Supplementary Data

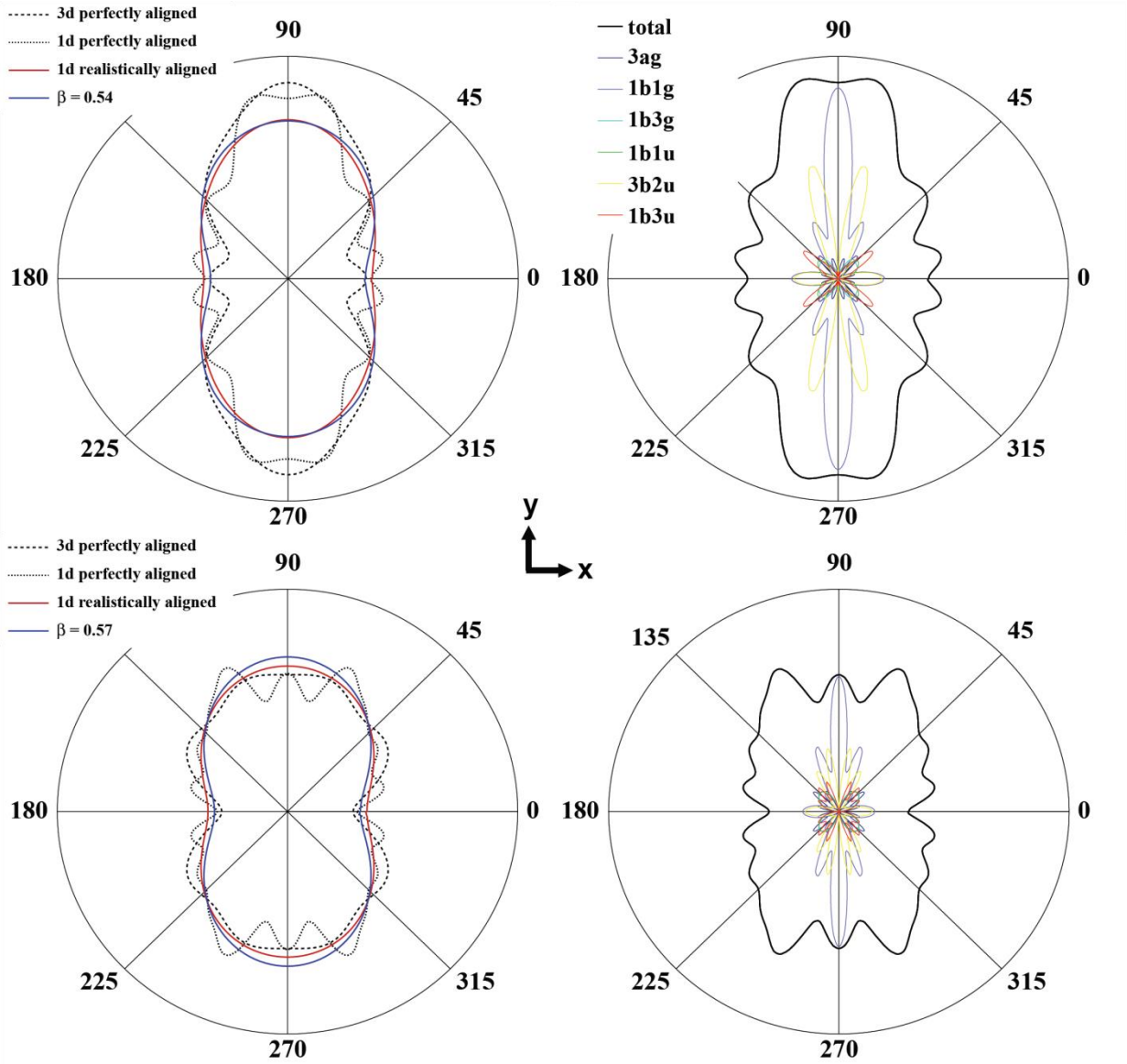

Figure S1: Calculated bromine (*2p*) molecular-frame photoelectron angular distributions (MFPADs) for 1,4-dibromobenzene molecules at 20 eV (top) and 35 eV (bottom) photoelectron kinetic energy obtained from the DFT calculations. The polarization axis of the X-rays is along the y-axis (at 90°/270°) and the X-ray beam propagation direction along the x-axis (at 0°/180°). In the left panels, the MFPADs are shown for perfectly 3-D aligned molecules with the Br-Br axis along the y-axis and the molecular plane in the yz-plane (dashed lines), perfectly 1-D aligned molecules with the Br-Br axis along the y-axis and the molecular plane freely rotating around the Br-Br axis (dotted lines), and for 1-D aligned molecules averaged over a Br-Br axis distribution corresponding to a two-dimensional Gaussian with a FWHM of 50° in order to take into account the experimentally achieved degree of alignment (red solid line). For comparison, the