TUNABLE PICOSECOND OPTICAL PARAMETRIC AMPLIFIERS FOR TIME RESOLVED RESONANCE RAMAN SPECTROSCOPY

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A picosecond optical parametric amplifier, OPA, system suitable for pump and probe spectroscopy has been developed. Two OPAs are simultaneously pumped by a titanium sapphire regenerative amplifier to produce several microjoules output over the 470 to 2000 nm wavelength range. One OPA used as the probe operates with c. 25 cm^{-1} linewidth over this tuning range. The system is optimised for TR³ spectroscopy. Some preliminary experiments on Trolox, a water soluble Vitamin E derivative, are presented.

Keywords: Optical parametric amplifier; OPA; picosecond; time resolved; Raman; TR³

INTRODUCTION

Many ultrafast time-resolved techniques require two broadly and independently tunable, synchronised light pulses. Recent advances in short pulse laser technology and non-linear crystal materials such as BBO have encouraged the rapid development of optical parametric oscillators (OPOs) and traveling wave optical parametric amplifiers (OPAs) capable of meeting the needs of ultrafast spectroscopists. We

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have developed kilohertz repetition rate OPA systems providing a stable, high repetition rate, high spectral brightness laser source tunable through the UV and visible wavelengths [1]. The system is optimised for femtosecond/picosecond, pump and probe time-resolved absorption, reflectance and resonance Raman spectroscopies.

Description of the System

Each OPA is based, see Figure 1, on a Type I BBO (5 mm, 29°) crystal which is pumped by a single titanium sapphire regenerative amplifier operating at 1 kHz repetition rate around 800 nm, 600–800 μJ pulse energy and ~ 1 ps pulse width. A three stage pump arrangement is used. The first stage generates seed light by optical parametric generation, OPG, ('superfluorescence' generation). A 60 cm lens focuses a $\sim 20 \mu\text{J}$ split of 400 nm pump light into the BBO crystal. Tilting this lens creates an aberrated focus elongated in the direction of angle walk-off between pump signal and idler within the crystal. Since the total gain is a stronger function of effective crystal length than of pump intensity this enhances the OPG process. For the second stage the same pump beam and the OPG light are retroreflected back to the crystal. The pump beam is refocused into the crystal. Group velocity mismatch accrued in the OPG stage is compensated by a 'magic' mirror. The output from this stage is a beam with several 10's of nJ of energy and provides good quality seed light for the final amplifier stage. Both OPAs use this configuration but OPA 1 uses a grating dispersion element to spectrally filter the pulse prior to injection into

FIGURE 1 OPA1. BBO = 29° cut Type I 5 mm long BBO crystal, f_1 , f_2 , f_3 = 60, 20 and 50 cm lens respectively, mm = mirror compensating for group velocity mismatch, dm = dichroic mirrors to reflect pump and transmit signal, G = Grating, S = Slit.

the final amplification stage. This also reconstitutes the beam with no spatial chirp before final amplification and lifts the seed beam in the vertical plane so that the amplified light can be picked off.

For the last stage the pump beam energy in OPA1 is typically 80–120 μJ and in OPA2 60–80 μJ . Care is taken to maintain good spatial beam quality in the pump and to minimise beam divergence because these have adverse effects on efficiency and linewidth. The overall pump to signal conversion efficiency of OPA1 and OPA2 is 10% and 15% respectively.

Typical performance curves for the OPAs is shown in Figure 2. Using both OPAs and a combination of non-linear conversion processes continuous tuning from 220–2200 nm at > 0.1 –1 μJ at the sample is possible. We estimate the spatial beam quality to be < 2 times diffraction limited and the time bandwidth product 1.8 times that of a Gaussian pulse. Shot to shot stability is around $\pm 10\%$ but constant output is routinely maintained over 10 hours or more.

FIGURE 2 Signal and idler tuning curves of OPA1 and OPA2.

SPECTROSCOPY: TR³ SPECTROSCOPY OF RADICALS FROM THE PHOTOIONISATION OF VITAMIN E ANALOGUES

The potential of the new system is illustrated by recent results in which ultrafast spectroscopy has been used to study the photoionisation of Trolox C, a water soluble vitamin E analogue. Scheme 1 shows how in biological membranes and lipoproteins vitamin E (α -tocopherol) is oxidised by the lipid peroxyl radical (LOO $\cdot$) and therefore interrupts the very damaging chain reaction of lipid peroxidation.

