Final Report: Bright Coherent Optical Waveforms from the IR to the VUV

Scientific Accomplishments: Four exciting advances resulted from this award
1. Revealing the Role of Electron-Electron Correlations during the Dissociation of Highly Excited D2 + using Attosecond XUV Pulses
2. Attosecond VUV Coherent Control of Molecular Dynamics
3. Attosecond Coherent Control of Single and Double Photoionization in Argon
4. Chemical dynamics relevant to ionospheric chemistry, interstellar processes and highenergy materials

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ABSTRACT

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1. Revealing the Role of Electron-Electron Correlations during the Dissociation of Highly Excited D2 + using Attosecond XUV Pulses 2. Attosecond VUV Coherent Control of Molecular Dynamics 3. Attosecond Coherent Control of Single and Double Photoionization in Argon 4. Chemical dynamics relevant to ionospheric chemistry, interstellar processes and highenergy materials

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received Paper


TOTAL: 1

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:
Number of Papers published in non peer-reviewed journals:

(c) Presentations
Invited and Keynote Presentations-
Invited talk, Uppsala University, Jan 2014.
Invited talk, AMOLF, Amsterdam, Jan 2014.
Invited talk, APS March Meeting, Denver, CO, March 2014.
Small Lecture, College of William and Mary, March 2014.
Irons Public Lecture, Rutgers University, March 2014.
Colloquium, Princeton University Mechanical Engineering, April 2014.
Colloquium, Cornell University Applied Physics, April 2014.
Colloquium, MIT Chemistry, May 2014.
Colloquium, CUNY Physics, May 2014.
Invited talk, CLEO-QELS Special Symposium for Howard Schlossberg at AFOSR, San Jose, CA, June 2014.
Invited talk, Conference on Light induced dynamics and control of correlated quantum systems, Hohwacht (Germany), June 2014.
Ahmed Zewail Prize talk, Annual Meeting of the American Chemical Society, “For the demonstration, development, and elucidation of the principles of femtosecond two-dimensional Fourier-transform spectroscopy, widely used for the investigation of diverse ultrafast phenomena.”, New Orleans, LA, April 2013. (Presented by David Jonas)

Number of Presentations: 21.00

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Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received    Paper


TOTAL: 2

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received    Paper


TOTAL: 1

Number of Manuscripts:

Books

Received    Book

TOTAL:
Patents Submitted

Patents Awarded

Awards
2015 Honorary Degree of Doctor of Science, National University of Ireland
2015 Elected to Member, American Philosophical Society
2015 Honorary Degree of Doctor of Science, University College Dublin
2015 Honorary Degree of Doctor of Science, Trinity College Dublin
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2012 Willis Lamb Award for Laser Science and Quantum Optics (shared, Margaret Murnane and Henry Kapteyn)
2012 Chair, President’s Committee for the US National Medal of Science (2012-2014) (Murnane)

Graduate Students

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**Student Metrics**

This section only applies to graduating undergraduates supported by this agreement in this reporting period.

- The number of undergraduates funded by this agreement who graduated during this period: **3.00**
- The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields: **0.00**
- The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense: **0.00**
- The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: **0.00**

Names of Personnel receiving masters degrees

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Names of personnel receiving PHDs

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Names of other research staff

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Total Number: 

Sub Contractors (DD882)
Inventions (DD882)

Scientific Progress

Technology Transfer
Four exciting advances resulted from this award –

1. Revealing the Role of Electron-Electron Correlations during the Dissociation of Highly Excited D\textsubscript{2}\textsuperscript{+} using Attosecond XUV Pulses [1]

Understanding electron-electron correlation in matter ranging from the atoms to solids represents a grand challenge for both experiment and theory. For experiment, the challenge is that in real molecular and materials systems, electron-electron interactions occur on attosecond time scales on up. Fortunately, advances in generating attosecond pulses of ionizing radiation are providing new capabilities for uncovering these electron-electron correlations. In our work we used attosecond pulse trains of extreme ultraviolet radiation to coherently populate and probe highly excited states of D\textsubscript{2}\textsuperscript{+} that undergo rapid Coulomb-explosion. By using electron-ion coincidence 3D momentum imaging coupled with advanced ab-initio simulations, we find that contrary to past understanding, the presence of correlations between the two electrons in D\textsubscript{2} can populate excited states that are not normally accessible. Moreover, these correlations strongly persist throughout the entire dissociation process, demonstrating that the entire Coulomb explosion occurs in a strong non-Born Oppenheimer regime. The good agreement between theory and experiment demonstrates that electron-electron correlations can play an important role even in the simplest of molecular systems.

