theta=21^\circ$ ), in a type I difference frequency mixing configuration (a half way plate is used to correct the polarization of the dye laser). By tuning the dye wavelength and the crystal angle (for correct phase-matching), mid-IR pulses of about 6 ps in length and several nJ in energy result. The crystal is, in principle, transparent between 0.3 and 6  $\mu\text{m}$ , but HIO<sub>3</sub> impurities cause an absorption maximum around 3  $\mu\text{m}$ , thus limiting, together with the applicable dye wavelengths of the Kiton Red and Rhodamine dye jet, the useful range of between 3.58  $\mu\text{m}$  and 5.55  $\mu\text{m}$ .

To generate mid-IR pulses of longer wavelength, which are especially important in the study of PBX's, since the PBX's often contain nitro-compounds which absorb around  $1560\text{ cm}^{-1}$ , a different set-up was used. In this case, a two crystal mixing scheme is used with minor modifications to the laser set-up. The dye in the amplifier chain was changed to Rhodamine 6G to reach the necessary dye wavelengths. In the first stage of the two crystal set-up, a KD\*P crystal (Cleveland crystals,  $10\times 10\times 10\text{ mm}$ , type II,  $\theta=48^\circ$ ) is used for difference frequency mixing of the dye beam with 1064 nm. The 1064 nm beam, resulting from the separated output of the regenerative amplifier is split 10(pump):1 (crystal). The available dye wavelengths (546-592 nm) yield near IR pulses between 1121 and 1334 nm with horizontal polarization. The generated near IR is monitored and optimized using a Ge-PIN photodiode transmitted through a near IR band pass filter. In the second stage, the tunable near IR and the leftover 1064 nm (dye is blocked by a filter) are difference frequency mixed in a AgGaS<sub>2</sub> crystal (Cleveland Crystal,  $5\times 5\times 5\text{ mm}$  type I,  $\theta=40^\circ$ ) resulting in mid-IR pulses. In principle, we could reach mid-IR wavelengths between 482 and  $1905\text{ cm}^{-1}$  but the absorption properties of the AgGaS<sub>2</sub> crystal (transparent between 0.5 and  $13\text{ }\mu\text{m}$ ) limit the mid-IR out put from 770 to  $1905\text{ cm}^{-1}$ . The IR range is further limited by the MCT detectors to a lower limit of  $\approx 800\text{ cm}^{-1}$  (total from  $5.25\text{--}12.5\text{ }\mu\text{m}$ ).

The temporal resolution of the two different crystal set-ups is determined by the pulse length of the pump pulse: the remaining fundamental of the regenerative amplifier. The pulse length of the 1064 nm fundamental is about 100 ps, for the harmonics the pulse lengths are about 70 ps and 60 ps for 532 nm and 355/266 nm respectively. Thus, our temporal resolution is about 20 ps by applying standard deconvolution methods. The optical delay line (computer controlled) of the pump beam, determines the maximum time scale of the experiment, about 8 ns, but it can be doubled to 16 ns by implementing a double pass set-up.

