

## Mapping Atomic Motions with Ultrabright Electron (and X-ray) Sources: The Chemists' Gedanken Experiment Enters the Lab Frame

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Electron sources have achieved sufficient brightness to literally light up atomic motions on the primary timescales of chemistry. The greater stability of high brightness electron sources in comparison to x-rays, with comparable on detector signal, results in significantly improve SNR over other possible sources for structural studies in the relevant 100 fs time domain. The main differences are related to ease of sample preparation. The higher SNR with electron sources is critical to achieving low enough excitation to avoid multiphoton processes in the phototriggering of the structural dynamics. In this context, recent advances in rf pulse compression and relativistic regimes for electron sources will be touched up. However, the most robust e source is the simple compact electron gun concept that has now reached new brightness levels capable of resolving unit cells up to 4 nm (scale of protein systems). These sources provide a direct observation of the far from equilibrium atomic motions central to chemistry for which general reduction principles are emerging. Studies of formally a photoinduced charge transfer process in charge ordered organic systems has directly observed the most strongly coupled modes that stabilize the charge separated state (Gao et al Nature 2013). It was discovered that this nominally 280 dimensional problem distilled down to projections along a few principle reaction coordinates. Similar reduction in dimensionality has also been observed for ring closing reactions in organic systems (Jean-Ruel et al JPC B 2013). Even more dramatic reduction in complexity has been observed for the material,  $\text{Me}_4\text{P}[\text{Pt}(\text{dmit})_2]_2$ , which exhibits a photo-induced metal to metal centre charge transfer process. The large-amplitude modes can be identified by eye from the full atomically resolved movie and involve a dimer expansion and a librational mode. These studies will be further amplified by recent studies of spin cross over molecular systems and a direct observation of Pauli explosion in alkali halides (Hada et al, Nature Comm, 2014) – the reverse of the classic “electron harpooning” reaction that helped establish transition state concepts. This reduction principle to a few key modes appears to be general, even for very complex systems. The far from equilibrium motions that sample the highly anharmonic barrier region are strongly coupled, which in turn leads to highly localized motions projected onto the reaction coordinate. In this respect, one of the marvels of chemistry, and biology by extension, is that despite the enormous number of possible nuclear configurations for any given construct, chemical processes reduce to a relatively small number of reaction mechanisms. We now are beginning to see the underlying physics for these generalized reaction mechanisms. The “magic of chemistry” is this enormous reduction in dimensionality in the barrier crossing region that ultimately makes chemical concepts transferrable. With a large enough basis, it may be possible to characterize reaction mechanisms in terms of reaction modes, or reaction power spectra, in analogy to the characterization of equilibrium fluctuations in terms of vibrational normal modes. In this respect, recent results from the LCLS will be presented as part of road map to connect the underlying chemistry to biological functions.