Electronic Supplementary Material (ESI) for Faraday Discussions.

Supporting Information:

Theoretical Modeling of Voltage Effects and the Chemical Mechanism in Surface-Enhanced Raman Scattering

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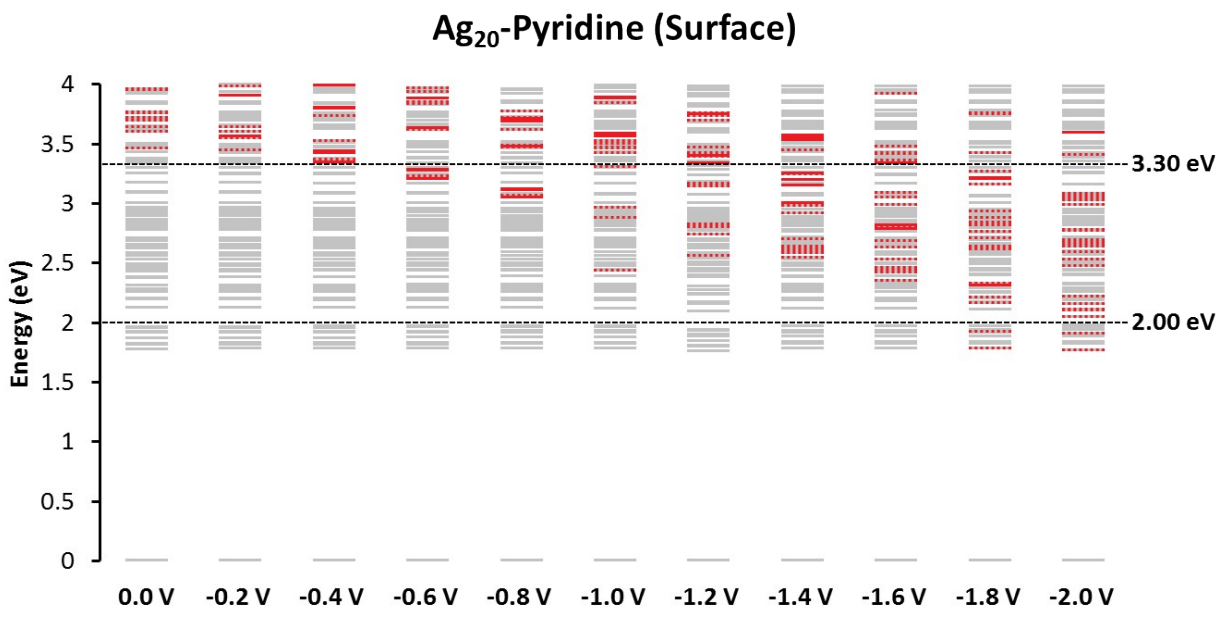

Figure S1. Excited-state energies for the Ag_{20}-pyridine Surface complex at the INDO/SCI level with applied potentials from 0.0 to -2.0 V. Solid red lines correspond to states with > 50% Ag_{20} → pyridine CT character, dotted red lines to states with 20-50% CT character, and gray lines to local Ag_{20} excited states.