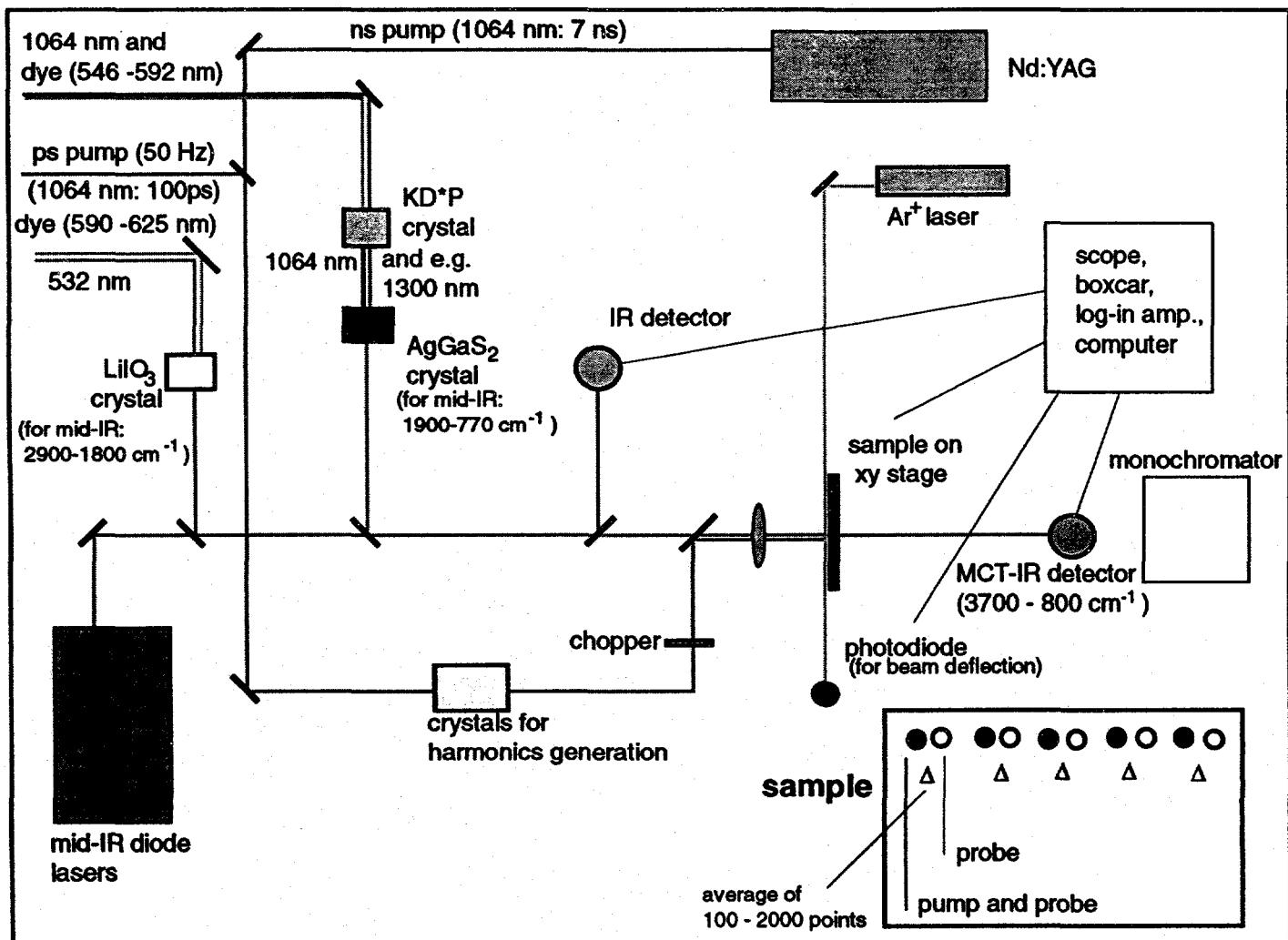


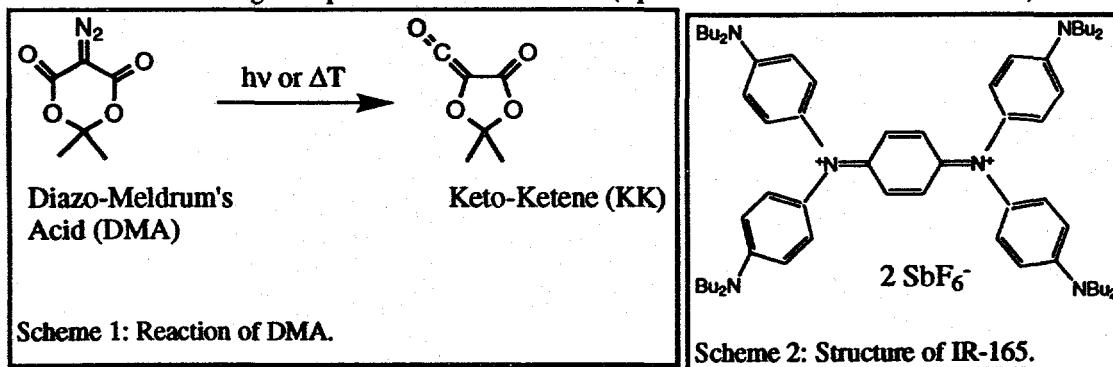
Fig. 2: Detailed scheme of the set-up in the sample area

