Supplemental Material for:
Direct detection of dimer orbitals in $Ba_5AlIr_2O_{11}$

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(Dated: December 26, 2018)

I. DETAILS OF THE DFT CALCULATIONS

Fig. S1 show the crystal structure of $Ba_5AlIr_2O_{11}$. It has an orthorhombic structure with space group *Pnma* (No. 62). There are two inequivalent Ir sites and a total of eight Ir sites in the unit cell. The lattice parameters and the atomic positions used in the DFT calculations are taken from Ref.[1]. The DFT part of calculations have been done using the Vienna Ab-initio Simulation Package (VASP)[2] with projector augmented-wave (PAW) pseudopotentials[3,4] and Perdew-Burke-Ernzerhof parametrization of the generalized gradient approximation (GGA-PBE) exchange-correlation functionals[5]. The energy cutoff of the plane-wave basis was set to be 400 eV, and a Γ-centered $5 \times 15 \times 8$ K-point grid was used.

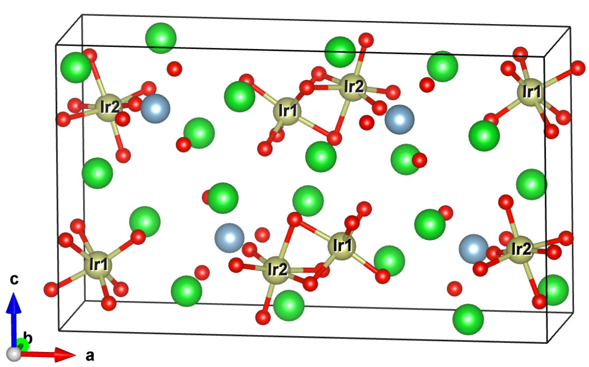

FIG. S1. The unit cell of $Ba_5AlIr_2O_{11}$.

II. DETAILS OF RIXS CROSS-SECTION

The Hamiltonian describing the valence electrons of the Ir1-Ir2 cluster can be written as,

$$\hat{H}_{\text{tot}} = \hat{H}^1 + \hat{H}^2 + \hat{V}^{12}, \tag{S1}$$

$$\hat{H}^{1(2)} = \hat{H}_U + \hat{H}_{\text{SOC}} + \hat{H}^{1(2)}_{\text{CF}}. \tag{S2}$$

The Hamiltonian $\hat{H}_{\text{inter}}$ for the intermediate configuration of the RIXS process where a $2p$ core-hole is created in either of the two Ir sites is obtained by adding a core-hole potential term $\hat{V}_{\text{core}}$ and a SOC term of the core electrons $\hat{H}_{\text{core-SOC}}$ to $\hat{H}_{\text{tot}}$,

$$\hat{H}^{1(2)}_{\text{inter}} = \hat{H}_{\text{init}} + \hat{V}^{1(2)}_{\text{core}} + \hat{H}^{1(2)}_{\text{core-SOC}}, \tag{S3}$$

where, 1(2) means that the core-hole is created in site Ir1(Ir2).

$$\hat{V}_{\text{core}} = -U_{dp} \sum_{\alpha,\beta} \hat{d}^\dagger_\alpha \hat{d}_\alpha (1 - \hat{p}^\dagger_\beta \hat{p}_\beta) \tag{S4}$$

$$+ \sum_{\alpha\beta\gamma\delta} F_{\alpha\beta\gamma\delta} \hat{p}^\dagger_\alpha \hat{d}^\dagger_\beta \hat{p}_\gamma \hat{d}_\delta + h.c. \tag{S5}$$

$$+ \sum_{\alpha\beta\gamma\delta} G_{\alpha\beta\gamma\delta} \hat{p}^\dagger_\alpha \hat{d}^\dagger_\beta \hat{d}_\gamma \hat{p}_\delta + h.c. \tag{S6}$$