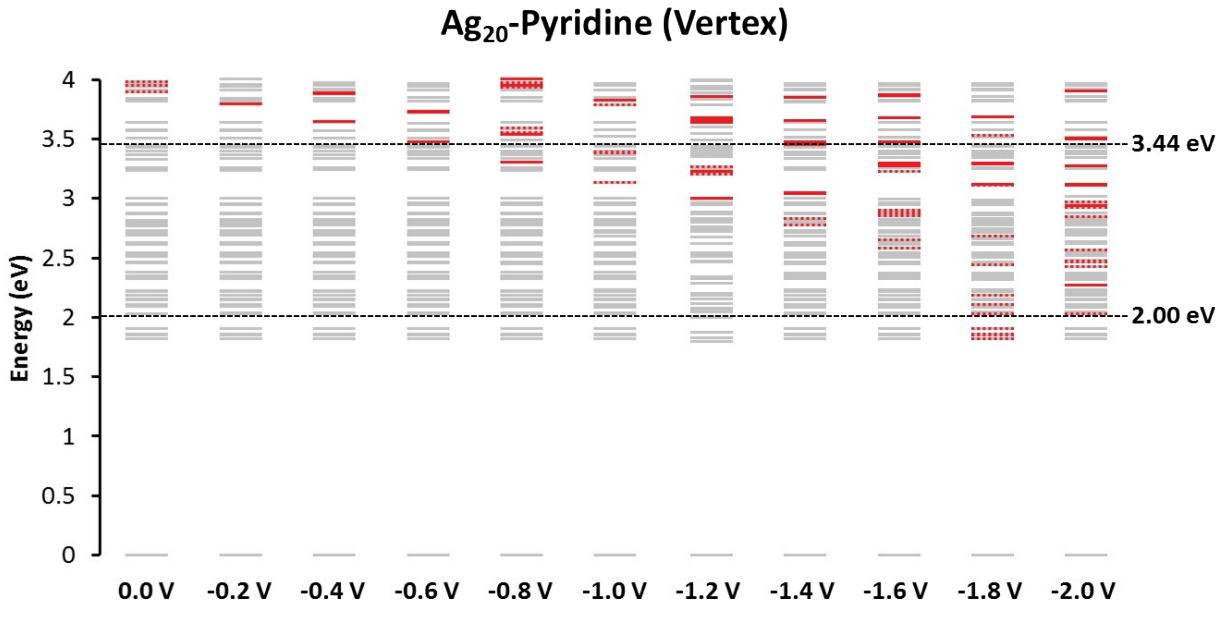

Figure S2. Excited-state energies for the Ag_{20}-pyridine Vertex complex at the INDO/SCI level with applied potentials from 0.0 to -2.0 V. Solid red lines correspond to states with > 50% Ag_{20} → pyridine CT character, dotted red lines to states with 20-50% CT character, and gray lines to local Ag_{20} excited states.

