MARCOS DANTUS – 20 KEY PUBLICATIONS

All the publications before 2002 were obtained with lasers built by Dantus.

PRINCIPAL AREAS OF WORK:

1. FEMTOCHEMISTRY AND ULTRAFAST ELECTRON DIFFRACTION
2. ULTRAFAST REACTION DYNAMICS
3. COHERENT CONTROL
4. ULTRAFAST LASER TECHNOLOGY
5. ULTRAFAST SPECTROSCOPY, MATERIALS DISCOVERY, AND PROCESSING
6. ULTRAFAST SPECTROSCOPY FOR BIOMEDICAL SCIENCES
7. ULTRAFAST SPECTROSCOPY FOR DEFENSE

FEMTOCHEMISTRY AND ULTRAFAST ELECTRON DIFFRACTION

1. *Real-time femtosecond probing of ''transition states'' in chemical reactions*, M Dantus, MJ Rosker, AH Zewail, Journal of Chemical Physics **87**, 2395 (1987).
https://doi.org/10.1063/1.453122

    Fundamental processes in chemistry such as bond formation and bond cleavage were considered too fast to be measurable. Dantus designed and built a femtosecond laser spectroscopy lab to study the spectroscopy of transient species with lifetimes shorter than a picosecond. This publication showed the spectroscopic signatures of "transition states" in the direct dissociation of iodine from ICN, with lifetimes shorter than 100 fs. Dantus authored the first 20 publications from this laboratory which addressed bond dissociation, pre-dissociative states, transition states, and isomerization, as well as molecular vibrations and rotations. These experiments involved gas phase, molecular beams, and liquids. This publication heralded the field of Femtochemistry and led to the 1999 Chemistry Nobel Prize.

2. *Ultrafast electron diffraction. 5. Experimental time resolution and applications*, M Dantus, SB Kim, JC Williamson, AH Zewail, The Journal of Physical Chemistry **98**, 2782 (1994).
https://doi.org/10.1021/j100062a011

    It has been the dream of many scientists to follow a complex chemical reaction from start to finish as if it were a slow-motion molecular movie. This ability to view chemical reactions is particularly important in cases where the structure of transition states is unknown. For such a dream to become reality, one needs a method with sub-Angstrom resolution and femtosecond time resolution that is capable of tracking the internuclear distances of multiple atoms. Dantus, who proposed gas-phase electron diffraction as one of his Ph.D. candidacy topics in 1987, and in his PhD exam in 1991, designed and built such a system as a postdoc in Zewail's group. Ultrafast electron diffraction allows one to obtain chemical movies showing how chemical bond lengths and angles change during a chemical reaction. It has taken three decades for the rest of the world to surpass the results presented in this publication. This publication was the seed for the field of Ultrafast Electron Diffraction, a field now pursued in multiple laboratories worldwide.

ULTRAFAST REACTION DYNAMICS

3. *Femtosecond Photoassociation Spectroscopy - Coherent Bond Formation,* U Marvet and M Dantus, Chemical Physics Letters **245**, 393 (1995). https://doi.org/10.1016/0009-2614(95)01018-5

    Studying bimolecular chemical reactions with femtosecond time resolution was considered impossible because reactive encounters between free reagents occur at random times and with random orientations. This apparent impasse was resolved by taking advantage of the photoassociation process, whereby two free moieties absorb a photon to reach a bound state. The method femtosecond photoassociation spectroscopy was introduced and used to study the reaction Hg+ Hg + hν → Hg_2. The results demonstrated coherent bond formation on the femtosecond time scale from free unbound mercury atoms. The product Hg_2 molecule was formed in the D_{1u} state and showed a high degree of rotational anisotropy induced by the polarization of the binding femtosecond pulse. This was the first of four papers describing the photoassociation process from both semiclassical and quantum mechanical points of view.

4. *Femtosecond observation of a concerted chemical reaction,* U Marvet, M Dantus, Chemical physics letters **256**, 57 (1996). https://doi.org/10.1016/0009-2614(96)00408-3

    With increased time resolution, one can determine if a reaction is indeed concerted or sequential. A time-resolved study is presented of the photodissociation of methylene iodide (CH_2I_2) to produce a carbene diradical and molecular iodine. This reaction pathway occurs only at high excitation energies (vacuum ultraviolet) and is initiated in this case by a two-photon transition at $\lambda_{\text{equivalent}} = 155$ nm. Discrimination over competing pathways is achieved by wavelength-selective monitoring of the nascent I_2 dynamics. The results show clear evidence that breakage of the two carbon-iodine bonds and formation of the iodine-iodine bond is concerted. The reaction takes place in less than 100 fs and is characterized by coherent vibrational motion in the iodine molecule. This is likely the first femtosecond time-resolved study of a concerted chemical reaction.

