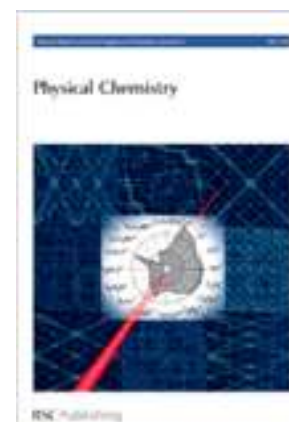
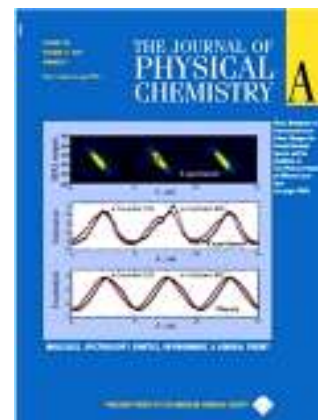
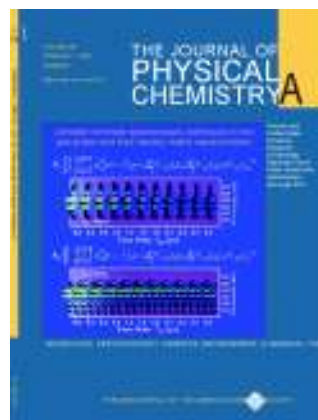


Controlling NLO processes, vibrational and electronic excitation, and strong field chemistry

Prof. Marcos Dantus

Prof. Vadim V. Lozovoy



Biophotonic
SOLUTIONS INC.
ULTRAFAST PULSE SHAPING & COMPRESSION



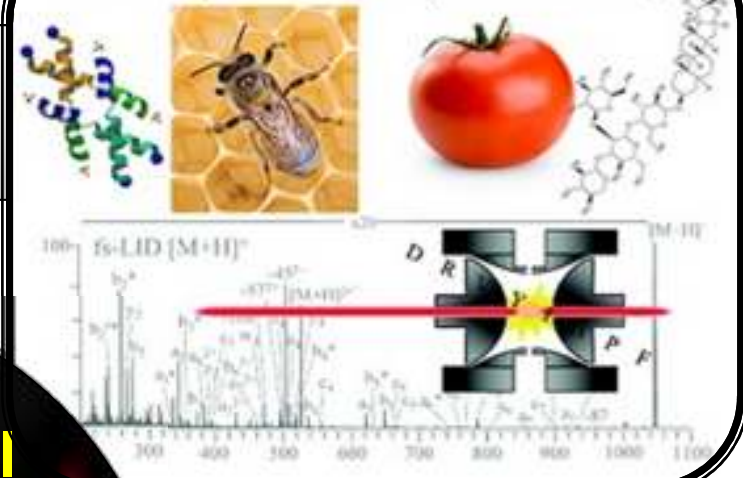
COI Disclosure: Dantus is the founder and president of Biophotonic Solutions Inc.

Sensing



Dantus Group

Biological Mass Spectrometry

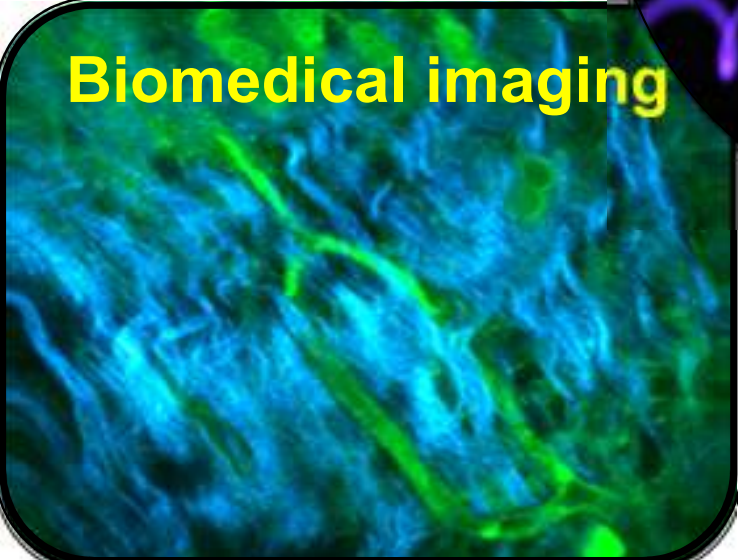


Phase Control

Laser Design

Multidisciplinary
Collaborations with
Universities and Industry

Biomedical imaging



Optimized Laser Processing

Si wafer micromachining 35 fs TL pulses



Si wafer micromachining 40k fs² chirp



Multiphoton Intrapulse Interference (MII)

General approach to control n-photon transitions and non-linear optical processes

Walowicz, Pastirk, Comstock, Shane, Xu, Coello, Lozovoy and Dantus

J. Phys. Chem. A **106**, 9369 (2002).

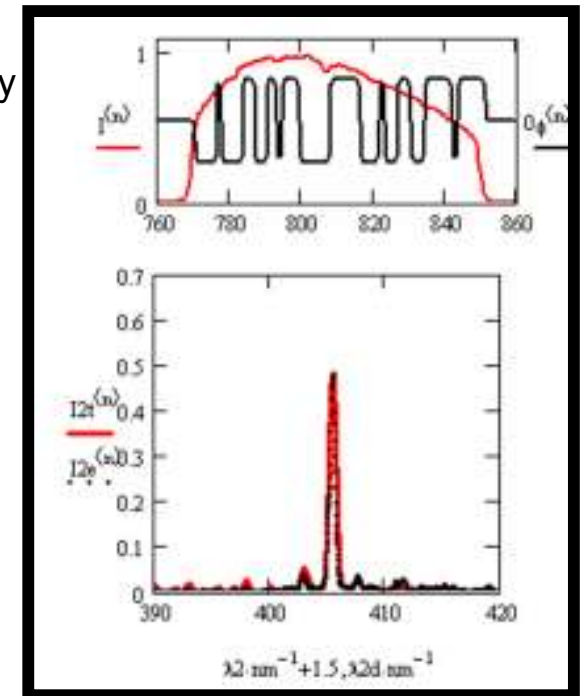
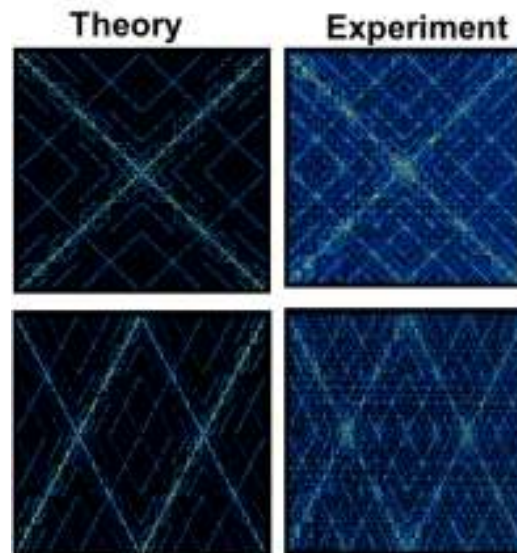
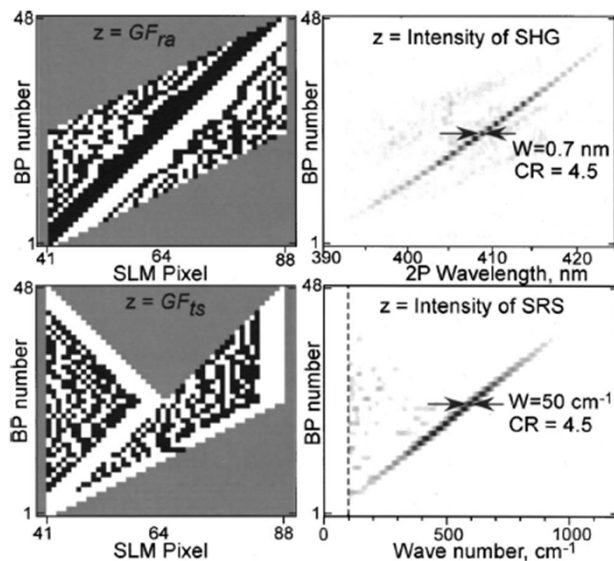
J. Chem. Phys. **118**, 3187 (2003). Two vs. three photon

Optics Express **12**, 1061-1066 (2004). Binary phases

Optics Express **13**, 10882 (2005). Selective excitation

Physical Review A **74**, 041805(R) (2006). **pseudorandom Galois fields**

Applied Optics, **49**, (32), 6348-6353 (2010). Two-photon excitation spectroscopy



Binary Phase Modulation: Physical Review A **74**, 041805(R) (2006)

Pulse Characterization and Compression

Pastirk, Xu, Gunn, Dela Cruz, Zhu, Martin, Rezan, Fry, Mackay, Coello, Harris, Shane, Gunaratne, Borukhovich, Tseng, Weinacht, Nogueira, Cruz, Pestov, Lozovoy and Dantus

Optics Letters **29**, 775-777 (2004).First

J. Opt. Society B **23**, 750-759 (2006).Quantitative

Opt. Express **14**, 8885-8889 (2006).Remote

Opt. Express **14**, 9537-9543 (2006).Pre amp

Opt. Express **14**, 10939-10944 (2006).Octave spanning

Opt. Express **15**, 16061 (2007) Surface SHG

Opt. Express, **15**, 1932-1938 (2007).THG in air

Laser Focus World **43**, 101-104, (2007)

J. Opt. Soc. Am. B **25**, A140-A150 (2008)

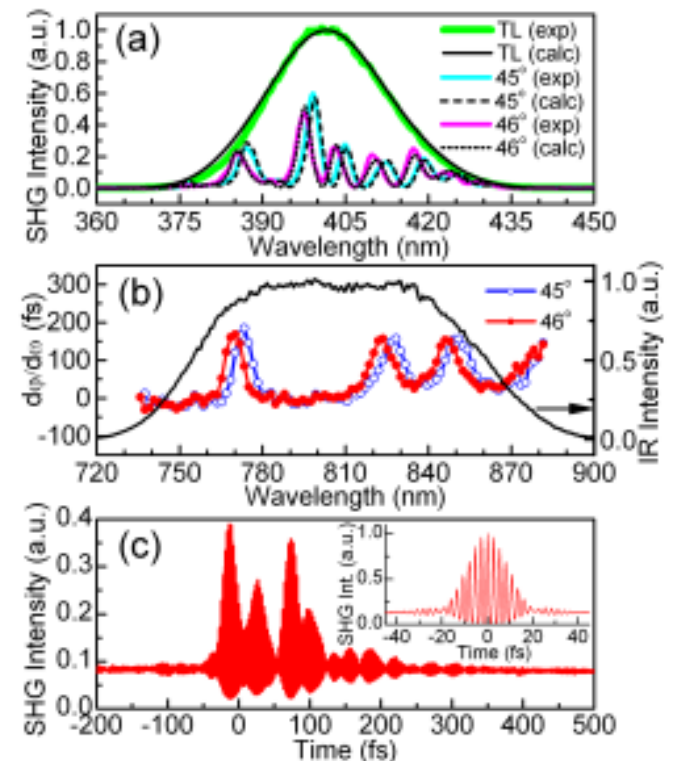
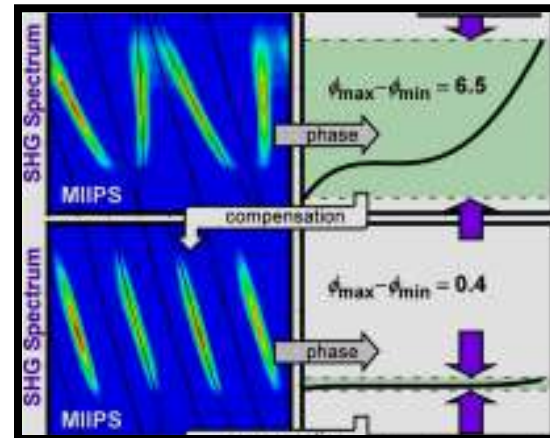
Interference without interferometer

Opt. Express **16**, 592-597 (2008).MIIPS 2

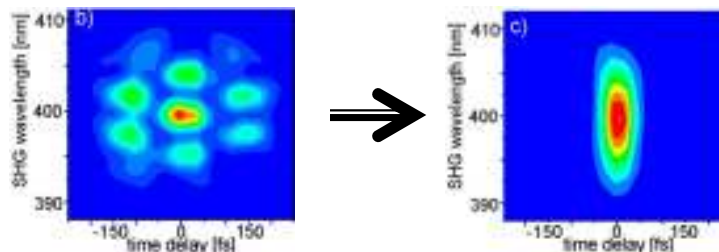
Opt. Express, **16**, Issue 14, pp. 10033-10038 (2008)

