PICOSECOND LASER STUDIES OF MOLECULAR DYNAMICS IN LIQUIDS

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Abstract

A very high repetition rate dye laser amplifier is described and used to extend the useful wavelength range for the anisotropic absorption technique into the ultraviolet. The amplifier was found to preserve the pulse characteristics of the original synchronously pumped dye laser pulses, which are also described. Rotational correlation functions for 1,4-diphenyl-1,3-butadiene obtained using both UV pump and probe are consistent with a slip boundary condition.

Introduction

Over the last few years synchronously pumped dye lasers have been used to study a range of relaxation processes\(^1\). In our laboratory particular emphasis has been placed on studies of rotational diffusion and of radiationless processes involving large amplitude motion\(^2\). This paper describes the extension of pump-probe techniques into the ultraviolet through the use of a very high repetition rate amplifier, and the application of these techniques to the study of photochemical isomerization. We begin with a description of the structure of the picosecond pulses obtained from synchronously pumped dye lasers.

Synchronously Pumped Dye Lasers

The quality of the pulses obtained from a synchronously pumped dye laser depends strongly on the quality of the ion laser mode locking. We have measured the argon pulse duration by two techniques: cross correlation and gain profile derivative. Figure 1 shows a cross correlation measurement of the argon laser pulse with a dye pulse of a few ps duration. The argon laser pulse duration in Figure 1 is 96ps. The argon laser (Coherent CR12) was operated with a 30% output coupler and the mode locker was driven with about 1W of rf power from a Rockland 5600A synthesizer. In the second technique the dye laser was operated in an oscillator-amplifier configuration, with the amplifier pumped by a portion of the mode locked argon ion laser. The gain of the amplifier was measured as a function of the relative delay between the pump and oscillator pulses. The resulting curve was well fit by the integral of a Gaussian function with a standard deviation of 40ps indicating that the ion laser output pulses have a FWHM of approximately 92ps. We feel more confident about the cross correlation results.

The zero background second harmonic autocorrelation technique\(^3\) is used extensively to measure the duration of ultrashort pulses. If the pulses are not transform limited, it is important to account for the influence of coherence in these measurements\(^4\). For very badly mode locked pulses the presence of a coherence spike is obvious in the autocorrelation trace, but for pulses that are only a factor of 2-3 times broader than transform limit a

![Fig. 1. Cross correlation trace of a typical argon ion laser pulse train with Rhodamine 6G dye laser pulses of a few picoseconds duration.](image-url)
smooth autocorrelation trace may be obtained, making interpretation significantly more problematical. We have previously presented\textsuperscript{4} an analysis of autocorrelations in terms of the noise burst model of Pike and Herscher\textsuperscript{5}. Here the autocorrelation function $G(\tau)$ is written as

$$G(\tau) = G_p(\tau) \left[ 1 + G_N(\tau) \right]$$

(1)

where $G_p(\tau)$ is the autocorrelation of the pulse envelope and the term in brackets corresponds to the autocorrelation of the pulse substructure. The FWHM of $G_N(\tau)$ should correspond to the Fourier transform of the spectrum. This correspondence is displayed in Figure 2. Particularly striking is the strong cavity length dependence of the spectral width of the dye laser pulses when they are nearly synchronized with the pumping pulses.

Table I presents the temporal and spectral parameters for dye laser pulses obtained with three different tuning elements of different spectral bandwidth. For the birefringent filter (BRF) and wedge etalon, the autocorrelations were fit to the noise burst model as described by McDonald et al.\textsuperscript{4} The spectra in all cases fit Gaussian functions much better than do Lorenzians, implying that transform limit pulses should also be Gaussian or at least nearly so. Autocorrelation traces of the pulses generated with the 0.25mm etalon and BRF combination fit a single Gaussian well, though fits of these traces to an autocorrelation function derived from a sech$^2(\tau)$ pulse profile\textsuperscript{6} are unambiguously better. For these pulses the time bandwidth product is close to that expected for bandwidth limit pulses; a situation for which the noise burst model is inappropriate. The small deviation from Gaussian shape of the autocorrelation for the pulses obtained with the three plate BRF plus etalon tuning elements could be due to a distribution of pulse widths caused by small interruptions of lasing.\textsuperscript{7} With this in mind too much significance should not be attached to the improved fit to a sech$^2(\tau)$ autocorrelation.

Table I. Characteristics of Synchronously Pumped Dye Laser Pulses.

