

Ultrafast Electronic-Nuclear Dynamics from the Molecule's Point of View

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Molecular dynamics involves ultrafast rearrangements of both electronic charge and vibrational energy and the non-Born-Oppenheimer coupling of these degrees of freedom is a ubiquitous feature in polyatomic systems. Time-Resolved Photoelectron Spectroscopy (TRPES) is a powerful probe of these processes in polyatomic molecules because it is sensitive both electronic and vibrational dynamics [1]. The TRPES method, in both its energy- and angle-resolved implementations, has been applied to a broad range of problems [2]. Ideally, one would like to observe these ultrafast processes from the molecule's point of view – the Molecular Frame – thereby avoiding the loss of information due to orientational averaging. This can be achieved by Time-Resolved Coincidence Imaging Spectroscopy (TRCIS) which images 3D recoil vectors of both photofragments and photoelectrons, in coincidence and as a function of time. This permits Molecular Frame imaging of valence electronic dynamics during a chemical reaction [3].

In order to enhance studies of ultrafast chemical dynamics, we apply the tools of Quantum Control, using specifically the non-resonant Dynamic Stark Effect. Dynamic Stark Control (DSC), which uses the electric field intensity envelope of a laser pulse rather than its frequency content, can control photochemical reactions *without* any net absorption of light [4]. DSC is also the interaction underlying molecular alignment and applies to field-free 1D and full 3D alignment [5]. Using laser alignment, we can transiently fix a molecule in space, yielding a more general approach to direct Molecular Frame imaging of valence electronic dynamics during a chemical reaction [6, 7].

The burgeoning field of Attosecond Science, which offers direct observation of purely electronic dynamics, emerged out of the physics of Strong Field Ionization (SFI). In strong fields, a new laser-matter physics emerges for polyatomic systems [8] wherein both the single active electron picture and the adiabatic electron response, both implicit in the standard models, can fail dramatically. This has important consequences for all attosecond strong field spectroscopies of polyatomic molecules, including high harmonic generation (HHG) [9]. We present an experimental method, Channel-Resolved Above Threshold Ionization (CRATI), which directly unveils the electronic continua participating in the attosecond molecular response [10]. Using molecular alignment techniques, the CRATI method can be applied in the Molecular Frame, offering the Molecule's View of laser-driven electronic dynamics [11].

[1] Nature **401**, 52, (1999). [2] Chemical Reviews **104**, 1719 (2004). [3] Science **311**, 219 (2006). [4] Science **314**, 278 (2006). [5] Physical Review Letters **94**, 143002 (2005); **97**, 173001 (2006). [6] Science **323**, 1464 (2009). [7] Nature Physics **7**, 612 (2011). [8] Physical Review Letters **86**, 51 (2001); **93**, 203402 (2004); **93**, 213003 (2004). [9] Science **322**, 1207 (2008). [10] Science **335**, 1336 (2012). [11] Physical Review Letters **110**, 023004 (2013)