

Imaging the Ultrafast Electronic Dynamics of Polyatomic Molecules:  
Molecular Frame Photoelectron Imaging, Quantum Control, Attosecond Strong Field Physics

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The most general molecular dynamic processes involve the coupled flow of both valence electronic charge and vibrational energy. Time-Resolved Photoelectron Spectroscopy (TRPES) is a powerful probe of ultrafast non-adiabatic dynamics in polyatomic molecules, as it simultaneously observes both electronic and vibrational dynamics [1]. The most detailed information, however, obtains from observing these electronic dynamics in the Molecular Frame. Time-Resolved Coincidence Imaging Spectroscopy (TRCIS) images the kinematically complete 3D momentum vectors of both photoions and photoelectrons in coincidence and as a function of time. This allows for study of the time evolution of both scalar and vector correlations during molecular processes such as chemical reaction. One important Molecular Frame vector correlation permits dynamical imaging of electronic wavefunction evolution [2]. Another general method, based on nonresonant laser pre-alignment, also permits direct time-resolved imaging of electronic wavefunction evolution in the Molecular Frame [3]. Furthermore, this method permits disentangling of the purely electronic dynamics from the strongly coupled nuclear dynamics, even during a non-adiabatic chemical reaction [4].

Since electric forces underlie all of solid state and molecular physics, controlling material processes with electric fields is a natural approach. We discuss Quantum Control using the non-resonant, non-perturbative 2<sup>nd</sup> order Dynamic Stark Effect as a new and powerful tool. Dynamic Stark Control (DSC), which uses the electric field intensity envelope of a laser pulse rather than its frequency content, can be used to control non-adiabatic molecular dynamics without any net absorption of light [5]. We illustrate the use of DSC in creating molecular frame alignment, a method important for time-resolved diffraction experiments. Using a cross-polarized pulse sequence, we demonstrate full 3D field-free axis alignment of an asymmetric top rotor – transiently ‘fixing the molecule in space’ in all three dimensions in order to make a field-free measurement [6].

As laser fields get stronger still, new laser-matter physics emerges for polyatomic systems wherein both the single active electron continuum and the adiabatic approximation, both implicit in the standard (quasi-static) atomic models, can fail dramatically. A new Nonadiabatic Multi-Electron (NME) dynamics emerges [7] which has important consequences for all strong field processes in polyatomic molecules, including high harmonic generation (HHG) and attosecond spectroscopy. Evidence for multiple electronic continua is seen in the HHG spectroscopy of polyatomic molecules [8]. We present a new attosecond molecular physics method, Channel-Resolved Above Threshold Ionization (CRATI), which directly and unambiguously reveals the multiple electronic continua active in the attosecond strong field dynamics of polyatomic molecules [9].

[1] Nature 401, 52, (1999).

[2] Science 311, 219 (2006).

[3] Science 323, 1464 (2009).

[4] Nature Physics 10.1038/nphys1980 (2011)

[5] Science 314, 278 (2006).

[6] Physical Review Letters 97, 173001 (2006); 97, 173001 (2006).

[7] Physical Review Letters 86, 51 (2001); 93, 203402 (2004); 93, 213003 (2004).

[8] Science 322, 1207 (2008)

[9] Nature Physics (*under review, May 2011*)