Supplementary Information for Exploring charge-transfer effects at metal-molecule interfaces through modeling Surface-Enhanced Raman Spectroscopy (SERS)

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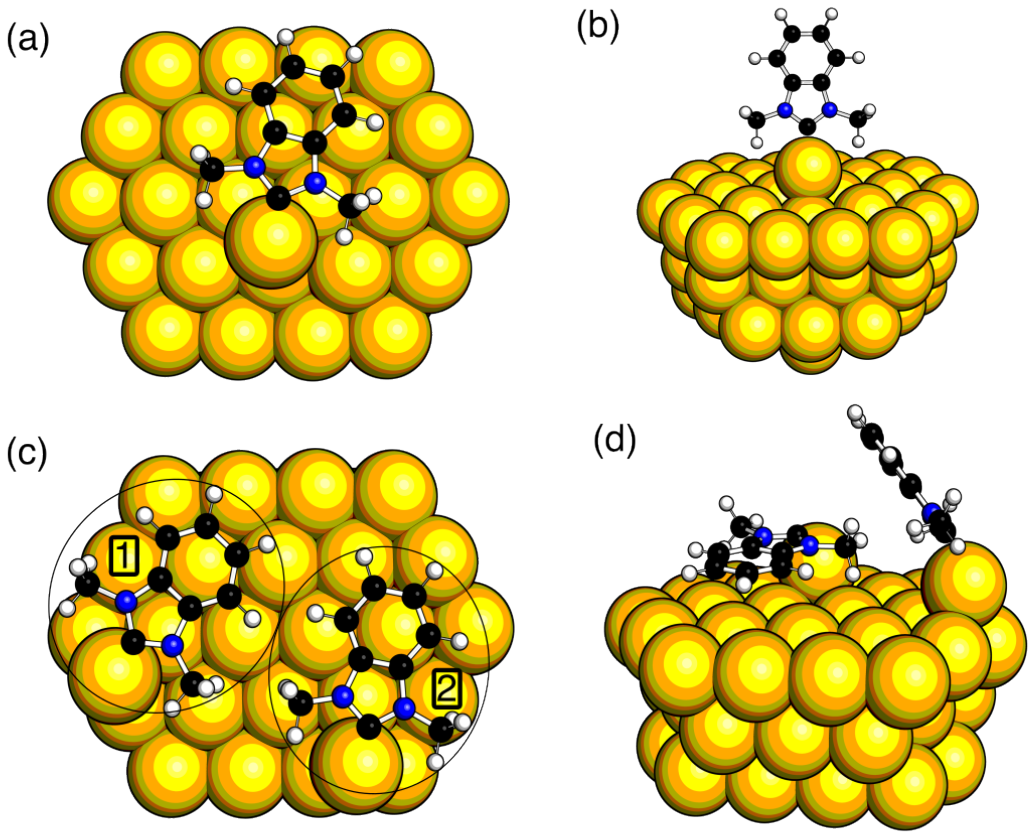

FIG. S1. Visualization of different NHC-Au_{58} geometries, where (a) is the flat configuration and (b) is the vertical for the NHC monomer, and (c) is the flat configuration and (d) is the mixed configurations for two NHCs.

I. SYSTEMS

The geometry of the N-Heterocyclic Carbenes (NHCs) are shown graphically in Figure S1. In our discussion of the two flat NHCs, which can be seen in Figure S1(c), F1 refers to the NHC circled and labeled with the number 1, while F2 refers to the NHC circled and labeled with the number 2.

II. EXTENDED RAMAN BOND DECOMPOSITIONS

For ease of visualization, we have provided extended Raman bond decompositions for the NHC molecules. Specifically, figure S2 shows these decompositions for the two flat NHC molecules and the mixed NHC configuration on the Au_{58} surface.