2GHZ Octave spanning

Opt. Letters **35**, 1422-1424 (2010).MIIPS sonogram

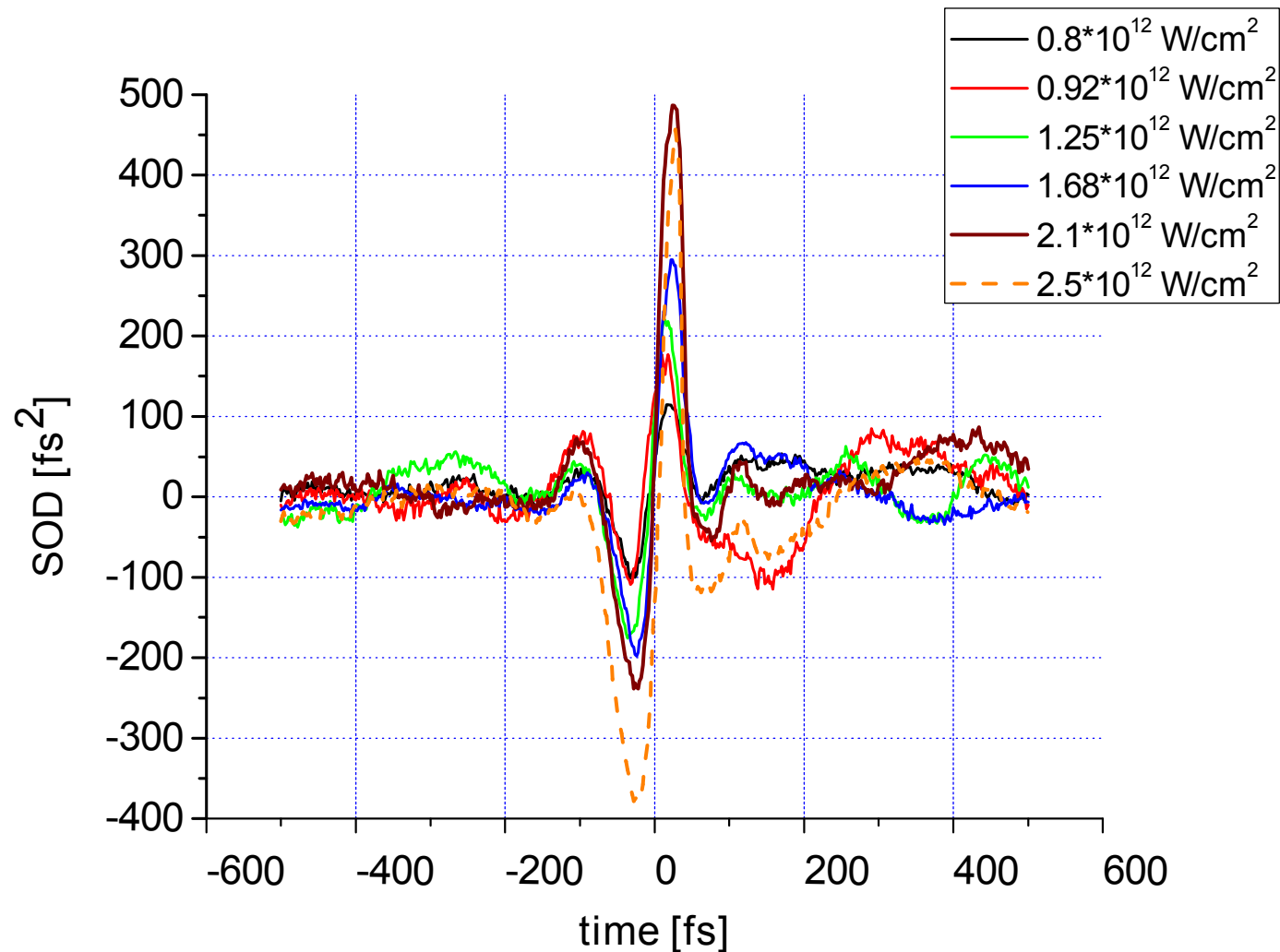


Preamp
Shaping

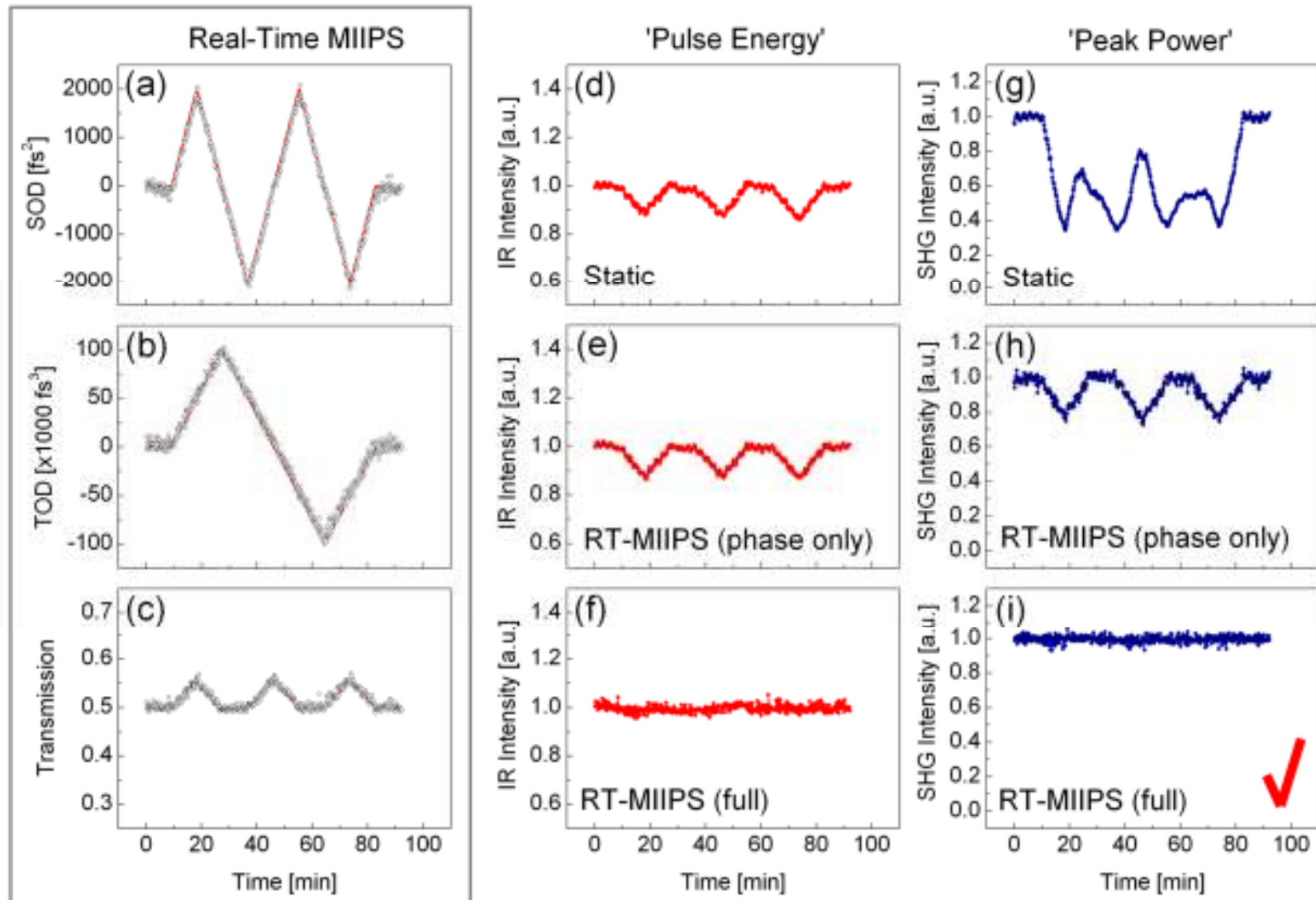


Transient SOD changes measured by single shot MIIPS

Results from 1mm quartz



Experimental Results: Active SOD+TOD+Amplitude Compensation



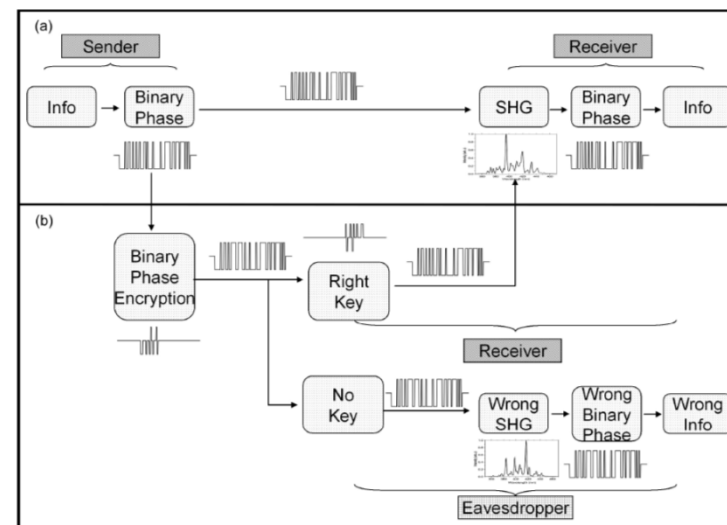
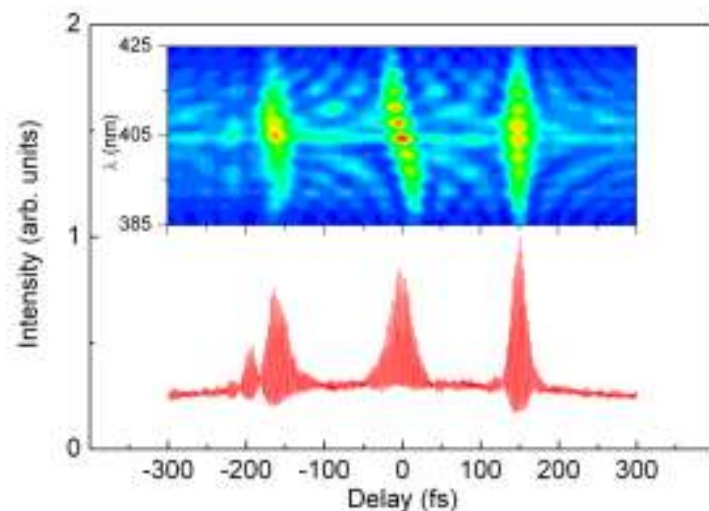
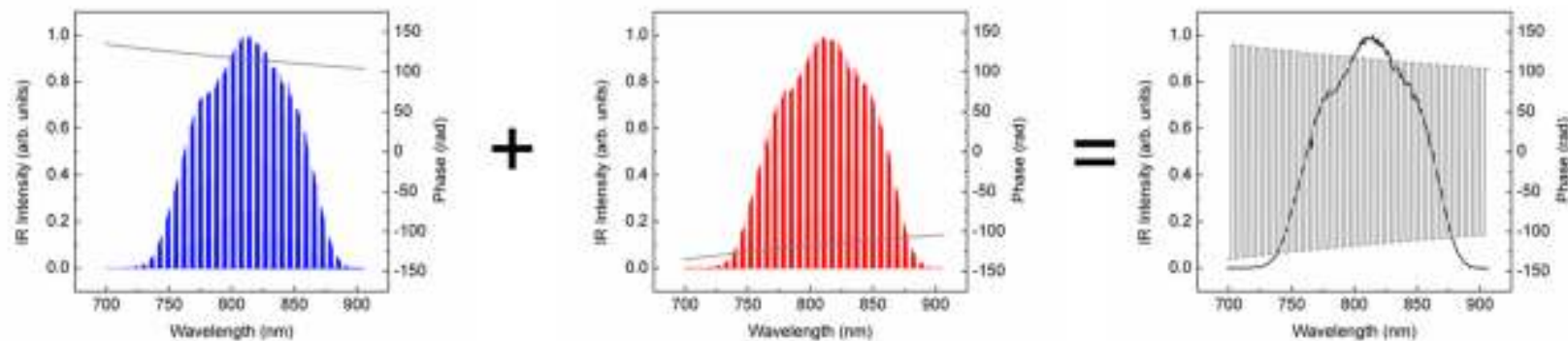
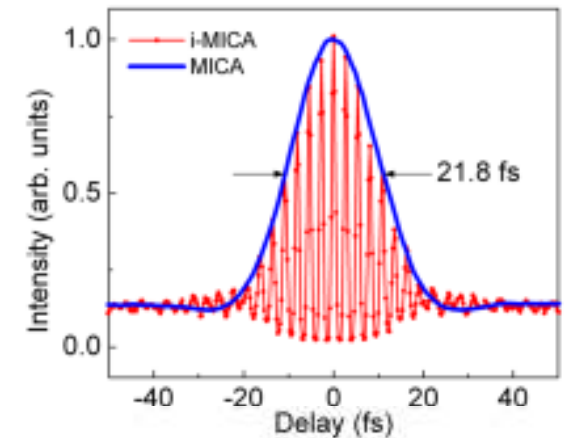
Pulse Shaping and Communications

Pestov, Xu, Coello, Nogueira, Cruz, Lozovoy, and Dantus

Optics Express, **17**, 14351 (2009) Multi-comb Shaping

Optics and Photonics News **20**, 42-43 (2009).

Optics Express, **16**, 15109 (2008) Asynchronous encrypted information transmission with sub-6 fs with 2.12 GHz repetition rate laser.



Metrology and GVD Measurements (sub-fs² accuracy)

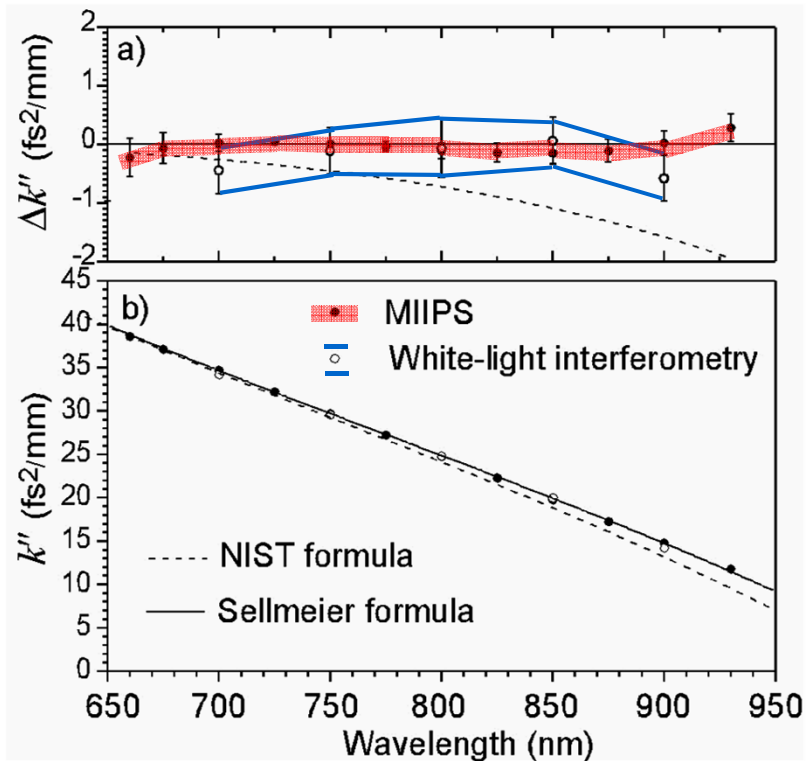
Coello, Xu, Miller, Wrzesinski, Gord, Roy, Devi, Pestov, Lozovoy and Dantus

Appl. Opt. 46, 8394 (2007) **Water and ocular GVD**

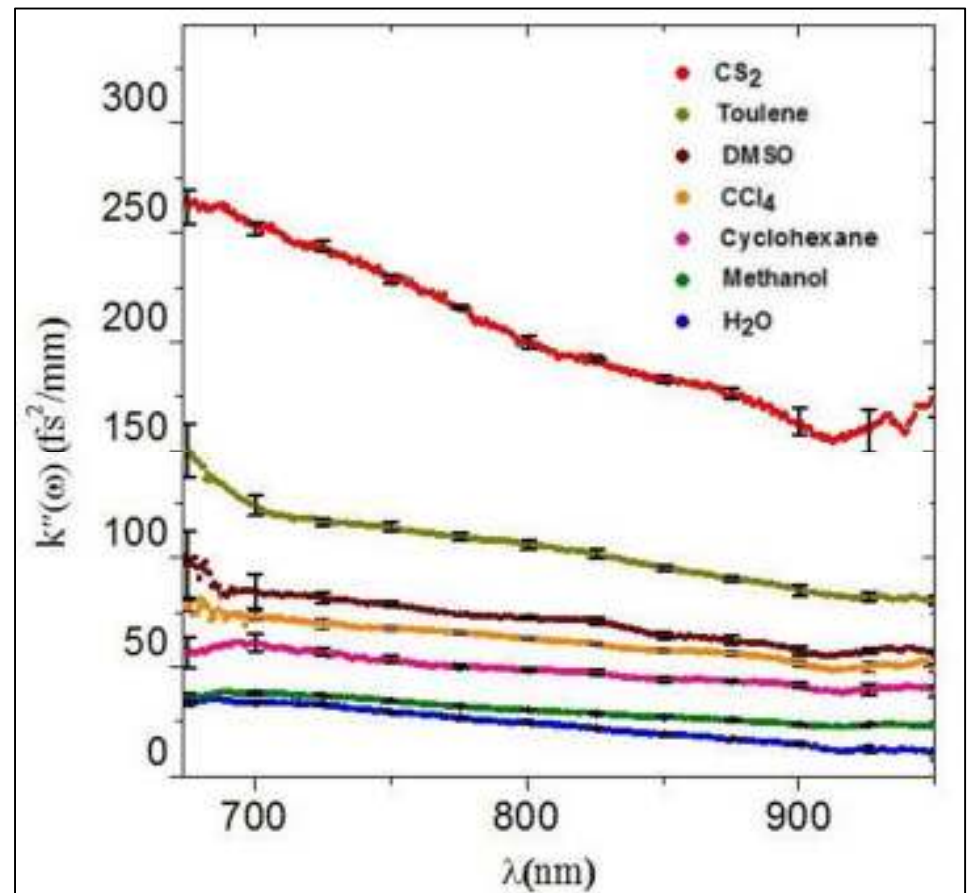
Optics Express **19**, 5163-5170 (2011) **GVD of atmospheric gases**

AIP Advances **1**, 032166 (2011) **GVD of solvents**

Dispersion of water



Dispersion of common solvents



Microscopy Imaging

Pastirk, Xu, Dela Cruz, Walowicz, Comstock, Schelhas, Andegecko, Weisel, Xi, Freudiger, Min, Holtom, Xie, Saytashev, Arkhipov, Winkler, Zuraski, Pestov, Lozovoy and Dantus

J. Phys. Chem. A **108**, 53 – 58 (2003)..

Optics Express 11, 1695-1701 (2003).

PNAS **101**, 16996-17001 (2004). **Selective two-photon microscopy through biological tissue**

Optics Express 12, 4144 (2004).

J. Photochem. Photobio. A **180**, 307 (2006).

Nanomed.Nanotec.Bio. Med. **2**, 177 (2006).

Opt. Commun. 281, 1841 (2008)

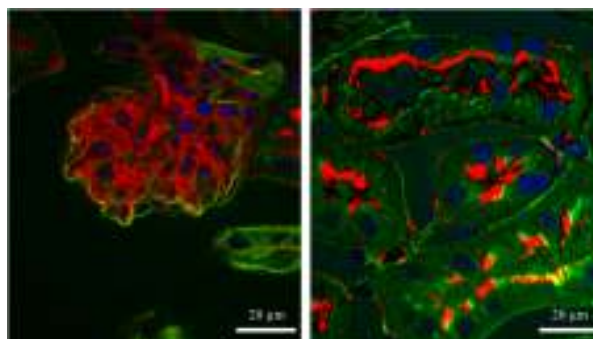
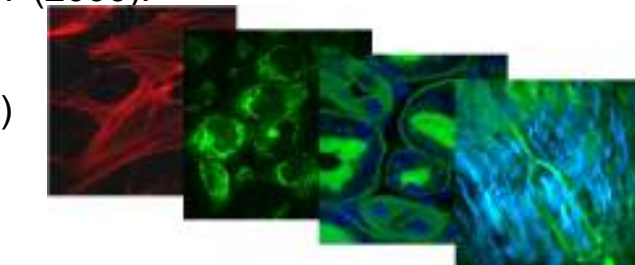
J. Biomed. Opt., 14, 014002 (2009)

BioOptics World 2 23-24 (2009)

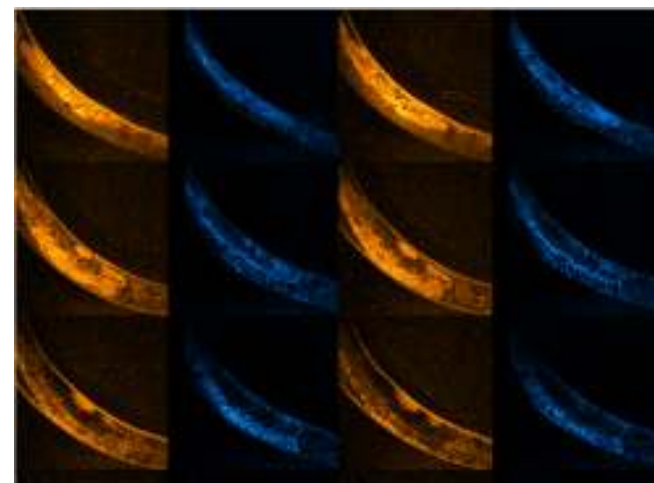
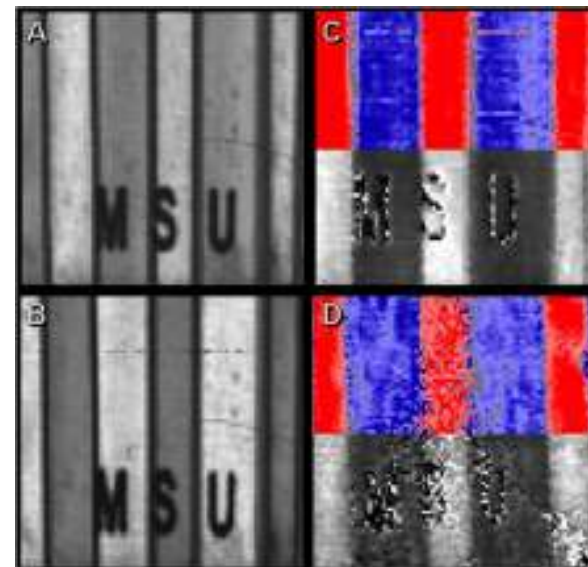
J. Opt. **12**, 084006 (2010).

Nature Photonics, **5**, 103–109 (2011). **Video rate selective SRS**

J. Photochem. Photobio B: **115**, 42 (2012). **Photodamage**



Quantum Control-Based
Functional Imaging Through Biological Tissue



Standoff Detection

Inspired by Dudovich Oron Silberberg Nature 418, 512 (2002)

Li, Harris, Xu, wrzesinski, Pastirk, Bremer, Butcher, Lozovoy and Dantus

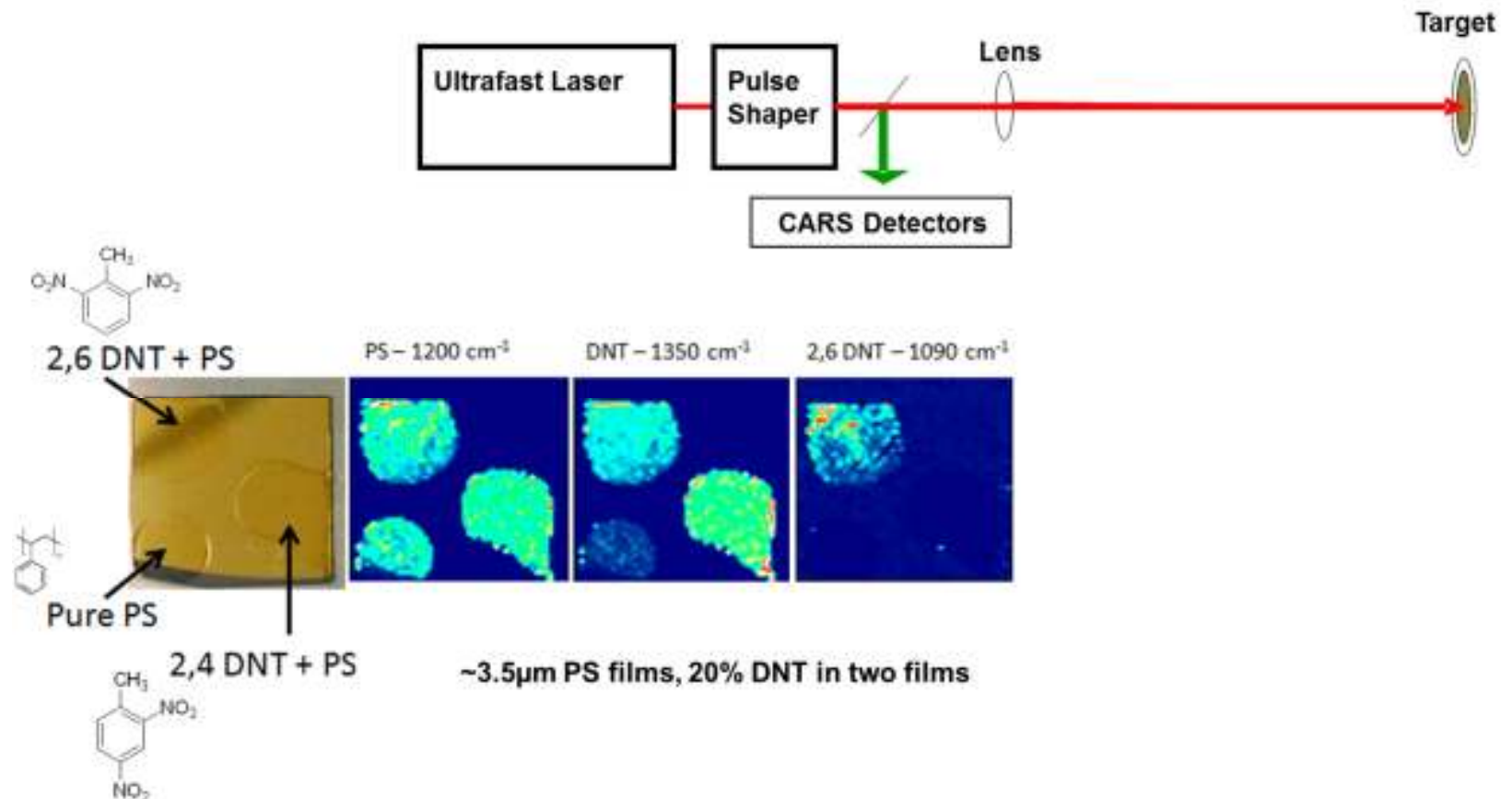
Opt. Express 16, 5499-5504 (2008)

Int. J. High Speed Electronics and Syst. **18**, 63 (2008).

Optics & Photonics News 19, 46 (2008)

Appl. Opt. **48**, B17 (2009)

Applied Physics Letters **99**, 101109 (2011).



Gas phase CARS

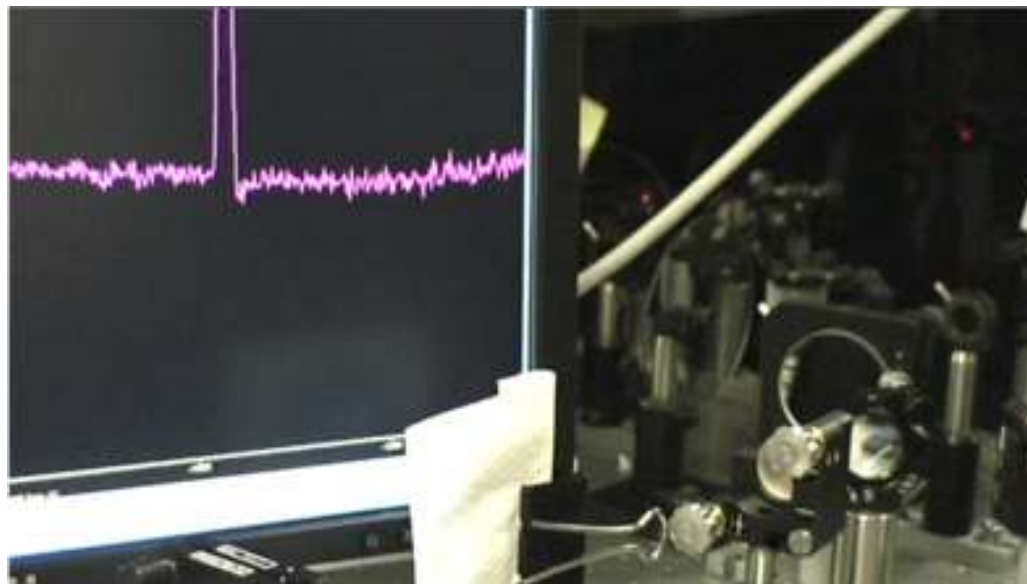
Roy, Wrzesinski, Pestov, Gunaratne, Gord, Xu, Yue, Bremer, Lozovoy and Dantus

Applied Physics Letters, L09-03549R1 (2009)

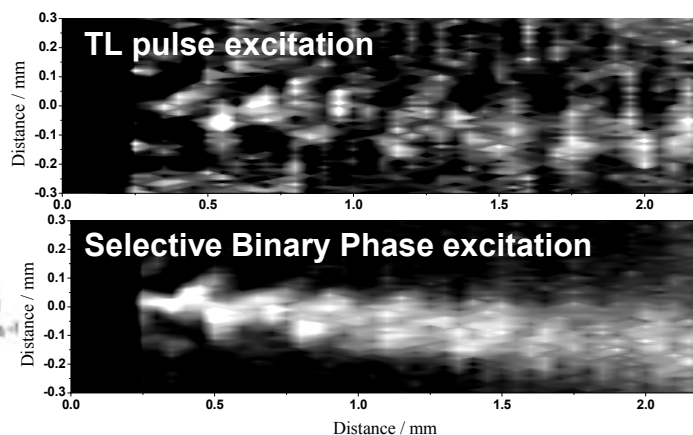
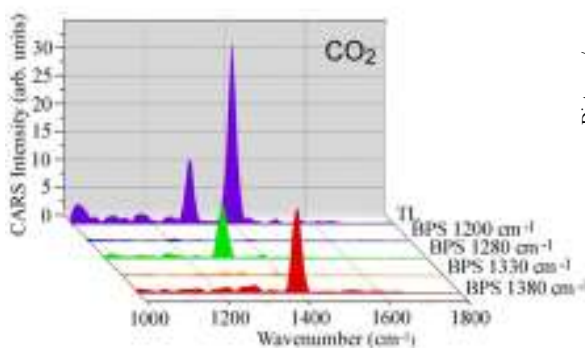
Optics and Photonics News **21**, 49 (2010).