To reach longer delays (which are important to follow reactions further than their initial steps), we have integrated a second mid-IR and pump source into our set-up. A ns Nd:YAG (Continuum NY60-10) is now used as the pump. The laser runs at a

maximum repetition rate of 10 Hz and is equipped with doubling crystals to yield the harmonics of the laser. At 1064 nm, the pulse length is about 7 ns with a maximum energy of 225 mJ, at 532 nm, it is 6 ns with 100 mJ, at 355 nm, it is about 6 ns with 55 mJ, and at 266 nm, it is also about 6 ns with 35 mJ. The pump beam is aligned onto the same optical path as the ps pump beam as shown in Fig. 1 and 2. To probe the longer time scale, we use CW mid-IR diodes (Laser Photonics) with liquid nitrogen dewar (Laser Photonics L5736), temperature (Laser Analytics, model CTS) and current controller (ILX Lightwave model 3545), shown in Fig. 2. These laser diodes can be tuned over a range of about 100  $\text{cm}^{-1}$  by changing the temperature and current of the diode. The wavelength of the diode is measured with a monochromator and MCT IR detectors (Graseby Infrared, model 1710138, same as for the ps experiments), a boxcar integrator (Stanford Research Instruments, model SR 250, interface SR 245, and power supply SR 280), and a digitizer (DSP 2012S, with averaging memory 4100 in a LeCroy 8013A with a GPIB 8901A), which is interfaced to a computer. This setup has a temporal resolution of micro to milliseconds, thus giving us a total temporal resolution for the complete set-up ranging from the ps to ms. The details of the sample area are shown in Fig. 2. The probe beam is divided into a reference and a sample beam which are detected with separate MCT diodes. The data is acquired using a boxcar integrator, digitizer and computer interface. The pump beam frequency is divided by two using an optical chopper and is collinearly aligned with the probe beam and focused with the same lens onto the sample. Typical beam diameters for the pump beam (on the sample) are about 350  $\mu\text{m}$  and for the probe beam about 180  $\mu\text{m}$ , ensuring that only the irradiated area is probed. Due to the nature of our samples, i.e., crystalline energetic material in a solid matrix, only single shot experiments of each irradiated area are possible; with each laser pulse the material is decomposed or ablated at the high pump energies. Therefore, a typical sample consists of a thin coating of our probe molecules in a polymer matrix (polymethyl-methacrylate, PMMA or polyvinylchloride, PVC) either as free standing film or on a polymer substrate (polypropylene, PP). The polymer film is mounted in an aluminum frame on an XY translation stage (Klinger, model CC1.2), which is also computer controlled. The moving of the stage is synchronized with the 50 Hz repetition rate of the pump beam. Due to the nature of the single shot experiments, the pulse to pulse variation of pump and probe beam, and sample inhomogeneities, it is necessary to average many shots, typically 100 to 2000, depending on the change of the IR transmission beam and sample quality. We use the reference and sample beams to measure the sample/probe beam quality. As shown in Fig. 2, we measure the difference of the IR transmission between a pair of probe pulses. By dividing the pump beam down to 25 Hz with the optical chopper (DigiRad, model L980), one measured point is a reference point with no pump beam, whereas the next point is measured with pump and probe beam overlapping. Then, between 100 and 2000 differences are averaged for each time delay. As mentioned before, the samples ablate at higher pump energies, which could possibly interfere with the measurements by scattering/absorption/removal of the ejected fragments. Therefore, we use a beam deflection method above the sample to determine the onset of ablation. Briefly, the beam of an air cooled Ar<sup>+</sup> laser (Cyonics, model 2201-10BL) is aligned parallel to the sample surface and the intensity of the beam is measured with a photodiode and oscilloscope. The ejected fragments and the thermal shock wave scatter the laser beam, thereby determining the onset of ablation. In a proof of principle demonstration, we use the ps set-up in the one crystal configuration.

### Sample Preparation

Samples used for the first test of our set-up were prepared by coating onto a polypropylene sheet (0.5 mm thick) with a Mayer #20 rod (wet thickness  $\approx$  50  $\mu\text{m}$ ). We used two different films, one prepared for irradiation in the UV (266 nm) and one prepared for irradiation at 1064 nm, to allow a comparison of the photochemical reaction with the thermal reaction. For the photo-chemical induced reaction, we used a mixture of 750 mg of PMMA and 200 mg of a diazocompound (5-diazo Meldrum's acid, DMA) in 15 ml of THF. This diazo compound is sensitive to UV irradiation<sup>3</sup> and has two features which make it a perfect test molecule. It has the strong azo absorption band in the mid-IR (2176  $\text{cm}^{-1}$ ) and has one known reaction product (keto-ketene), shown in scheme 1, which has also a strong absorption band in the mid-IR (reported between 2000 and 2200  $\text{cm}^{-1}$ <sup>4</sup>). For the thermal reaction of the diazo compound we used 1064 nm irradiation to excite a "heater" dye (IR-165, shown in scheme 2) which dumps its energy into the matrix within a few picoseconds<sup>5</sup>, raising the matrix "temperature" to one to two thousand Kelvin.



