Supplementary Materials

Core-valence double ionization of SF_6 involving S2p, F1s and S1s inner shells

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1 Determinant expansions of the dication states at the S2p edge

For the S2p edge, the core-hole orbital angular momentum $l_C = 1$ admits three sublevels, with the dication's orbital angular-momentum projection $M_L^{\text{dic}} \in \{-1, 0, +1\}$ depending on which component of the S2p MO is the hole. Denote by i_m the dication configuration with the core hole carrying $M_L^{\text{dic}} = m$, and let j be the valence-hole MO. The Slater determinants of the dication configuration (i_m, j) with specified spin assignments are $|\Phi^{(i_m\sigma,\, j\sigma')}\rangle$, the same notation used in the main text. For each $(s_V = 1/2, j_C, J_{\text{dic}}, M_J)$ dication state, the wavefunction is built by Clebsch–Gordan coupling of $l_C = 1$ with the LS-triplet or LS-singlet spin manifold, followed by the coupling to total $(J_{\text{tot}}, M_{J,\text{tot}}) = (1, m_\gamma)$ with the photoelectron pair (Section **??**). We display the $M_J = 0$ wavefunctions for brevity. The $M_J = \pm 1$ components are obtained by analogous CG decomposition.

Spin determinants of the partial jj-coupling substates (dication).

$j_C = 1/2, J_{\text{dic}} = 0$ **multiplet (1 state):**

$$\big|s_V = 1/2,\, j_C = 1/2,\, J_{\text{dic}} = 0,\, M_J = 0\big\rangle = \frac{\sqrt{3}}{3}\big|\Phi^{(i_{-1}\alpha,\, j\alpha)}\big\rangle - \frac{\sqrt{6}}{6}\big|\Phi^{(i_0\alpha,\, j\beta)}\big\rangle - \frac{\sqrt{6}}{6}\big|\Phi^{(i_0\beta,\, j\alpha)}\big\rangle + \frac{\sqrt{3}}{3}\big|\Phi^{(i_{+1}\beta,\, j\beta)}\big\rangle. \quad (1)$$

$j_C = 1/2, J_{\text{dic}} = 1$ **multiplet (3 states):**

$$\big|1/2,\, 1/2,\, 1,\, -1\big\rangle = -\frac{\sqrt{6}}{3}\big|\Phi^{(i_{-1}\alpha,\, j\beta)}\big\rangle + \frac{\sqrt{3}}{3}\big|\Phi^{(i_0\beta,\, j\beta)}\big\rangle, \quad (2)$$

$$\big|1/2,\, 1/2,\, 1,\, 0\big\rangle = -\frac{\sqrt{3}}{3}\big|\Phi^{(i_{-1}\alpha,\, j\alpha)}\big\rangle + \frac{\sqrt{6}}{6}\big|\Phi^{(i_0\beta,\, j\alpha)}\big\rangle - \frac{\sqrt{6}}{6}\big|\Phi^{(i_0\alpha,\, j\beta)}\big\rangle + \frac{\sqrt{3}}{3}\big|\Phi^{(i_{+1}\beta,\, j\beta)}\big\rangle, \quad (3)$$

$$\big|1/2,\, 1/2,\, 1,\, +1\big\rangle = -\frac{\sqrt{3}}{3}\big|\Phi^{(i_0\alpha,\, j\alpha)}\big\rangle + \frac{\sqrt{6}}{3}\big|\Phi^{(i_{+1}\beta,\, j\alpha)}\big\rangle. \quad (4)$$

$j_C = 3/2, J_{\text{dic}} = 1$ **multiplet (3 states):**

$$\left|1/2, 3/2, 1, -1\right\rangle = -\frac{\sqrt{3}}{2}\left|\Phi^{(i_{-1}\beta,\, j\alpha)}\right\rangle + \frac{\sqrt{3}}{6}\left|\Phi^{(i_{-1}\alpha,\, j\beta)}\right\rangle + \frac{\sqrt{6}}{6}\left|\Phi^{(i_0\beta,\, j\beta)}\right\rangle, \tag{5}$$

$$\left|1/2, 3/2, 1, 0\right\rangle = -\frac{\sqrt{6}}{6}\left|\Phi^{(i_{-1}\alpha,\, j\alpha)}\right\rangle - \frac{\sqrt{3}}{3}\left|\Phi^{(i_0\beta,\, j\alpha)}\right\rangle + \frac{\sqrt{3}}{3}\left|\Phi^{(i_0\alpha,\, j\beta)}\right\rangle + \frac{\sqrt{6}}{6}\left|\Phi^{(i_{+1}\beta,\, j\beta)}\right\rangle, \tag{6}$$

$$\left|1/2, 3/2, 1, +1\right\rangle = -\frac{\sqrt{6}}{6}\left|\Phi^{(i_0\alpha,\, j\alpha)}\right\rangle - \frac{\sqrt{3}}{6}\left|\Phi^{(i_{+1}\beta,\, j\alpha)}\right\rangle + \frac{\sqrt{3}}{2}\left|\Phi^{(i_{+1}\alpha,\, j\beta)}\right\rangle. \tag{7}$$

$j_C = 3/2, J_{\text{dic}} = 2$ **multiplet (5 states):**

$$\left|1/2, 3/2, 2, -2\right\rangle = \left|\Phi^{(i_{-1}\beta,\, j\beta)}\right\rangle, \tag{8}$$

$$\left|1/2, 3/2, 2, -1\right\rangle = 1/2\left|\Phi^{(i_{-1}\beta,\, j\alpha)}\right\rangle + 1/2\left|\Phi^{(i_{-1}\alpha,\, j\beta)}\right\rangle + \frac{\sqrt{2}}{2}\left|\Phi^{(i_0\beta,\, j\beta)}\right\rangle, \tag{9}$$

$$\left|1/2, 3/2, 2, 0\right\rangle = \frac{\sqrt{6}}{6}\left|\Phi^{(i_{-1}\alpha,\, j\alpha)}\right\rangle + \frac{\sqrt{3}}{3}\left|\Phi^{(i_0\beta,\, j\alpha)}\right\rangle + \frac{\sqrt{3}}{3}\left|\Phi^{(i_0\alpha,\, j\beta)}\right\rangle + \frac{\sqrt{6}}{6}\left|\Phi^{(i_{+1}\beta,\, j\beta)}\right\rangle, \tag{10}$$

$$\left|1/2, 3/2, 2, +1\right\rangle = \frac{\sqrt{2}}{2}\left|\Phi^{(i_0\alpha,\, j\alpha)}\right\rangle + 1/2\left|\Phi^{(i_{+1}\beta,\, j\alpha)}\right\rangle + 1/2\left|\Phi^{(i_{+1}\alpha,\, j\beta)}\right\rangle, \tag{11}$$

$$\left|1/2, 3/2, 2, +2\right\rangle = \left|\Phi^{(i_{+1}\alpha,\, j\alpha)}\right\rangle. \tag{12}$$

The projected N-electron final states

For all the 12 dication states listed above, we considered direct products with the spin-resolved states of the photoelectron pair (48 in total), and projected into the $S_{\text{total}} = 0$ subspace. The 30 nonzero projections are listed below. It is worth emphasizing that the projections are not normalized states, in general.