J. Raman Spec. **42**, 393-398 (2011)

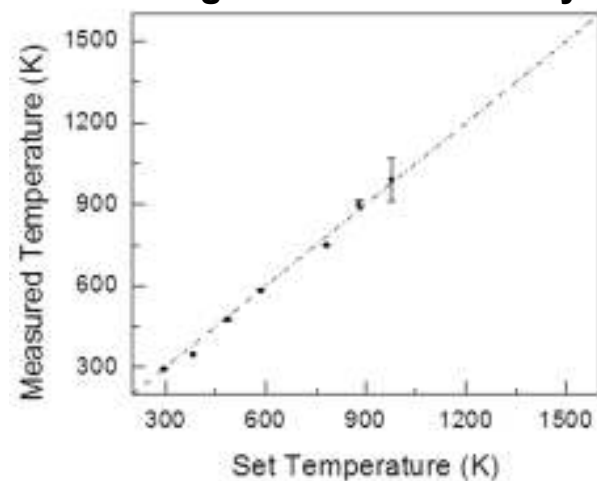
J. Phys. Chem. A, (2012)



Selective Single Beam CARS



Single shot thermometry



Micromachining & LIBS

Gunaratne, Kangas, Singh, Gross, Zhu, Parker, Parker, Nie, Lozovoy and Dantus

Chemical Physics Letters **423**, 197-201 (2006) Metals

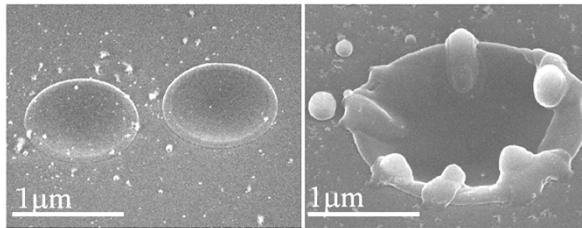
J. Appl. Phys. **106**, 123101 (2009) Silicon

Chem. Phys. Lett. (2012) LIBS using fiber oscillator

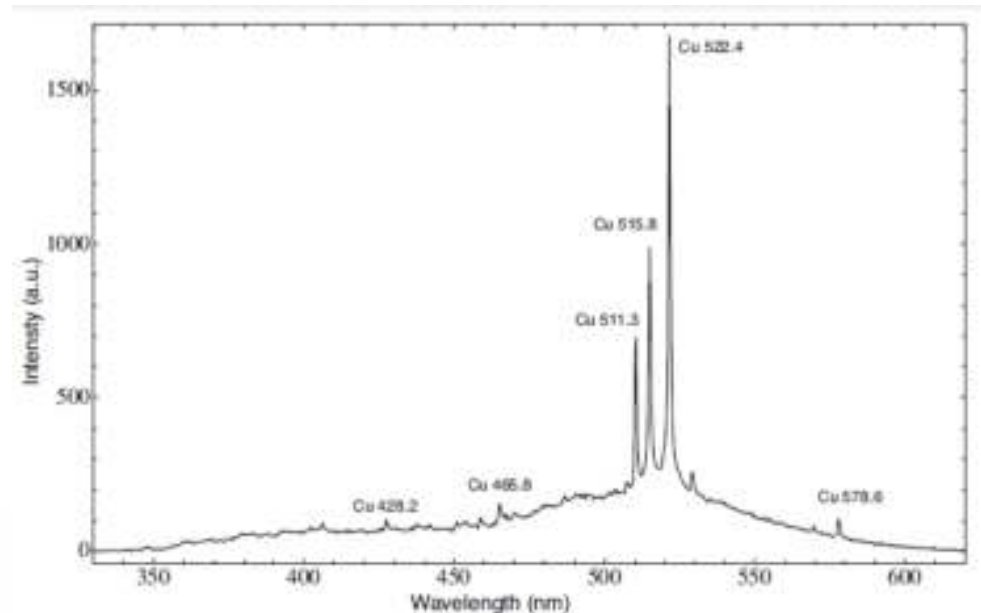
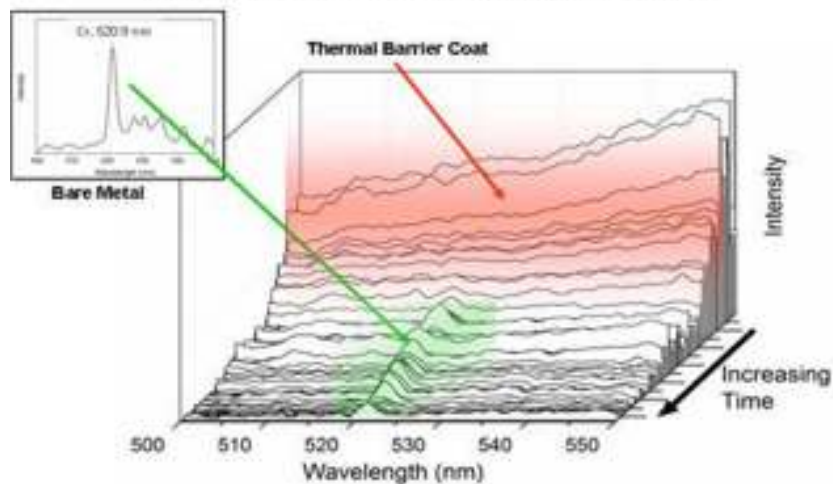
Single shot ablation of silicon

TL

Chirped



In-situ Laser Induced Breakdown Spectroscopy (LIBS)
for real-time monitoring of the machining process



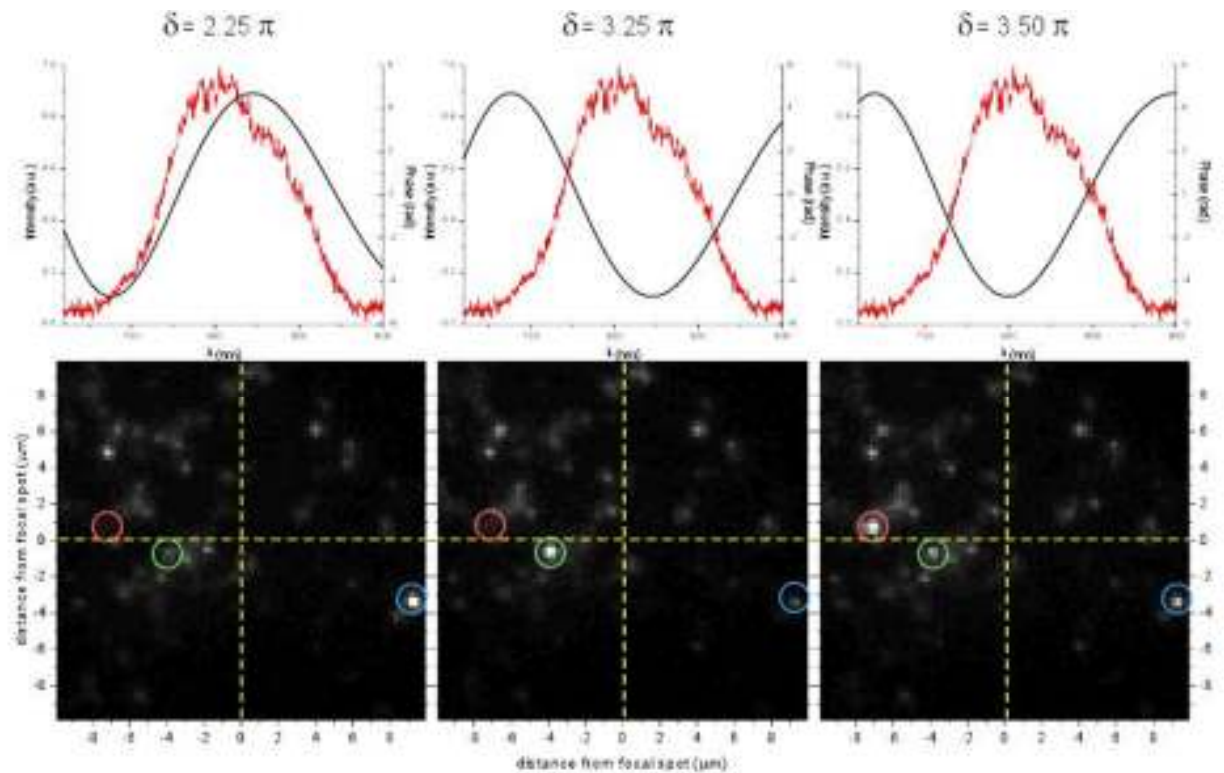
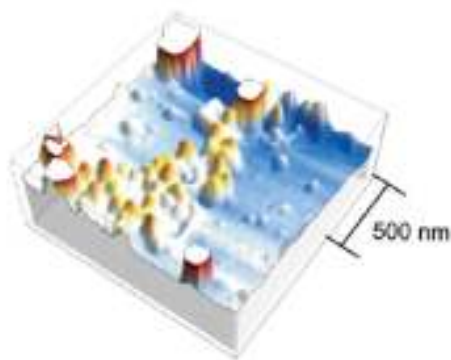
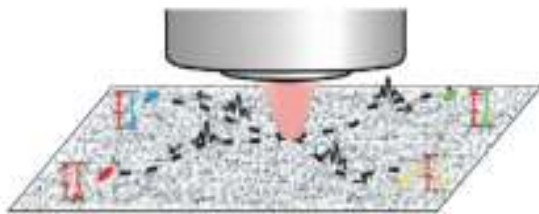
Plasmonics and nanoparticles

Gunn, Ewald, High, Lozovoy and Dantus

Nano Letters 6, 2804-2809 (2006).

J. Phys. Chem. C C **114**, (29), 12375 (2010).

Measurement and Control of Ultrashort Optical Pulse Propagation in Metal Nanoparticle-Covered Dielectric Surfaces; Up to distances >100x focal spot.



Two-photon induced luminescence, far from focal spot
Surface Plasmon Transmission through nanoparticle wires.

Solvation Dynamics

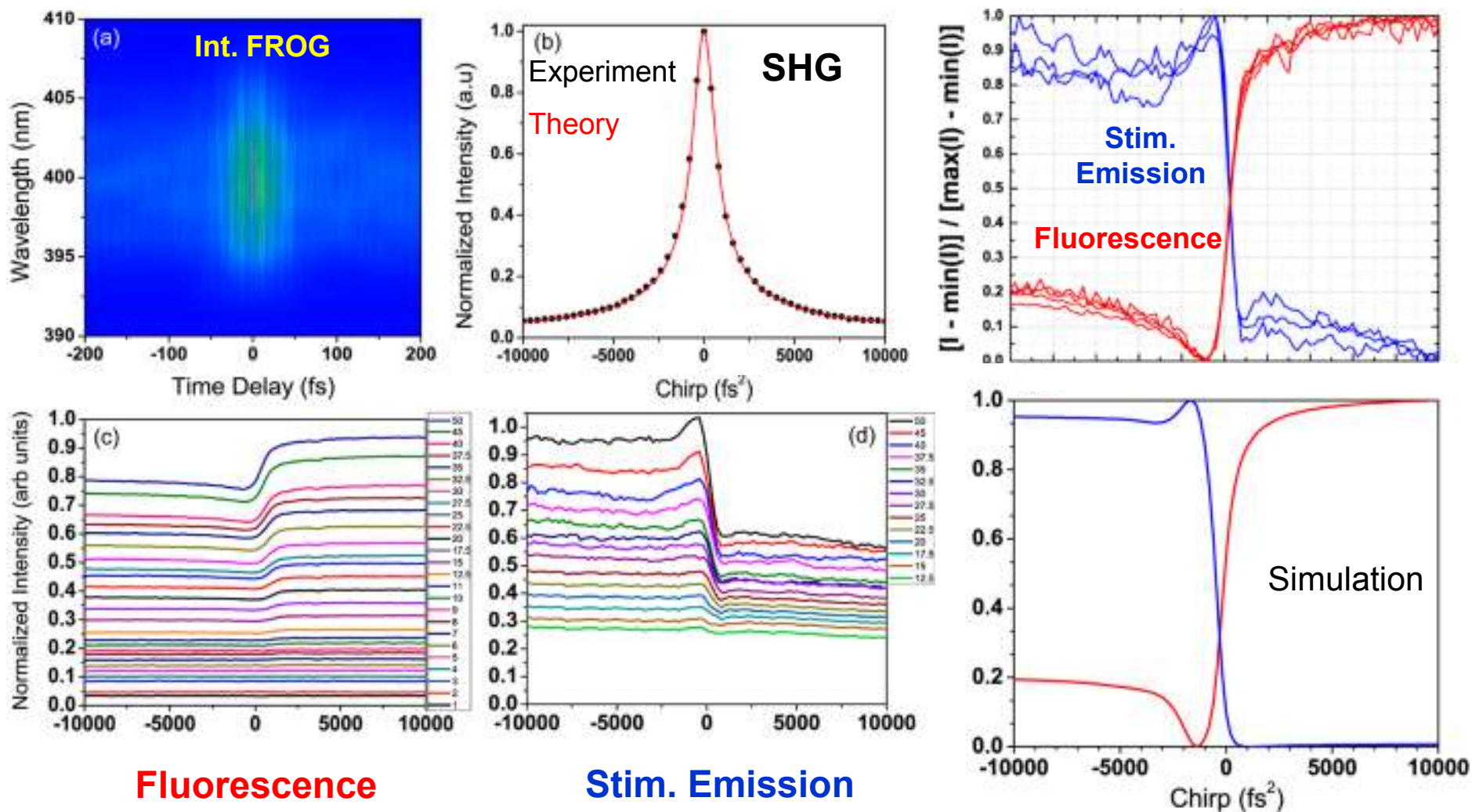
Konar, Shah, Lozovoy and Dantus

J. Phys. Chem. Letters **3**, 2458 (2012)

Revisiting the chirp effect observed by Bardeen and Shank,

Later by Wilson's group

Intensity Invariant



Solvation Dynamics

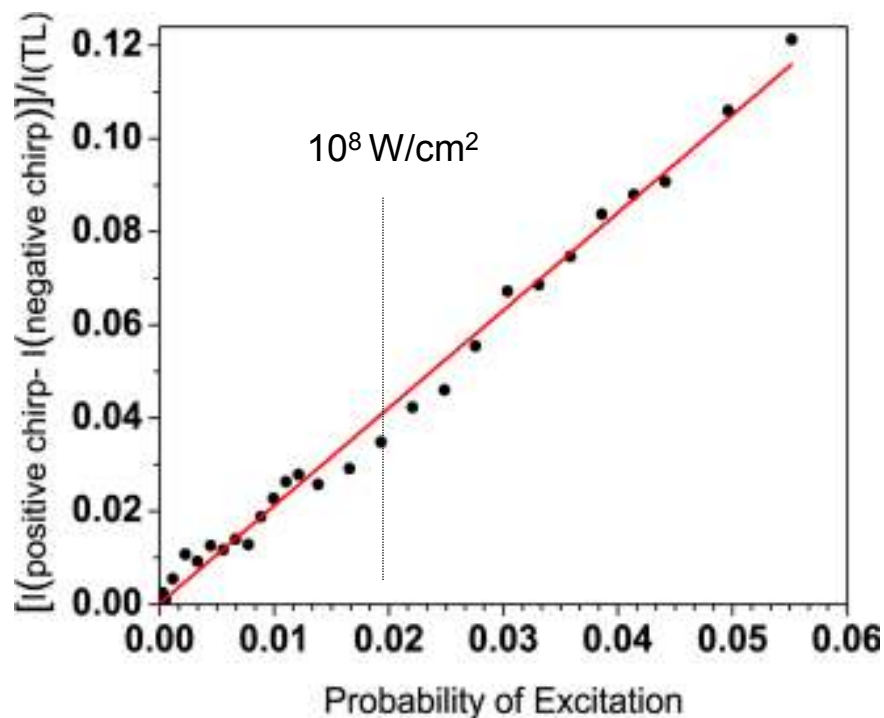
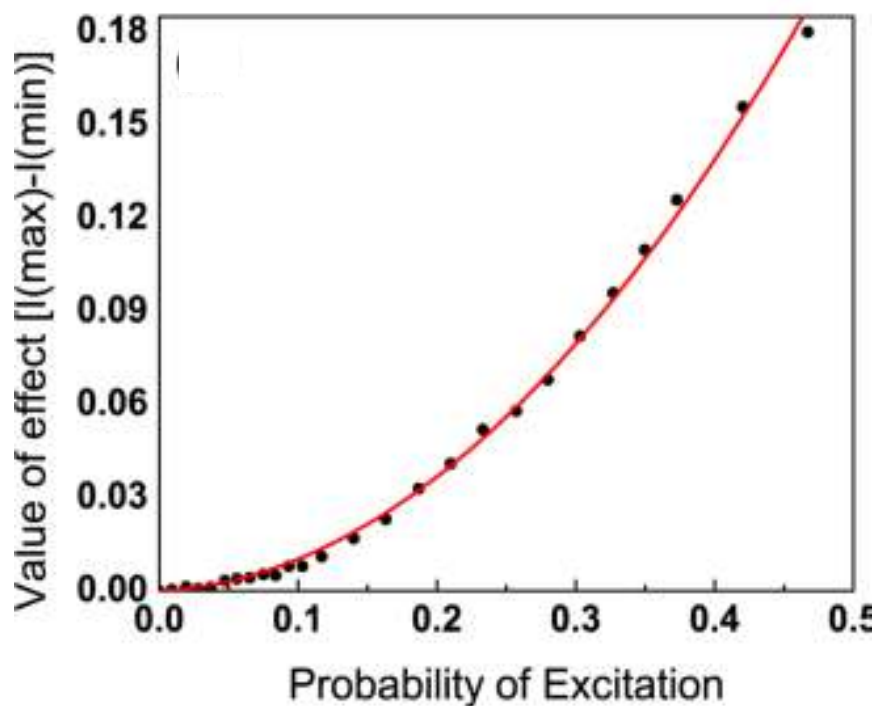
Konar, Shah, Lozovoy and Dantus

J. Phys. Chem. Letters **3**, 2458 (2012)

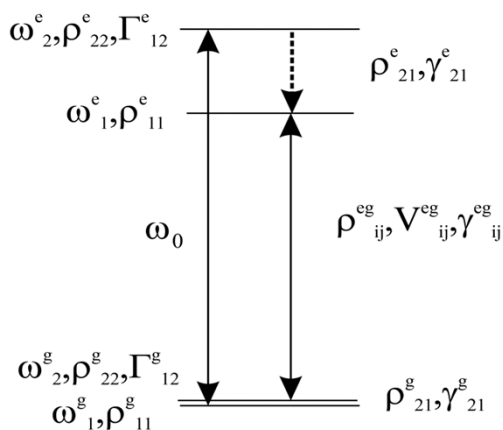
$$\text{Normalized Effect} = [\text{Max}(I_{FL}) - \text{Min}(I_{FL})] / (I_{FL} TL)$$

If found to be $= x$

Because $I_{FL} TL = x$ then **Effect** = x^2



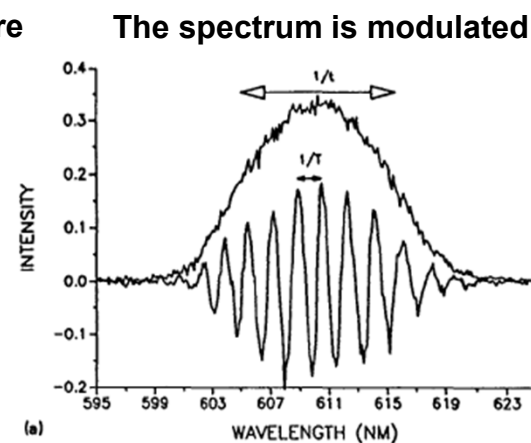
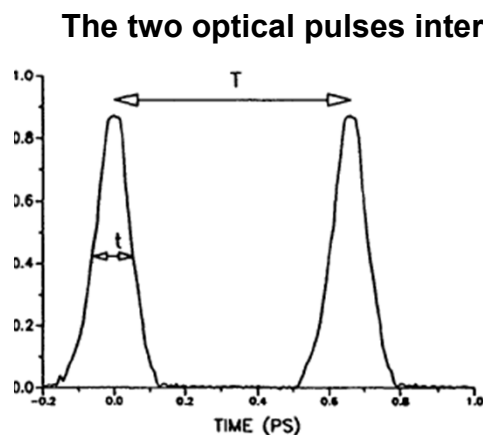
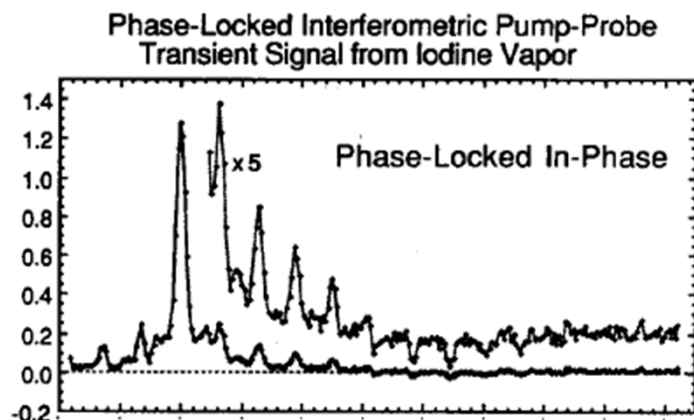
Excitation Range from 0.02% to 6%