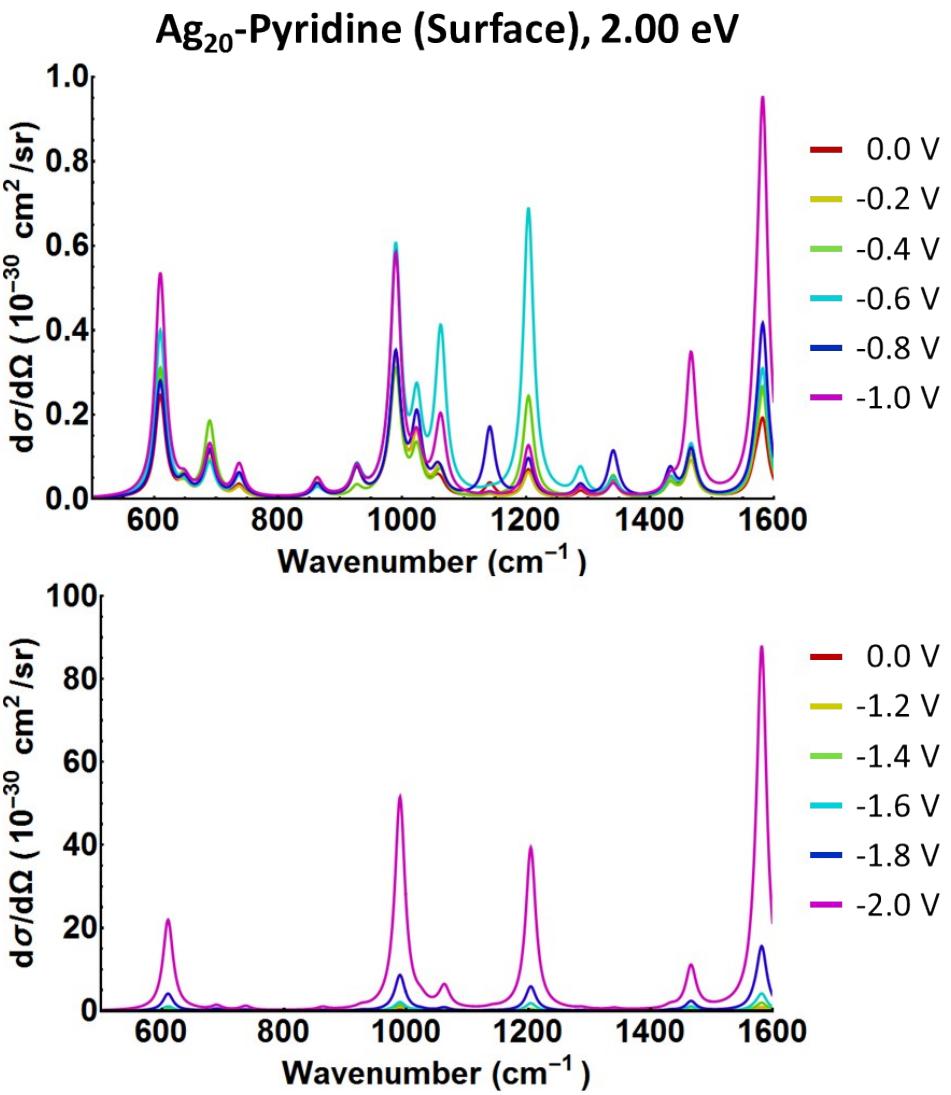

Figure S3. Normal Raman spectra for the Surface geometry of the Ag_{20}-pyridine complex at the INDO/SCI level, showing the effect of applied potentials from 0.0 to -2.0 V within the OESA model.

