Supporting Information for:

Electronic Structure of Heavy Halogen Atoms Adsorbed on the Cu(111) Surface: A Combined ARPES and First Principles Calculations Study

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Detailed analysis on the change of Cu(111) surface bands by the adsorption of I/Br atoms

For the clean Cu(111) surface, there are two surface bands starting around -0.53 eV at the Γ-point (figure S1(a)), due to the fact that there are two surface layers in the slab model. The bands are not degenerated in energy since we have relaxed only one side of the slab but constrained the other side to reproduce the bulk geometry. Since the adsorption of the I and Br atoms affects only one side of the slab, one band goes up in energy while the other remains nearly at the same energy position. This behavior is seen by the fatbands of the surface Cu atoms in the clean Cu(111), I/Cu(111), and Br/Cu(111) surfaces in figures S1(a)-(c). The fatband structure of Cu atoms at the center of the slab in figures S1(d)-(f), however, does not change when the I or Br atoms are adsorbed.

Figure S1. Orbital-resolved fat band structures of the clean Cu(111) surface and, I/Cu(111) and Br/Cu(111) overlayers. Upper three panels ((a)-(c)) are the fat band structures of the surface Cu atoms in each case, while lower three panels ((d)-(f)) are those of the Cu atoms at the center of the slab. Red, green, and blue fat bands present the projections of the band structure onto the s-, p-, and d-orbitals, respectively.
Figure S2. (a) ARPES intensity curves, as a function of the binding energy, $E_B$, integrated over $k_y$ from -0.05 to 0.05 Å$^{-1}$ with fixed $k_x = -0.1$ Å$^{-1}$ for Cu(111) (violet line), Br/Cu(111) (red line) and I/Cu(111) (black line); state 1 and 3 are the spin-splitting Iodine-induced states; state 2 is a molecular state; SS is the surface state of the bare Cu(111) surface; Constant energy maps measured at (b) -1.98, (c) -1.90 eV, and (d) -1.82 eV evidencing the evolution of the second iodine-induced states (peak 3).
Figure S3. Charge density maps for (a) the I/Cu(111) and (b) Br/Cu(111) overlayers. The black lines depict the contours of the density at 0.005 e⁻/Å³.