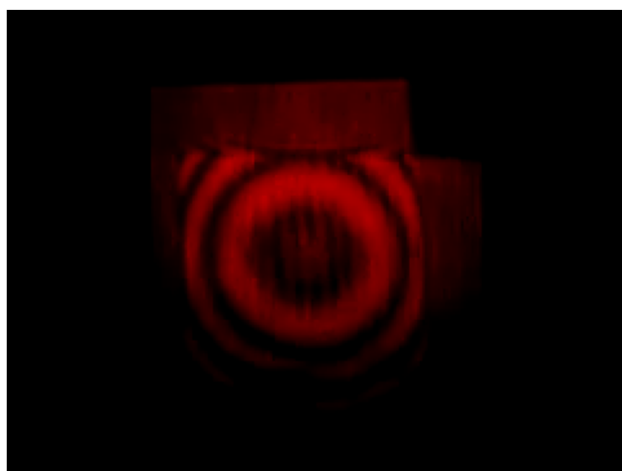
Quadratic Intensity Dependence

Measuring Interference Between Laser Pulses and Wave Packets Without Imposing

Scherer et al. JCP 93, 856 (1990), JCP 95, 1487 (1991)



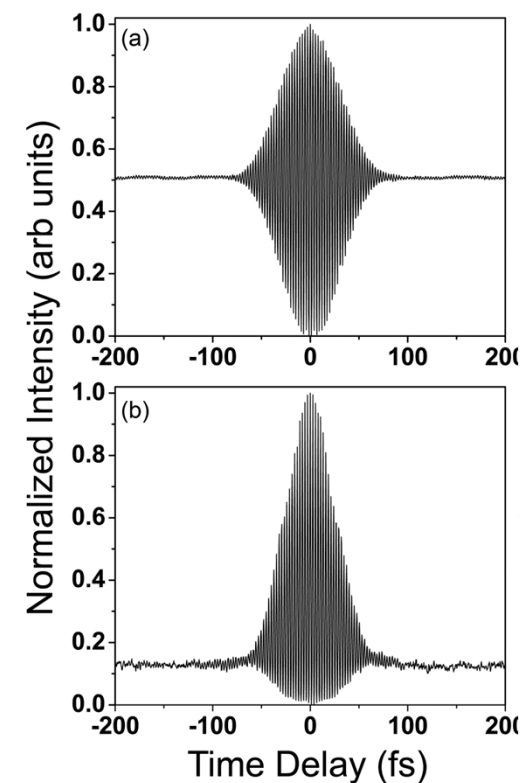
Michelson Interferometer



1st order autocorrelation



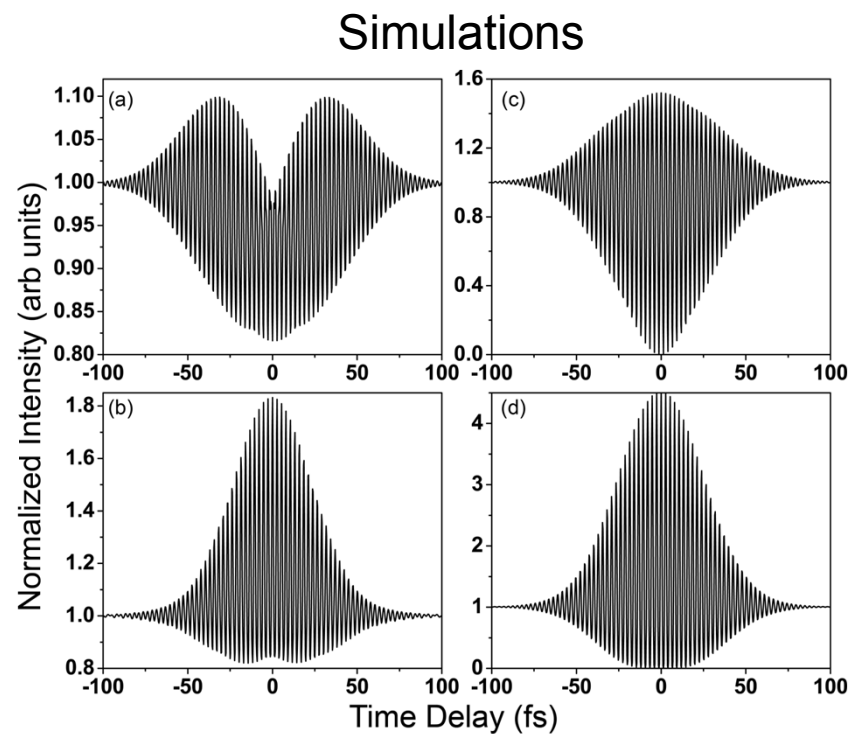
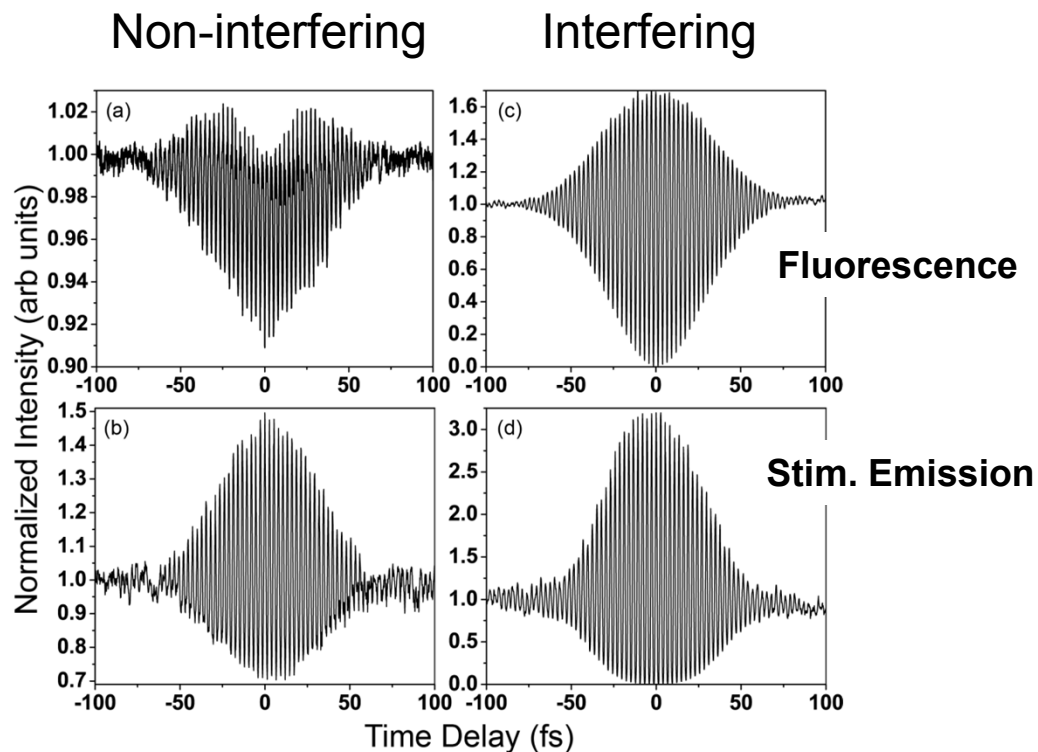
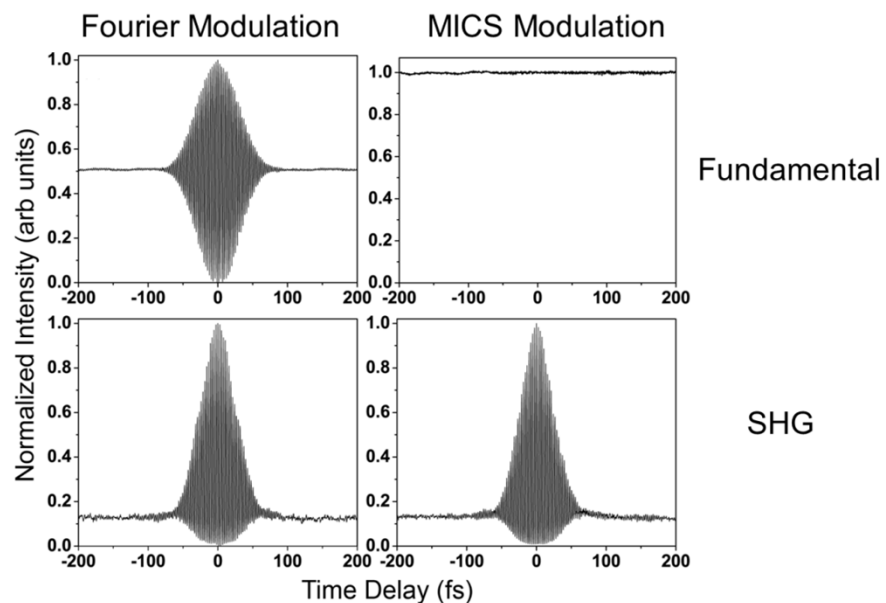
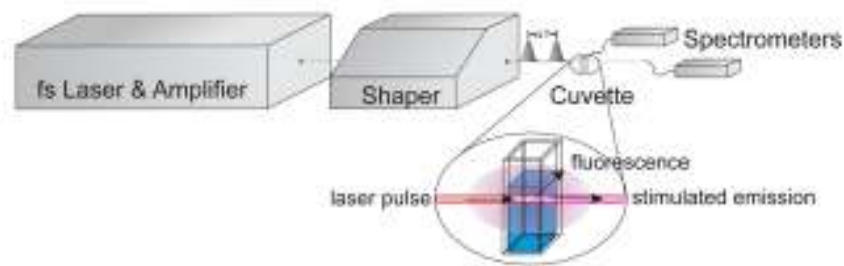
2nd order autocorrelation



Solvation Dynamics

Konar, Shah, Lozovoy and Dantus

J. Phys. Chem. Letters **3**, 1329 (2012).



Fiber Laser Design

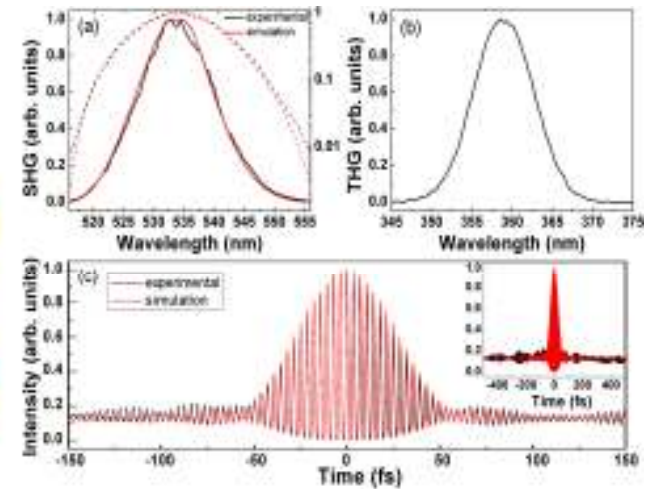
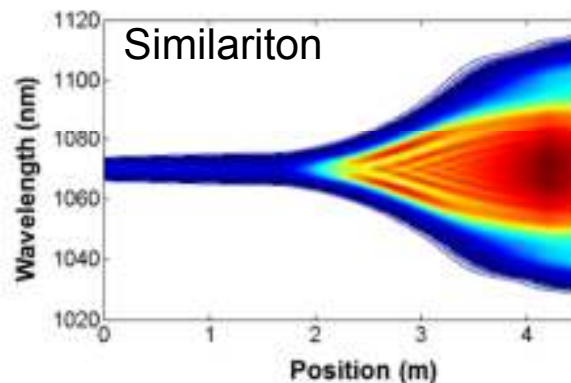
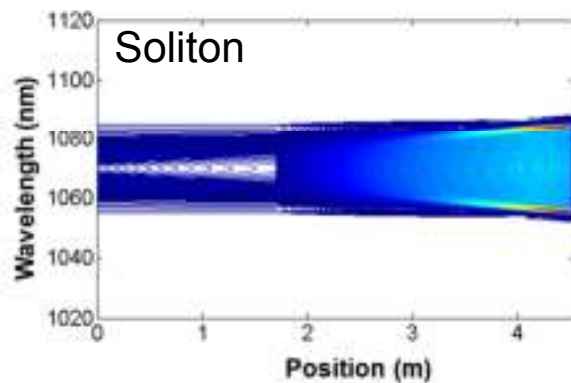
Nie, Pestov, Wise, Chong, Liu, Gale, Wabnitz, Renninger, Saytashev, Arkhipov, Lozovoy and Dantus

Optics Express **19**, 12074-12080 (2011) 42 fs, 10nJ Yb fiber laser

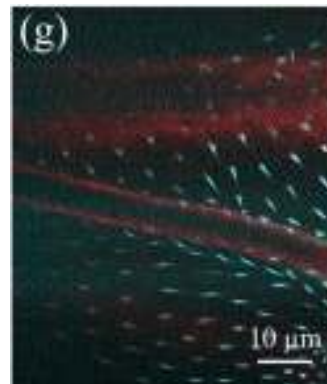
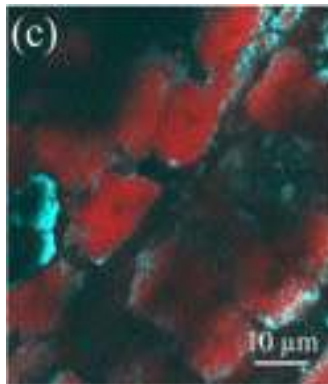
Optics and Photonics News **22**, 47 (2011) Self similar evolution

Optics Express **20**, 14213 (2012) Osc. with bandwidth greater than gain

Biomed. Optics Express **B**, 1750 (2012) Imaging with sub-30fs Yb fiber



Sub-30fs Ytterbium oscillator



Compact <9fs fiber lasers



Strong Field

Pastirk, Kangas, Dela Cruz, Shane, Gunaratne, Zhu, Harris, Lozovoy and Dantus

J. Phys. Chem. A **109**, 2413-2416 (2005) binary phases for multidimensional analysis

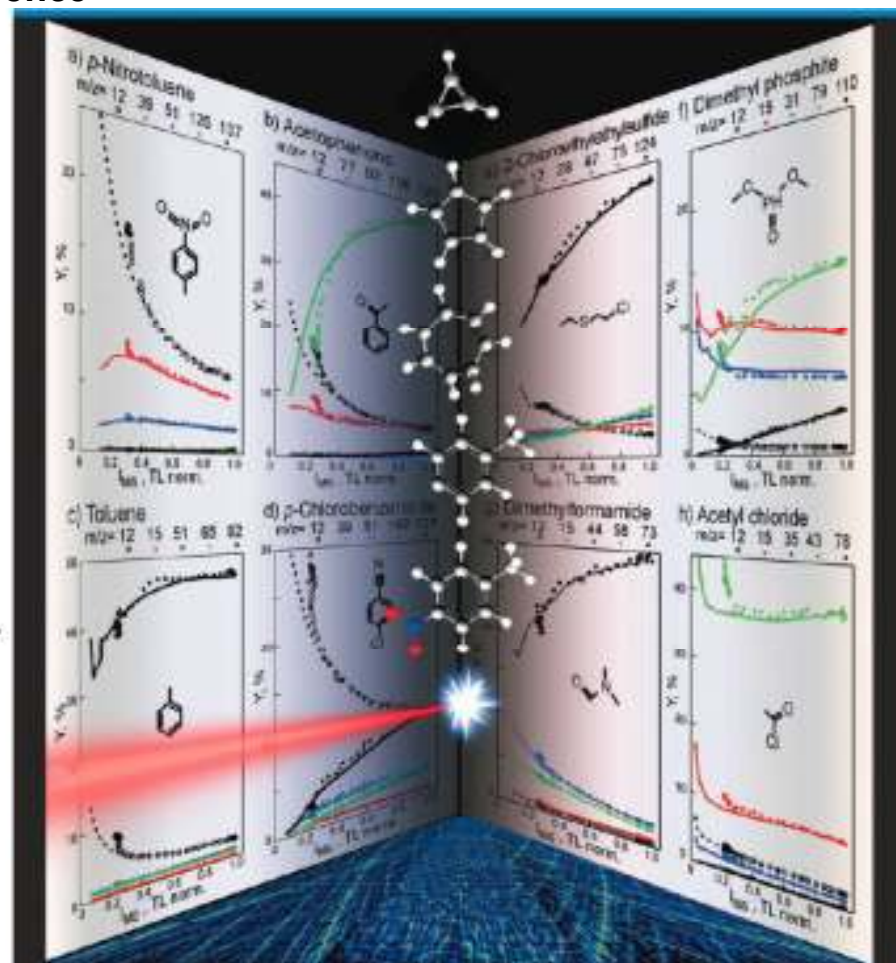
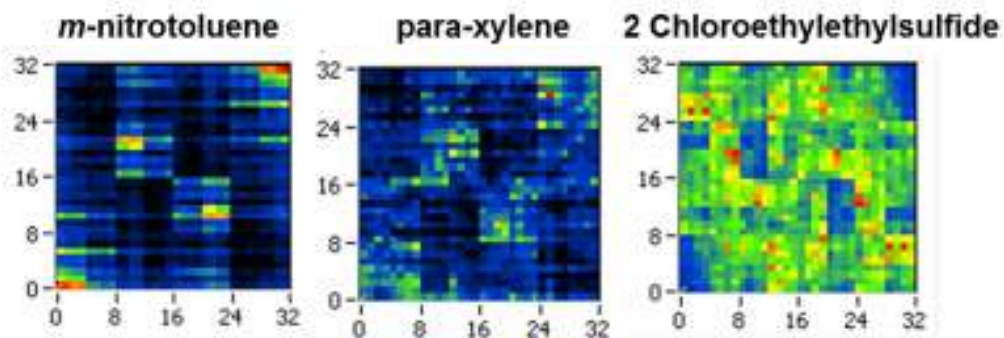
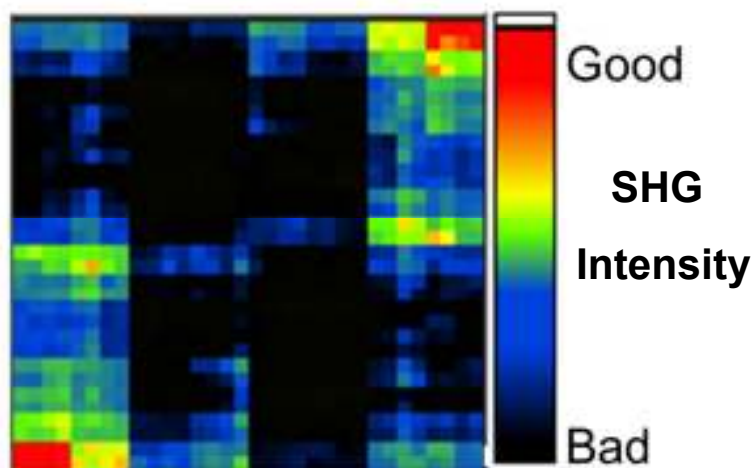
J. Phys. Chem. A **110**, 11388-11391 (2006) search space mapping