5. *H_2 roaming chemistry and the formation of H_3^+ from organic molecules in strong laser fields*, N Ekanayake, M Nairat, B Kaderiya, P Feizollah, B Jochim, T Severt, B Berry, K R Pandiri, K D Carnes, S Pathak, D Rolles, A Rudenko, I Ben-Itzhak, C A Mancuso, B S Fales, J E Jackson, B G Levine, M Dantus, Nature Communications **9**, 5186 (2018). https://doi.org/10.1038/s41467-018-07577-0

    H_3^+ is considered one of the most important molecules in the universe. It is responsible for the cooling process essential for the formation of stars and for the creation of most water and organic molecules in the universe. Despite this importance, little is known about the dynamics of chemical processes involving H_3^+, because there is no trigger to time bimolecular processes involved with femtosecond time resolution. This study uses a femtosecond laser pulse to initiate the production of tri-hydrogen cations from hydrocarbons. The formation takes place through a roaming chemical mechanism involving neutral hydrogen molecules. This finding is important in the context of roaming chemical reactions, given that it is the first time-resolved measurement of a roaming reaction and because the roaming partner is a hydrogen molecule.

COHERENT CONTROL

6. *Experimental coherent laser control of physicochemical processes*, M Dantus, VV Lozovoy, Chemical Reviews **104**, 1813 (2004). https://doi.org/10.1021/cr020668r

   Understanding a particular process often improves the ability to control it. Controlling chemical reactions is a goal that has experienced many setbacks. This publication provides the background and intellectual rationale for the most successful approaches for controlling chemical reactions taking advantage of the coherent properties of lasers and the broad bandwidth of femtosecond pulses. Hundreds of different experiments were grouped by approach, for example pump-dump, ω+3ω, chirp, multiphoton intrapulse interference, four-wave mixing, and genetic algorithms, and analyzed. Subsequently, comparisons and critical insights were distilled from the massive analysis. This article is a valuable reference in the field.

7. *Multiphoton intrapulse interference. II. Control of two-and three-photon laser induced fluorescence with shaped pulses,* VV Lozovoy, I Pastirk, KA Walowicz, M Dantus, Journal of Chemical Physics **118**, 3187 (2003). https://doi.org/10.1063/1.1531620

   Nonlinear optical processes are controlled by modulating the phase of ultrafast laser pulses taking advantage of multiphoton intrapulse interference. Experimental results show orders of magnitude control over two- and three-photon excitation of large organic molecules in solution using specific phase functions. Calculations of second- and third-order effects on the amplitude of the electric field spectrum are used to simulate the data and demonstrate that the observed control is not caused by simple changes in peak intensity. These findings had an important impact on multimodal two- and three-photon fluorescence imaging of biological samples.

8. *Isomeric identification by laser control mass spectrometry* JM Dela Cruz, VV Lozovoy, M. Dantus, Journal of Mass Spectrometry **42** 178 (2007). https://doi.org/10.1002/jms.1148

   The influence shaped femtosecond laser pulses have on molecular photofragmentation and ionization, coupled with the intrinsic sensitivity of mass spectrometry, results in a powerful tool for fast, accurate, reproducible and quantitative isomeric identification. Complex phase functions are introduced to enhance differences during the laser–molecule interactions, which depend on geometric structure, resulting in different fragmentation fingerprints. A full account is given on the setup and results leading to a technique that can be used to distinguish between compounds normally indistinguishable by conventional electron ionization mass spectrometry. We demonstrate geometric and structural isomer identification of cis-/trans-3-heptene, cis-/trans-4-methyl-2-pentene, o-/p-cresol and o-/p-xylene. For the positional isomers of xylene we present a complete dataset consisting of 1024 different phases to explore phase complexity. A selection of two phases from that data can then be used to achieve quantitative identification in mixtures of xylene isomers. Finally, we evaluate receiver operational curves obtained from our experimental data to demonstrate the reliability that can be achieved by femtosecond laser control mass spectrometry.