Specifically, we probed the Coulomb explosion of deuterium (D\textsubscript{2}) following single-photon ionization by a 42 eV extreme ultraviolet (XUV) pulse, to make a remarkable and unexpected observation. Photoionization of D\textsubscript{2} leaves most molecules in the D\textsubscript{2}\textsuperscript{+} ion ground state. However, some fraction of the molecules undergo a shake-up excitation, where a second electron is excited simultaneously during photoionization. These excited state D\textsubscript{2}** molecules dissociate, with characteristic energies and timescales that are accessible in experiment, and that are only now fully theoretically tractable. By using a time-delayed infrared probe pulse combined with electron-ion coincidence imaging techniques, we can map the energy and angular distributions of the molecular fragments. When combined with advanced ab-initio calculations that include the coupled nuclear and electron-electron motions, this allows us to make two surprising findings.
First, the shake-up dynamics is not dominated by excitation to the $2p\pi_u$ state—as has been identified previously and as might be expected from a dipole $s \rightarrow p$ transition. Rather, a hybrid state dominated by $2s\sigma_g$ is populated as a result of strong electron-electron correlations in the photoionization process. Second, throughout the Coulomb explosion, the characters of the $2p\pi_u$ and $2s\sigma_g$ states are mixed due to strong electron-electron correlations, demonstrating that the entire Coulomb explosion occurs in a non-Born Oppenheimer regime. This imprints a unique signature on the energy and angular distribution of the molecular fragments.

2. Attosecond VUV Coherent Control of Molecular Dynamics [2]
A breakthrough showing that we can precisely control molecular dynamics on both nuclear (i.e. femtosecond) and electronic (i.e. attosecond) timescales to control the electronic state and outcome of a reaction was published in PNAS. By using VUV light pulses that are tunable in wavelength with adjustable attosecond time structure, we show that it is possible to switch population between electronic excited states, and use this ability to select specific pathways for ionization or dissociation of a molecule. This results represents a milestone advance because almost two decades after attosecond physics was demonstrated, attosecond chemistry has not yet been fully established because the wavelength and bandwidth of attosecond pulses did not match the (VUV) wavelengths and (~<eV) spectral features involved in molecular quantum state control.

![Fig. 2: Attosecond control of the excitation and ionization pathways of D$_2$ on short timescales using complex narrow-band attosecond pulses.](image)

(Right) Simplified potential energy surfaces of the D$_2$ and D$_2^+$. The purple and red arrows represent the VUV harmonics and IR laser pulses used to coherently control the populations of the excited neutral and ion states in the Franck-Condon region through two-pathway quantum interference of electronic wave packets in B, B* (single photon) and EF (two photon) states. (Lower left inset) Calculated electron wave functions of the EF and B excited neutral states. Theoretical predictions show that the electronically excited populations can be switched between the even B and odd parity EF potentials on attosecond timescales, which can in turn control how the molecule vibrates. (Upper left inset) The experimental photoelectron, D$_2^+$ and D$^+$ yields modulate on full and half-cycle attosecond timescales, as the delay between the pump VUV+IR and probe IR pulses is scanned.
Specifically, we used attosecond pulse trains from a comb of VUV harmonics to steer the excited states and dissociation pathways in the simplest molecule - deuterium. We took advantage of interfering electronic wave packets in the excited neutral and singly-ionized molecule to switch the excited electronic state on attosecond timescales, and coherently guide the nuclear wave packets to dictate the way a neutral molecule vibrates. This also allowed us to steer and manipulate the ionization channels. The observed richness and complexity of the dynamics, even in this very simplest of molecules, is both remarkable and daunting, and presents intriguing new possibilities for state-selective chemistry. Finally, through advanced theory, we succeeded in observing and rigorously modeling multi-scale quantum control in a molecule for the first time.

We note that our results represent the first successful scheme for manipulating a chemical reaction using attosecond capabilities. A large component of the attosecond community is increasingly doctrinaire in focusing on isolated attosecond pulses as a requirement to capture the fastest dynamics. Much of this work has evolved into studies that place priority on measuring the shortest possible timescales without a clear physical question, or indeed without any particular connection to new or consequential physical phenomena. Our paper shows where these fast timescales can be relevant to the outcome of a physical process, but to do this requires electronic excitation in a molecule with precise (i.e. attosecond) timing and multi-state selectivity. Our work shows this requires using more complex narrow-band attosecond pulse trains, not broadband attosecond pulses.

3. Attosecond Coherent Control of Single and Double Photoionization in Argon [3]

This work is the first to apply quantum control techniques to double photoionization, which is a fundamental process where a single, high-energy photon ionizes two electrons simultaneously from an atom. To extend coherent control concepts to higher photon energies and shorter time scales, and access core-hole, inner-valance or doubly-excited systems where autoionization, Auger decay, interatomic Coulomb decay, and other ultrafast processes play a role, ultrafast pulses at high photon energies are required. Tabletop high harmonics represent a unique light source that is perfectly synchronized to the driving laser, which can be used to manipulate the fastest electron and molecular dynamics in matter.