$j_C = 1/2$ **(12 states):**

$$\mathscr{P}\left[\left|s_V = 1/2,\, j_C = 1/2, J_{\text{dic}} = 0,\, M_J = 0\right\rangle_D \otimes \left|S_{\text{pair}} = 1, M_{\text{pair}} = -1\right\rangle_P\right] = \frac{1}{3}\left|\Phi^{(i_{-1}\beta,\, j\beta)}\, \psi^\beta_{\mathbf{k}_1}\psi^\beta_{\mathbf{k}_2}\right\rangle. \tag{13}$$

$$\begin{aligned}\mathscr{P}\left[\left|1/2, 1/2, 0, 0\right\rangle_D \left|1, 0\right\rangle_P\right] = &+\frac{1}{6}\left|\Phi^{(i_0\alpha,\, j\beta)}\, \psi^\alpha_{\mathbf{k}_1}\psi^\beta_{\mathbf{k}_2}\right\rangle + \frac{1}{6}\left|\Phi^{(i_0\alpha,\, j\beta)}\, \psi^\beta_{\mathbf{k}_1}\psi^\alpha_{\mathbf{k}_2}\right\rangle \\ &+\frac{1}{6}\left|\Phi^{(i_0\beta,\, j\alpha)}\, \psi^\alpha_{\mathbf{k}_1}\psi^\beta_{\mathbf{k}_2}\right\rangle + \frac{1}{6}\left|\Phi^{(i_0\beta,\, j\alpha)}\, \psi^\beta_{\mathbf{k}_1}\psi^\alpha_{\mathbf{k}_2}\right\rangle.\end{aligned} \tag{14}$$

$$\mathscr{P}\left[\left|1/2, 1/2, 0, 0\right\rangle_D \left|1, +1\right\rangle_P\right] = +\frac{1}{3}\left|\Phi^{(i_{+1}\alpha,\, j\alpha)}\, \psi^\alpha_{\mathbf{k}_1}\psi^\alpha_{\mathbf{k}_2}\right\rangle. \tag{15}$$

$$\begin{aligned}\mathscr{P}\left[\left|1/2, 1/2, 1, -1\right\rangle_D \left|0, 0\right\rangle_P\right] = &-\frac{\sqrt{3}}{6}\left|\Phi^{(i_{-1}\alpha,\, j\beta)}\, \psi^\alpha_{\mathbf{k}_1}\psi^\beta_{\mathbf{k}_2}\right\rangle + \frac{\sqrt{3}}{6}\left|\Phi^{(i_{-1}\alpha,\, j\beta)}\, \psi^\beta_{\mathbf{k}_1}\psi^\alpha_{\mathbf{k}_2}\right\rangle \\ &+\frac{\sqrt{3}}{6}\left|\Phi^{(i_{-1}\beta,\, j\alpha)}\, \psi^\alpha_{\mathbf{k}_1}\psi^\beta_{\mathbf{k}_2}\right\rangle - \frac{\sqrt{3}}{6}\left|\Phi^{(i_{-1}\beta,\, j\alpha)}\, \psi^\beta_{\mathbf{k}_1}\psi^\alpha_{\mathbf{k}_2}\right\rangle.\end{aligned} \tag{16}$$

$$\mathscr{P}\Big[\big|1/2,\,1/2,1,-1\big\rangle_D\big|1,0\big\rangle_P\Big] = +\frac{1}{6}\,\big|\Phi^{(i_{-1}\alpha,\,j\beta)}\,\psi^{\alpha}_{\mathbf{k}_1}\,\psi^{\beta}_{\mathbf{k}_2}\big\rangle + \frac{1}{6}\,\big|\Phi^{(i_{-1}\alpha,\,j\beta)}\,\psi^{\beta}_{\mathbf{k}_1}\,\psi^{\alpha}_{\mathbf{k}_2}\big\rangle + \frac{1}{6}\,\big|\Phi^{(i_{-1}\beta,\,j\alpha)}\,\psi^{\alpha}_{\mathbf{k}_1}\,\psi^{\beta}_{\mathbf{k}_2}\big\rangle + \frac{1}{6}\,\big|\Phi^{(i_{-1}\beta,\,j\alpha)}\,\psi^{\beta}_{\mathbf{k}_1}\,\psi^{\alpha}_{\mathbf{k}_2}\big\rangle. \tag{17}$$

$$\mathscr{P}\Big[\big|1/2,\,1/2,1,-1\big\rangle_D\big|1,+1\big\rangle_P\Big] = +\frac{1}{3}\,\big|\Phi^{(i_0\alpha,\,j\alpha)}\,\psi^{\alpha}_{\mathbf{k}_1}\,\psi^{\alpha}_{\mathbf{k}_2}\big\rangle. \tag{18}$$

$$\mathscr{P}\Big[\big|1/2,\,1/2,1,0\big\rangle_D\big|0,0\big\rangle_P\Big] = -\frac{\sqrt{3}}{6}\,\big|\Phi^{(i_0\alpha,\,j\beta)}\,\psi^{\alpha}_{\mathbf{k}_1}\,\psi^{\beta}_{\mathbf{k}_2}\big\rangle + \frac{\sqrt{3}}{6}\,\big|\Phi^{(i_0\alpha,\,j\beta)}\,\psi^{\beta}_{\mathbf{k}_1}\,\psi^{\alpha}_{\mathbf{k}_2}\big\rangle + \frac{\sqrt{3}}{6}\,\big|\Phi^{(i_0\beta,\,j\alpha)}\,\psi^{\alpha}_{\mathbf{k}_1}\,\psi^{\beta}_{\mathbf{k}_2}\big\rangle - \frac{\sqrt{3}}{6}\,\big|\Phi^{(i_0\beta,\,j\alpha)}\,\psi^{\beta}_{\mathbf{k}_1}\,\psi^{\alpha}_{\mathbf{k}_2}\big\rangle. \tag{19}$$