9. *Control of electron recollision and molecular nonsequential double ionization*, S Li, D Sierra-Costa, MJ Michie, I Ben-Itzhak, M. Dantus, Comm. Phys. **3**, 35 (2020). https://doi.org/10.1038/s42005-020-0297-3

Intense laser pulses lasting a few optical cycles, are able to ionize molecules via different mechanisms. One such mechanism involves a process whereby within one optical period an electron tunnels away from the molecule and is then accelerated and driven back as the laser field reverses its direction, colliding with the parent molecule and causing correlated non-sequential double ionization (NSDI). Here we report control over NSDI via spectral-phase pulse shaping of femtosecond laser pulses. The measurements are carried out on ethane molecules using shaped pulses. We find that the shaped pulses can enhance or suppress the yield of dications resulting from electron recollision by factors of 3 to 6. This type of shaped pulses is likely to impact all phenomena stemming from electron recollision processes induced by strong laser fields such as above threshold ionization, high harmonic generation, attosecond pulse generation, and laser-induced electron diffraction.

ULTRAFAST LASER TECHNOLOGY

10. *Multiphoton intrapulse interference. IV. Ultrashort laser pulse spectral phase characterization and compensation*, VV Lozovoy, I Pastirk, M Dantus, Optics letters **29**, 775 (2004). https://doi.org/10.1364/OL.29.000775

    Advances in ultrafast laser spectroscopy depends on reproducible laser pulses. In this publication, Dantus demonstrated it is possible to characterize femtosecond pulses without autocorrelation. Moreover, the method takes advantage of a pulse shaper that both characterizes and compresses the pulses to their theoretical transform limit. This publication, the fourth in a series of pulse shaping breakthroughs in the Dantus group, extends the multiphoton intrapulse interference (MII) theory for controlling two- and three-photon processes. Experimental results showed unprecedented accuracy in the measurement of chirp and higher order dispersion in femtosecond laser pulses without the need for conventional autocorrelation or splitting the input beam into two or more beams. This technology, multiphoton intrapulse interference phase scan (MIIPS), was commercialized and it now enables ultrafast research in over 100 laboratories worldwide. MII has enabled coherent (phase dependent) control of molecules in solution, and even of single molecules. MIIPS-enabled pulse shapers are presently used for chemically resolved biomedical imaging and two-dimensional spectroscopy. The automated pulse compression feature of MIIPS has enabled the design of the most advanced femtosecond fiber laser sources, some of which are now incorporated in industrial systems.

11. *Generation of 42-fs and 10-nJ pulses from a fiber laser with self-similar evolution in the gain segment*, B Nie, D Pestov, FW Wise, M Dantus, Optics Express **19**, 12074 (2011). https://doi.org/10.1364/OE.19.012074

    A double-clad Yb-doped all-normal-dispersion fiber laser with a narrow intra-cavity spectral filter is demonstrated to produce 22 nJ pulses at 42.5 MHz repetition rate. These pulses are characterized and compressed via mulitphoton intrapulse interference phase scan to as short as 42 fs and 10 nJ/pulse. Adaptive compression underlies the achievement of 250-kW peak power, which enables efficient second and third harmonic generation with spectra spanning 30 nm and 20 nm, respectively. This laser design was a breakthrough in fiber laser technology.

ULTRAFAST SPECTROSCOPY, MATERIALS DISCOVERY AND PROCESSING

12. *Cascaded free-induction decay four-wave mixing,* VV Lozovoy, I Pastirk, MG Comstock, M Dantus, Chemical Physics **266**, 205 (2001). https://doi.org/10.1016/S0301-0104(01)00229-4

    This article reports the observation of cascaded optical free-induction decay four-wave mixing (FID-FWM) signal. This process can take place when nonlinear optical measurements are carried out with pulses that are orders of magnitude shorter than the dephasing time of the sample. Experimental observations and theoretical calculations show that the coherent emission from the first laser pulse participates as a time-delayed local electric field to yield the cascaded signal. We arrived at this conclusion based on pulse sequences of degenerate noncollinear femtosecond pulses for which three-pulse FWM is forbidden. Further confirmation was obtained from experiments where the time delay between two pulses were used to form ground or excited state populations, the signal reflected the corresponding ground or excited state dynamics. Although FID is long lived, the femtosecond resolution was found to be maintained in our measurements on gas phase molecular iodine. This is because the FID is modulated in the femtosecond time scale by the molecular dynamics of the system; its intensity and modulation were confirmed using femtosecond time-gated up-conversion measurements.