In our work we showed that by spectrally separating a comb of high harmonics into VUV and XUV components, we can coherently populate Rydberg states of Ar and Ar⁺ close to the single and double ionization thresholds. Then, in the presence of two IR fields, one co-propagating and phase-locked with the VUV/XUV pump pulse and another that is time-delayed relative to the combined VUV/XUV/IR pump pulse, we show that we can coherently control both Ar⁺ and Ar⁴⁺ total yields using.

![Fig. 3: Schematic showing the relevant energy levels for coherently controlling both single and double ionization pathways in Ar. The tuning range of the harmonics is also shown. The inset shows the ion yield difference when controlling single ionization using quantum interferences alone in (a), or a combination of quantum and optical interferences in (b).](image-url)
two-quantum-pathway electron wave packet interference processes. Furthermore, by tuning the energy of the VUV/XUV photons around different resonant Ar and Ar$^+$ states, we demonstrate an ability to fine-tune the phases of the optical and quantum interferences produced by the combined action of the IR laser and VUV/XUV harmonic fields. This work demonstrates for the first time that attosecond coherent control methods can manipulate double ionization processes on attosecond time scales, where electron-electron interactions play an important role. Double photoionization is a fundamental mechanism where a single photon can ionize two electrons simultaneously from an atom, providing insight into electron/electron dynamical correlation processes. Understanding and coherently controlling these correlations in simple atoms and molecules, where theoretical models are possible, will help develop the more advanced concepts necessary to control ultrafast dynamics in complex molecular systems or novel, strongly-correlated materials.

4. Chemical dynamics relevant to ionospheric chemistry, interstellar processes and high-energy materials [4, 5]

Molecular studies of internal conversion of electronic energy into nuclear motion have, until recently, largely focused on the first one or two excited states. Higher excited states, near 7-10 eV, have been little-explored due to the lack of good experimental approaches - but are critical to ionospheric chemistry, interstellar processes and high-energy materials. Dynamics in this energy range may be expected to exhibit very fast internal conversion, depositing enough vibrational energy to cause molecular dissociation on timescales faster than the validity regime of statistical theories. To probe these processes for the first time on the few-femtosecond timescales on which they occur, we performed time-resolved photoelectron-photoion coincidence (PEPICO) experiments on acetone (which is a prototype for organic molecules in the atmosphere) and methyl azide (a high energy density molecule). In these experiments an 8 eV pump pulse creates a highly excited state in the molecule, and a time-delayed 3.1 eV probe pulse ionizes the excited electron. To untangle the dissociation pathways, we detect the full 3D momentum vectors of the departing electron and of any ionic fragments produced from excess nuclear motion in the cation.

![Diagram related to text](image-url)

**Fig. 4:** a) An energy level diagram illustrating highly excited states of acetone and the two lowest cation states, with arrows indicating various pump-probe pathways investigated. b) An illustration of HHG upconversion techniques and PEPICO detection. c) Photoelectron energy vs. time plots in coincidence with acetone molecular ion (left) and the acetyl fragment ion (right).
This new capability allows us to uncover the correct dissociation pathways for highly-excited molecules. In acetone we re-assign the 8 eV state as a Rydberg-valence mixed state between $n_2 \rightarrow 3p$ and $\pi \rightarrow \pi^*$, which internally converts to lower Rydberg states with a time constant of 340 fs. This mixing produces a non-separable electronic wavefunction, which can frustrate typical photoelectron imaging experiments and produce incorrect state assignments. The flexibility of our waveguide-based low-order harmonic generation allows us to measure 1-photon ionization with the 7th and 9th harmonics under identical experimental conditions as our pump-probe experiments, providing reliable identification by a comparison between 1 and 2-photon processes and access to multiple cation states.

In methyl azide we find Rydberg-Rydberg mixing between series converging to different ion states: $(HOMO \rightarrow 3p)$ and $(HOMO - 1 \rightarrow 3s)$. This mixing opens up relaxation pathways which are otherwise symmetry-forbidden, and represents an unanticipated phenomenon in the ultrafast dynamics of low Rydberg molecules. This mixed Rydberg state undergoes fast (~20 fs) wavepacket motion before undergoing a surprisingly quick (~25 fs) internal conversion. Again, the unambiguous assignment of the mixed electronic state required access to both relevant cation states as well as comparison to 1-photon ionization data provided by high harmonic generation.

Fig. 5: After ionization, the methyl azide ion may undergo a sequential 3-body breakup. In our 8.0 eV pump – 1.6 eV probe experiment, we measure the time-dependent branching ratios, revealing how the excited state dynamics influence the post-ionization breakup. Time-dependent photoelectron spectra taken in coincidence with the fragment reveal the mixed character of the excited electronic state.

Publications from ARO Support
**Honors during grant**

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