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Femtosecond Pump Probe Spectroscopy of Novel Corroles

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Abstract. We present our experimental results on the femtosecond (fs) pump-probe dynamics of four novel Corroles (a) Tritolyl Corrole (TTC) (b) Germanium Tritolyl Corrole (Ge-TTC) (c) Phosphorus Tritolyl Corrole (P-TTC) (d) Triphenyl Corrole (TPC). The photo-physical response of these Corroles was studied with ~ 60 fs, 1 kHz laser pulses at a wavelength of 600 nm. The transient response of change in probe transmission with pump and without pump at 100 Hz modulation was acquired. Photo-induced absorption (change in transmission was negative) was observed for all Corroles. The recovery time for TTC was ~ 60 ps. With the introduction of Ge the life time was estimated was ~ 53 ps while for phosphorous substitution the life time observed was ~ 286 ps. TPC had an excited life time of ~ 35 ps.

Keywords: Z-scan, Two photon absorption (2PA), Corroles, Picosecond, Femtosecond, Pump-probe

PACS: 42.65.-k, 42.70.Jk, 42.65.A, 87.15.ht

INTRODUCTION

The relaxation mechanisms of photo-induced excitation are one of the most important aspects that determine the performance of devices in applications such as optical switches and optical limiting filters. Detailed knowledge of photo-excited dynamics of potential molecules is required in view of their applications in photonics. Corroles have set of highly delocalized π electrons through which it exhibit large nonlinearity which makes them good candidates for such applications. Corroles are very special organic systems in that they offer tremendous opportunities by substituting different atoms and functional groups in its core [1,2]. The general ultrafast spectroscopic techniques to investigate the transient kinetics utilize ultrashort laser pulses (ps or fs) in a pump probe configuration. With conventional techniques such as Z-scan the interpretation of mechanisms of nonlinear response requires careful analysis. However, the dynamic information of the measured nonlinearity will not be revealed [3-5]. Therefore, in order to observe an ultrafast process such as the translation or rotation of part of a molecule, energy transfer, charge transport or the formation or breaking of a chemical bond, a measurement technique with a temporal resolution in the range of fs to ps is required. In the pump probe spectroscopy technique a beam

Functional Materials

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consisting of a train of ultrafast laser pulses is split into pump and probe beams. The pump and probe beams are sent along different optical paths and then focused into a sample with a time delay between them. The pump is used to trigger a photo-induced process in the sample and the probe beam is used to probe the process, for example molecules or atoms in their excited states, making it possible to follow its evolution back to the ground state. The evolution of this process is then followed by monitoring the delayed probe pulse, for example by absorption or reflection and varying this delay time [6-8]. The limit of time resolution is determined solely by the width of laser pulses used.

EXPERIMENTAL DETAILS

The experiments were performed using 600 nm pulses from TOPAS-C (Coherent). The output of MICRA (Coherent) oscillator (~ 15 fs FWHM, 800 nm, 80 MHz) was amplified by Ti:sapphire laser system (Legend) delivering ~ 40 fs, 800 nm pulses at 1 kHz which was then fed to a optical parametric amplifier. The translation stage was controlled by motion controller (ESP 300) which was automated to computer. Data acquisition was done by LabVIEW programming. Appropriate time constant and sensitivity of the lock-in-amplifier were chosen acquiring the taking data via GPIB. The optically induced transmission changes of the probe signal were measured by periodical blocking of the pump beam with mechanical chopper (198A, Signal Recovery). The pump was chopped at 109 Hz frequency. The probe delay was given through translation stage which is automated and connected to PC. The angle between pump and probe was $\sim 10^\circ$. Pump Intensity was controlled using a half wave plate and polarizer. The pump to probe intensity ratio was maintained at 10:1. The pulse duration was estimated to be ~ 70 fs at the sample.

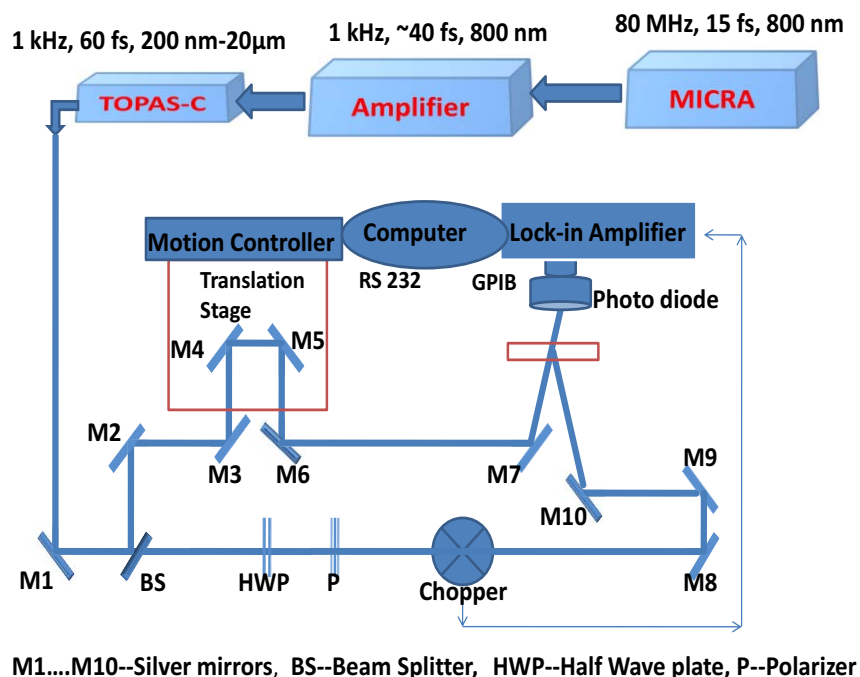


Figure 1 Typical pump-probe experimental set up.