Journal of Modern Optics **53**, 2533 (2006) chemical recognition

ChemPhysChem, **7**, 2471-2473 (2006) control using binary phases

J. Phys. Chem. A.112,3789 (2008) No evidence of interference

Binary Search Space Mapping



Mass Spectrometry Analysis and Imaging

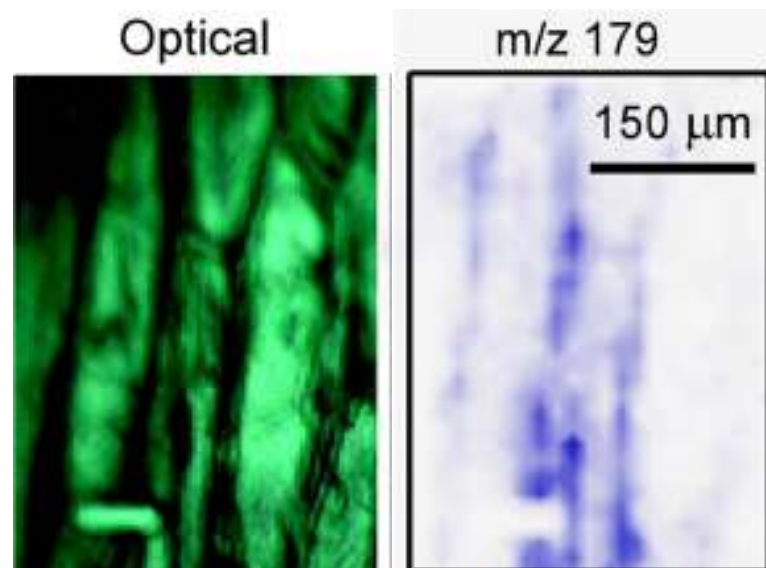
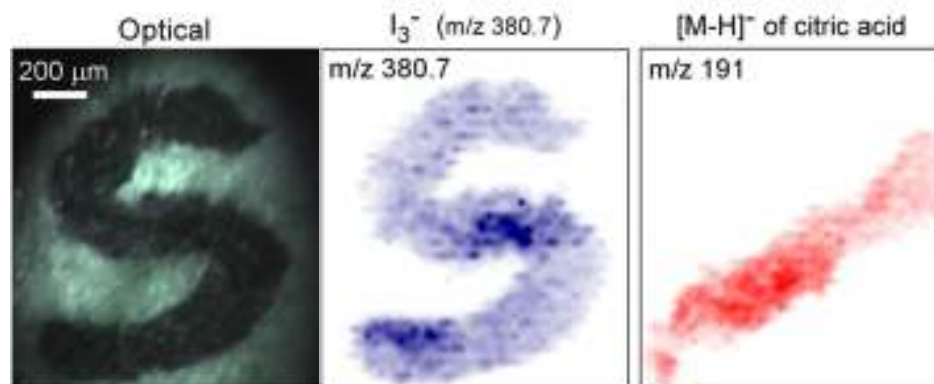
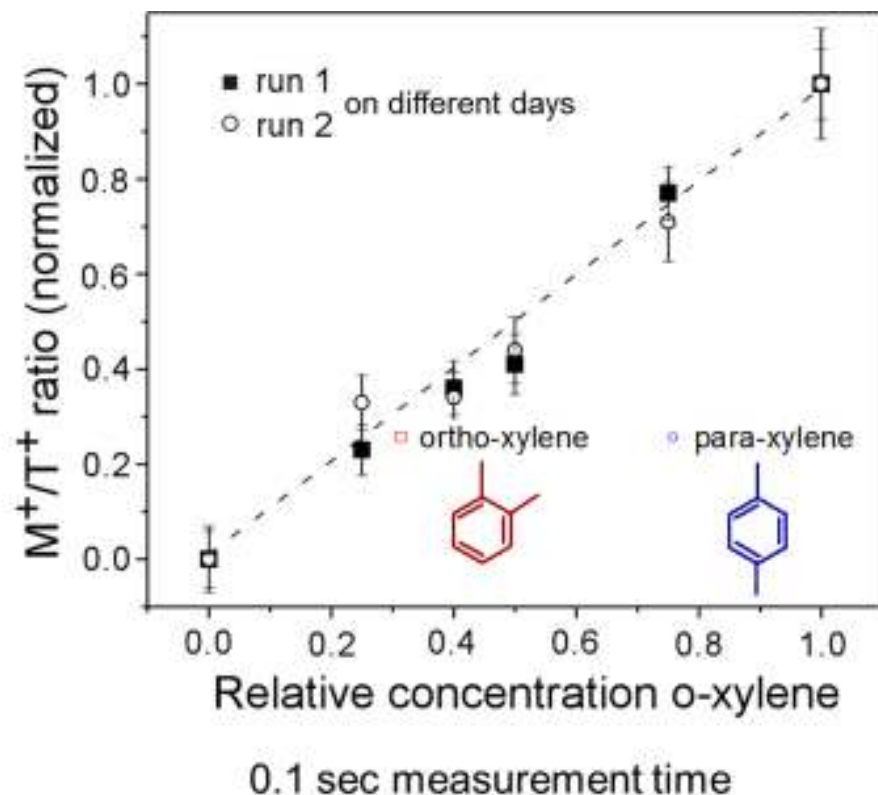
Dela Cruz, Pastirk, Coello, Jones, Gunaratne, Lozovoy and Dantus

J. Phys. Chem. A **109**, 8447-8450 (2005) **quantitative isomer identification**

Journal of Mass Spectrometry **42** 178 (2006) Isomer identification

Applied Optics, in press (2007). multidimensional

Anal. Chem. **82**, 2753 (2010) **Atmospheric pressure femtosecond laser imaging mass spectrometry**



Mass Spec. Proteomics and Metabolomics

Kalcic, Gunaratne, Jones, Reid, Winkler, Smith, Safran, Stemmer, Palumbo, Lozovoy and Dantus

J. Am. Chem. Soc. 131, 940 (2009) FS-LID

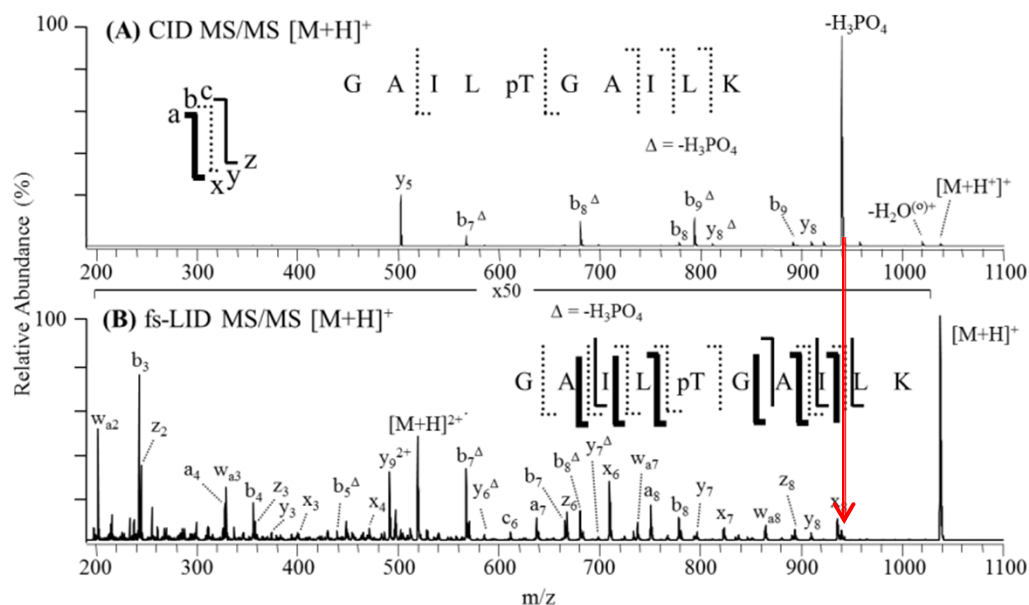
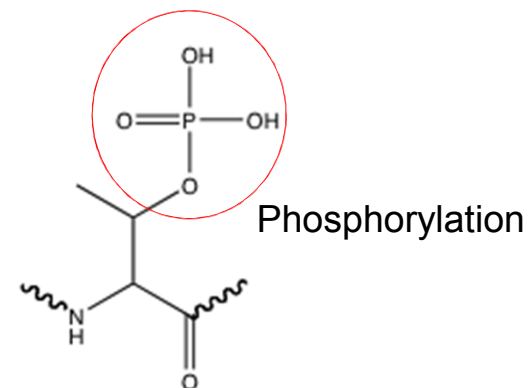
J. Phys. Chem. A, **114**, 10380 (2010).

Journal of the American Society for Mass Spectrometry **12**, 2031 (2010).

Mass Spectrometry Reviews **30**, 600 (2011) Phosphoproteomics

Journal of Physical Chemistry A **116**, 2764 (2012) The mechanism

Breaking strong chemical bonds while leaving weak ones intact



Post-translational modifications: a challenge for proteomics *Proteomics* 6,1525-6 (2004)

Tumor antigen p53: (*Science* Molecule of the year 1993), has >18 phosphorylation sites.

DNA winds around Histones, gene regulation and DNA repair depend on histone PTM's.

Coherent Control

Marvet, Gross, Backhaus, Schmidt, Pastirk, Brown, Grimberg, Gunaratne, Zhu, Shah, Goswami, Lozovoy and Dantus

Photoassociation

Chem. Phys. Letters **245**, 393 (1995) J. Chem. Phys. **106**, 8013 (1997) Chem. Phys. Letters **306**, 18 (1999)

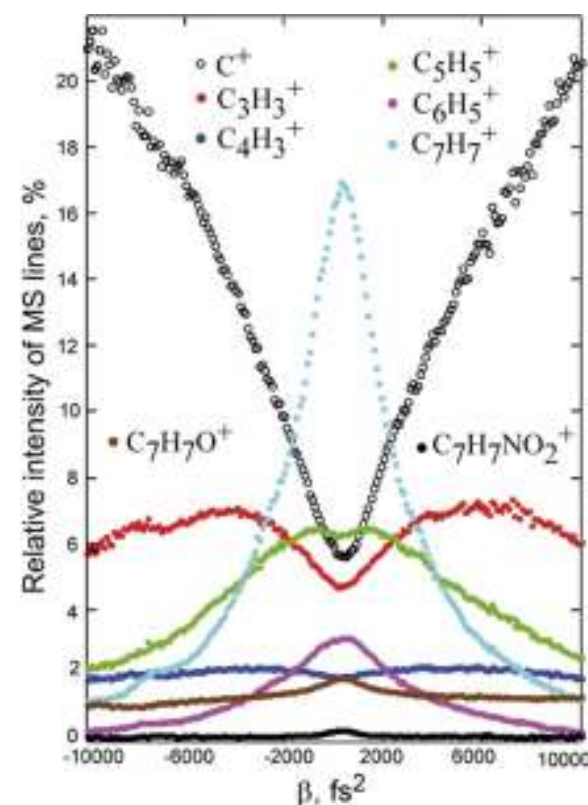
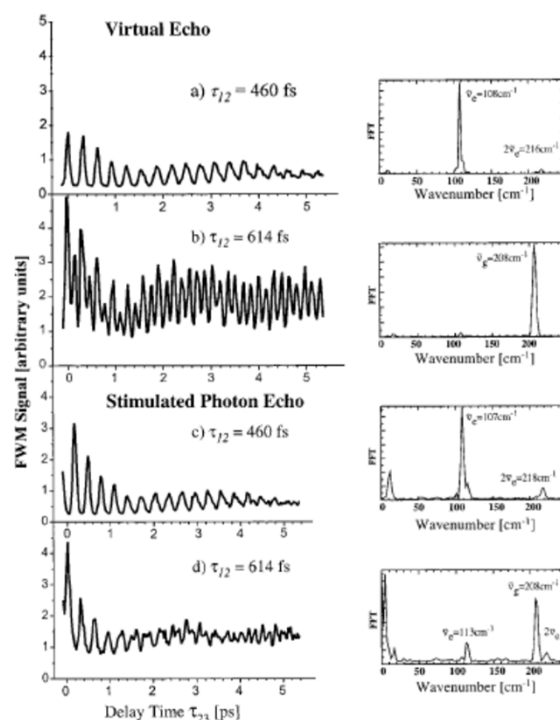
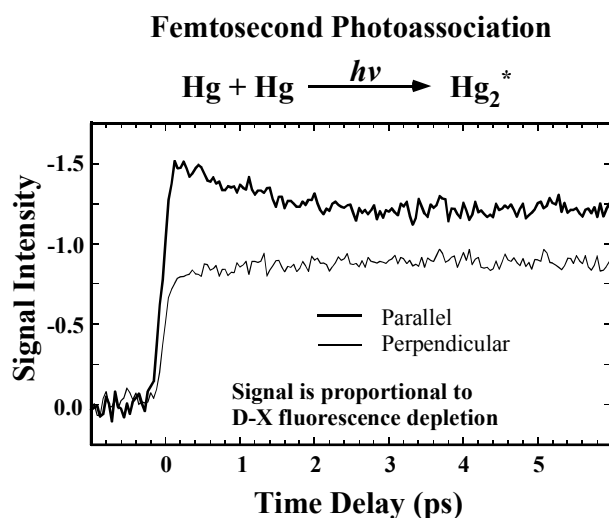
Chirp control of chemical reaction J. Chem. Phys. **108**, 4375-4378 (1998)

Four Wave Mixing (includes CARS) J. Chem. Phys. **111**, 3779 (1999) J. Phys. Chem. A **103**, 10226 (1999)

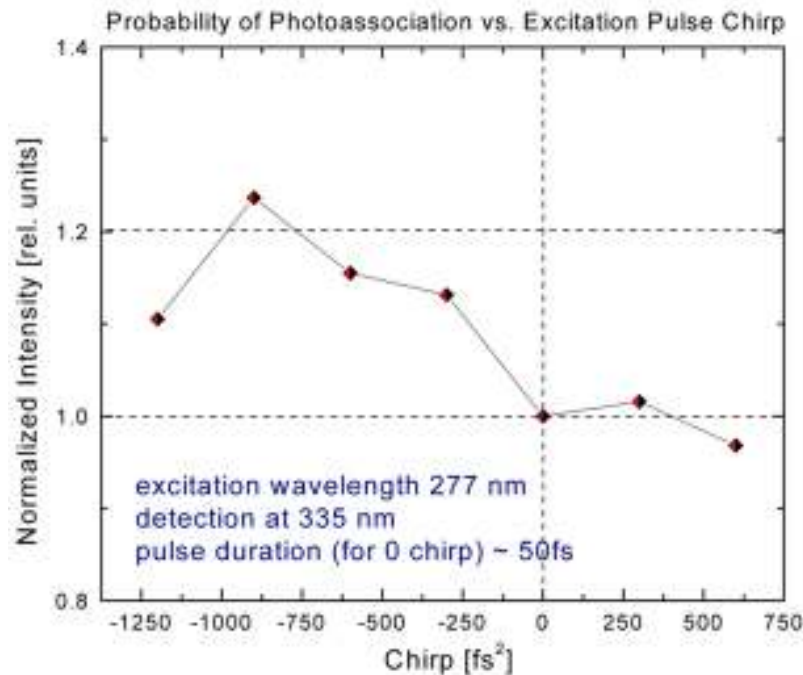
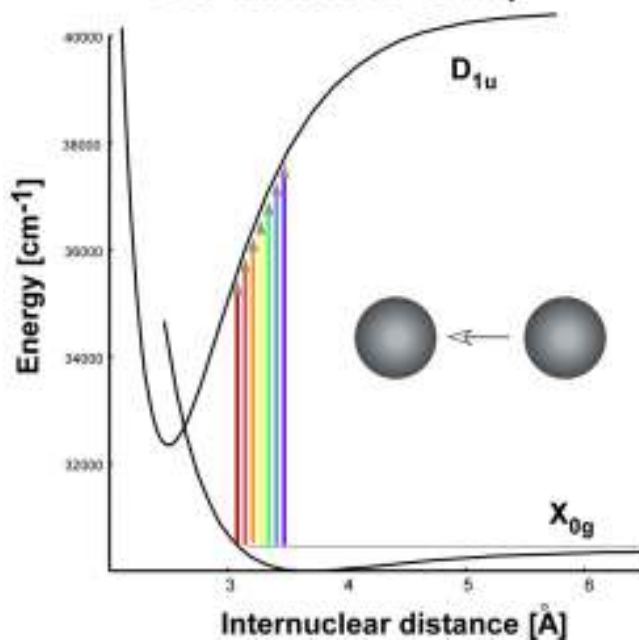
Temporal symmetry Chem. Phys. **338**, 259 (2007).

Comment (no toluene found from acetophenone) J. Phys. Chem. A **113**, 5264 (2009)

Dynamics observed in acetophenone J. Phys. Chem. A **115**, 1305 (2011)



The Effect of Chirp



Back of the Envelope Calculation

$$\frac{\Delta V}{\Delta R} = 10^4 \text{ cm}^{-1} / \text{\AA}$$

The relative velocity of the mercury atoms

$$\bar{v} = -300 \text{ m/s} = -3 \times 10^{-3} \text{ \AA/fs}$$

The expected chirp in the absorption spectrum

$$\varphi = -30 \text{ cm}^{-1} / \text{fs}$$

The calculated chirp required

$$\phi = -\frac{1}{30c} = -10^3 \text{ fs}^2$$

Unpublished data by I. Pastirk, presented

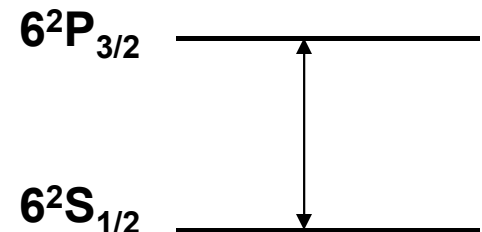
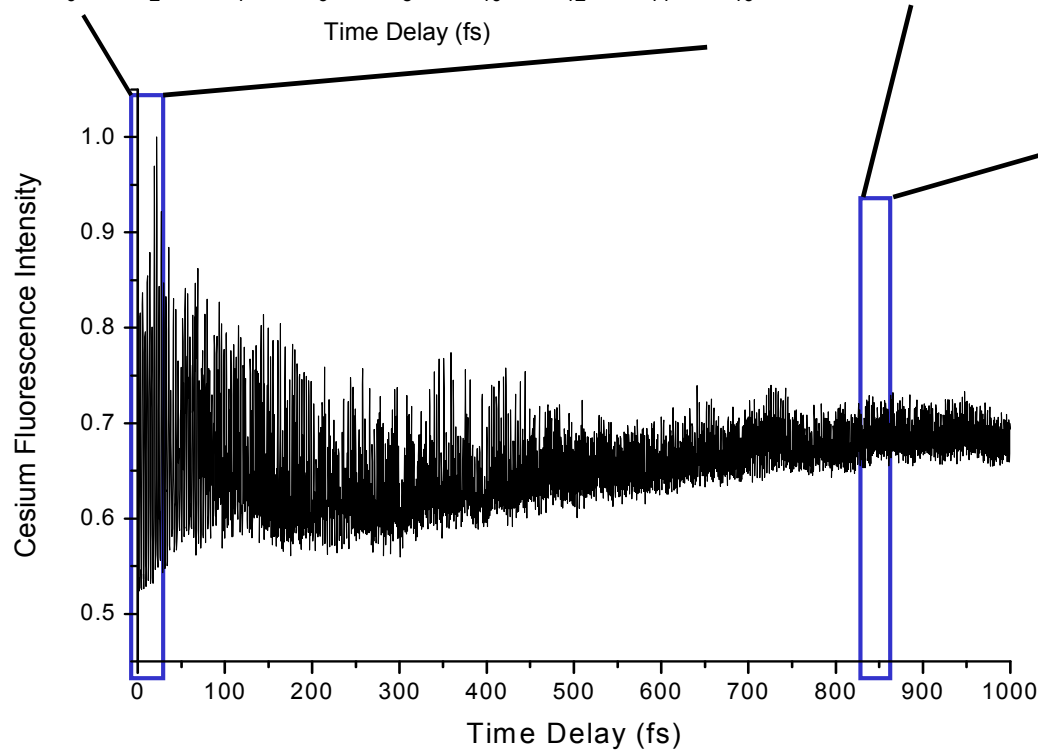
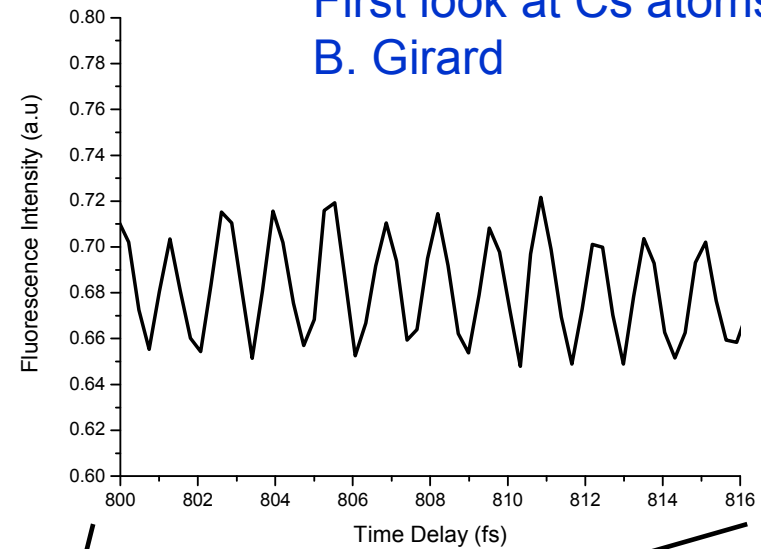
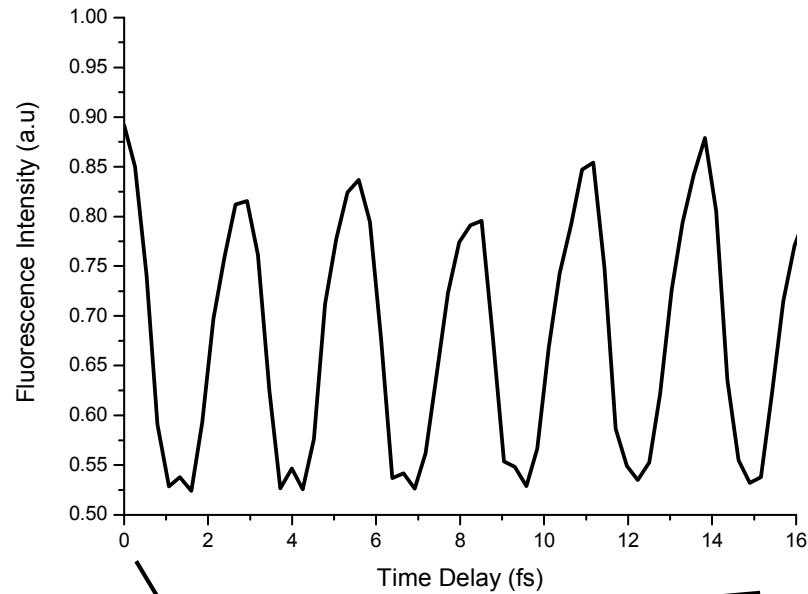
Cold Molecule 2001: Coherent Control and Cold Molecules