calculated photoelectron angular distributions for randomly oriented molecules are also shown (blue solid lines). In the right panels, the MFPADs for the six molecular orbitals that contribute to the bromine (*2p*) photoelectron line, weighted by their relative contribution according to the DFT calculations, are shown for perfectly 1-D aligned molecules along with their sum, which corresponds to the dotted lines in the left panels.

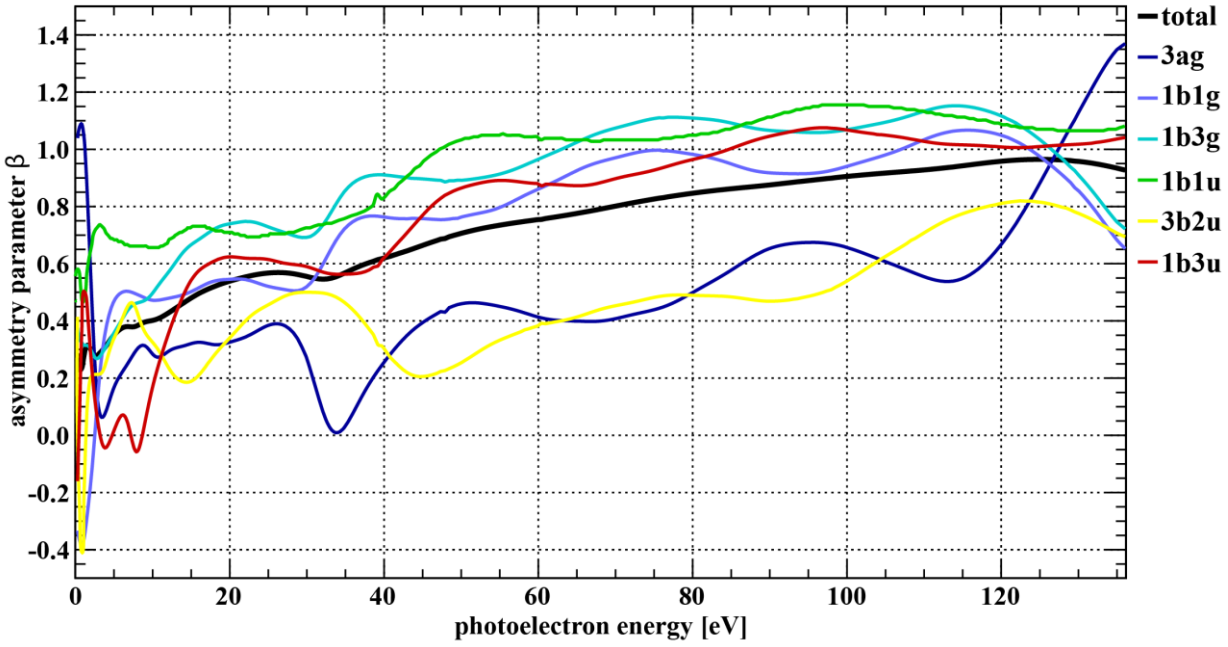

Figure S2: Calculated bromine (*2p*) photoelectron angular distribution parameter β for 1,4-dibromobenzene molecules as a function of photoelectron kinetic energy obtained from the DFT calculations. The β-parameters for the six molecular orbitals that contribute to the bromine (*2p*) photoelectron line are shown as colored lines, while the averaged β-parameter, obtained as the sum of the individual components weighted by their individual partial cross sections according to the DFT calculations, is shown as a thick black line.