The nonlinear optical properties of these molecules were studied using the Z-scan technique (discussed in [8-12]) and are reported elsewhere [13]. The fs pump-probe experimental setup is described in figure 1. The intensity of pump pulses was controlled by a half wave plate and the polarizer combination. The silver mirrors with >95% reflectivity and less dispersion were used in this set up. The pump diameter was ~4 mm and the probe diameter was ~1.5 mm. Both the beams were *not focused* in the sample. The probe beam was ensured to be within the envelope of pump beam area throughout the probe delay scan for achieving good signal. Temporal step size of the scan was ~0.5 ps.

RESULTS AND DISCUSSION

Figures 2(a)-(d) show the degenerate pump probe data for all four Corroles. We fitted the data using the following formula $\Delta T/T = A \exp-(t-t_0)/\tau$ where ΔT is the time dependent change in probe transmission, induced by the pump at time 't' after the pump excitation and T is the probe transmission in the absence of pump. At initial times, after excitation, there is an ultrafast decrease of transmission of the probe beam, which indicated photo-induced absorption. Our data were fitted using a single exponential decay function since we used 600 nm pulses (and that too unfocused) where we expect the excitation only to the first excited singlet state.

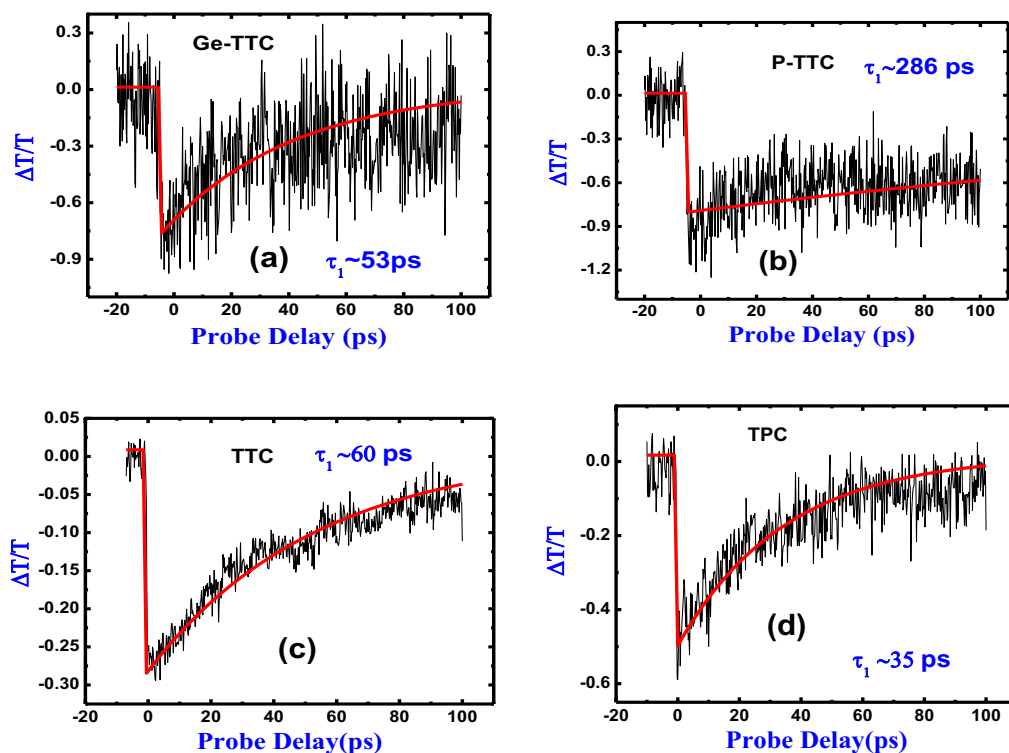


Figure 2 Degenerate pump probe data at 600 nm obtained using ~60 fs pulses (a) GeTTC (b) PTTC (c) TTC (d) TPC. Solvent used was chloroform.

The lifetimes estimated from the fits were ~53 ps for Ge-TTC, ~286 ps for P-TTC, ~60 ps for TTC and ~35 ps for TPC. The error in the measurements is estimated to be $\pm 15\%$. We attribute these lifetimes to the de-excitation times from the S_1 states of these molecules to the ground state through non-radiative means. The fluorescence lifetimes are expected to be in the ns regime. Since these molecules are fluorescent further detailed analysis is required to accurately assign the lifetimes obtained to various relaxation mechanisms. If one were to excite the molecules with focused 800 nm pulses (as was done for Z-scan in our earlier experiments [11,13]) one would expect two-photon absorption and excitation of the molecules directly into the S_n states and lifetimes of the higher excited states could also be retrieved. Further experiments with picosecond pulses are in progress.

CONCLUSIONS

The excited state dynamics of Corroles studied using fs pulses were found to be single exponential. The excitation mechanism confirms the lifetime observed is related to the first excited state of these molecules.

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