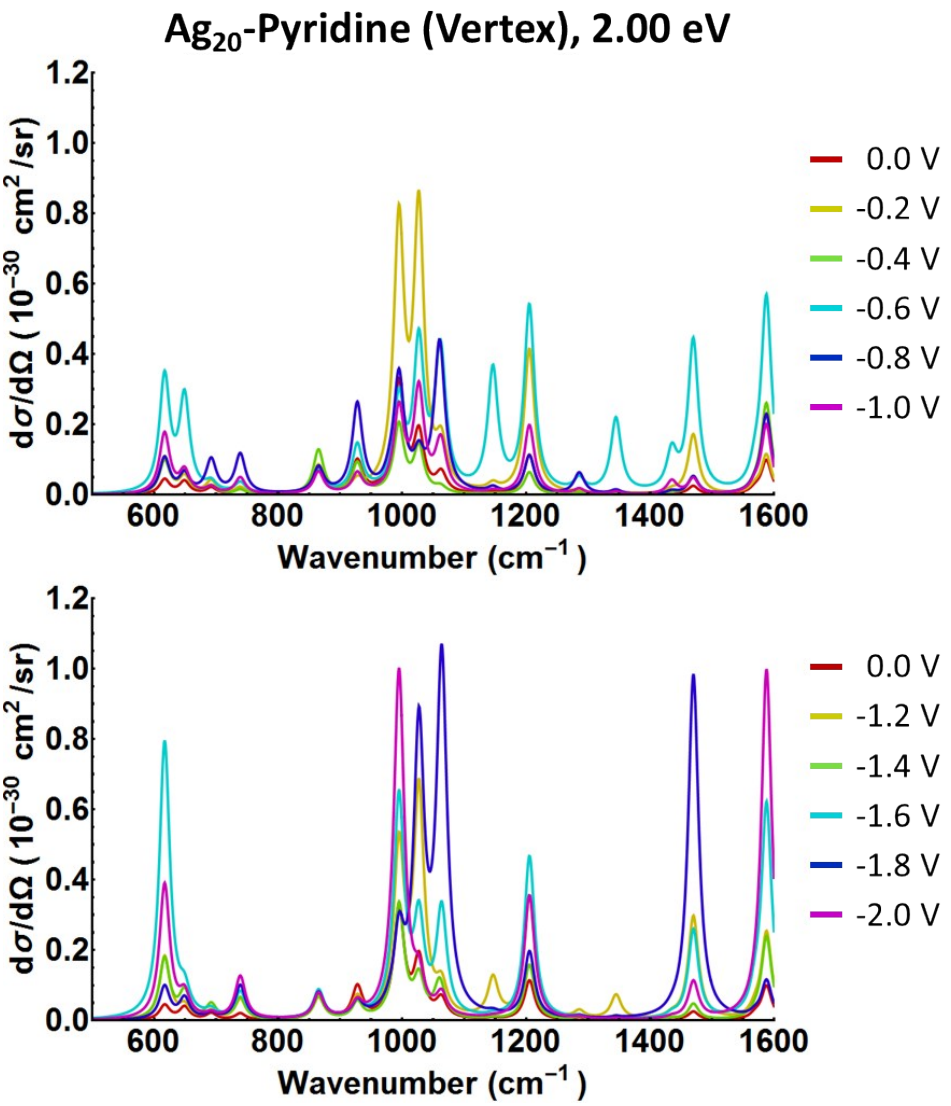

Figure S4. Normal Raman spectra for the Vertex geometry of the Ag_{20}-pyridine complex at the INDO/SCI level, showing the effect of applied potentials from 0.0 to -2.0 V within the OESA model.

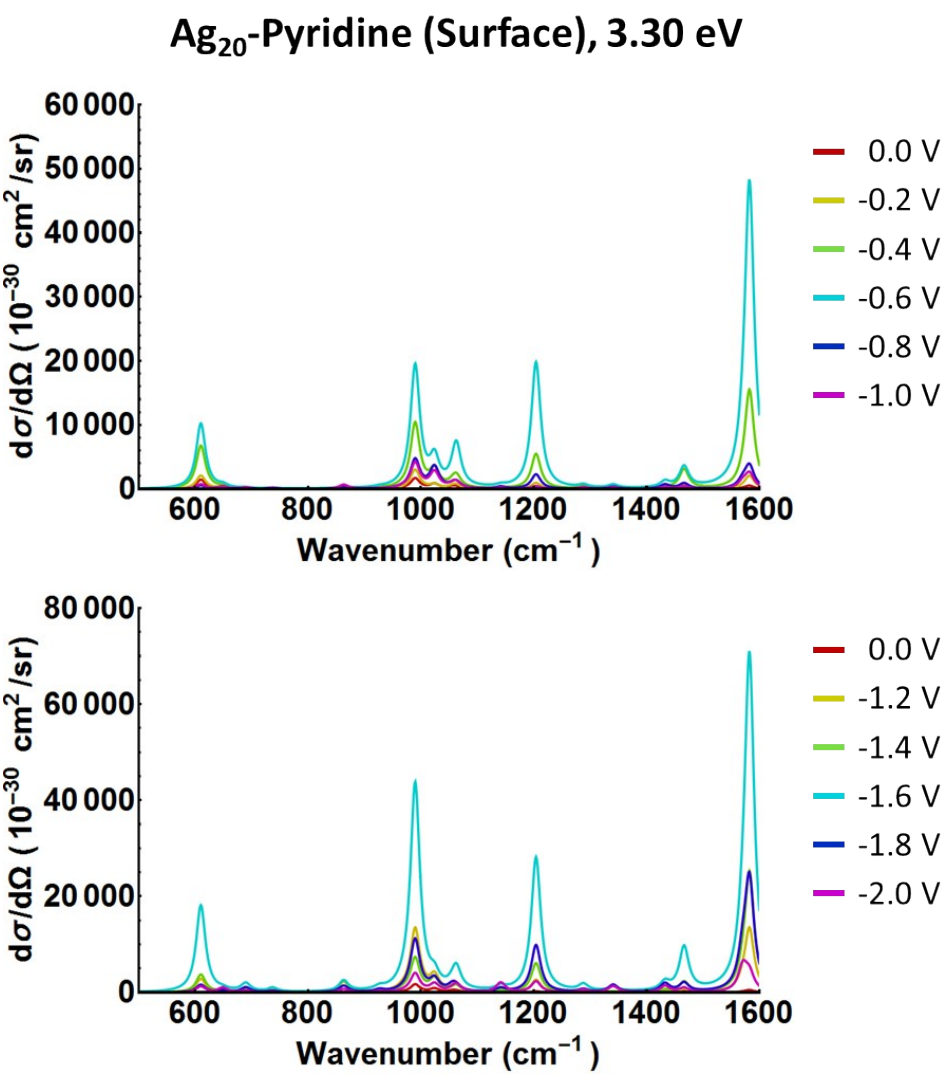

Figure S5. Resonance Raman spectra for the Surface geometry of the Ag_{20}-pyridine complex at the INDO/SCI level, showing the effect of applied potentials from 0.0 to -2.0 V within the OESA model.

