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LASER-INDUCED REACTIONS IN A DEEP ULTRA VIOLET RESIST SYSTEM: STUDIED WITH PICOSECOND INFRARED SPECTROSCOPY

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Author(s):

T. Lippert, CST-1
A. Koskelo, CST-1
P.O. Stoutland, CST-6

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Laser-induced Reactions in a Deep UV Resist System: Studied with Picosecond Infrared Spectroscopy

T. Lippert, A. Koskelo, P. O. Stoutland

Division of Chemical Science and Technology, Mail Stop J-567, Los Alamos National Laboratory, Los Alamos, NM 87545, lippert@lanl.gov

ABSTRACT

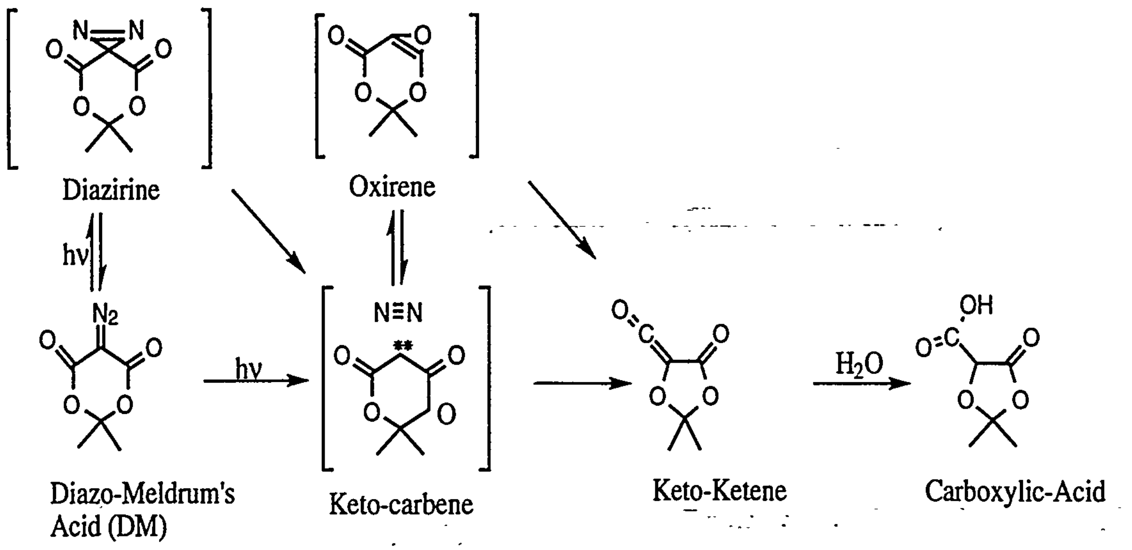
One of the most technologically important uses of organic photochemistry is in the imaging industry where radiation-sensitive organic monomers and polymers are used in photoresists. A widely-used class of compounds for imaging applications are diazoketones; these compounds undergo a photoinduced Wolff rearrangement to form a ketene intermediate which subsequently hydrolyses to a base-soluble, carboxylic acid. Another use of organic molecules in polymer matrices is for dopant induced ablation of polymers. 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 using picosecond infrared spectroscopy. In particular, irradiation of DM with a 60 ps 266 nm laser pulse results in immediate bleaching of the diazo infrared band ($\nu = 2172\ \mathrm{cm}^{-1}$). Similarly, a new band appears within our instrument response at 2161 cm^{-1} (FWHM $= 29\ \mathrm{cm}^{-1}$) and is stable to greater than 6 ns.; we assign this band to the ketene photoproduct of the Wolff rearrangement. Using deconvolution techniques we estimate a limit for its rate of formation of $\tau < 20$ ps. The linear dependence of the absorbance change with the pump power (266 nm) even above the threshold of ablation suggest that material ejection take place after 6ns.

INTRODUCTION

One of the most technologically important uses of organic photochemistry is in the imaging industry where radiation-sensitive organic monomers and polymers are used in photoresists.[1] Common examples include systems in which photochemically formed acids become soluble in aqueous base (i.e. positive photoresists)[2] and where organic dopants sensitize a polymer towards ablation.[3] The chemistry which occurs in these systems is the basis for the manufacture of high-density electronic circuits, as well as for the production of printing plates.

