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Exciting and probing attosecond multielectron dynamics in chiral molecules at FERMI

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Little is known about attosecond multielectron dynamics in photo-excited chiral molecules and their coupling to vibronic dynamics triggered by photoexcitation. Such photodynamics is of great importance for understanding photo-processes triggered in chiral molecules by electromagnetic radiation in outer space; this has important implications in bio-astrophysics and in the search for the origin of life and homochirality on Earth. The difficulty in studying such dynamics is due to a combination of factors. First, even localized excitations quickly redistribute among many degrees of freedom along the multidimensional landscape of the excited molecular states. Thus, it is very hard to follow the individual pathways. Second, the photoelectron spectrum of excited molecules corresponding to Rydberg excitations and valence holes of the final-state cation has a fundamentally many-body nature, and is challenging to resolve both computationally and experimentally due to broad featureless regions of overlapping lines.

We have discovered a strategy for contrastive detection of such states by exploiting several unique and powerful features of our spectroscopic scheme: it is (i) sub-cycle, (ii) interferometric and (iii) differential. The detection is enabled by the interference of two quantum pathways generated by the two phase-locked linearly polarized pulses in orthogonal configuration readily available at FERMI. The advantages are: (i) the phase-dependent signal arises only when the w and 2w pathways interfere, providing unique sensitivity to dynamics excited by the w-field; (ii) by tuning w, we can select a specific intermediate resonance for creating an excited many-body state.

This interferometric spectroscopy combines "the best of the two worlds": high temporal resolution due to the sub-cycle phase lock, and high spectral resolution due to long duration of involved pulses. At FERMI, we can routinely achieve <40 meV spectral resolution and <40 as temporal resolution –the cutting edge of attosecond spectroscopy. The detection relies on measuring angle- and energy-resolved photoelectron distribution – one of the most direct spectroscopic tools. The interferometric detection of photoelectron signals offers an additional level of selectivity and robustness. Our observable comes from the interference of two quantum pathways: the reference –one-photon ionization by the 2w field, and the signal –the resonant photoexcitation by the w field into an excited state with an inner-valence hole that experiences Auger-Meitner decay assisted by absorption of the second w photon. Since the interference requires that both pathways lead to the same final state, i.e. the same energy/emission angle of the electron, the same state of the parent ion, and the same states of all fragments in case of fragmentation, it is an extremely selective probe of photodynamic pathways. The interferometric, i.e. two-color phase delay-dependent signal, is fundamentally sub-cycle and thus, for w~10 eV, only sensitive to multielectron dynamics occurring in less than 40 as after excitation with the first w photon. In fact, the majority of excitation pathways will yield fragmentation before the absorption of the second w photon, destroying the purity of the final quantum state and with it the interference with the reference 2w pathway. Thus, the two-color phase-dependent photoionization signal is a unique messenger of attosecond multielectron dynamics and subsequent chemical change.

Finally we use differential measurement to complete contrastive detection scheme. By subtracting photoelectron spectra recorded for the same two-color phase but for two slightly different photon frequencies w and w+dw we eliminate non-resonant background.

In our experiment we resolved the enantio-sensitive molecular phase associated with the laser-assisted Auger-Meitner decay and involving the contribution of 8 two-hole one-particle states in a chiral molecule propylene oxide. The multielectron states are associated with holes in Homo, Homo-1, Homo-2 and electron in Rydberg orbitals 3p,4p,3s in excellent agreement with calculations using ADC-family of methods. Understanding

enantio-sensitive attosecond multielectron dynamics in excited chiral molecules is an important unsolved challenge in several fields: ultrafast spectroscopy, femtosecond mass-spectrometry, chemistry to name just a few. Addressing this challenge for randomly oriented chiral molecules brings our research well beyond the current state of the art in those fields.

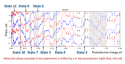

Figure 1: Fig. 1Experimental results obtained at FERMI. The enantio-sensitive molecular phase associated with two-hole one particle states (vertical lines) vs photoelectron energy, blue - right enantiomer, red -left enantiomer.

Authors: FACCIALA', Davide (CNR-IFN); AYUSO, David (Department of Chemistry, Molecular Sciences Research Hub, Imperial College London, W12 0BZ London, UK); LÖHR, Alexander G. (Max Born Institute for Nonlinear Optics and Short Pulse Spectroscopy (MBI Berlin)); SCHNEIDER, Alexander; SENFTLEBEN, Arne (University of Kassel); ROOS, Aycke; CALLEGARI, Carlo (Elettra - Sincrotrone Trieste); VOZZI, Caterina (CNR-IFN); CHRISTOU, Elena Aethra (Max Born Institute for Nonlinear Optics and Short Pulse Spectroscopy); GHOSH, Jayanta; MIKOSCH, Jochen; TERENTJEVAS, Justas (Max-Born Institute); PRINCE, Kevin (Elettra Sincrotrone Trieste); UEDA, Kiyoshi; OBERTI, Linda (Politecnico di Milano); GERMEROTH, Lukas; RUBERTI, Marco (Imperial College London); MIRAHMADI, Marjansadat (Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie Berlin); PADOVANI LEKSCHAS, Maximilian; DI FRAIA, Michele; PLEKAN, Oksana (Beamline scientist at FERMI/LDM); MAIER, Pablo Martin (Max Born Institute for Nonlinear Optics and Short Pulse Spectroscopy, Max-Born-Straße 2A, 12489 Berlin, Germany); FLORES, Philip Caesar (Max Born Institute); Dr KOLORENC, Premysl (Faculty of Mathematics and Physics, Charles University); HEILEMANN, Rico; PATCHKOVSKII, Serguei (Max-Born-Institut, Max-Born-Str. 2A, 12489 Berlin, Germany); BAUMERT, Thomas; Dr AVERBUKH, Vitali (imperial College London); SMIRNOVA, Olga

Presenter: FACCIALA', Davide (CNR-IFN)

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