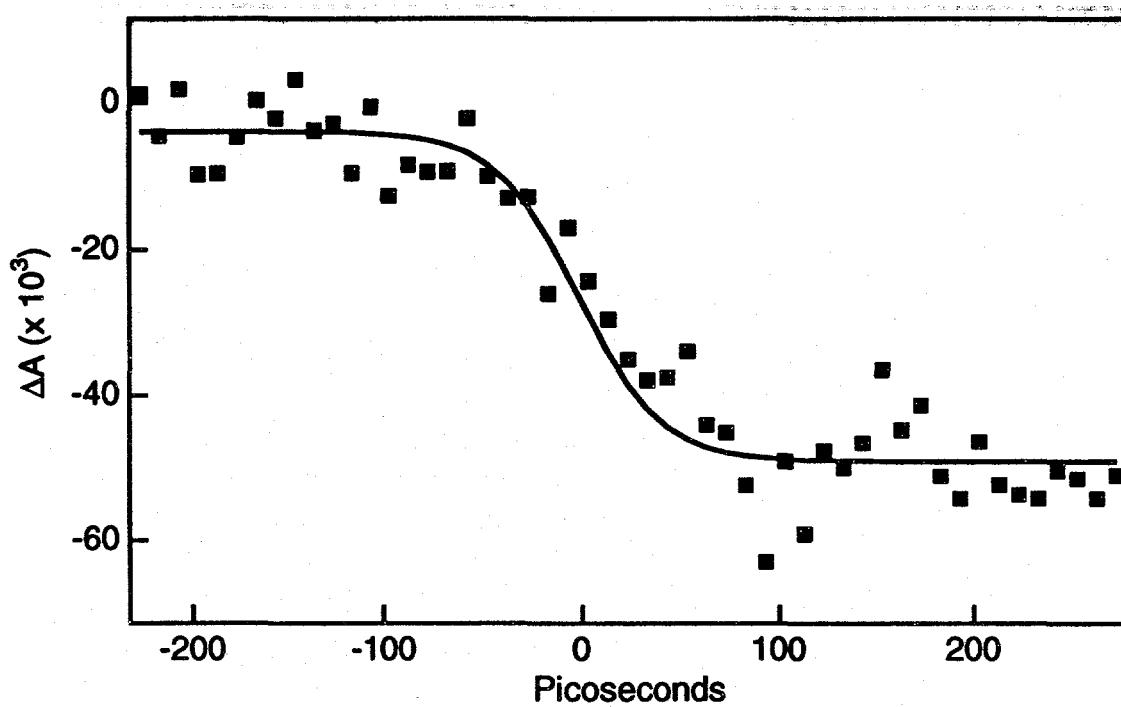


Fig. 3: Change of absorbance as a function of time from -200 to 300 ps at  $2190\text{ cm}^{-1}$ . The solid line is the instrument response.