where, the first line is the direct Coulomb interaction between a $5d$ electron and a $2p$ core-hole and it is parameterized by U_{dp}. We set $U_{dp} = 2.0$ eV in our simulations. The second and third lines describe the exchange interaction between $5d$ and $2p$ electrons. $F_{\alpha\beta\gamma\delta}$ is parameterized by F^0_{dp}, F^2_{dp} and $G_{\alpha\beta\gamma\delta}$ is parameterized by G^1_{dp}, G^3_{dp}. $F^0_{dp}, F^2_{dp}, G^1_{dp}, G^3_{dp}$ are calculated by Cowan's atomic code[6] and they are: $F^0_{dp} = 0.088$ eV, $F^2_{dp} = 1.107$ eV, $G^1_{dp} = 0.957$ eV and $G^3_{dp} = 0.569$ eV. We tested the core-hole potential by changing its strength and it turns out to have minimal effect on the final RIXS spectrum.

The final state generated by the RIXS process is[7],

$$|F_i\rangle = \hat{D}'^\dagger_i \frac{1}{\omega_{\text{inc}} - \hat{H}_{\text{inter}} + E_g + i\Gamma_c/2} \hat{D}_i |g\rangle, \tag{S7}$$

and the RIXS intensity is,

$$I(\omega, \omega_{inc}) \propto \sum_f \left| \sum_{i=1}^{8} e^{-i\vec{Q}\cdot\vec{R}_i} \langle f \,|\, F_i \rangle \right|^2 \delta(\omega - E_f + E_g), \tag{S8}$$

where $|g(f)\rangle$ are the ground (excited) eigenstates of $\hat{H}_{\text{init}}$, and $\hat{D}_i$ is the dipolar transition operator from $2p$ to $5d$

shell on the i-th Ir site. Γ_c is the core-hole life time broadening and is set to be 5.0 eV. $\vec{Q} = \vec{k}_f - \vec{k}_i$, where $\vec{k}_i$ and $\vec{k}_f$ are the wave vectors of the incident and outgoing photons, respectively. $\vec{R}_i$ are the positions of Ir-sites.

III. MORE SIMULATED RIXS SPECTRA

We plot more simulated RIXS spectra in Fig. S2. As we can see, the simulated RIXS spectra at small t is much more sensitive to $\Delta\mu$ than that at large t. At $t = 0.18$ eV, there are also obvious changes in simulated RIXS spectra when $\Delta\mu > 0.2$ eV.

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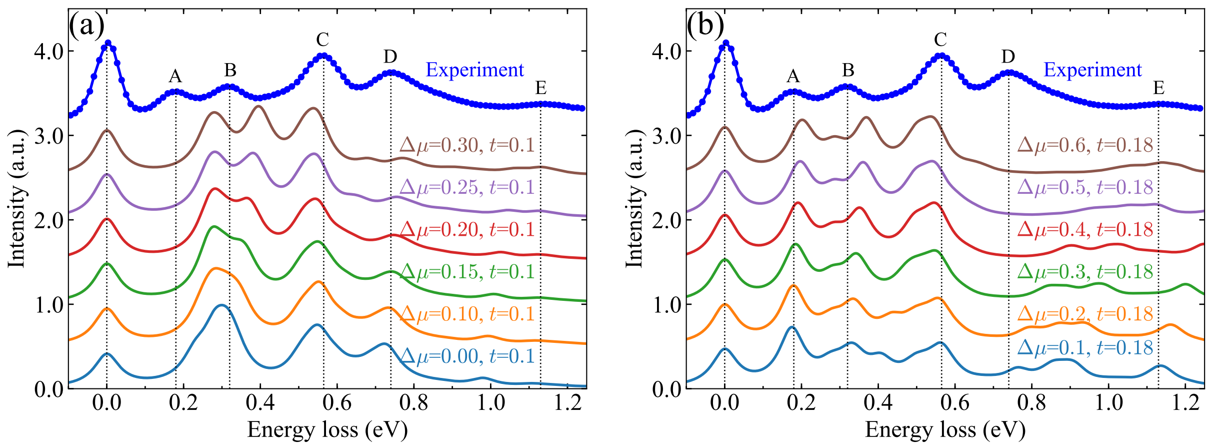

FIG. S2. More RIXS spectra as a function of $\Delta\mu$ at (a) $t = 0.1$ eV and (b) $t = 0.18$ eV.