One of the most widely-used class of compounds for imaging applications are diazoketones.[4] These compounds undergo a photoinduced Wolff[5] rearrangement to form a ketene intermediate which subsequently hydrolyses to a base-soluble carboxylic acid.[6] As part of a program to develop diagnostics for laser-driven reactions in polymer matrices[7], 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.[8] It has historically been difficult to study the chemistry of such resists 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 occurring in UV photoresists with infrared spectroscopy. Herein, we describe the first room temperature observation of intermediates in the photochemistry of DM with ultrafast infrared spectroscopy.

Shown below is the generally accepted mechanism for the photodecomposition of diazo Meldrum's acid.[9]



Reaction scheme of the photochemistry of Diazo Meldrums Acid.

It is widely believed that the initial event is loss of nitrogen and formation of a keto-ketene, most likely through a short-lived carbene intermediate. This keto-ketene is hydrolzed by water present in the polymeric matrix to form a ketenehydrate[10] and finally a carboxylic acid. Various other intermediates have also been discussed. For example, it has been reported that isomerization to a diazirine may take place[11], and that a oxirene[12] may also be present. For resist applications the key species is the carboxylic acid which results in the resist being base soluble.

For ablation applications, the ketene of DM (and its rate of formation and lifetime) is important as it has been reported to be involved in a multiple photon cyclic absorption process leading to heating and ultimately ablation.[9] Room-temperature transient experiments have suggested that the keto-ketene forms within 200 ns[13], and is hydrolyzed on a seconds timescale. Low temperature experiments coupled with infrared spectroscopy have also identified the keto-ketene intermediate ($\nu_{\text{ketene}} = 2143\ \text{cm}^{-1}$).[14] Nevertheless there are only limited data about reactions in polymer matrices at room temperature available.

EXPERIMENTAL

We have examined the photodecompositon of DM in a PMMA matrix[15] with picosecond infrared spectroscopy. The general experimental procedure has been described previously[16] and shown in Fig. 1.

Briefly, our infrared probe pulse, tunable from 2900 - 1800 cm^{-1}, is generated by difference frequency mixing a tunable 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 (266nm, 60 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.[17] 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.

