



**Figure S1.** Resonance enhanced multiphoton ionization (REMPI) spectra of the FA-W cluster obtained by using (A) picosecond and (B) nanosecond laser pulses. The frequency of the ionization pulse is 32249 cm<sup>-1</sup> (310 nm) for (A) (1+1' REMPI) and  $\nu_{\text{exc}}$  for (B) (1+1 REMPI).  $S_1$ - $S_0$  origin transitions of related clusters are labeled. The time-resolved IR spectra are measured by monitoring the origin band of the FA-W<sup>CO</sup> cluster marked by an arrow. Although the widths of the bands in the picosecond spectrum are broader due to the lower spectral resolution of the picosecond pulse, the transition of the FA-W<sup>CO</sup> cluster is clearly separated from that of the FA-W<sub>2</sub><sup>CO</sup> cluster. This observation ensures a selective probe of dynamics of FA-W<sup>CO</sup>.