$$\mathscr{P}\Big[\big|1/2,\,1/2,1,0\big\rangle_D\big|1,-1\big\rangle_P\Big] = -\frac{1}{3}\,\big|\Phi^{(i_{-1}\beta,\,j\beta)}\,\psi^{\beta}_{\mathbf{k}_1}\,\psi^{\beta}_{\mathbf{k}_2}\big\rangle. \tag{20}$$

$$\mathscr{P}\Big[\big|1/2,\,1/2,1,0\big\rangle_D\big|1,+1\big\rangle_P\Big] = +\frac{1}{3}\,\big|\Phi^{(i_{+1}\alpha,\,j\alpha)}\,\psi^{\alpha}_{\mathbf{k}_1}\,\psi^{\alpha}_{\mathbf{k}_2}\big\rangle. \tag{21}$$

$$\mathscr{P}\Big[\big|1/2,\,1/2,1,+1\big\rangle_D\big|0,0\big\rangle_P\Big] = -\frac{\sqrt{3}}{6}\,\big|\Phi^{(i_{+1}\alpha,\,j\beta)}\,\psi^{\alpha}_{\mathbf{k}_1}\,\psi^{\beta}_{\mathbf{k}_2}\big\rangle + \frac{\sqrt{3}}{6}\,\big|\Phi^{(i_{+1}\alpha,\,j\beta)}\,\psi^{\beta}_{\mathbf{k}_1}\,\psi^{\alpha}_{\mathbf{k}_2}\big\rangle + \frac{\sqrt{3}}{6}\,\big|\Phi^{(i_{+1}\beta,\,j\alpha)}\,\psi^{\alpha}_{\mathbf{k}_1}\,\psi^{\beta}_{\mathbf{k}_2}\big\rangle - \frac{\sqrt{3}}{6}\,\big|\Phi^{(i_{+1}\beta,\,j\alpha)}\,\psi^{\beta}_{\mathbf{k}_1}\,\psi^{\alpha}_{\mathbf{k}_2}\big\rangle. \tag{22}$$

$$\mathscr{P}\Big[\big|1/2,\,1/2,1,+1\big\rangle_D\big|1,-1\big\rangle_P\Big] = -\frac{1}{3}\,\big|\Phi^{(i_0\beta,\,j\beta)}\,\psi^{\beta}_{\mathbf{k}_1}\,\psi^{\beta}_{\mathbf{k}_2}\big\rangle. \tag{23}$$

$$\mathscr{P}\Big[\big|1/2,\,1/2,1,+1\big\rangle_D\big|1,0\big\rangle_P\Big] = -\frac{1}{6}\,\big|\Phi^{(i_{+1}\alpha,\,j\beta)}\,\psi^{\alpha}_{\mathbf{k}_1}\,\psi^{\beta}_{\mathbf{k}_2}\big\rangle - \frac{1}{6}\,\big|\Phi^{(i_{+1}\alpha,\,j\beta)}\,\psi^{\beta}_{\mathbf{k}_1}\,\psi^{\alpha}_{\mathbf{k}_2}\big\rangle - \frac{1}{6}\,\big|\Phi^{(i_{+1}\beta,\,j\alpha)}\,\psi^{\alpha}_{\mathbf{k}_1}\,\psi^{\beta}_{\mathbf{k}_2}\big\rangle - \frac{1}{6}\,\big|\Phi^{(i_{+1}\beta,\,j\alpha)}\,\psi^{\beta}_{\mathbf{k}_1}\,\psi^{\alpha}_{\mathbf{k}_2}\big\rangle. \tag{24}$$

$j_C = 3/2$ **(18 states):**

$$\mathscr{P}\Big[\big|1/2,\,3/2,1,-1\big\rangle_D\big|0,0\big\rangle_P\Big] = +\frac{\sqrt{6}}{6}\,\big|\Phi^{(i_{-1}\alpha,\,j\beta)}\,\psi^{\alpha}_{\mathbf{k}_1}\,\psi^{\beta}_{\mathbf{k}_2}\big\rangle - \frac{\sqrt{6}}{6}\,\big|\Phi^{(i_{-1}\alpha,\,j\beta)}\,\psi^{\beta}_{\mathbf{k}_1}\,\psi^{\alpha}_{\mathbf{k}_2}\big\rangle - \frac{\sqrt{6}}{6}\,\big|\Phi^{(i_{-1}\beta,\,j\alpha)}\,\psi^{\alpha}_{\mathbf{k}_1}\,\psi^{\beta}_{\mathbf{k}_2}\big\rangle + \frac{\sqrt{6}}{6}\,\big|\Phi^{(i_{-1}\beta,\,j\alpha)}\,\psi^{\beta}_{\mathbf{k}_1}\,\psi^{\alpha}_{\mathbf{k}_2}\big\rangle. \tag{25}$$

$$\mathscr{P}\Big[\big|1/2,\,3/2,1,-1\big\rangle_D\big|1,0\big\rangle_P\Big] = +\frac{\sqrt{2}}{12}\,\big|\Phi^{(i_{-1}\alpha,\,j\beta)}\,\psi^{\alpha}_{\mathbf{k}_1}\,\psi^{\beta}_{\mathbf{k}_2}\big\rangle + \frac{\sqrt{2}}{12}\,\big|\Phi^{(i_{-1}\alpha,\,j\beta)}\,\psi^{\beta}_{\mathbf{k}_1}\,\psi^{\alpha}_{\mathbf{k}_2}\big\rangle + \frac{\sqrt{2}}{12}\,\big|\Phi^{(i_{-1}\beta,\,j\alpha)}\,\psi^{\alpha}_{\mathbf{k}_1}\,\psi^{\beta}_{\mathbf{k}_2}\big\rangle + \frac{\sqrt{2}}{12}\,\big|\Phi^{(i_{-1}\beta,\,j\alpha)}\,\psi^{\beta}_{\mathbf{k}_1}\,\psi^{\alpha}_{\mathbf{k}_2}\big\rangle. \tag{26}$$

$$\mathscr{P}\Big[\big|1/2,3/2,1,-1\big\rangle_D\big|1,+1\big\rangle_P\Big] = +\,\frac{\sqrt{2}}{6}\,\big|\Phi^{(i_0\alpha,\,j\alpha)}\,\psi^{\alpha}_{\mathbf{k}_1}\,\psi^{\alpha}_{\mathbf{k}_2}\big\rangle\,. \tag{27}$$