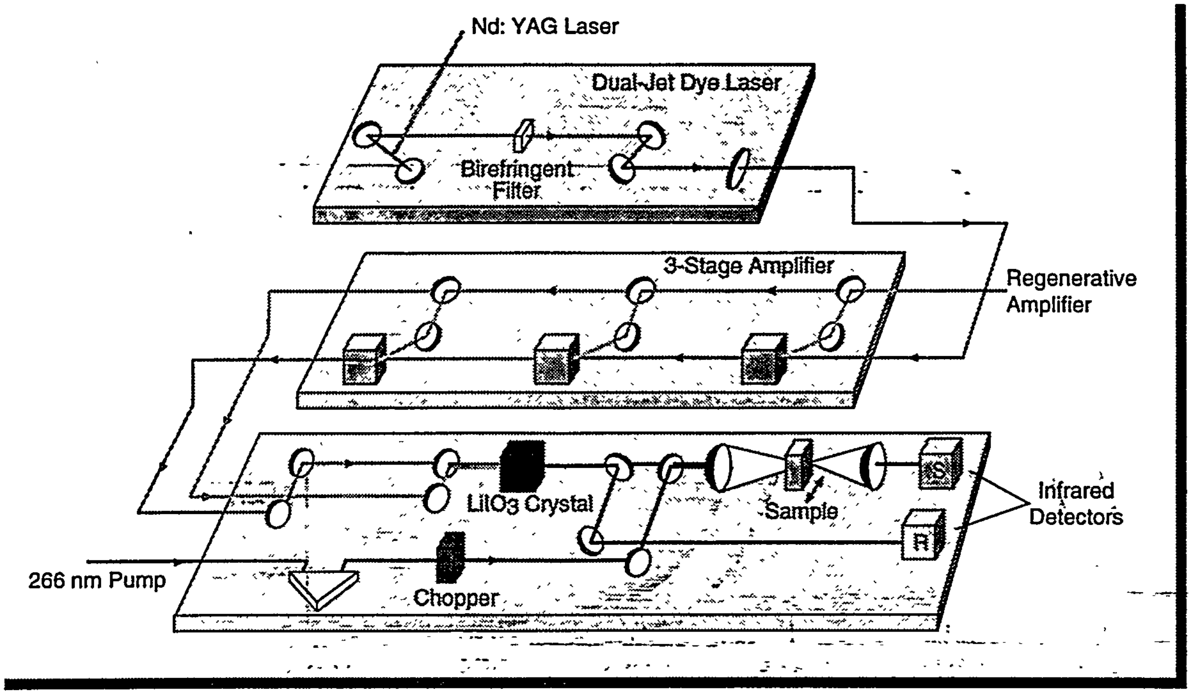


Figure 1: Schematic of the exprimental set-up.

RESULTS

The change of the IR absorbance was monitored in the diazo/ketene 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} change to the bleaching of the diazo Meldrum's acid, and the 2150 cm^{-1} to the appearance of the keto-ketene intermediate. 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. 2 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 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}. 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 (Fig. 3) was consistent with a single photon event, and a quantum yield of decomposition of 0.8 ± 0.2.[18] The quantum yield for the ketene appearance is about the same, suggesting that side reactions are not significant.

The linear dependence of the absorbance change over the applied energy range, varying from below to above the threshold of ablation (≈ 70 μJ), suggests that ablation take not place during this time scale (6 ns). The ejection of material would be expected to alter the observed signal due to scattering.