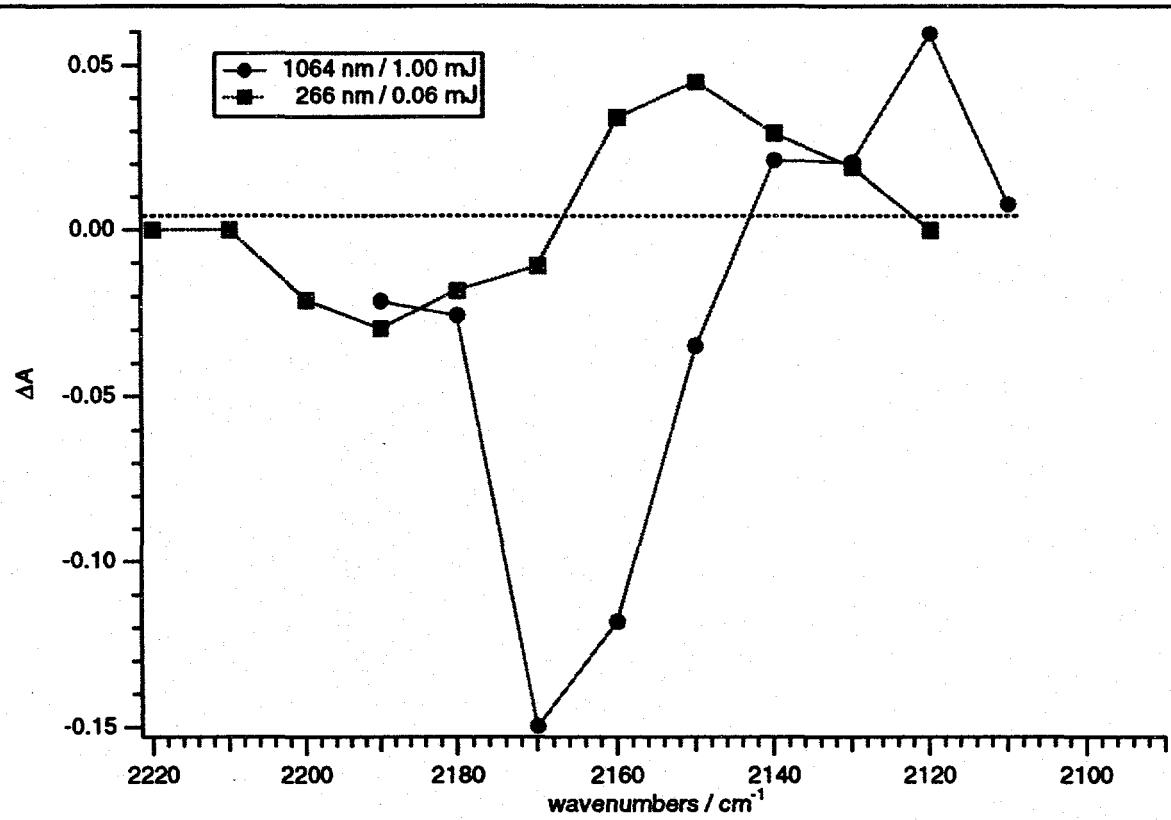


Fig. 4: IR-difference spectra between  $2220$  and  $2100\text{ cm}^{-1}$  after irradiation at  $266$  and  $1064\text{ nm}$ . Spectra averaged over  $1\text{ ns}$ .

## Results and Discussion

### 266 nm excitation

The change of the IR absorbance was monitored following 266 nm excitation with 30-130  $\mu$ J per pulse in the diazo/ketene region from 2120 to 2210  $\text{cm}^{-1}$  at intervals of 10  $\text{cm}^{-1}$ . Maximum changes in absorption occurred at 2190  $\text{cm}^{-1}$  where a decrease in absorbance was observed, and at 2150  $\text{cm}^{-1}$  where an increase in absorbance was observed. We assign the 2190  $\text{cm}^{-1}$  change to the bleaching of the diazo Meldrum's acid, and the 2150  $\text{cm}^{-1}$  to the appearance of the keto-ketene intermediate. In Fig. 3 is shown the bleaching of the azoband monitored at 2190  $\text{cm}^{-1}$ . We took similar traces at various wavenumbers, creating a difference spectra in the mid-IR (shown in Fig. 4). As the bands due to the starting diazo compound and the keto-ketene overlap significantly, we have fit the difference spectra to the difference of the DM infrared spectra and a gaussian function representing the keto-ketene (maximum around 2161  $\text{cm}^{-1}$ )<sup>6</sup>.

### 1064 nm excitation

The resulting difference spectra (Fig. 4) are similar to that seen with 266 nm excitation. Here we pump with 0.2-1.0 mJ per pulse of 1064 nm. The product bands are red shifted slightly and are less intense than those seen for 266 nm. Varying the laser energy resulted in changes in the intensities of the bands, but not the band positions. This suggests that we are observing bands from a reaction product (ketene) and not exclusively from thermal effects that would result in an energy dependent red shift at increasing laser energies, but only minor intensity changes. The product band is centered at 2120 - 2145  $\text{cm}^{-1}$ , and is less intense than seen in the photochemical experiments. The red shift of the observed product band is probably due a red shift of IR bands with increasing temperature (change of density and anharmonicity)<sup>7</sup>. A typical shift<sup>8</sup> for similar IR bands (from static measurements) yields a shift of about 4  $\text{cm}^{-1}$  / 100°C. The observed red shift would then account for a temperature jump of about 1000°C, which is well within the range of the estimated (laser energy, heat capacity etc.) temperature increase<sup>9</sup>.

## Conclusions

We have built a set-up to study laser driven reactions in solid matrices (e.g. polymers) using time resolved IR spectroscopy. The first experiments have provided one of the first examples of how ultrafast infrared spectroscopy may be used to examine laser-driven reactions in polymeric matrices. The photochemical as well as the thermal initiated reaction of a model compound has been studied in a PMMA matrix. While the initial reaction products are probably the same, the band position and intensity of difference spectra of the UV and thermal initiated reaction are different. These variations are probably due to additional side reactions, temperature effects and different matrix interactions at elevated temperatures.

## Acknowledgement

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