

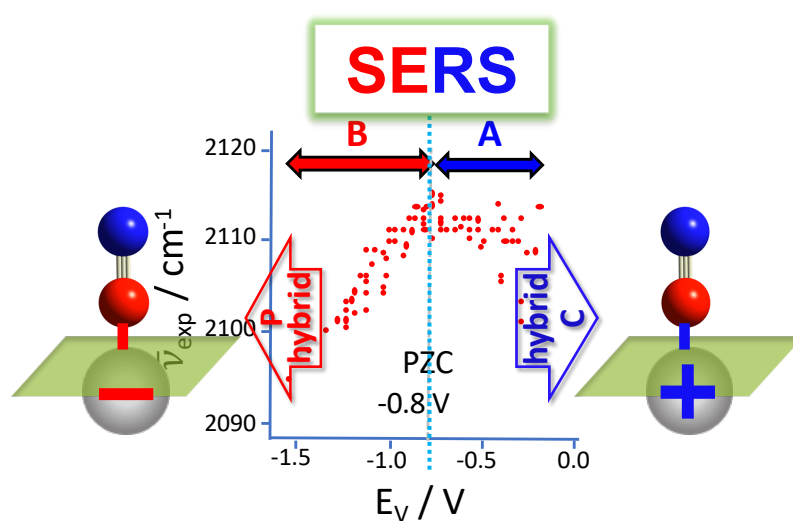
# Proving the Dual Electronic Structure of Charged Metal-Molecule Interfaces: SERS of Cyanide Adsorbed on a Nanostructured Silver Electrode

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## Supporting Information



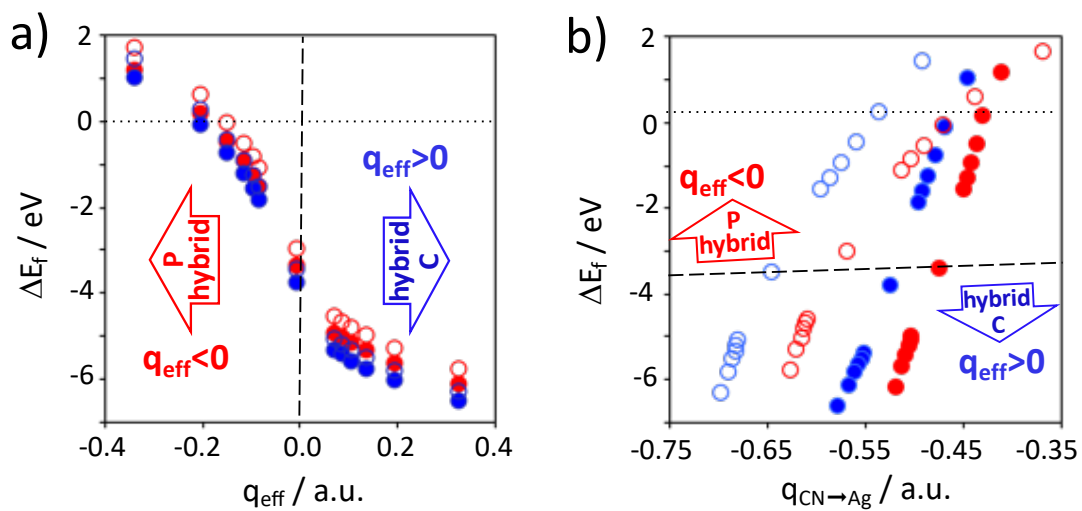


Figure S1. Dependence on the effective charge ( $q_{\text{eff}}$ ) of the calculated B3LPY/LanL2DZ (full circles) and B3LYP/def2-TZVPP (empty circles) a) energies of formation ( $\Delta E_f$ ) and b) injected Mulliken charges ( $q_{\text{CN} \rightarrow \text{Ag}}$ ) of top-C (blue) and top-N (red) stick-like complexes shown in Figure 1.

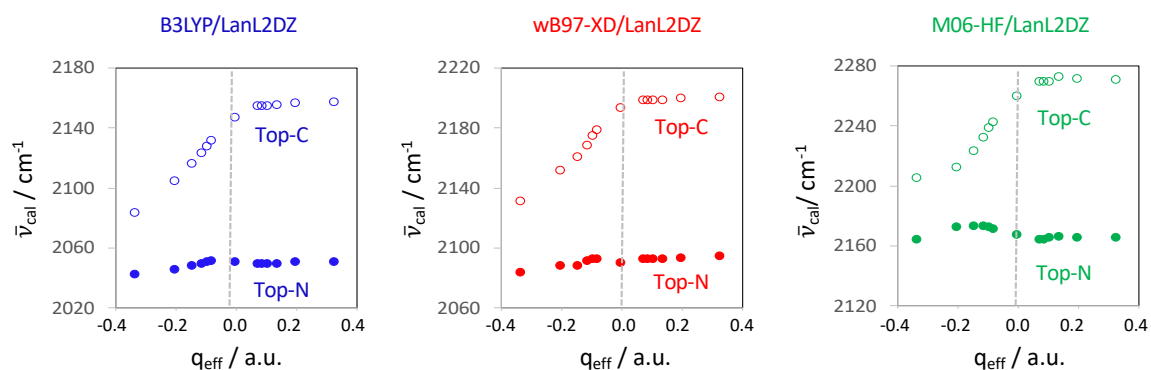


Figure S2. Dependence of the B3LYP/LanL2DZ, wB97-XD/LanL2DZ and M06-HF/LanL2DZ calculated wavenumbers of the  $\nu(\text{CN}^-)$  vibration ( $\bar{\nu}_{\text{cal}}$ ) on the effective charge ( $q_{\text{eff}}$ ) of top-C (empty circles) and top-N (full circles) linear  $[\text{Ag}_n^q\text{-CN}]^{q-1}$  complexes.

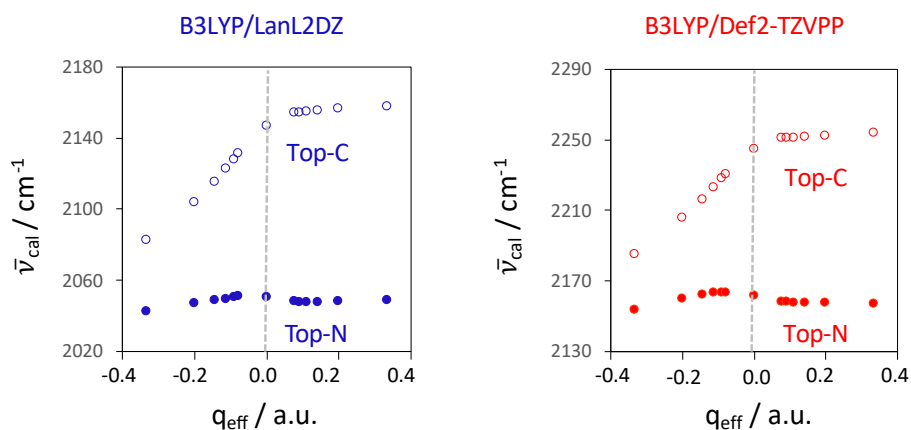


Figure S3. Dependence of the B3LYP/LanL2DZ and B3LYP/Def2-TZVPP calculated wavenumbers of the  $\nu(\text{CN}^-)$  vibration ( $\bar{\nu}_{\text{cal}}$ ) on the effective charge ( $q_{\text{eff}}$ ) of top-C (empty circles) and top-N (full circles) linear  $[\text{Ag}_n^q\text{-CN}]^{q-1}$  complexes.