$$\begin{aligned}\mathscr{P}\Big[\big|1/2,3/2,1,0\big\rangle_D\big|0,0\big\rangle_P\Big] = &+\frac{\sqrt{6}}{6}\,\big|\Phi^{(i_0\alpha,\,j\beta)}\,\psi^{\alpha}_{\mathbf{k}_1}\,\psi^{\beta}_{\mathbf{k}_2}\big\rangle - \frac{\sqrt{6}}{6}\,\big|\Phi^{(i_0\alpha,\,j\beta)}\,\psi^{\beta}_{\mathbf{k}_1}\,\psi^{\alpha}_{\mathbf{k}_2}\big\rangle\\ &-\frac{\sqrt{6}}{6}\,\big|\Phi^{(i_0\beta,\,j\alpha)}\,\psi^{\alpha}_{\mathbf{k}_1}\,\psi^{\beta}_{\mathbf{k}_2}\big\rangle + \frac{\sqrt{6}}{6}\,\big|\Phi^{(i_0\beta,\,j\alpha)}\,\psi^{\beta}_{\mathbf{k}_1}\,\psi^{\alpha}_{\mathbf{k}_2}\big\rangle\,.\end{aligned} \tag{28}$$

$$\mathscr{P}\Big[\big|1/2,3/2,1,0\big\rangle_D\big|1,-1\big\rangle_P\Big] = -\,\frac{\sqrt{2}}{6}\,\big|\Phi^{(i_{-1}\beta,\,j\beta)}\,\psi^{\beta}_{\mathbf{k}_1}\,\psi^{\beta}_{\mathbf{k}_2}\big\rangle\,. \tag{29}$$

$$\mathscr{P}\Big[\big|1/2,3/2,1,0\big\rangle_D\big|1,+1\big\rangle_P\Big] = +\,\frac{\sqrt{2}}{6}\,\big|\Phi^{(i_{+1}\alpha,\,j\alpha)}\,\psi^{\alpha}_{\mathbf{k}_1}\,\psi^{\alpha}_{\mathbf{k}_2}\big\rangle\,. \tag{30}$$

$$\begin{aligned}\mathscr{P}\Big[\big|1/2,3/2,1,+1\big\rangle_D\big|0,0\big\rangle_P\Big] = &+\frac{\sqrt{6}}{6}\,\big|\Phi^{(i_{+1}\alpha,\,j\beta)}\,\psi^{\alpha}_{\mathbf{k}_1}\,\psi^{\beta}_{\mathbf{k}_2}\big\rangle - \frac{\sqrt{6}}{6}\,\big|\Phi^{(i_{+1}\alpha,\,j\beta)}\,\psi^{\beta}_{\mathbf{k}_1}\,\psi^{\alpha}_{\mathbf{k}_2}\big\rangle\\ &-\frac{\sqrt{6}}{6}\,\big|\Phi^{(i_{+1}\beta,\,j\alpha)}\,\psi^{\alpha}_{\mathbf{k}_1}\,\psi^{\beta}_{\mathbf{k}_2}\big\rangle + \frac{\sqrt{6}}{6}\,\big|\Phi^{(i_{+1}\beta,\,j\alpha)}\,\psi^{\beta}_{\mathbf{k}_1}\,\psi^{\alpha}_{\mathbf{k}_2}\big\rangle\,.\end{aligned} \tag{31}$$

$$\mathscr{P}\Big[\big|1/2,3/2,1,+1\big\rangle_D\big|1,-1\big\rangle_P\Big] = -\,\frac{\sqrt{2}}{6}\,\big|\Phi^{(i_0\beta,\,j\beta)}\,\psi^{\beta}_{\mathbf{k}_1}\,\psi^{\beta}_{\mathbf{k}_2}\big\rangle\,. \tag{32}$$

$$\begin{aligned}\mathscr{P}\Big[\big|1/2,3/2,1,+1\big\rangle_D\big|1,0\big\rangle_P\Big] = &-\frac{\sqrt{2}}{12}\,\big|\Phi^{(i_{+1}\alpha,\,j\beta)}\,\psi^{\alpha}_{\mathbf{k}_1}\,\psi^{\beta}_{\mathbf{k}_2}\big\rangle - \frac{\sqrt{2}}{12}\,\big|\Phi^{(i_{+1}\alpha,\,j\beta)}\,\psi^{\beta}_{\mathbf{k}_1}\,\psi^{\alpha}_{\mathbf{k}_2}\big\rangle\\ &-\frac{\sqrt{2}}{12}\,\big|\Phi^{(i_{+1}\beta,\,j\alpha)}\,\psi^{\alpha}_{\mathbf{k}_1}\,\psi^{\beta}_{\mathbf{k}_2}\big\rangle - \frac{\sqrt{2}}{12}\,\big|\Phi^{(i_{+1}\beta,\,j\alpha)}\,\psi^{\beta}_{\mathbf{k}_1}\,\psi^{\alpha}_{\mathbf{k}_2}\big\rangle\,.\end{aligned} \tag{33}$$

$$\mathscr{P}\Big[\big|1/2,3/2,2,-2\big\rangle_D\big|1,+1\big\rangle_P\Big] = +\,\frac{\sqrt{3}}{3}\,\big|\Phi^{(i_{-1}\alpha,\,j\alpha)}\,\psi^{\alpha}_{\mathbf{k}_1}\,\psi^{\alpha}_{\mathbf{k}_2}\big\rangle\,. \tag{34}$$

$$\begin{aligned}\mathscr{P}\Big[\big|1/2,3/2,2,-1\big\rangle_D\big|1,0\big\rangle_P\Big] = &-\frac{\sqrt{6}}{12}\,\big|\Phi^{(i_{-1}\alpha,\,j\beta)}\,\psi^{\alpha}_{\mathbf{k}_1}\,\psi^{\beta}_{\mathbf{k}_2}\big\rangle - \frac{\sqrt{6}}{12}\,\big|\Phi^{(i_{-1}\alpha,\,j\beta)}\,\psi^{\beta}_{\mathbf{k}_1}\,\psi^{\alpha}_{\mathbf{k}_2}\big\rangle\\ &-\frac{\sqrt{6}}{12}\,\big|\Phi^{(i_{-1}\beta,\,j\alpha)}\,\psi^{\alpha}_{\mathbf{k}_1}\,\psi^{\beta}_{\mathbf{k}_2}\big\rangle - \frac{\sqrt{6}}{12}\,\big|\Phi^{(i_{-1}\beta,\,j\alpha)}\,\psi^{\beta}_{\mathbf{k}_1}\,\psi^{\alpha}_{\mathbf{k}_2}\big\rangle\,.\end{aligned} \tag{35}$$