Gif-sur-Yvette, France,

October 21-25, 2001

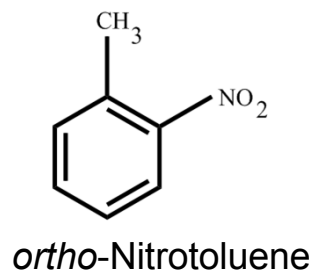
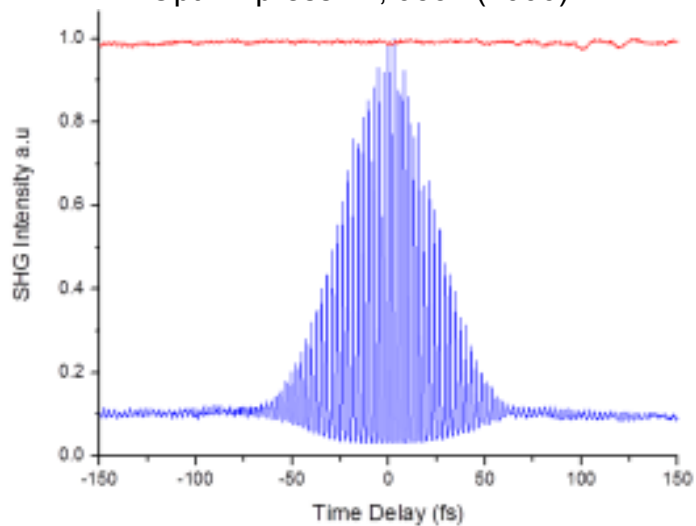
Looking for electronic coherence in strong fields

First look at Cs atoms
B. Girard

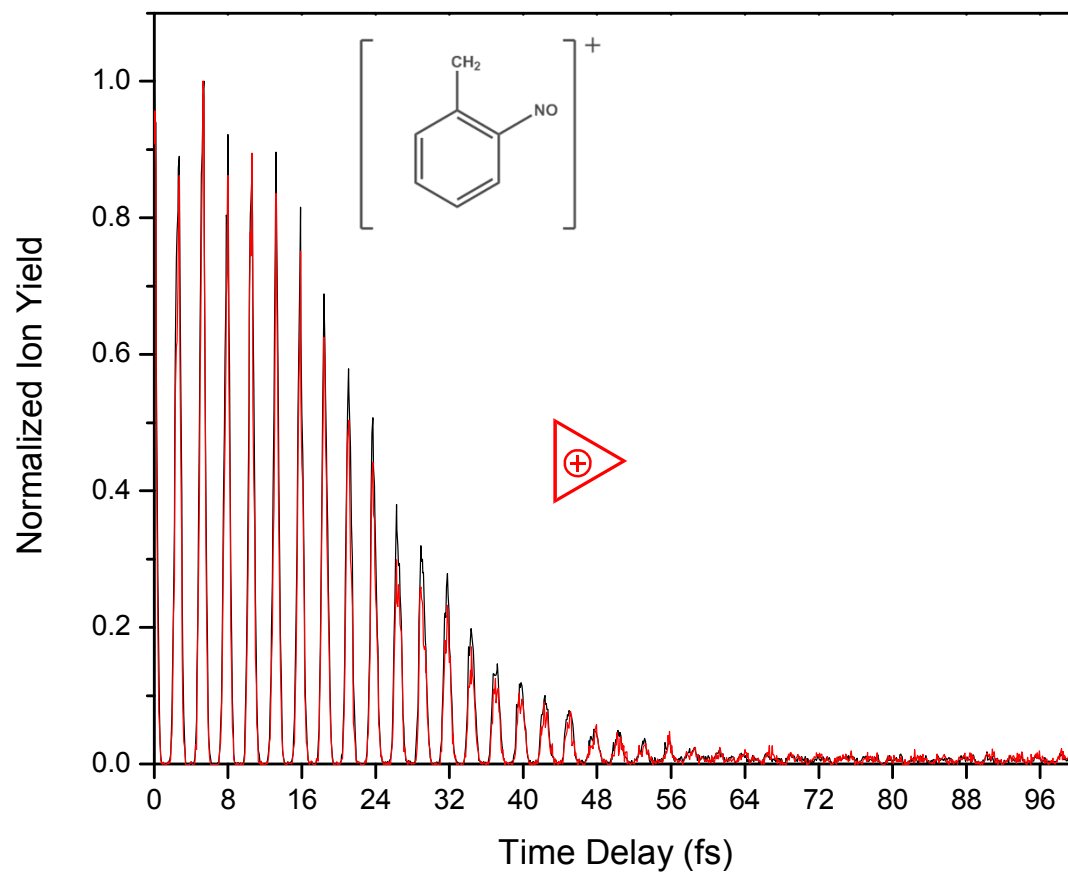


Looking for evidence of electronic coherence in o-NT photodissociation

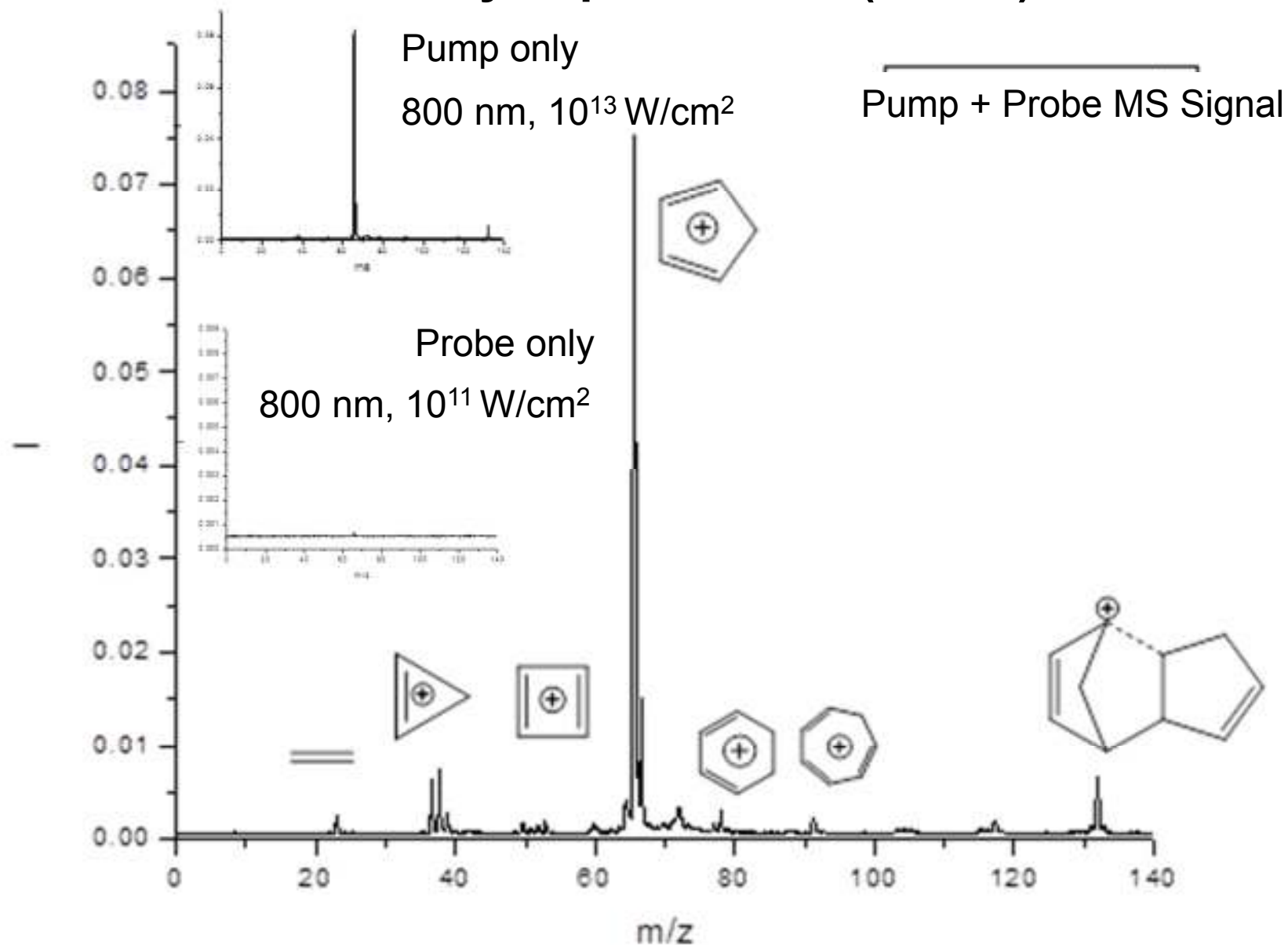
Opt. Express 14, 9537 (2006)



Peak Intensity = $8 \times 10^{13} \text{ W/cm}^2$

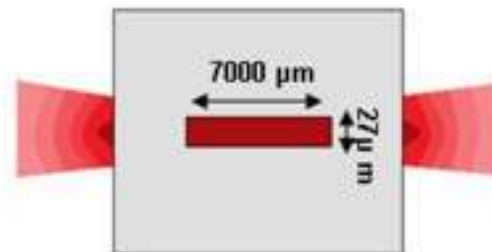
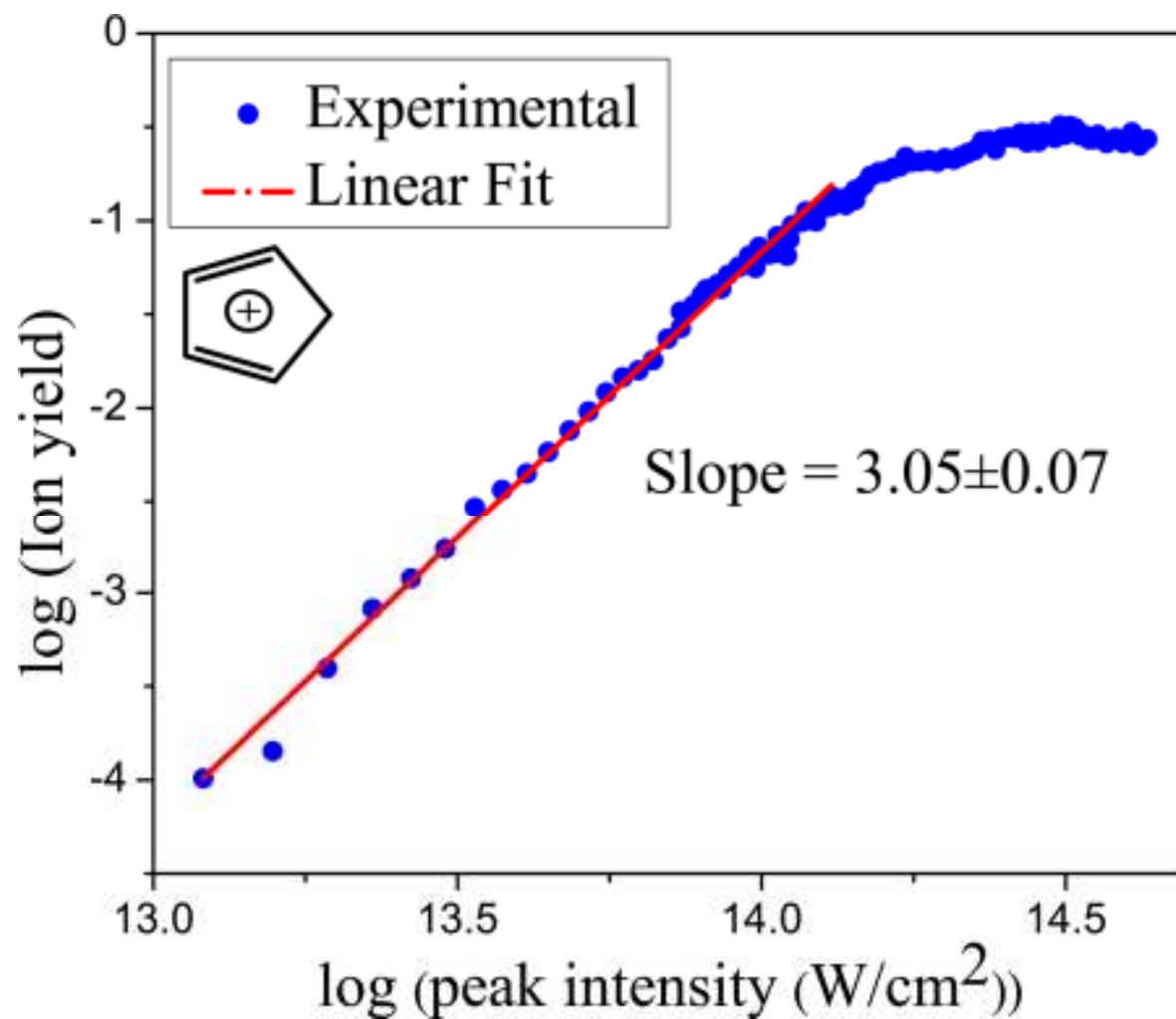


Dicyclopentadiene (DCDP)

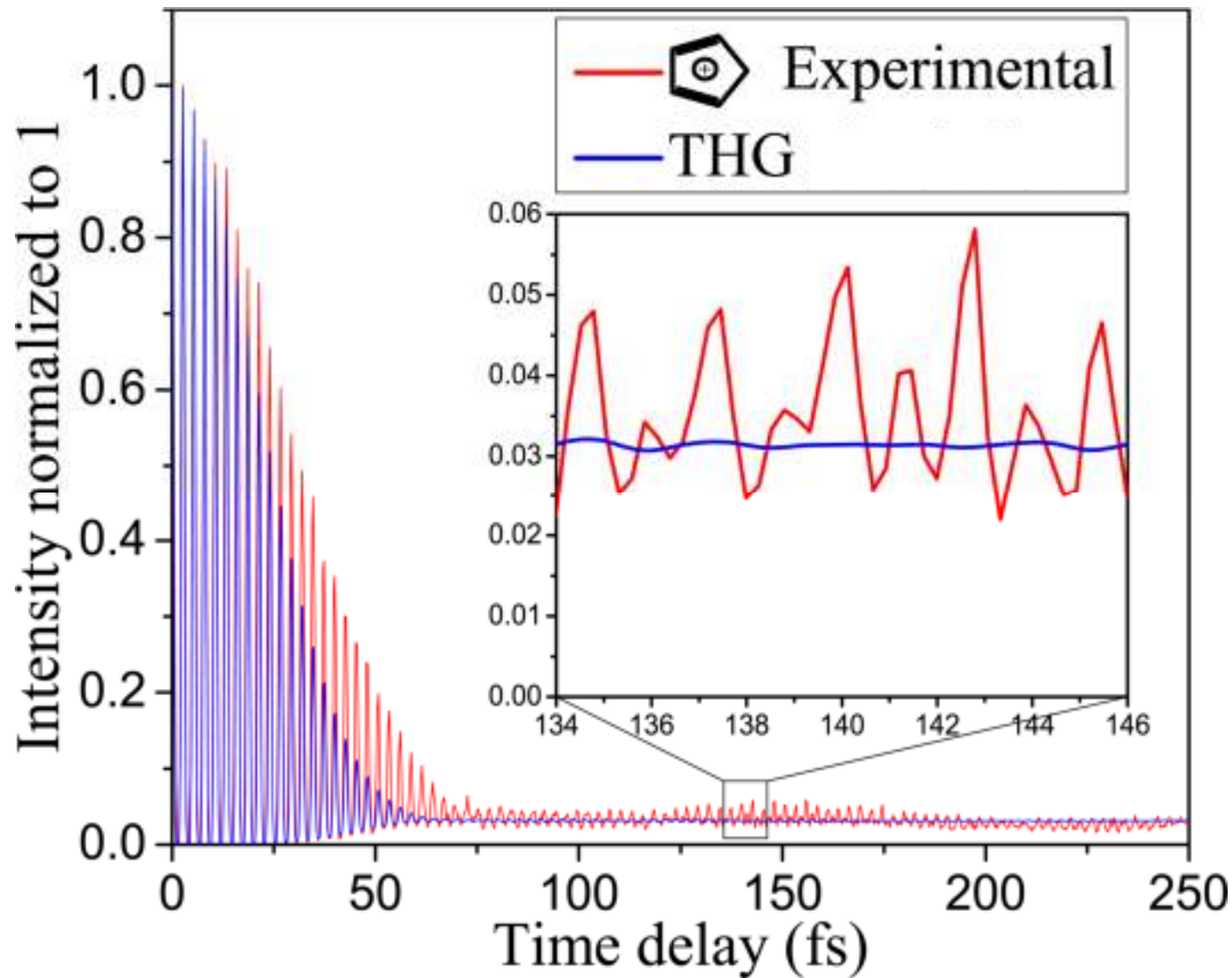


Goswami, Shah, Konar, Lozovoy and Dantus to be submitted (2012)

Power Dependence Fit for CPD⁺

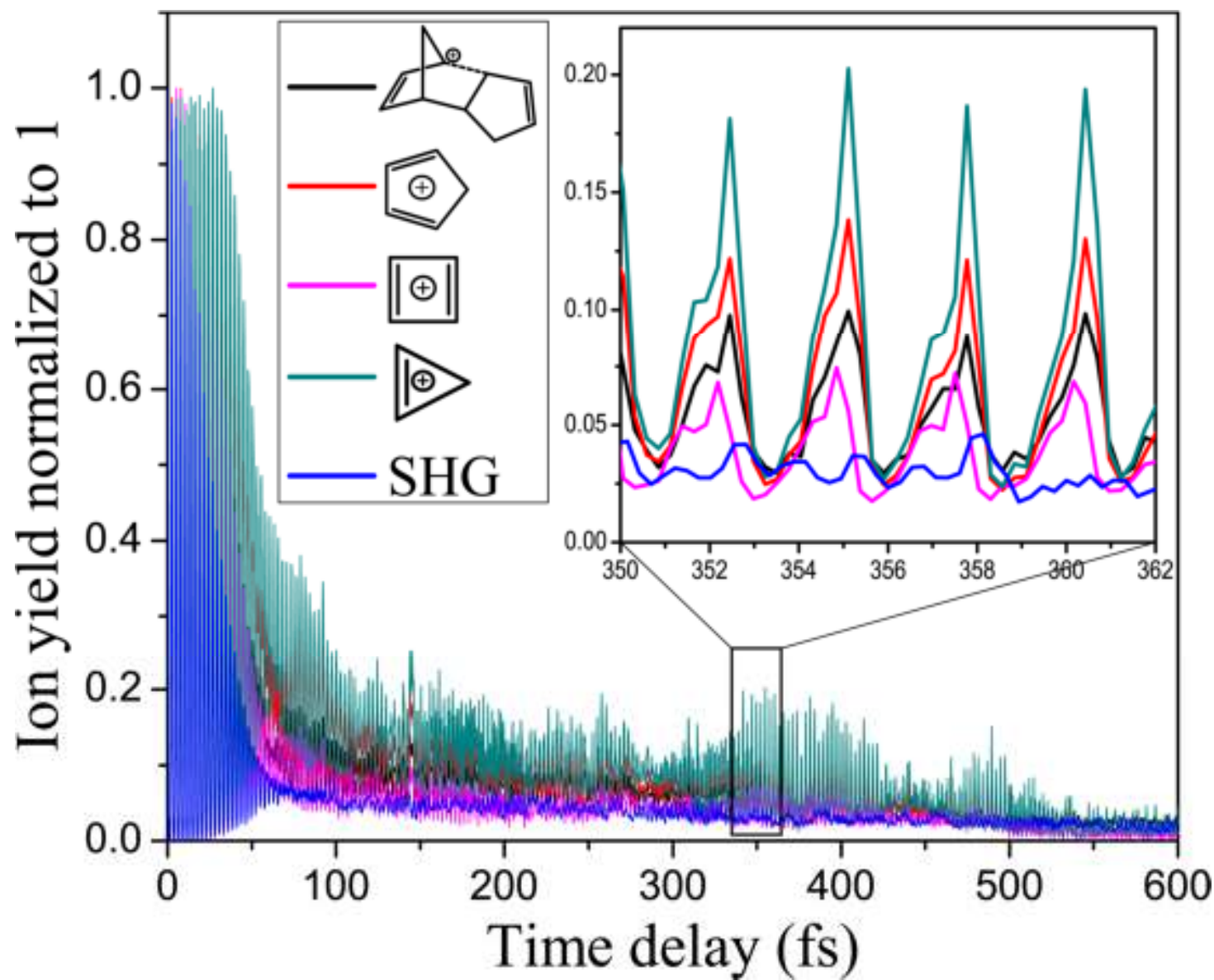


Comparison to Third Harmonic Generation Signal



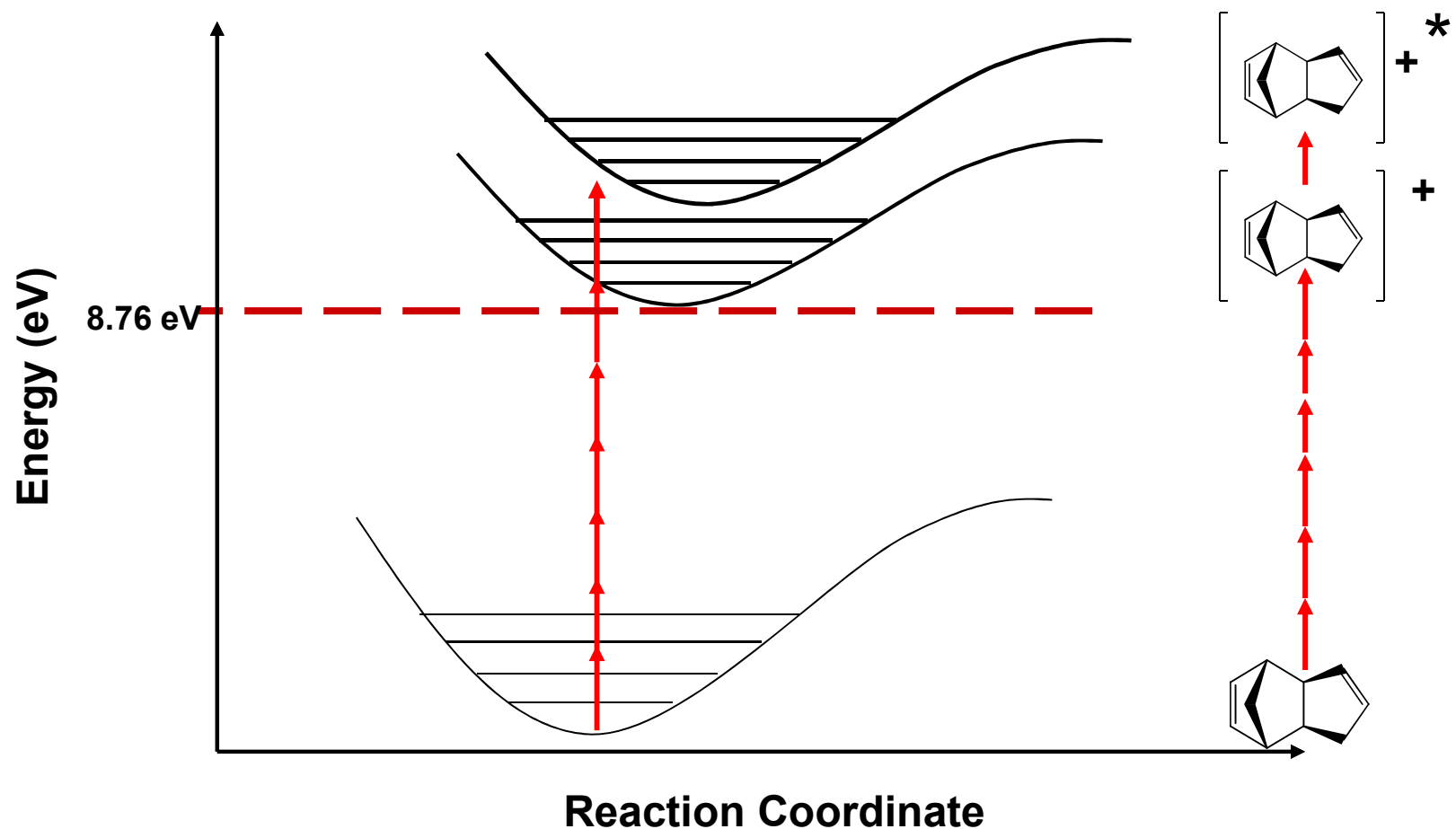
Goswami, Shah, Konar, Lozovoy and Dantus to be submitted (2012)

