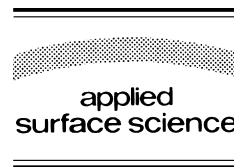applied
surface science

Laser–material interactions probed with picosecond infrared spectroscopy

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Abstract

Picosecond infrared spectroscopy in the mid-IR has been applied to the study of laser–material interactions on an ultrafast time scale. We excite the sample with one pulse at 1064 or 266 nm and probe some time later in the mid IR ($2900–1400$ cm^{-1}). We study photochemical reactions by exciting the sample directly in the UV. Alternatively, we initiate thermal reactions by exciting a 'heater' dye at 1.064 μm, which quickly converts the photon energy into heat. The potential of this technique to study reactions in the solid state was demonstrated for the photochemically induced (266 nm) Wolff rearrangement in a polymer matrix. This reaction is the basis of most positive photoresists. We were able to assign the key intermediate (ketene) in real time at room temperature for the first time. Thermal initiation also resulted in Wolff rearrangement. The position, amplitude and width of the product bands changed, probably due to additional side reactions and temperature effects.

Keywords: Picosecond infrared spectroscopy; Ablation; Polymer; Photoresist

1. Introduction

One of the most widely used class of compounds for imaging applications are diazoketones. [1] These compounds undergo a photoinduced Wolff rearrangement to form a ketene intermediate which subsequently hydrolyses to a base-soluble carboxylic acid (shown in Scheme 1) [2]. As part of a program to develop diagnostics for laser-driven reactions in polymer matrices we have investigated the photo-induced decomposition of 5-diazo-2,2-dimethyl-1,3-dioxane-4,6-dione (5-diazo Meldrum's acid, DM) in a PMMA matrix. This particular diazoketone is sensitive to deep UV (200–260 nm) making it suitable for high resolution lithographic applications [3].

Thermally induced reactions in polymers are also of increasing interest for fundamental and applied research. In particular, various imaging systems are based on putting energy into a thin polymer film with a laser. The energy is put into a dye (shown in Scheme 2) that converts the energy into heat within a few picoseconds. Subsequently, the films start to decompose, break up, and eventually ablate [4]. Additional energetic materials are thought to increase

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[1] Widely used in this regard are a variety of naphthoquinone diazides in Novalak resins, including the commercially available naphthoquinone diazides (Shipley-AZ1350J, Kodak-Photoresist 820, Hunt-HPR 204). See Ref. [1].

Scheme 1. Mechanism of the photodecomposition of diazo Meldrum's acid.
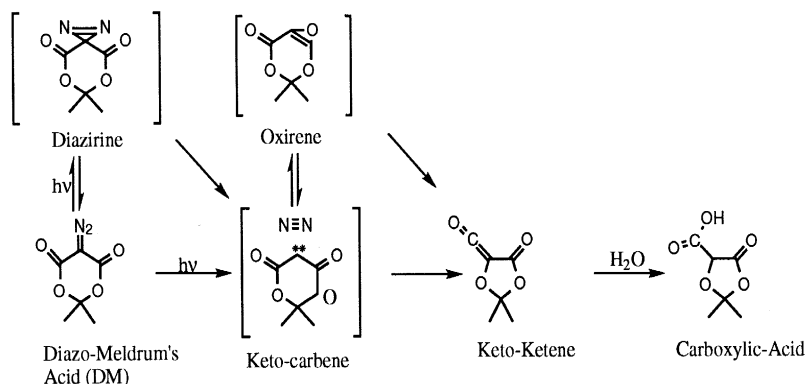
the efficiency of these process. One possible candidate is again DM, which is also known to undergo a thermally induced Wolff rearrangement [5].

It has historically been difficult to study the chemistry of such systems as many of the intermediates are short-lived and absorb only in the UV. Recent advances in ultrafast infrared spectroscopy, however, now allow us to directly examine the initial steps with infrared spectroscopy. Herein, we describe the first observation of intermediates in the photochemistry [6] and thermochemistry of DM with ultrafast infrared spectroscopy.