$$\mathscr{P}\Big[\big|1/2,3/2,2,-1\big\rangle_D\big|1,+1\big\rangle_P\Big] = +\,\frac{\sqrt{6}}{6}\,\big|\Phi^{(i_0\alpha,\,j\alpha)}\,\psi^{\alpha}_{\mathbf{k}_1}\,\psi^{\alpha}_{\mathbf{k}_2}\big\rangle\,. \tag{36}$$

$$\mathscr{P}\Big[\big|1/2,3/2,2,0\big\rangle_D\big|1,-1\big\rangle_P\Big] = +\,\frac{\sqrt{2}}{6}\,\big|\Phi^{(i_{-1}\beta,\,j\beta)}\,\psi^{\beta}_{\mathbf{k}_1}\,\psi^{\beta}_{\mathbf{k}_2}\big\rangle\,. \tag{37}$$

$$\mathscr{P}\Big[\big|1/2,3/2,2,0\big\rangle_D\big|1,0\big\rangle_P\Big] = -\frac{\sqrt{2}}{6}\big|\Phi^{(i_0\alpha,\,j\beta)}\,\psi^{\alpha}_{\mathbf{k}_1}\psi^{\beta}_{\mathbf{k}_2}\big\rangle - \frac{\sqrt{2}}{6}\big|\Phi^{(i_0\alpha,\,j\beta)}\,\psi^{\beta}_{\mathbf{k}_1}\psi^{\alpha}_{\mathbf{k}_2}\big\rangle - \frac{\sqrt{2}}{6}\big|\Phi^{(i_0\beta,\,j\alpha)}\,\psi^{\alpha}_{\mathbf{k}_1}\psi^{\beta}_{\mathbf{k}_2}\big\rangle - \frac{\sqrt{2}}{6}\big|\Phi^{(i_0\beta,\,j\alpha)}\,\psi^{\beta}_{\mathbf{k}_1}\psi^{\alpha}_{\mathbf{k}_2}\big\rangle. \tag{38}$$

$$\mathscr{P}\Big[\big|1/2,3/2,2,0\big\rangle_D\big|1,+1\big\rangle_P\Big] = +\frac{\sqrt{2}}{6}\big|\Phi^{(i_{+1}\alpha,\,j\alpha)}\,\psi^{\alpha}_{\mathbf{k}_1}\psi^{\alpha}_{\mathbf{k}_2}\big\rangle. \tag{39}$$

$$\mathscr{P}\Big[\big|1/2,3/2,2,+1\big\rangle_D\big|1,-1\big\rangle_P\Big] = +\frac{\sqrt{6}}{6}\big|\Phi^{(i_0\beta,\,j\beta)}\,\psi^{\beta}_{\mathbf{k}_1}\psi^{\beta}_{\mathbf{k}_2}\big\rangle. \tag{40}$$

$$\mathscr{P}\Big[\big|1/2,3/2,2,+1\big\rangle_D\big|1,0\big\rangle_P\Big] = -\frac{\sqrt{6}}{12}\big|\Phi^{(i_{+1}\alpha,\,j\beta)}\,\psi^{\alpha}_{\mathbf{k}_1}\psi^{\beta}_{\mathbf{k}_2}\big\rangle - \frac{\sqrt{6}}{12}\big|\Phi^{(i_{+1}\alpha,\,j\beta)}\,\psi^{\beta}_{\mathbf{k}_1}\psi^{\alpha}_{\mathbf{k}_2}\big\rangle - \frac{\sqrt{6}}{12}\big|\Phi^{(i_{+1}\beta,\,j\alpha)}\,\psi^{\alpha}_{\mathbf{k}_1}\psi^{\beta}_{\mathbf{k}_2}\big\rangle - \frac{\sqrt{6}}{12}\big|\Phi^{(i_{+1}\beta,\,j\alpha)}\,\psi^{\beta}_{\mathbf{k}_1}\psi^{\alpha}_{\mathbf{k}_2}\big\rangle. \tag{41}$$

$$\mathscr{P}\Big[\big|1/2,3/2,2,+2\big\rangle_D\big|1,-1\big\rangle_P\Big] = +\frac{\sqrt{3}}{3}\big|\Phi^{(i_{+1}\beta,\,j\beta)}\,\psi^{\beta}_{\mathbf{k}_1}\psi^{\beta}_{\mathbf{k}_2}\big\rangle. \tag{42}$$

Angle-averaged squared amplitudes.
Each Slater determinant $\big|\Phi^{(i_m\sigma_c,\,j\sigma_v)}\,\psi^{\sigma_1}_{\mathbf{k}_1}\psi^{\sigma_2}_{\mathbf{k}_2}\big\rangle$ contributing to a substate has one of two spin patterns:

- **F-type:** the dication carries opposite spins ($\sigma_c \neq \sigma_v$) and the photoelectron pair carries mixed spins ($\sigma_1 \neq \sigma_2$). This determinant contributes via the $\alpha\beta$ direct channel and yields, after one-centre angle averaging, $\mathscr{F}_{ij} \equiv \mathscr{D}_i\mathscr{S}_j + \mathscr{D}_j\mathscr{S}_i$.
- **G-type:** the dication carries parallel spins ($\sigma_c = \sigma_v$) and the photoelectron pair carries parallel-but-anti-aligned spins ($\sigma_1 = \sigma_2 \neq \sigma_c$). This determinant contributes via the $\alpha\alpha/\beta\beta$ direct channel and yields the exchange integral $\mathscr{G}_{ij}$.

A direct inspection of the 30 states shows that *each state contains determinants of exactly one type*. No state mixes F-type and G-type determinants. Of the 30, 14 are purely F-type and 16 are purely G-type. Within a given state, the angle-averaged squared transition amplitude $|T_f|^2$ would in general contain both diagonal ($|a_n|^2$) and off-diagonal ($a_n^* a_m$) contributions from the determinants $|n\rangle, |m\rangle$ in the state's expansion. The off-diagonal terms reduce, after the one-center and no-cross-Dyson approximations used in the main text, to overlaps $\langle n|m\rangle$ between distinct Slater determinants. Inspection of the 30 states shows that the determinants within each state are pairwise distinct in their full spin-orbital labels $(m,\sigma_c,\sigma_v,\sigma_1,\sigma_2)$. In other words, no two determinants in the same state share all five labels, and they are therefore mutually orthogonal. All off-diagonal contributions vanish, and the angle-averaged squared amplitude reduces to a simple incoherent sum,

$$\big|T_f\big|^2 \simeq \sum_n |a_n|^2\,\mathscr{A}_n, \qquad \mathscr{A}_n = \begin{cases} \mathscr{F} & \text{(F-type state)}, \\ \mathscr{G}_{ij} & \text{(G-type state)}. \end{cases} \tag{43}$$

Since each state is purely F-type or purely G-type, the squared amplitude reduces to a single number times $\mathscr{F}_{ij}$ or $\mathscr{G}_{ij}$.