Long lived electronic coherence – DCPD fragments



Goswami, Shah, Konar, Lozovoy and Dantus to be submitted (2012)

Multiphoton Ionization of Di-Cyclopentadiene

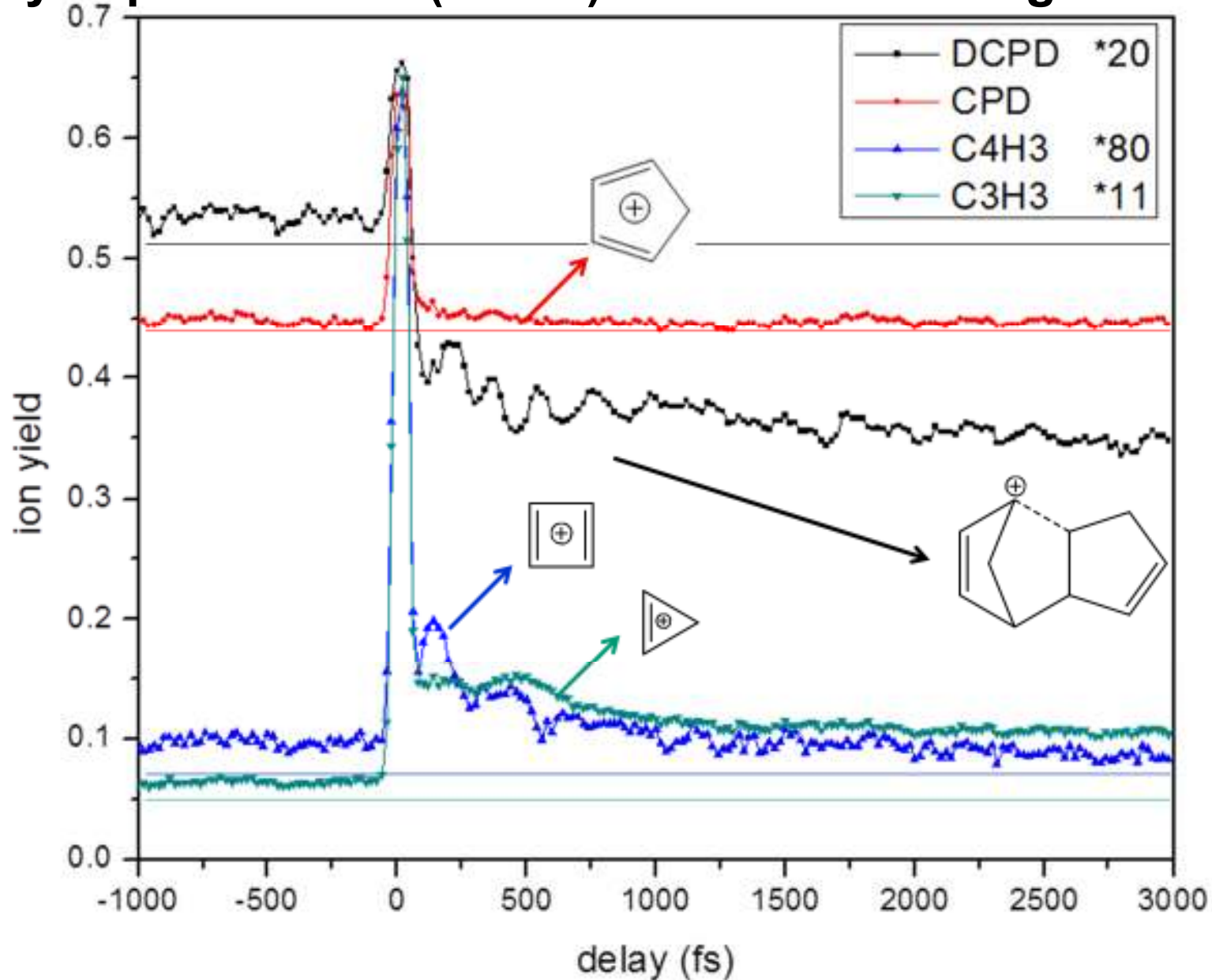


↑ = 1.5 eV, 800nm

Electronic coherence occurs between the ground and first excited state ion states

Baker *et al.*, *Anal Chem*, 42, (1970)

Dicyclopentadiene⁺ (DCDP) time-resolved fragmentation



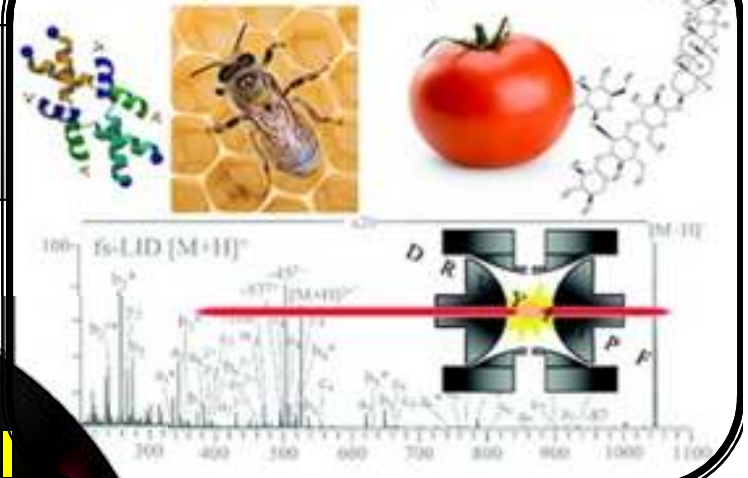
Goswami, Shah, Konar, Lozovoy and Dantus to be submitted (2012)

Sensing



Dantus Group

Biological Mass Spectrometry

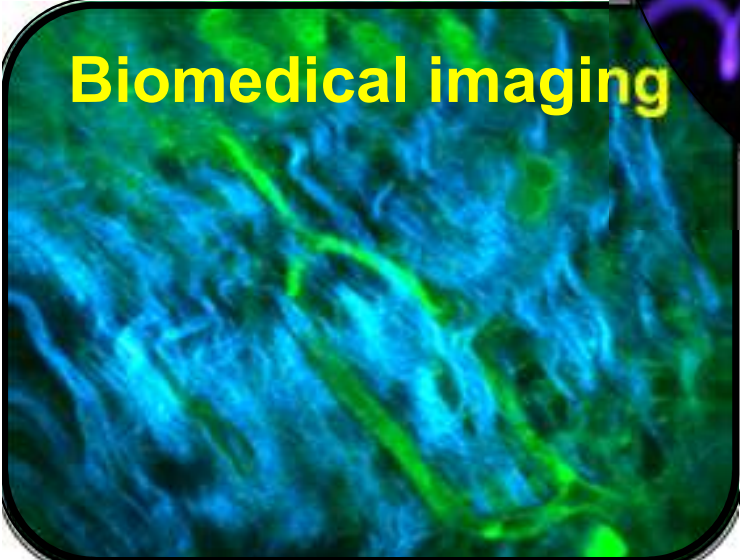


Phase Control

Laser Design

Multidisciplinary
Collaborations with
Universities and Industry

Biomedical imaging



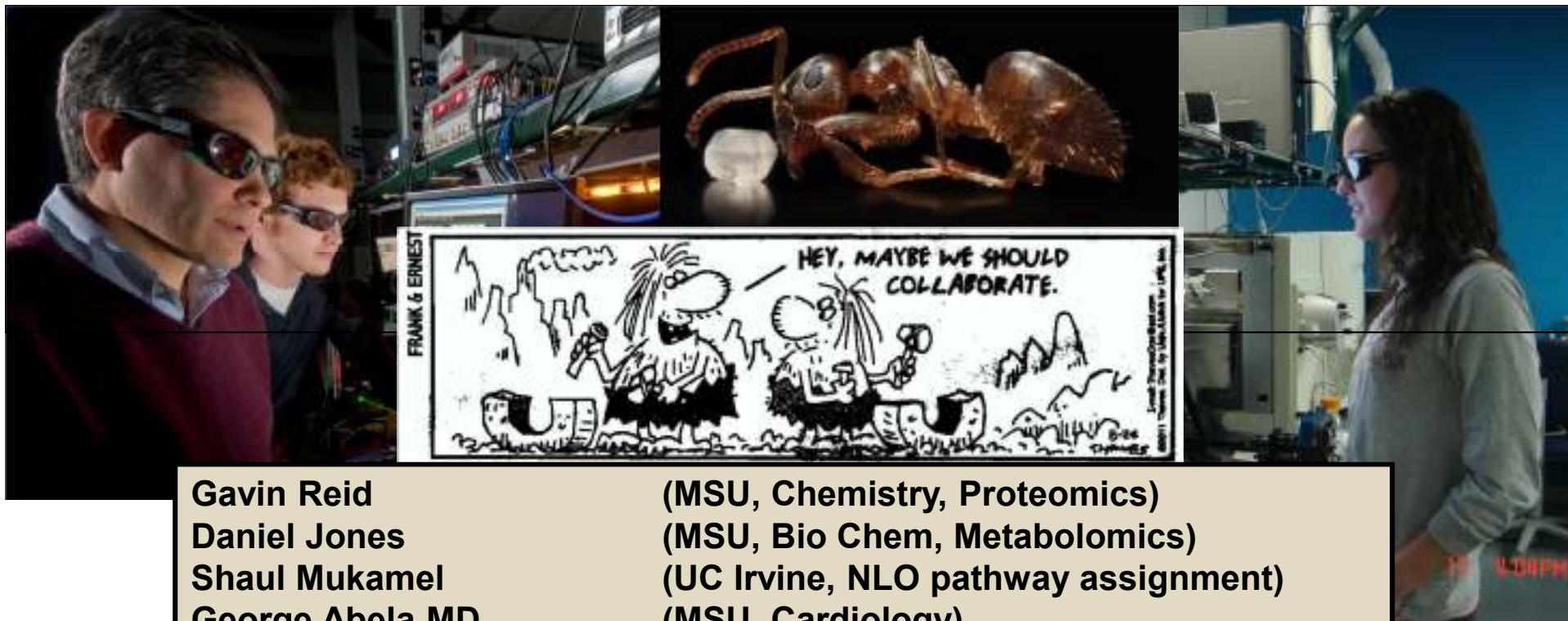
Optimized Laser Processing

Si wafer micromachining 35 fs TL pulses



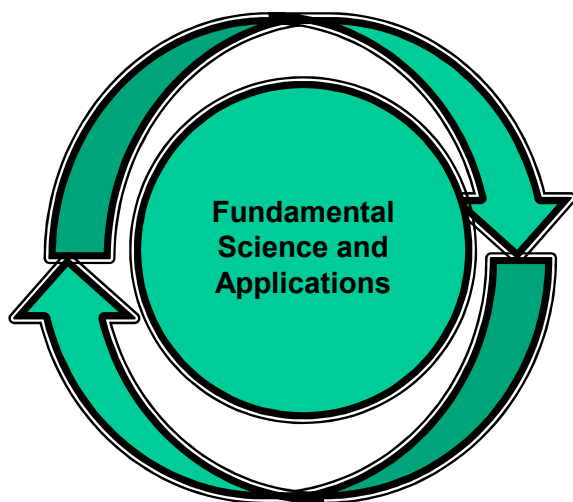
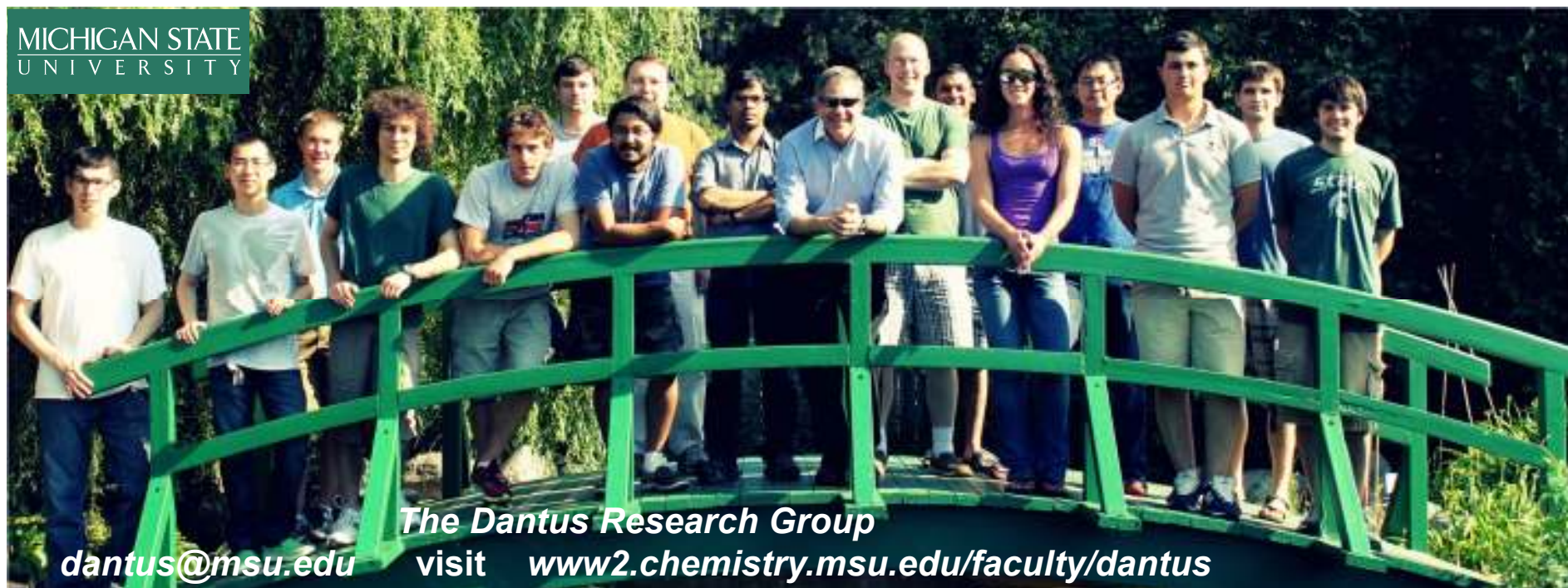
Si wafer micromachining 40k fs² chirp





Gavin Reid	(MSU, Chemistry, Proteomics)
Daniel Jones	(MSU, Bio Chem, Metabolomics)
Shaul Mukamel	(UC Irvine, NLO pathway assignment)
George Abela MD	(MSU, Cardiology)
Chong-Yu Ruan	(MSU, ultrafast electron diffraction)
James Resau MD	(Van Andel Institute, cancer)
Stephen Boppart	(UIUC, femtosecond endoscopy)
Jim Gord	(Air Force Research Lab, CARS)
Sukesh Roy	(Spectral Engines LLC, CARS, Machining)
Flavio Cruz	(UNICAMP, Brazil, Novel laser sources)
Sunney Xie	(Harvard, CARS microscopy)
Rich Mathis	(Berkeley, low frequency in biomolecules)
Frank Wise	(Cornell, fiber laser design)
Thomas Weinacht	(SUNY Stony Brook, UV pulse shaping)
Maurice Jansen	(Free Univ. Amsterdam, PEPICO)
Shaul Mukamel	(UC Irvine, NLO Theory)

Phase control enables fundamental research and applications



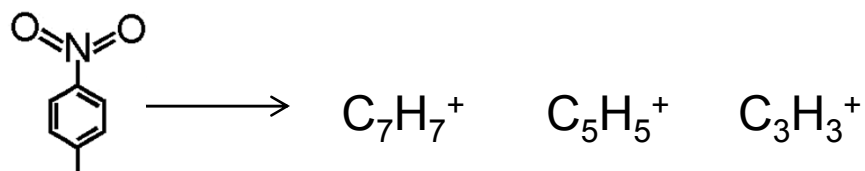
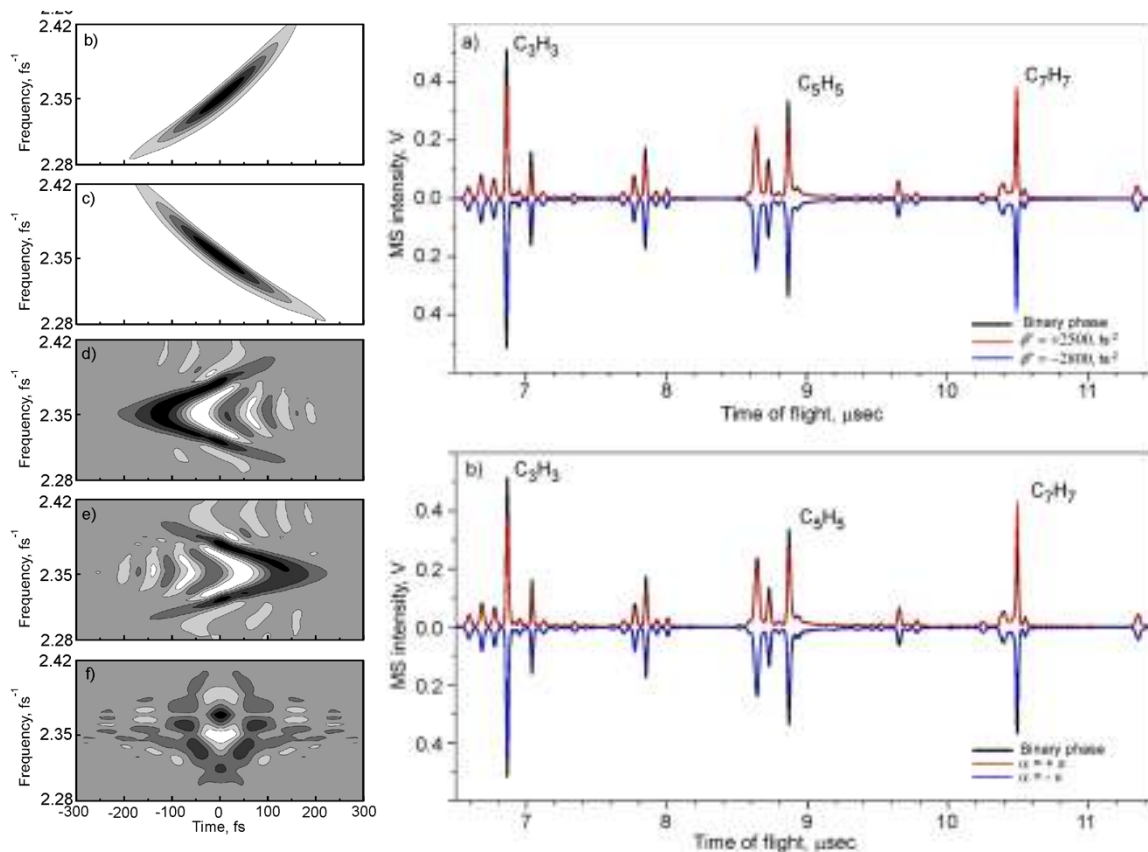
Biophotonic
SOLUTIONS INC.
ULTRAFAST PULSE SHAPING & COMPRESSION



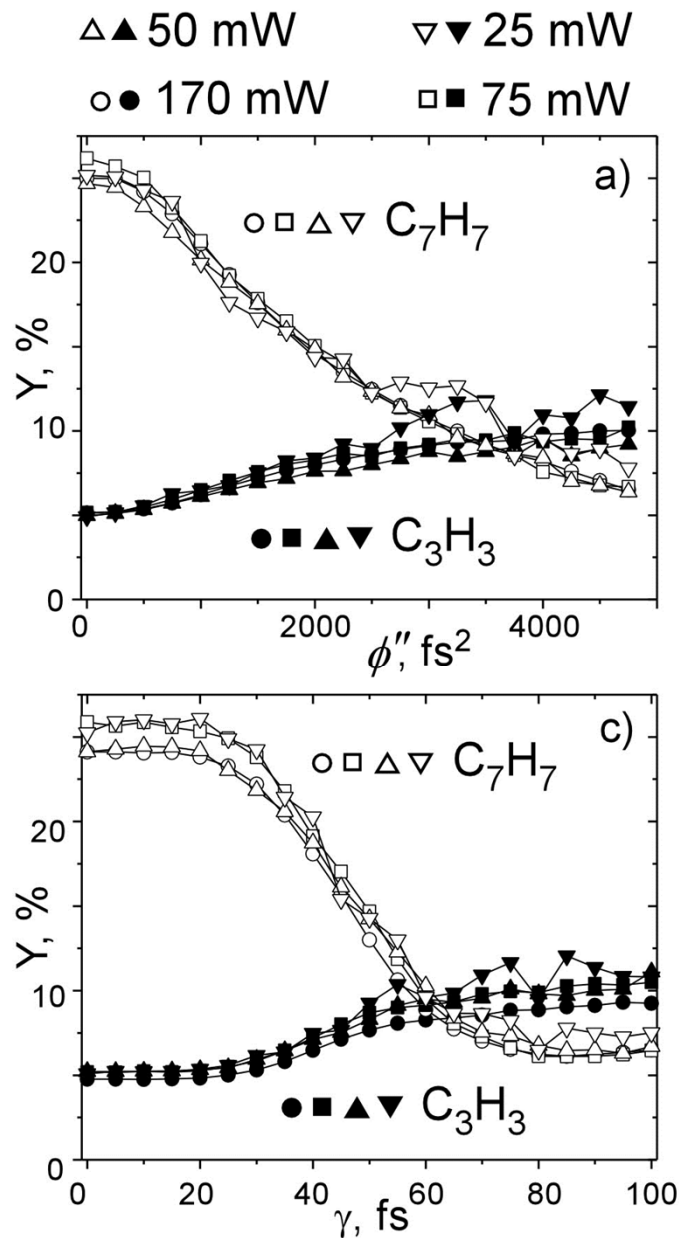
Backup Slides for Follow Up Discussion

Is photofragmentation pattern phase dependent?

