Ab Initio Solution of Structural Dynamics with Ultrafast Electron Diffraction and Charge Flipping

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Abstract: Ultrafast electron diffraction is used to probe the photo-induced structural dynamics of single crystal $(EDO\text{-}TTF)_2PF_6$ with femtosecond time resolution. Structure factor phases at key time points are solved *ab initio* using the charge-flipping method.

OCIS codes: 320.2250 Femtosecond phenomena; (320.7130) Ultrafast processes in condensed matter, including semiconductors

1. Introduction

Diffraction methods have played an important role in determining the structure of molecules and crystals over the past hundred years. The advent of coherent femtosecond X-ray and electron pulse sources has enabled structural exploration of materials with a low radiation-damage threshold, as well as short-lived intermediate states in chemical reactions [1]. However, the general "phase problem" inherent to crystallography remains a challenge. Conventional diffraction studies can only measure the modulus of the structure factors; without the complex phase, the data cannot be easily inverted from momentum space to position space. A solution is to collect data at multiple sample orientations and apply constrained refinement of a rough structure against the three-dimensional set of intensities [2,3]. Recently, an iterative algorithm called Charge Flipping (CF) has been developed to offer a simpler, more efficient, and *ab initio* method for solving the phase problem [4,5]. It does so by modifying a random scattering function in momentum and position space alternatively to generate a highly localised and positive-definite solution with structure factor magnitudes matching given data.

As a proof of concept, we present preliminary work that combines the high-source intensity and sub-picosecond time resolution of our ultrafast electron diffraction (UED) setup with the CF method to directly reconstruct the time-dependent structure of $(EDO\text{-}TTF)_2PF_6$ (EDOP). This molecular system undergoes a photo-induced phase transition and exhibits femtosecond structural dynamics [6]. We have chosen it as our model system because it is an effective stand-in for more complex ones and has a multi-picosecond transient intermediate state whose structure has been determined from a refinement model alone [7].

2. Experimental Methods

Electron diffraction patterns were collected using our 95 kV DC electron gun with RF compression. A 270 nm laser pulse back-illuminates a 20 nm thick gold photocathode to release a high density electron bunch which is then accelerated to a kinetic energy of 95 keV and recompressed by 3-GHz RF cavity before arriving at the sample position with a duration of 430 fs.

Monocrystalline EDOP were grown and ultramicrotomed to 100-nm thick slices. The 500 × 500-μm samples are then mounted on standard TEM copper meshes. They are in turn placed on a sample holder assembly cooled to 230 K with a liquid nitrogen cold finger. Multiple crystal orientations are sampled using the rotation stage that supports the sample holder. Photoexcitation of the samples is provided by a pump pulse (wavelength: 800 nm, duration: 60 fs, repetition rate: 10 Hz, excitation fluence: 0.55 mJ/cm^2, spot size: 400 μm FWHM) from a Ti:Sapphire regeneratively amplified laser system. The polarisation was linear and chosen to be along the stacking axis of EDOP. The incident angle is varied to ensure that the excited fraction (~10%) is constant over the sampled orientations. The entire setup is held under a background vacuum pressure of 10^{-8} mbar.

The CF method is based on the assumption that distribution of scattered electron in momentum space is proportional to the Fourier transform of the electrostatic potential function. When the electron path length in the sample is long, there could be multiple scattering events and this proportionality would no longer be exact. In addition, the sample surface area is limited and does not allow arbitrarily high longitudinal rotations. As such, sample rotation would need to be minimised. We have performed simulations to determine the minimal momentum space coverage (i.e. orientation sampling) to ensure reasonable convergence of the CF algorithm. Calculations are also being done to study the effect of increased path length under sample rotation on CF structure solutions.

3. Preliminary Results

Using a low-temperature EDOP structure model from previous measurements, model calculations of kinematic electron diffraction show that full coverage of momentum space is not necessary for the CF algorithm. For a spatial resolution of 1 Å and a coverage as low as 50% (i.e. ±30° longitudinal rotation), convergence is achieved without any additional constraints and yields a structure solution which is comparable to the starting structure. The lower bound is reached and convergence fails when there is insufficient structure factor information perpendicular to the 0° plane to constrain the solution along the transverse direction.

We are focusing on three key points in the phase transition of EDOP: initial low-temperature state at $t < 0$ ps, the transient intermediate state at $t = 3$–10 ps, and the final high-temperature state $t > 1$ ns. For the first and last cases, diffraction measurements have been done with longitudinal rotations up 40° (see Fig. 1a); the scattering electrostatic potentials were reconstructed and found to be consistent with the known ones (see Fig. 1b). By taking the peak centroids in the potential as atomic positions, spatial resolutions of ~1.3 Å and ~2.1 Å were found along the directions longitudinal and transverse to the 0° plane.

Data collection is in progress to capture a similar data set for the intermediate state. Here, the challenge is to maintain subpicosecond time resolution while maintaining a fairly constant excitation density and obtaining sufficiently a high signal-to-noise level to extract useful structure factor intensities. When this is achieved, a full reconstruction of the transient molecular structure, comparable to the unexcited ones, would be obtained.

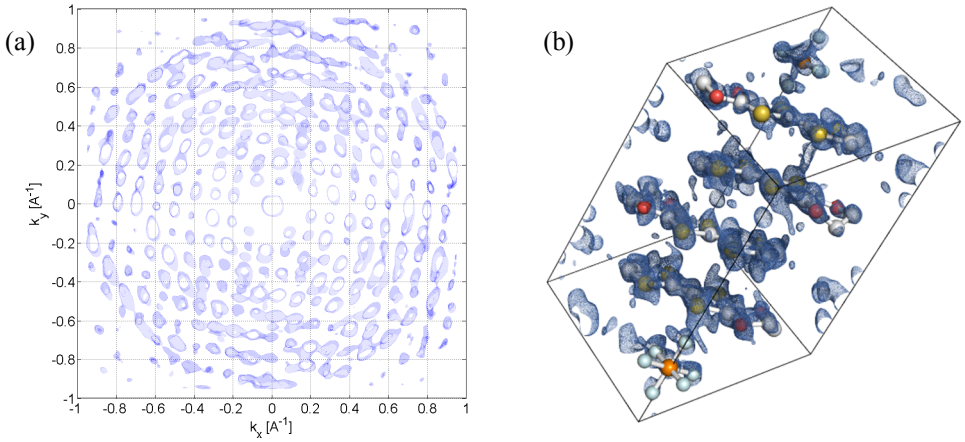

Figure 1. (a) Top view of 3D isosurface plot of measured electron diffraction intensities in momentum space (k_x,k_y-plane) and sample rotation angle (z-axis). (b) 3D isosurface plot of electrostatic potential of low-temperature of EDOP solved *ab initio* using our UED data and the CF algorithm, overlaid over the molecular structure from published data [7].

4. References

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