Observation of counterion effects and dimensionality reduction in single-crystal (EDO-TTF)₂SbF₆ with ultrafast electron diffraction

Lai Chung Liu[1], *Yifeng* Jiang[2], *Henrike M.* Mueller-Werkmeister[2], *Cheng* Lu[2], *Gustavo* Moriena[2], *Manabu* Ishikawa[2], *Yoshiaki* Nakano[2], *Hideki* Yamochi[2], and *R. J. Dwayne* Miller[1, *]

[1]Departments of Physics and Chemistry, University of Toronto, 80 St. George St., Toronto, Ontario, M5S 3H6, Canada

[2]Max Planck Institute for the Structure and Dynamics of Matter, Luruper Chaussee 149, 22607 Hamburg, Germany

[3]Institute of Chemistry, University Potsdam, Karl-Liebknecht-Strasse 24-25, 14476 Postdam, Germany

[4]Research Centre for Low Temperature and Material Sciences, Kyoto University, Sakyo-ku, Kyoto, 606-8501, Japan

[5]Division of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto, 606-8502, Japan

Abstract. Femtosecond electron diffraction is used to resolve structural dynamics in single-crystal (EDO-TTF)2XF6 (X = P, Sb). The retarded and lower-dimensional dynamics of the latter illustrate the dominant role of counterion motion in stabilizing electron transfer.

1 Introduction

The organic salts (EDO-TTF)₂XF₆, where EDO-TTF is 4,5-ethylenedioxy-trathiafulvalene and X is a pnictogen (P, As, Sb), are part of a class of molecules that undergo an insulator-to-metal (I–M) phase transition when subject to various perturbations [1, 2]. Below the transition temperature $T_{I–M}$, the material is in an insulator 'low temperature' (LT) phase, wherein the electron-donating EDO-TTF cations form stacks separated by sheets of electron-accepting XF₆ counterions and charge is localized on every other cation (Figure 1a). Above $T_{I–M}$, the molecules exist in the metallic 'high-temperature' (HT) phase: charge is delocalized evenly over all cations and conduction can occur along the stacking direction. Collective interactions lead to periodic distortions in the crystal structure: charged cations are flat while the neutral cations become bent, causing structural distortion and unit cell doubling during the I-M transition. This change in electron distribution can also be induced by photoexciting into a charge transfer band. At low excitation, it is found that this process is truly a localized

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[*] Corresponding author: dmiller@lphys.chem.utoronto.ca

molecular event, thus providing an ideal system for exploring electron transfer dynamics and the effects of spectators like the medium and counterions on reaction dynamics.

A 95-kV DC-RF hybrid electron diffractometer is used to image transient electron diffraction patterns in transmission, as described previously in [4, 5]. Single-crystals of (EDO-TTF)$_2$SbF$_6$ were prepared by electrocrystallization and (500 μm × 500 μm × 150 nm) samples are cleaved from them by ultramicrotomy. During the measurements, the samples are cooled to 180 K, well below T_{I-M} = 242 K to avoid thermal hysteresis.
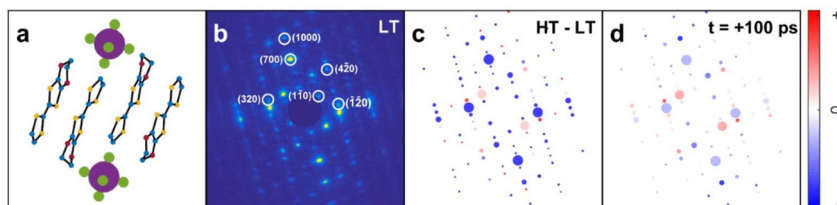

Fig. 1. (a) Crystal structure of (EDO-TTF)$_2$SbF$_6$. (b) Electron diffraction pattern of the LT phase. Integrated change in intensity between the ground LT state and (c) the HT state, and the photoexcited state after 100 ps [3].