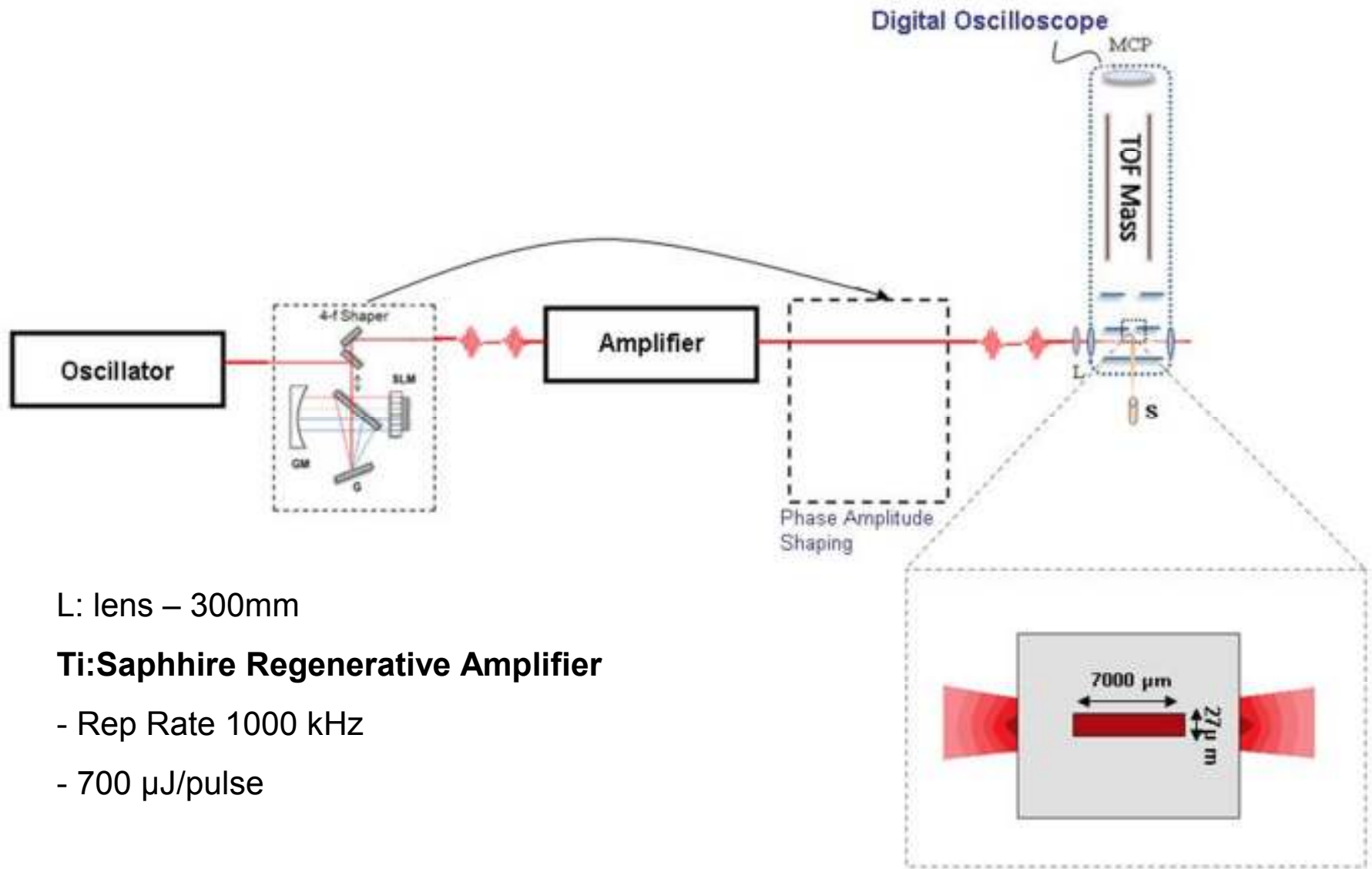
Comprehensive exploration on the role of phase coherence on the fragmentation of large molecules by intense shaped pulses



Zhu et al. J. Phys. Chem. A. 112, 3789 (2008)



Experimental Set-Up

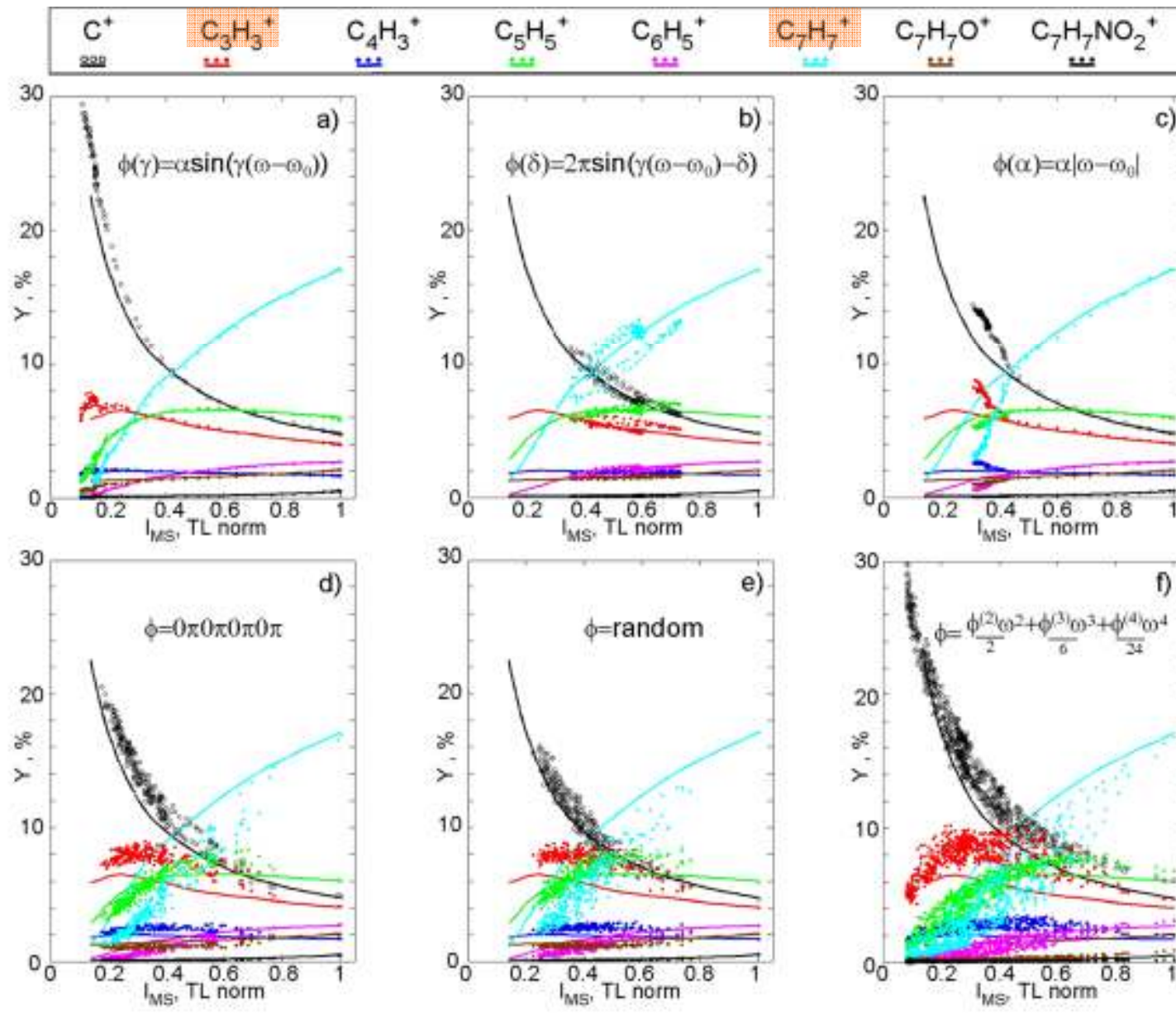


L: lens – 300mm

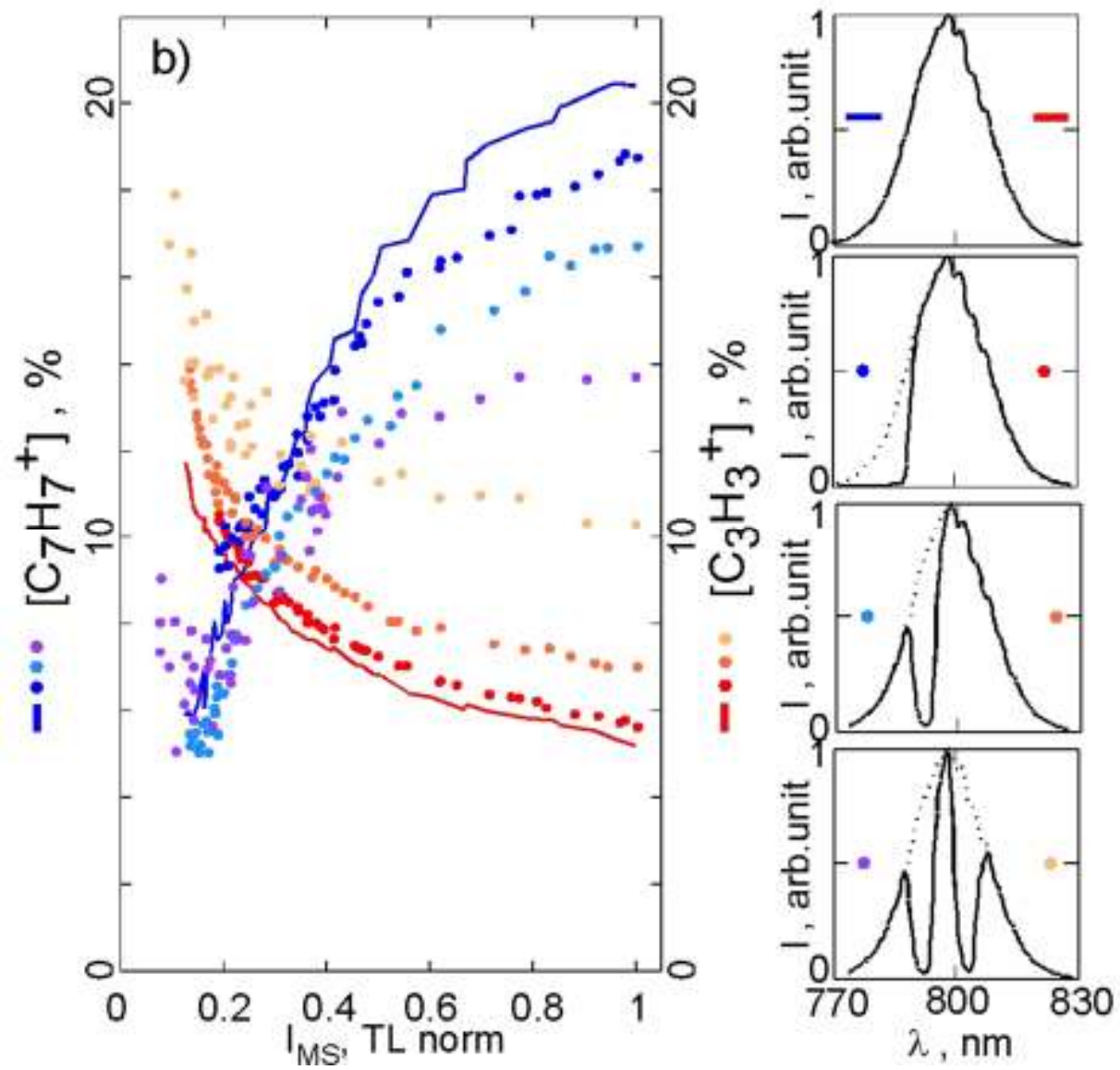
Ti:Sapphire Regenerative Amplifier

- Rep Rate 1000 kHz
- 700 $\mu\text{J}/\text{pulse}$

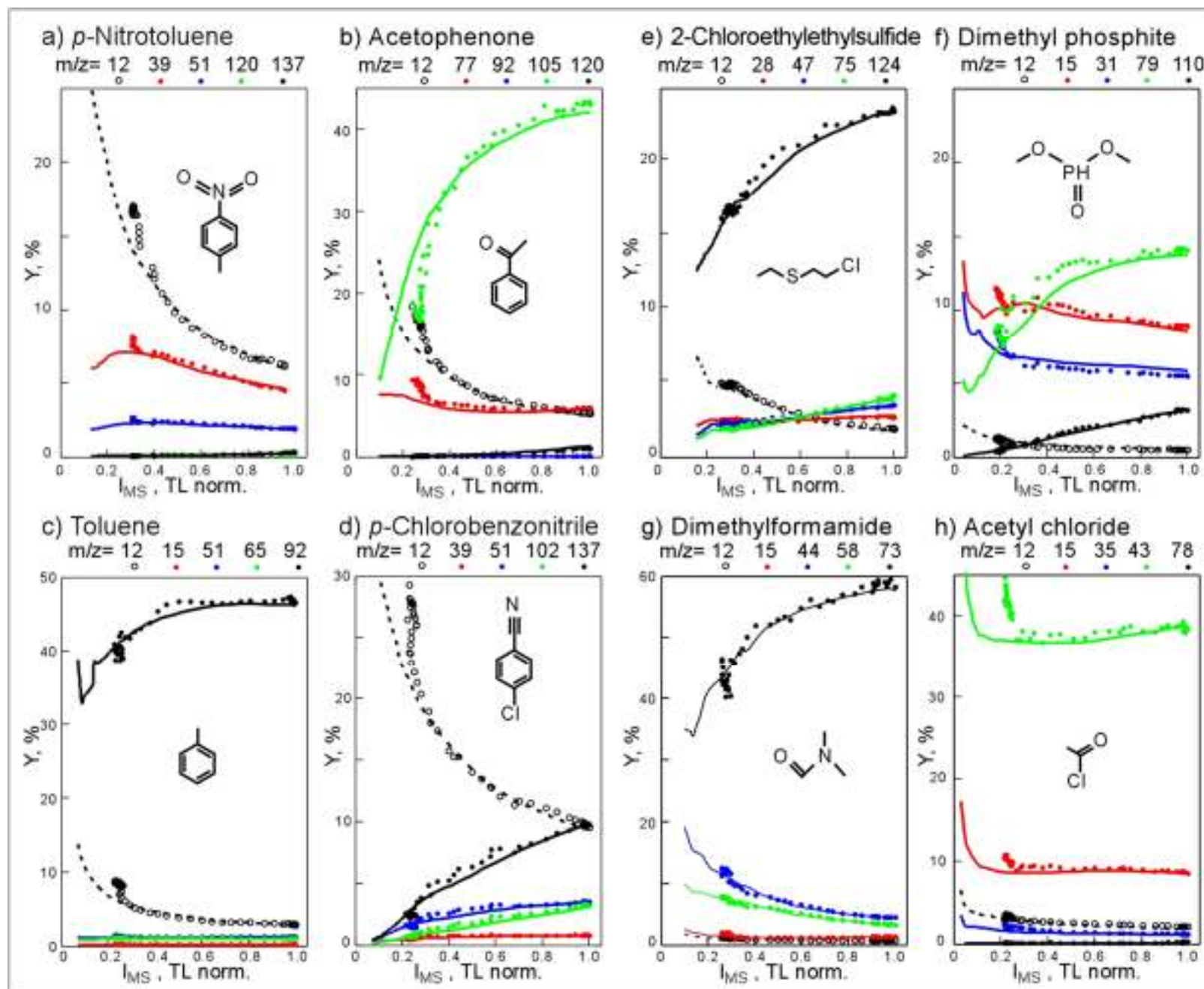
Is molecular response predictable?



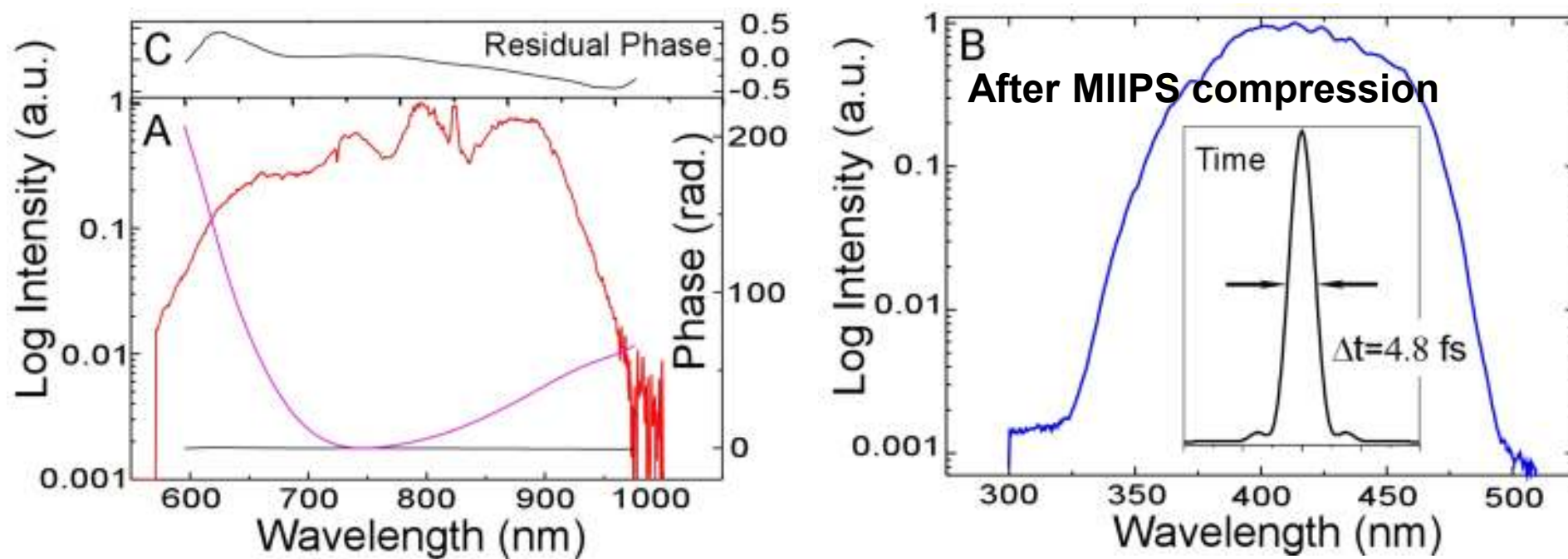
Effect of phase & amplitude shaping



Generalizing to other molecules



Experimental Single-Beam CARS Setup



2010 Pulse Shaping Workshop
August 20-22, 2010
Michigan State University



Teaching scientists worldwide how to use sub-5fs pulses routinely



2011 Pulse Shaping Workshop @ MSU Aug 19-21. Keynote by Andrew Weiner