SCHEME 1

Our ultimate goal is to study details of electron transfer reactions involving vitamin E. Photoionisation provides the most direct route to the generation and study of the neutral radical [5, 6] and, as in the one-electron oxidation reaction involving LOO $\cdot$, the radical cation might be expected to be a short-lived intermediate. The measured pK of the tocopheroxyl radical of -1.4 [7] suggests a picosecond lifetime for the radical cation after photoionisation. The kinetics of hydrated electron formation from Trolox C in a buffered neutral aqueous solution were observed after photoionisation with a 300 fs pulse at 277 nm. The curve in Figure 2 shows that the electron is formed in two steps: about half of the absorbance is formed within the risetime of the 300 fs pulse, whereas the remaining absorbance grows in with an approximately 5 ps time constant. The electron absorbance then decays with a lifetime of about 25 ps before reaching a value which is stable on the

nanosecond timescale. Both the 5 ps and 25 ps processes have k_H/k_D of about 2.3, indicating that they are linked to the transfer of a proton [8].

We provisionally suggest that the delayed electron formation is due to deprotonation of the excited phenol which results in the autoionisation of the excited phenolate anion. The picosecond decay of the electron is proposed to be due to recombination with the geminate radical cation. Recombination is incomplete due to competition with deprotonation of the radical cation. The rate of electron decay therefore represents the combined rates of geminate radical pair separation and radical cation deprotonation. The rate of deprotonation has been estimated from observation of both the neutral and cation radicals by picosecond time-resolved resonance Raman spectroscopy, and our initial results suggest that this dominates the rate of electron decay. TR³ spectra obtained for Trolox in neutral aqueous solution are shown in Figure 4. Curves B and C show TR³ spectra obtained with pump and probe wavelengths of 283 and 425 nm as third and second harmonics respectively of the Ti:sapphire fundamental. At this probe wavelength both neutral and cation radicals are in resonance with extinction coefficients of the order of $4 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. At 5 ps delay between pump and probe pulses (Curve B) the spectrum consists mainly of the 1620 cm^{-1} peak attributable to the $\text{C}=\text{C}(\nu_{8a})$ stretching mode of the tocopheroxyl radical cation [5]. At a 1 ns delay (Curve C) the spectrum contains two peaks representing the $\text{C}-\text{O}(\nu_{7a})$ stretch at ca. 1490 cm^{-1} and the $\text{C}=\text{C}(\nu_{8a})$ stretch at 1600 cm^{-1} of the neutral tocopheroxyl radical. Further data show that the growth of the lower frequency band is complete at 100 ps, and appears to be correlated with the electron decay observed in the transient absorption experiments such as that shown in Figure 3. Curve A in Figure 4 shows the TR³ spectrum using pump and probe wavelengths of 273 and 470 nm respectively with a 20 ps delay. The probe wavelength in this example was obtained using the OPA system and the figure illustrates that spectra of good quality may be obtained with parametric amplification. The probe wavelength of 470 nm is more strongly in resonance with the radical cation (ϵ ca. $10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). A small shift to higher frequency is discernible between the ca 1620 cm^{-1} band in this spectrum and that of Figure 3C despite the approximately similar

FIGURE 3 Formation and decay of the transient absorbance of the hydrated electron at 830 nm in an aqueous solution of Trolox C containing phosphate buffer (50 mM, pH 7) on photolysis with a 300 fs laser pulse at 277 nm.

FIGURE 4 Picosecond TR³ spectra from neutral aqueous solution of Trolox C. Spectra B and C were obtained with pulse and probe wavelengths of 283 and 425 nm respectively, employing time delays between pump and probe pulses of 5 ps (B) and 1 ns (C). Spectrum A was obtained using a 20 ps delay between the pump pulse at 273 nm and the probe pulse at 470 nm.

bandwidth of the probe pulse and the expected shift of $20-25\text{ cm}^{-1}$ in the C=C band upon deprotonation of the radical cation. Further work is now in progress in order to extract kinetic information from these time resolved resonance Raman spectra.

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