Ab initio Calculation Approach to the Intramolecular Charge Ordering in (TTM-TTP) I$_3$

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Charge-ordering phenomena have been one of the main research subjects in molecular solids. In (TTM-TTP)I$_3$ crystal [1], a new type of charge-ordered (CO) state has been claimed by the Raman-scattering [2] and the X-ray [3] measurements. We call this state the “intra-molecule CO” state, where the inversion center on the middle point of the TTM-TTP molecule is lost and the charge is disproportionated within the molecule. This state cannot be described by the conventional theoretical treatment based on the single-site approximation of the molecule, i.e., based on the single molecular-orbital (MO) approximation.

We examine characteristics of the frontier molecular orbitals of the TTM-TTP (Fig.1.) molecule based on the multi-configuration ab initio calculation. It is shown that the energy levels of the singly-occupied molecular orbital (SOMO) and of the second highest-occupied molecular orbital (HOMO-1) are close to each other, i.e., this system can be regarded as an effectively two-orbital system. We find that the SOMO and HOMO-1 have common wave function with respect to the left and right parts of the TTM-TTP molecule and the SOMO has a bonding character of them while the HOMO-1 has an anti-bonding character. In order to clarify this nontrivial feature of these MOs, we divide virtually the TTM-TTP molecule into the three fragments; namely, left, right, and center fragments. Based on this three-fragment model, we clarify the relevant interactions between the fragments which can reproduce the MOs obtained from ab initio calculations. Furthermore, in order to analyze the symmetry breaking observed experimentally at low temperature, we take into account neighboring two TTM-TTP molecules and analyze the intra-molecular CO state explicitly. The MOs are reconstructed due to the mixing of each fragment, yielding the redistribution of the Mulliken charge, i.e., the electron disproportionation within the TTM-TTP molecule.