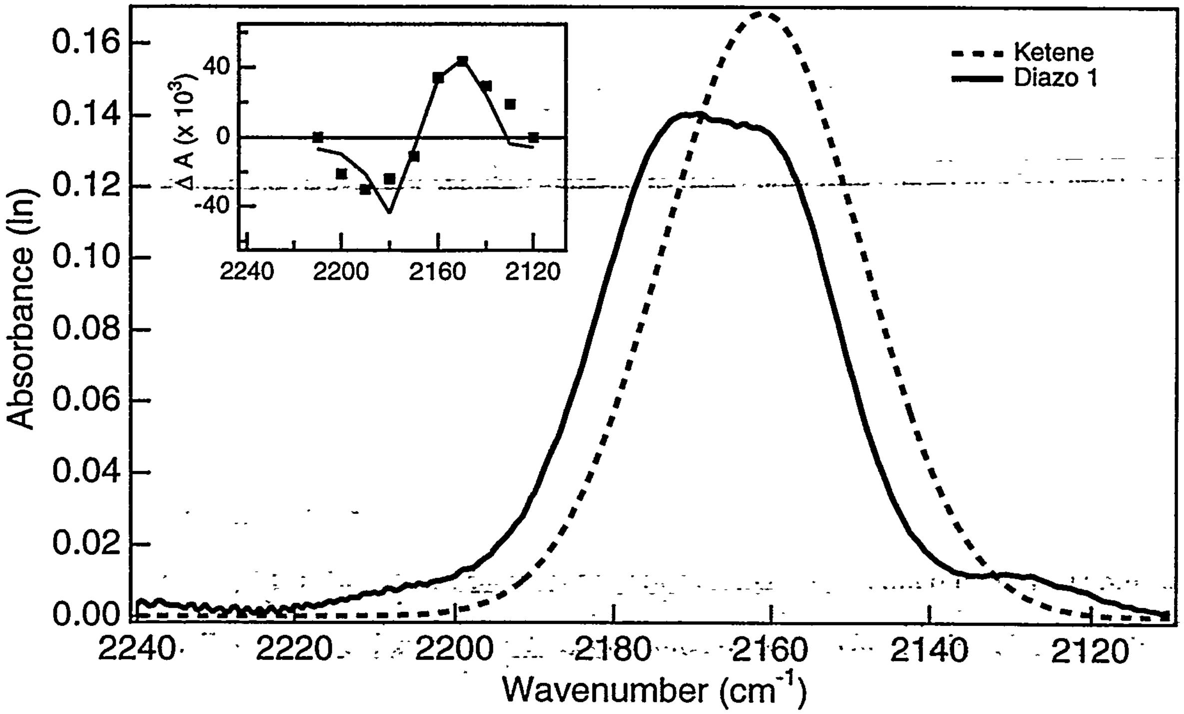


Figure 2: Spectra of DM (solid line), and the keto-ketene (dashed line) at 300 - 500 ps calculated by fitting the difference spectrum (inset) to the difference of the DM spectra and a gaussian function which best represents the ketene spectrum. The fit which results from the difference of the two spectra is shown in the inset.

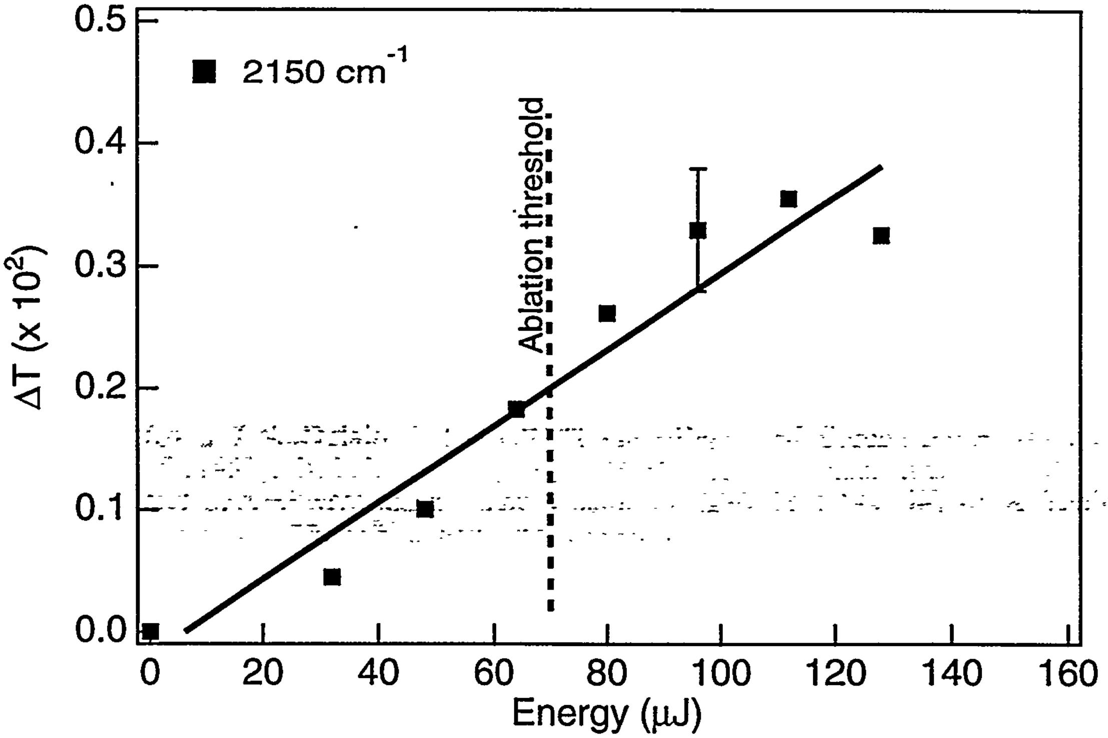


Figure 3: Dependence of the signal intensity on the laser energy (266 nm).

CONCLUSION

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 doesn't appear within 6 ns. Future experiments will center on extending our wavelength range so that we may observe the ketone moieties, and hopefully the keto-carbene itself, and on examining the effect of different matrices. Finally, in the near future we will be extending our measurements to examine a variety of other processes (e.g. ablation, curing, etc.) for which detailed structural information on ultrafast timescales has technological importance.

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(18) This agrees with the previously reported values of 0.6 and 1.0: references 9, and 13.