2. Experimental

We have examined the photodecomposition of DM in a PMMA matrix with picosecond infrared spectroscopy. The general experimental procedure has been described previously [7]. Briefly, our infrared probe pulse, tunable from 2900 to 1800 cm^{-1}, is generated by difference frequency mixing a tun-

able amplified dye laser pulse (ca. 600 nm, 5 ps) with the doubled 532 nm output of a regenerative YAG amplifier. Our excitation pulse is the frequency quadrupled output (266 nm, 60 ps) or the fundamental (1064 nm, 100 ps) of the regenerative amplifier. Using conventional deconvolution techniques, we can typically resolve 20 ps events. Time resolution is obtained by optical delay, and is variable from 0 to 6 ns. Samples consist of ~ 3 μm thick coatings of PMMA (Aldrich, $M_W = 120,000$) doped with DM (TCI America, ca. 20% by weight) on polypropylene sheets. For the thermal experiments samples consist of PMMA, DM and IR dye 165 (Glendale Protective, ca. 10% by weight) coated onto polypropylene sheets. The sheets are held taut with a metal frame, and are translated with a computer controlled stepper motor such that each location on the film is subjected to only a single laser shot. Both pump on and pump off data are taken which allow us to convert our data into ΔA units.

3. Results and discussion

3.1. 266 nm excitation

The change of the IR absorbance was monitored following 266 nm excitation in the diazo/ketene [8] region from 2120 to 2210 cm^{-1} at intervals of 10 cm^{-1}. Maximum changes in absorption occurred at 2190 cm^{-1} where a decrease in absorbance was observed, and at 2150 cm^{-1} where an increase in absorbance was observed. We assign the 2190 cm^{-1}
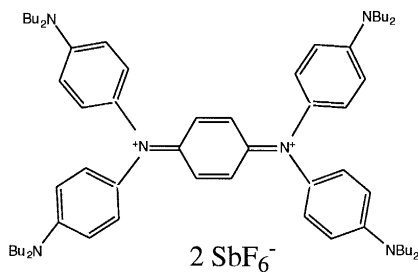
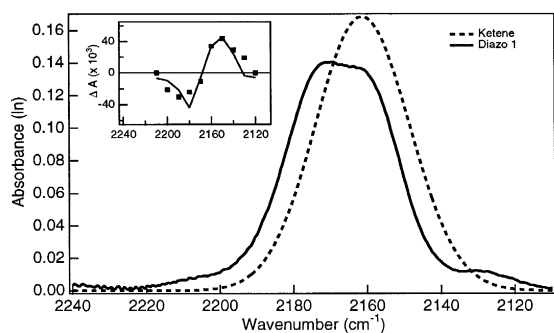Scheme 2. Structural formula of IR-165.

Fig. 1. Spectra of DM (solid line), and the keto-ketene (dashed line) at 300–500 ps calculated by fitting the difference spectrum (inset) to the difference of the DM spectra and a gaussian function which best represents the ketene spectrum. The fit which results from the difference of the two spectra is shown in the inset. The forth harmonic (266 nm) of a Nd:YAG laser with an energy of about 120 μJ has been applied. The diameter of the UV pulse was typically 400 μm, corresponding to a fluence of about 95 mJ cm^{-2}.
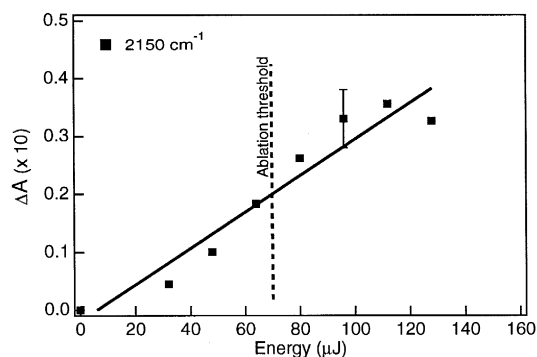

Fig. 2. Dependence of the signal intensity on the laser energy (266 nm). The irradiated area is about 1.25×10^{-3} cm^2. A typical error bar is shown in the graph. The bandwidth of the IR probe is ~ 8 cm^{-1}.

change to the bleaching of the diazo Meldrum's acid, and the 2150 cm^{-1} to the appearance of the keto-ketene intermediate [6,8]. The decrease in absorbance at 2190 cm^{-1} occurs within our instrument response and is constant for 6 ns as expected for the photodissociation. Similarly, the rise time of the 2150 cm^{-1} feature we assign to the keto-ketene can also be described by our instrument response. Using deconvolution techniques we assign an upper limit on the appearance of the keto-ketene of $\tau < 20$ ps; no change was seen out to 6 ns. In Fig. 1 is shown the difference spectra observed at 300–500 ps, generated by averaging the 300–500 ps data in each of the kinetic traces. 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 [2] and a gaussian function representing the keto-ketene.