The cross section for each j_C peak is the incoherent sum of $|T_f|^2$ over all substates within the multiplet. Tabulating the weights from Eqs. (13)–(42), grouped by (j_C, type):

Multiplet	$\sum_n \lvert a_n\rvert^2$ on F-type	$\sum_n \lvert a_n\rvert^2$ on G-type
$j_C = 1/2$	$4/3$	$2/3$
$j_C = 3/2$	$8/3$	$4/3$

(44)

Both the F-type and G-type sectors exhibit the same $j_C = 3/2 : j_C = 1/2 = 2:1$ ratio. The angle-integrated transition amplitudes for the two unresolved j_C peaks are therefore

$$A_f^{(j_C=3/2)} = \tfrac{8}{3}\mathscr{F} + \tfrac{4}{3}\mathscr{G}_{ij}, \tag{45}$$

$$A_f^{(j_C=1/2)} = \tfrac{4}{3}\mathscr{F} + \tfrac{2}{3}\mathscr{G}_{ij}. \tag{46}$$

Both amplitudes are proportional to the same combination $2\mathscr{F} + \mathscr{G}_{ij}$, so the two j_C peaks have *identical spectral shape*, with the $j_C = 3/2$ peak twice as intense as the $j_C = 1/2$ peak. In terms of the *LS* amplitudes $A_f^{(S_{\rm dic}=0)} \simeq 2\mathscr{F}$ and $A_f^{(S_{\rm dic}=1)} \simeq \frac{1}{3}(2\mathscr{F} + 4\mathscr{G}_{ij})$ of Eqs. (**??**)–(**??**) of the main text, Eqs. (45)–(46) read

$$A_f^{(j_C=3/2)} = A_f^{(S_{\rm dic}=0)} + A_f^{(S_{\rm dic}=1)}, \tag{47}$$

$$A_f^{(j_C=1/2)} = \tfrac{1}{2}\left[A_f^{(S_{\rm dic}=0)} + A_f^{(S_{\rm dic}=1)}\right]. \tag{48}$$

This is the form used in the code to combine the two pipeline outputs $A_f^{(S=0)}$ and $A_f^{(S=1)}$ into the two j_C peaks once SO coupling on the core hole is switched on.

The $2:1$ branching ratio is the same as the one familiar from single-hole core-level XPS spectra of S $2p$, where the $2p_{3/2} : 2p_{1/2}$ multiplet ratio is $(2\cdot 3/2+1) : (2\cdot 1/2+1) = 4:2 = 2:1$. In the present DPI context, this ratio is not assumed at the outset but is recovered as the output of the substate enumeration. Instead, it emerges from the combinatorics of the 30 dipole-allowed substates without any explicit invocation of statistics. This is consistent with the picture that, at the S $2p$ edge, the SO splitting acts only on the core hole, with the valence hole and the two photoelectrons coupling as spectators within the *LS* scheme.

Table S1. Per-state energies, in eV, for the CV channels over the S2p edge.

Label	ΔSCF energy [j_C=1/2]	ΔSCF energy [j_C=3/2]	ΔSCF energy [S]	ΔSCF energy [T]
$5a_{1g}$	15.70	14.62	15.21	14.74
$4t_{1u}$	9.30	8.05	8.11	7.76
$1t_{2g}$	5.20	4.09	4.39	4.39
$1t_{2u}$	2.40	1.28	1.60	1.60
$5t_{1u}$	2.19	1.08	1.41	1.34
$3e_g$	1.33	0.23	0.53	0.52
$1t_{1g}$	1.12	0.00	0.32	0.32

2 Molecular orbitals

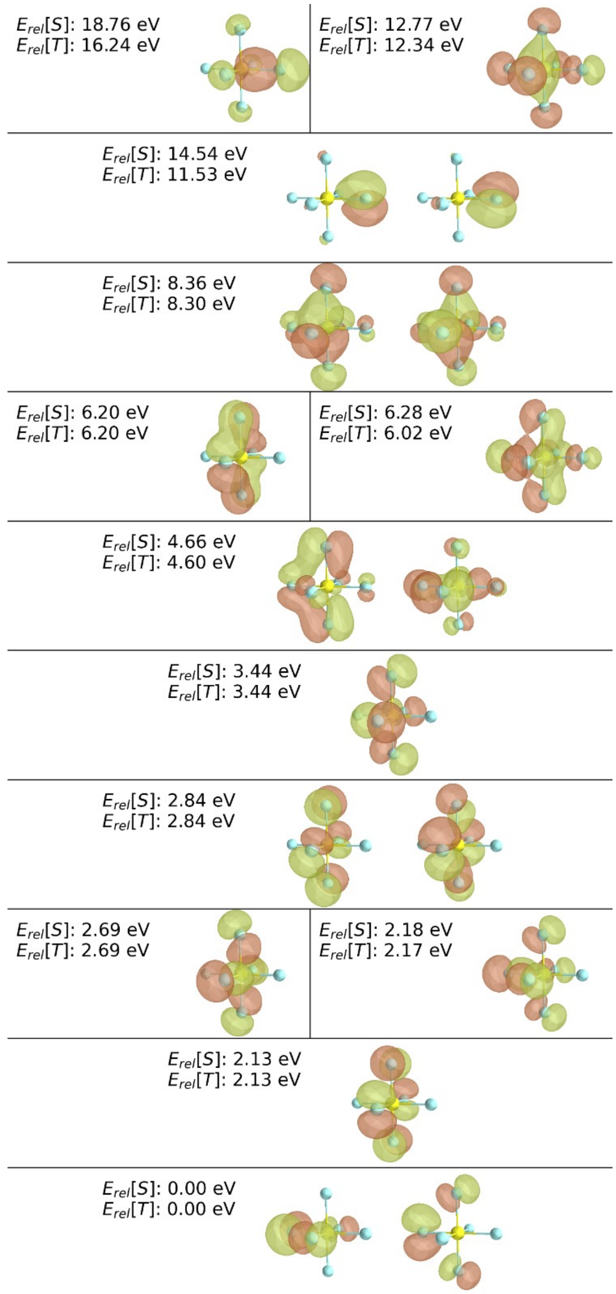

Figure S1. The V molecular orbitals of each CV state for the F1*s* calculation. The energies of the singlet and triplet dication states are also shown.