13. *Ultrafast Dynamics of a "Super" Photobase,* W Sheng, M Nairat, PD Pawlaczyk, E Mroczka, B Farris, E Pines, J. H. Geiger, B. Borhan, M. Dantus, Angewandte Chemie International Edition **57**, 14742 (2018). https://doi.org/10.1002/anie.201806787

    Chemical reactions requiring acidic or basic reagents are mixed and allowed to react. When these reactions require very strong acids or bases, the subsequent neutralization can be environmentally costly. Spatially and temporally addressable chemical reagents in the form of super photoacids or super photobases would revolutionize a number of industrial chemical processes. In this work, the energy of light is used to increase the free energy of a compound and altering its equilibrium constant. Here, a fluorene inspired Schiff base (**FR0**-SB) with a ground state pK_a of 7 is found to have an excited state pK_a^* of 21. Having such a high pK_a^* allows **FR0**-SB to abstract protons from alcohols in a picosecond timescale. The discovery of a "super photobase" indicates that our strategy to crate super photoreagents is valid and may have a significant impact in a number of chemical processes. Dantus is leading collaborative work aimed at novel super photoreagent discovery involving synthesis, theory, and characterization.

ULTRAFAST SPECTROSCOPY FOR BIOMEDICAL SCIENCES

14. *Highly specific label-free molecular imaging with spectrally tailored excitation-stimulated Raman scattering (STE-SRS) microscopy*, CW Freudiger, W Min, GR Holtom, B Xu, M Dantus, XS Xie, Nature photonics **5**, 103 (2011). https://doi.org/10.1038/nphoton.2010.294

    Chemically resolved microscopy promises to provide diagnostic information without the need for contrast reagents. This publication demonstrates for the first-time video rate chemically selective microscopy, of proteins and lipids, in unstained living organisms. The approach is a significant enhancement to the stimulated Raman microscopy work from Xie. Dantus' contribution to this work focused on the accurate phase manipulation of the femtosecond pulses, making video-rate chemically resolved imaging possible.

15. *Femtosecond laser-induced ionization/dissociation of protonated peptides*, CL. Kalcic, TC Gunaratne, AD Jones, M Dantus, and GE Reid, J. Am. Chem. Soc. **131**, 940 (2009). https://doi.org/10.1021/ja8089119

    The application of electrospray ionization (ESI) and matrix assisted laser desorption ionization (MALDI) techniques coupled with tandem mass spectrometry (MS/MS) for the identification and characterization of peptide ions has underpinned the emergent field of proteomics. However, the ability of MS/MS approaches to determine peptide sequences and characterize site specific post-translational modifications in peptides is highly dependent on the ion activation method and the selected precursor ion. Conventional approaches often result in incomplete backbone fragmentation, or the loss of labile groups from side chains containing post translational modifications such as phosphorylation. Thus, there has been great interest in the development of alternate activation methods. This publication describes the implementation and initial results obtained from femtosecond laser-induced ionization/dissociation (fs-LID), a novel strategy for peptide sequence and modification analysis using ultrashort (<35 fs) laser pulses for energy deposition and nonergodic dissociation in a quadrupole ion trap mass spectrometer. fs-LID is capable of phosphorylation mapping by breaking strong bonds while leaving weak bonds intact; and of overall providing a greater number of product ions useful for protein sequencing. This study was followed by additional studies where multiple phosphorylation sites were mapped without the need of special reagents.

16. *Stain-free histopathology by programmable supercontinuum pulses*, H Tu, Y Liu, D Turchinovich, M Marjanovic, JK Lyngsø, J Lægsgaard, , EJ Chaney, Y Zhao, S You, WL Wilson, B Xu, M Dantus, SA Boppart, Nature Photonics **10**, 534 (2016). https://doi.org/10.1038/nphoton.2016.94

    With the goal of providing richer chemical information than present H&E staining in histopathology, an imaging method was developed to provide seven different non-linear spectroscopic signals. The system was demonstrated on excised cancer tumors. The results showed a clear separation between a number of cellular and tissue components without the need for staining. This publication introduced a novel platform for label-free multimodal multiphoton microscopy. Most significantly, analysis of the tumor microenvironment led to improved understanding of the mesoscopic biological organization, tumor cell migration, and angiogenesis. This collaborative work was a significant step towards optical biopsies with greatly enhanced diagnostic information. Dantus' contributions involved pulse shaping for the compression of the industrial Yb laser (240 fs) to sub-10 fs duration and for achieving selective coherent Raman signals.