<table>
<thead>
<tr>
<th>Tuning Element</th>
<th>$\Delta \nu$ (GHz)</th>
<th>$\Delta t_p^*$ (ps)</th>
<th>$\Delta t_p \Delta \nu$</th>
<th>$t_N^{**}$ (ps)</th>
<th>$\Delta t_N \Delta \nu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Etalon plus BRF</td>
<td>21$^\dagger$</td>
<td>21.0$^{	ext{††}}$</td>
<td>.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BRF</td>
<td>142</td>
<td>9.2</td>
<td>1.31</td>
<td>2.9</td>
<td>.41</td>
</tr>
<tr>
<td>Wedge Etalon</td>
<td>360</td>
<td>8.0</td>
<td>2.9</td>
<td>1.3</td>
<td>.45</td>
</tr>
</tbody>
</table>

$^\dagger$ FWHM of the pulse envelope.

$^{**}$ FWHM of the coherence spike (pulse substructure).

$^\dagger$ Bandwidth values are ±5 GHz and in the case of the narrowest spectra required deconvolution from an ±16 GHz instrument response.

$^{	ext{††}}$ $\Delta t_p$ values for these near transform limit pulses were obtained directly from the FWHM of the autocorrelation.
Fig. 3. Autocorrelation traces for dye laser pulse with various tuning elements: a) 3 plate birefringent filter plus 25mm etalon; b) 3 plate birefringent filter; c) wedge etalon. Note the differences in time scales.

Figure 3 shows the change in shape of the autocorrelation as the spectral bandwidth increases. The pulses become shorter but not enough so to remain bandwidth limited. The presence of substructure within the pulse envelope causes a narrow Gaussian coherence spike to be superimposed on a slightly broader envelope autocorrelation, giving the impression of a double sided exponential.

Pump-Probe Experiments

Megahertz Repetition Rate Amplifier

Figure 4 shows the experimental arrangement we have used to perform pump-probe spectroscopy in the ultraviolet. The amplifier consists of a pair of simple lenses (5cm fl) a standard dye laser nozzle and a pair of mirrors which enable the picosecond pulse to pass twice through the gain medium during the passage of the pumping pulse. The amplifier is pumped by a cavity-dumped 3 W argon ion laser operating all lines, with an average power of 1.2 W at 756.7 kHz. We have performed experiments using the dye laser at the full repetition rate (i.e. amplifying one pulse in a hundred) and with the dye laser also cavity dumped at 756.7 kHz. The maximum double pass gain obtained for a noncavity-dumped dye laser is about 30 times. Significantly lower gains (2.75 times) are obtained when the dye laser is cavity-dumped. We believe that this large decrease is mainly due to poor beam quality and changes in confocal parameter rather than saturation, since lower gains were also observed when the cavity dumper was operated as a cw output coupler. Significantly higher gains should be possible with an improved optical design.

Fig. 4. Experimental arrangement. (CD: Cavity Dumper; C: compensator; VFC: voltage to frequency converter; MCA: multichannel analyzer) See ref. 9 for further details.
No pulse or spectral broadening was observed in the amplifier. In fact a small shortening was observed when the cavity-dumped dye laser pulses were amplified.

Rotational Diffusion Studies

The anisotropic absorption technique shown in Figure 4 was first used in the visible by Shank and Ippe[n][o]. As described in detail in our earlier study the observed signal may arise from either induced dichroism, induced birefringence or both. In the limit of perfect optics the time dependence of the signal is independent of its origin and is:

$$T(t) = [r(t)K(t)]^2$$ (2)

where \(r(t)\) is the rotational correlation function and \(K(t)\) the excited state decay law. If the focusing and collecting lenses are inside the crossed polarizers (see Fig. 4) or if a sample cell is used (in the present work a free flow jet was used), the time dependence of the signal may be significantly distorted by the presence of strain birefringence in the optics.

Figure 5 shows the anisotropic absorption signal from diphenyl butadiene (DPB) dissolved in tetracane. The excitation and probe wavelengths were both 303nm. The decay is well fit by a single exponential of 62ps. If DPB is approximated as a prolate rotor a single exponential correlation function is expected. The rapid spinning motion in DPB is not observable by this technique since it does not influence the transition moment direction. The rotational reorientation time obtained from Figure 5 corresponds to a slope of 66ps/cp. This compares very closely with that calculated from Stokes-Einstein-Debye theory with a slip boundary condition (62ps/cp).

The excited state lifetime of DPB is significantly shorter in alcohols than in alkane solvents. This is probably due to the stabilization of the twisted excited state by the polar solvent. The measured decay time for DPB in ethanol is 25±3ps. The excited state decay now contributes significantly to the measured relaxation time and the observed decay is notably shorter than would be expected simply from the change in viscosity between tetracane (2.25cp) and ethanol (1.2cp). We do not have at present a sufficiently accurate excited state lifetime to obtain a value of the rotational reorientation time in ethanol.

Acknowledgement

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References