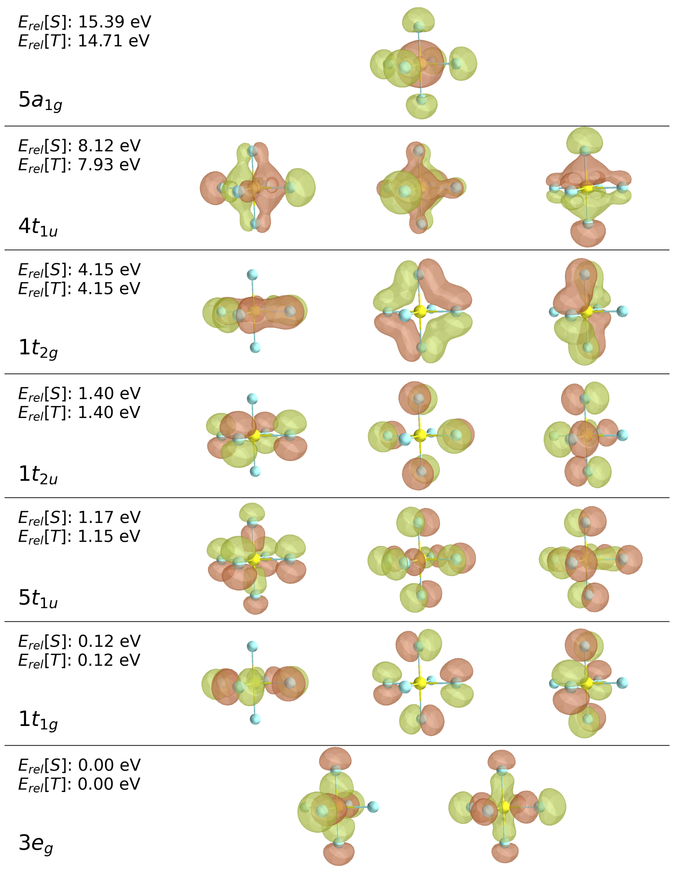

Figure S2. The V molecular orbitals of each CV state for the S1*s* calculation. The energies of the singlet and triplet dication states are also shown.

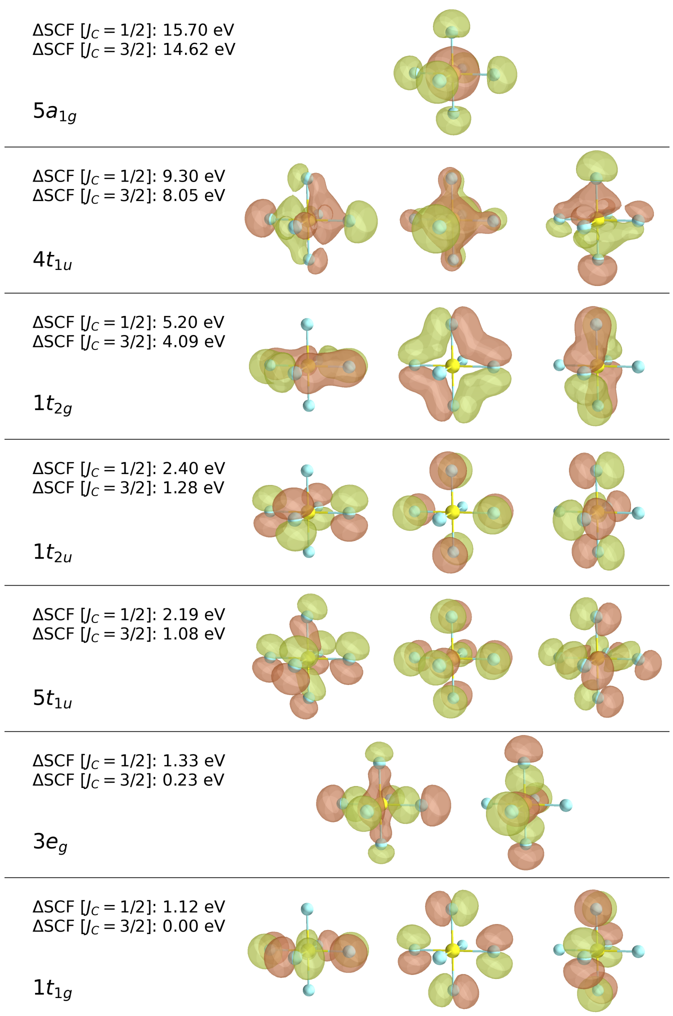

Figure S3. The V molecular orbitals of each CV state for the S2p calculation. The energies of the singlet and triplet dication states are also shown.