3 Results and Discussions

Previous studies on the photoinduced electron transfer process in (EDO-TTF)$_2$PF$_6$ using ultrafast electron diffraction (UED) followed the atomic motions convoluted to the electron transfer. Of the >100 possible nuclear modes or dimensions, the lattice reorganization could be completely reconstituted through the activation of three molecular modes [5]. These modes were not completely independent but shown to be highly correlated to the slowest mode, which primarily involves the observed counterion motion in response to changes in the local electric field as the dominant reaction mode.

A corollary to this conclusion is that substituting for a larger counterion should significantly change the dynamics or degree of correlation amongst the reaction modes. The present work and the UED measurements [3] herein support this prediction: the difference UED pattern of the thermal HT state does not match that of the photoexcited state at t = +100 ps (Figure 1c, d), suggesting that the photoinduced structural dynamics of the photo is distinct from the thermally driven one.

As seen in Figure 2, the changes in diffraction intensity are different between the PF$_6$ and SbF$_6$ derivatives not just in reciprocal space but in time as well. The former (panel b) is characterized by a sub-ps peak, a few-ps intermediate state, and a relaxation to the HT-like final state; the latter (panel a) only exhibits a multi-ps evolution to a non-thermal state.

The present work [3] uses a novel approach that allows the structural dynamics to be understood wholly within reciprocal space. We apply singular value decomposition (SVD) and global analysis to our datasets, yielding the fitted results in Figure 2c, d. In conjunction, Pearson correlation coefficients (P_{HT}, P_{LT}) are calculated for the time-resolved diffraction data with respect to the thermally accessible states to construct the respective conformation trajectories (Figure 2e, f). With these two approaches, we find that the three molecular modes of the PF$_6$ derivative found earlier [5] are recovered as the three principal SVD components and that the dimensionality of the SbF$_6$ dynamics is one less than the PF$_6$ one.

Given the clear counterion dependence, we conclude that it is the counterion motion that directs the lattice reorganization to stabilize the charge separation and in turn destabilize the charge order, moving the system towards the metallic state. The lower dimensionality also

provides evidence that the structural transition is dominated by only a few motions, as opposed to an equipartition over all possible motions.
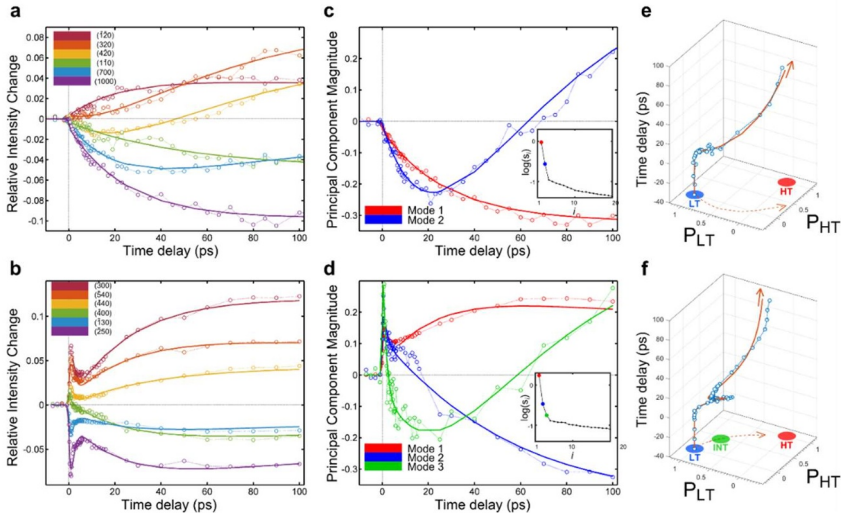

Fig. 2. Comparison of UED results for both $(EDO\text{-}TTF)_2XF_6$ derivatives, top panels for X = Sb and bottom panels for X = P. The left panels show relative change in the intensity of select diffraction spots. The middle panels show the results of the SVD analysis, wherein the thin lines are the major right-singular vectors, the thick lines are global exponential fits, and the insets are logarithmic plots of the singular values. The right panels are trajectories in Pearson correlation space [3].

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