Vibrational selection rules and charge order pattern in BEDT-TTF k-phase salts

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The salts of bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) molecule and its variants play a central role among molecular quantum materials. Most salts have stoichiometry $(\text{BEDT-TTF})_2^+ X^-$ (X^- is a closed-shell anion), i.e., one electron per pair of molecules. The presence of itinerant electrons gives rise to a plethora of quantum phenomena, like superconductivity, charge fluctuations, charge-ordering, ferroelectricity, spin liquids state and so forth.

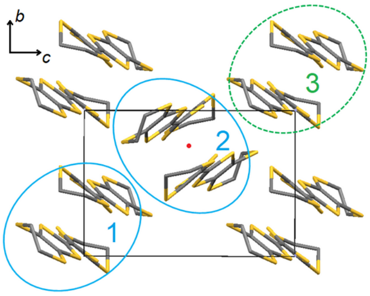

Figure 1: Typical chessboard pattern of k-BEDT-TTF salts. Hydrogens and anions not shown.

Vibrational spectroscopy is an invaluable tool for the characterization of BEDT-TTF salts. It has been indeed used for: Investigate the average charge residing on the molecules [1], as well as charge fluctuations and localization [2]; Estimate the Hubbard parameters (hopping integrals, on-site electron-electron repulsion) and the strength of electron-molecular vibration (e-mv) coupling [3,4]. The e-mv coupling indeed manifest itself by very strong IR bands due to out-of-phase coupling of totally symmetric vibrations in a dimerized structure.

The focus of this talk is on the so-called k-phase, characterized by BEDT-TTF dimers arranged in a chessboard pattern inside the crystal (Figure 1). This dimerized structure of course displays the strong e-mv induced bands in the IR, typically in the 1100-1300 cm^{-1} region. Some of these salts become superconductors, whereas some undergo a charge localization (charge order, CO), ending in a ferroelectric state. Everyone so far has assumed that the CO is within a dimer, namely the the intradimer inversion center (red dot in Figure 1) is lost. However, every vibrational spectroscopist knows the very stringent mutual exclusion selection rule: In the presence of an inversion center, no normal mode can be both IR and Raman active. When the inversion is lost, IR modes may become Raman active and vice-versa. Therefore, if the intradimer inversion center is lost at the CO transition, the strong IR e-mv induced band should become Raman active. Since no Raman band is seen in the relevant spectral region 1100-1300 cm^{-1}, I am proposing a change of paradigm: Different dimers (e.g. 1 and 2 in Figure 1) bear a different average charge, the inversion center is maintained [4]. This is a rather indirect proof. Here I shall present additional evidences in support of my hypothesis.

References

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