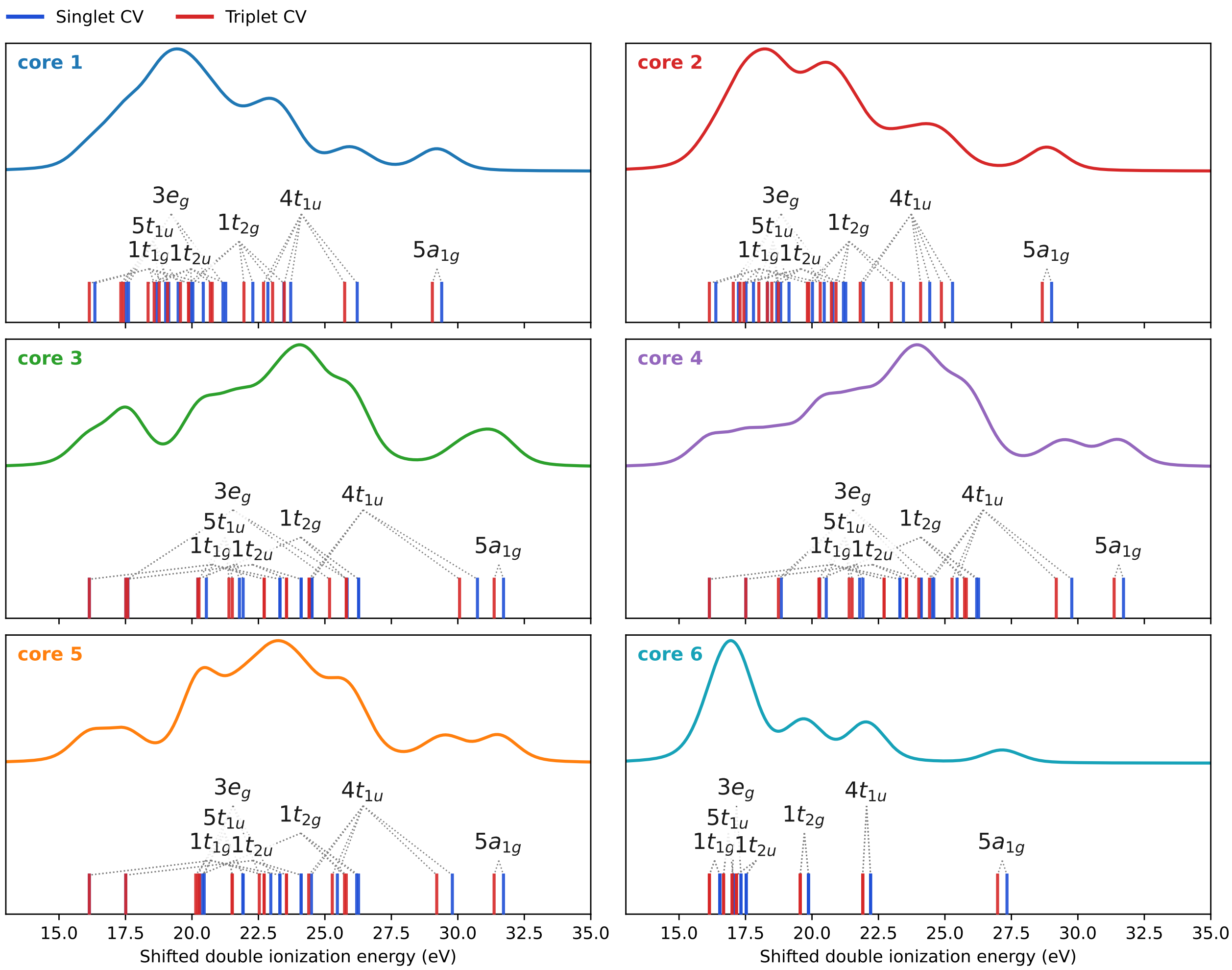

Figure S4. Density of CV states above the F1s edge per delocalized (O_h) F1s core orbital in the frozen-orbital limit approximation. The labels indicated in the graphics are associated with the valence ionized orbital.

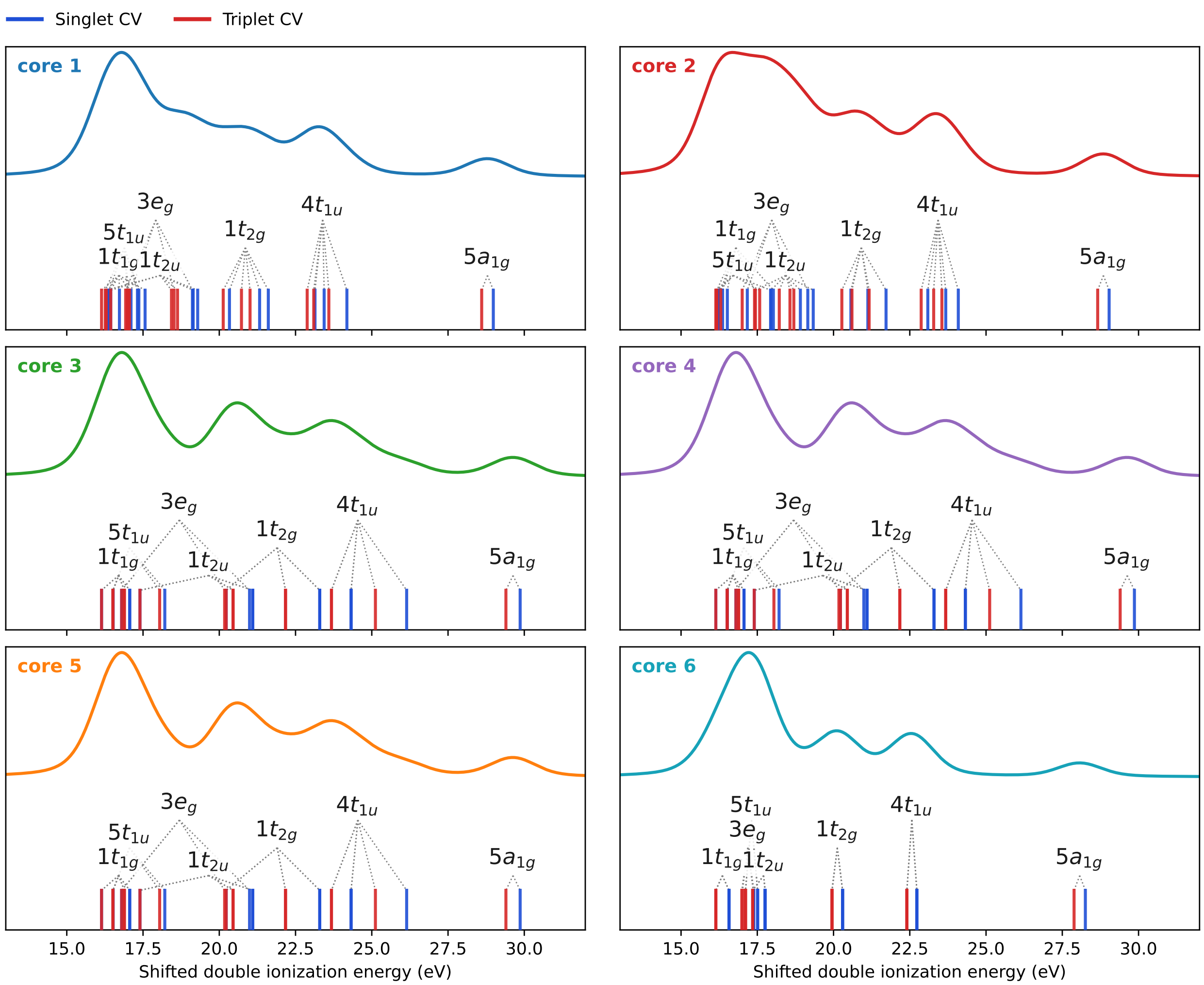

Figure S5. Density of CV states above the F1s edge per delocalized (O_h) F1s core orbital based on the ΔSCF calculations. The labels indicated in the graphics are associated with the valence ionized orbital.