The best fit yields a spectrum for the keto-ketene centered at 2161 cm^{-1} and with a width (FWHM) of 29 cm^{-1}. [3] Deviation from the experimental data at

some wavelengths suggests that the spectrum is more complex than a single gaussian as expected for dopants dispersed in polymeric matrices. The energy dependence of the signal intensities at 2150 cm^{-1} for 1 ns is shown in Fig. 2. The key point is that there is no dramatic change above the ablation threshold ablation (≈ 70 μJ), suggesting that ablation occurs on a longer time scale (i.e., > 6 ns). The ejection of material would be expected to increase the observed signal (ΔA at 2150 cm^{-1}) drastically due to light scattering. In addition, within the experimental error, the signal size is linear over the entire in laser energy, consistent with a one photon event and a quantum yield of decomposition of 0.8 ± 0.2. [4] The quantum yield for the ketene appearance is about the same, suggesting that side reactions are not significant.

3.2. 1064 nm excitation

Excitation at 1064 nm is used to excite a 'heater' dye which dumps its energy into the matrix within a few picoseconds, raising its 'temperature' up to a few thousand kelvin. The resulting difference spectra (Fig. 3) are similar to that seen with 266 nm excitation. 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

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[2] The IR spectra of DM in PMMA was recorded with an FTIR spectrometer and is identical to previous published data [8].

[3] The ketene has been measured previously [8] in KBr at 100–120 K. The band was centered at 2143 cm^{-1} with a FWHM of about 40 cm^{-1}.

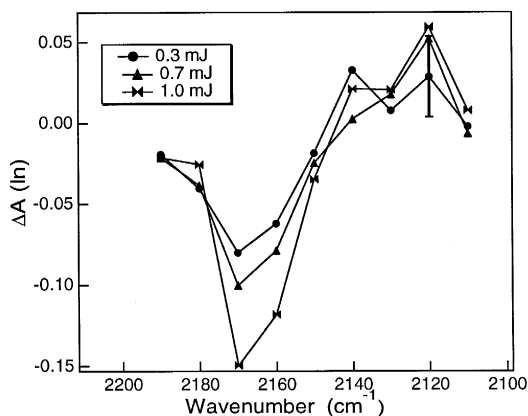[4] This agrees with the previously reported values of 0.6 and 1.0 [11].

Fig. 3. Change of the absorbance as a function of irradiation energy (1064 nm) for a time of 1 ns. The irradiated area is about 0.49×10^{-3} cm^2. A typical error bar is shown in the graph. The bandwidth of the IR probe is ~ 8 cm^{-1}.

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. [5] The product band is centered at 2135–2145 cm^{-1}, and is less intense than seen in the photochemical experiments. The band shift is likely due to a small temperature shift as the matrix is heated to 2000–4000 K (1 mJ/pulse excitation energy); the change in intensity relative to the 266 nm data is likely due to the presence of additional, *thermally* activated, side reactions.

The energy dependence of the increase in absorbance attributable to the ketene (at 1 ns) distinct from the photochemical result. The increase is not linear and can be described as roughly exponential (from additional data, not shown in Fig. 3) in laser energy as might be expected if Arrhenius behavior were followed. Interestingly, the DM band has a larger temperature dependence, suggesting that additional side reactions (that result in less ketene formed relative to the DM decomposed) may be more important at higher laser energies. We have not yet resolved the rate of appearance of the product bands; we estimate, however, that the bands appear in less than 1 ns. This is consistent with calculations based on known kinetic parameters [13] that predict reaction times of 2–200 ps at 2000–4000 K.

4. Conclusions

In summary, these experiments have provided the first example of how ultrafast infrared spectroscopy may be used to examine laser-driven reactions in polymeric matrices. We have determined that the photoinduced Wolff rearrangement of DM in a PMMA matrix is complete within 20 ps. The IR band assignable to the ketene is centered at 2161 cm^{-1} and has a width of 29 cm^{-1}. The rapid formation of the ketene is a key element of the high quantum yield of carboxylic acid formation, and for the use of DM as an ablation sensitizer. The power dependence data show that ablation does not appear within 6 ns. The thermally induced Wolff rearrangement can also be followed by ps-IR spectroscopy. While the initial reaction products are the same, the band position and intensity of the ketene are different. These variations are probably due to additional side reactions, temperature effects and different matrix interactions at elevated temperatures. In the near future we will resolve the kinetics of the reaction initiated with 1064 nm excitation, extend our IR wavelength range to 1000 cm^{-1}, and extend our time scale to the millisecond regime with the use of infrared diode lasers.

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[5] There exist several possibilities for the product band: the ketene, a red shifted diazo band, a red shifted ketene and a mixture of them. Considering the line shape of the difference spectra and the thermal initiated Wolff rearrangement [5], we favor the red shifted ketene as product band. Nevertheless we cannot totally neglect the other possibilities with the available data.

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