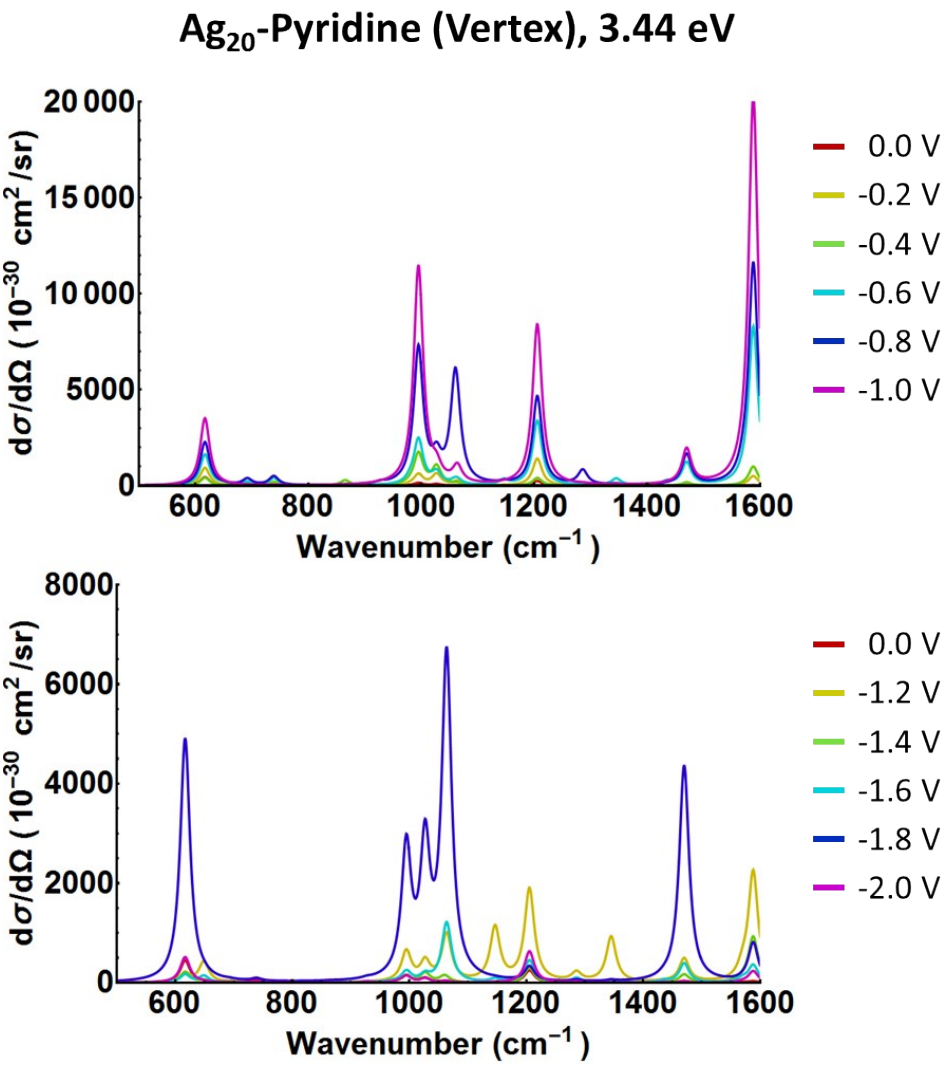

Figure S6. Resonance Raman spectra for the Vertex geometry of the Ag_{20}-pyridine complex at the INDO/SCI level, showing the effect of applied potentials from 0.0 to -2.0 V within the OESA model.