17. *Use of coherent control methods through scattering biological tissue to achieve functional imaging,* JMD Cruz, I Pastirk, M Comstock, VV Lozovoy, M Dantus, Proceedings of the National Academy of Sciences **101**, 16996 (2004). https://doi.org/10.1073/pnas.0407733101

    We test whether coherent control methods based on ultrashort-pulse phase shaping can be applied when the laser light propagates through biological tissue. Our results demonstrate experimentally that the spectral-phase properties of shaped laser pulses optimized to achieve selective two-photon excitation survive as the laser pulses propagate through tissue. This observation is used to obtain functional images based on selective two-photon excitation of a pH-sensitive chromophore in a sample that is placed behind a slice of biological tissue. Our observation of coherent control through scattering tissue suggests possibilities in multiphoton-based imaging and photodynamic therapy.

18. *Investigating the role of human serum albumin protein pocket on the excited state dynamics of indocyanine green using shaped femtosecond laser pulses*, M Nairat, A Konar, M Kaniecki, VV Lozovoy, M Dantus, Physical Chemistry Chemical Physics **17**, 5872 (2015). https://doi.org/10.1039/c4cp04984e

    Indocyanine green (ICG) is an important compound approved by the Food and Drug Administration for diagnosis and photodynamic therapy (PDT). In many cases, ICG is injected into the patient, and its long wavelength fluorescence is used to find tumors. Laser excitation leads to the creation of reactive oxidation species (ROS), which cause cell death. This publication uncovers how human serum albumin binds the photodynamic therapy agent and prevents the internal conversion that produces the therapeutic triplet state. This is significant because human serum albumin is ubiquitous in humans. Dantus' findings imply the phototherapy agent needs to be modified to enhance its therapeutic configuration, especially when injected.

19. *Multimodal nonlinear optical imaging of unstained retinas in the epi-direction with a sub-40 fs Yb-fiber laser*, GA Murashova, CA Mancuso, JL Canfield, S Sakami, K Palczewski, G Palczewska, M Dantus, Biomedical Optics Express **11**, 5228 (2017). https://doi.org/10.1364/BOE.8.005228

    Ultrafast lasers have potential use in ophthalmology for diagnoses through non-invasive imaging as well as for surgical therapies or for evaluating pharmacological therapies. New ultrafast laser sources, operating at 1.07 µm and sub-40 fs pulse durations, offer exciting possibilities in multiphoton imagining of the retina as the bulk of the eye is relatively transparent to this wavelength, three-photon excitation is not absorbed by DNA, and this wavelength has a greater penetration depth compared to the commonly used 800 nm Ti:Sapphire laser. In this work, we present the first epi-direction detected cross-section and depth-resolved images of unstained isolated retinas obtained using multiphoton microscopy with an ultrafast fiber laser centered at 1.07 µm and a ~38 fs pulse duration. Spectral and temporal characterization of the autofluorescence signals show two distinct regions; the first one from the nerve fiber layer to the inner receptor layer, and the second being the retinal pigmented epithelium and choroid.

ULTRAFAST SPECTROSCOPY FOR DEFENSE

20. *Highly selective standoff detection and imaging of trace chemicals in a complex background using single-beam coherent anti-Stokes Raman scattering*, MT Bremer, PJ Wrzesinski, N Butcher, VV Lozovoy, M Dantus, Applied Physics Letters **99**, 101109 (2011). https://doi.org/10.1063/1.3636436

    The threat of terrorist attacks in public spaces has necessitated the development of chemically resolved imaging at a distance. Taking advantage of the selectivity and sensitivity of coherent Raman spectroscopy, together with the use of sub-10 fs pulses and pulse shaping based on MII, Dantus designed and demonstrated a system to detect explosives in trace quantities, sub-microgram per centimeter squared, at distances of up to 10 meters. The spectroscopic approach demonstrated in this paper could have a significant impact on securing public spaces.