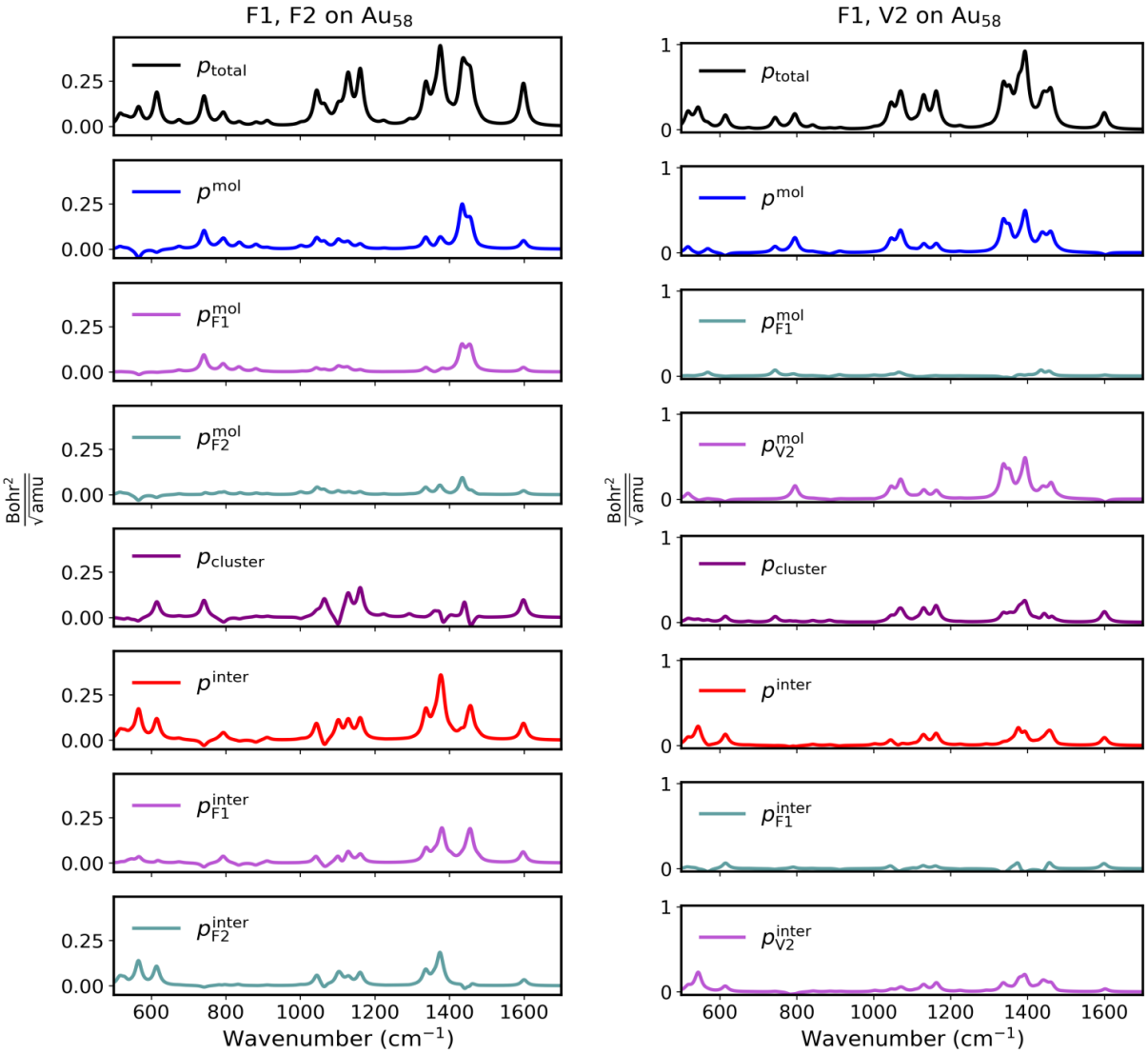

FIG. S2. Extended Raman bond decompositions for the NHC molecules. The left image corresponds to the extended system with two flat molecules, and the right image corresponds to the extended system with a mixed configuration.

All cartoons of the model systems and the visualization of the Raman bonds were generated

using PyMOL.[1]

III. TERS IMAGES OF BENZENE

For the free benzene, TERS images of three modes were generated. Due to the computational cost, only one mode was scanned for the benzene on Ag_{40} substrate. The incident frequencies were chosen based on the maximum absorption.

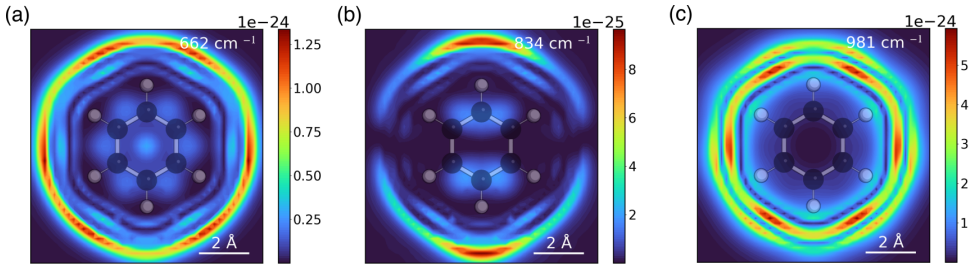

FIG. S3. TERS images of a free benzene molecule generated from a Ag_{20} tip.

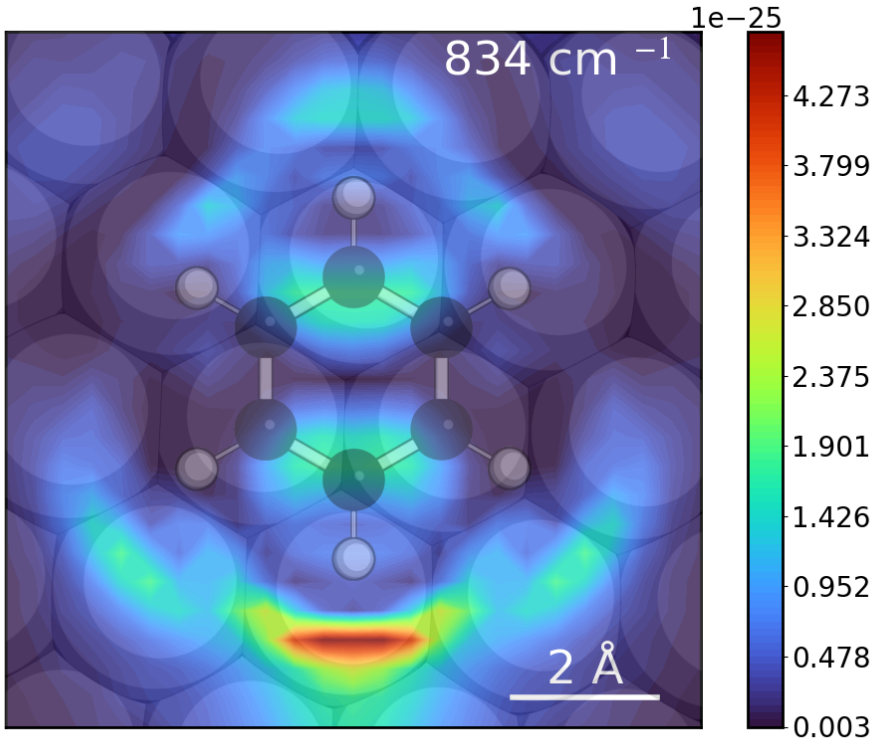

FIG. S4. TERS image of a benzene molecule on Ag_{40} substrate scanned with a Ag_{20} tip.

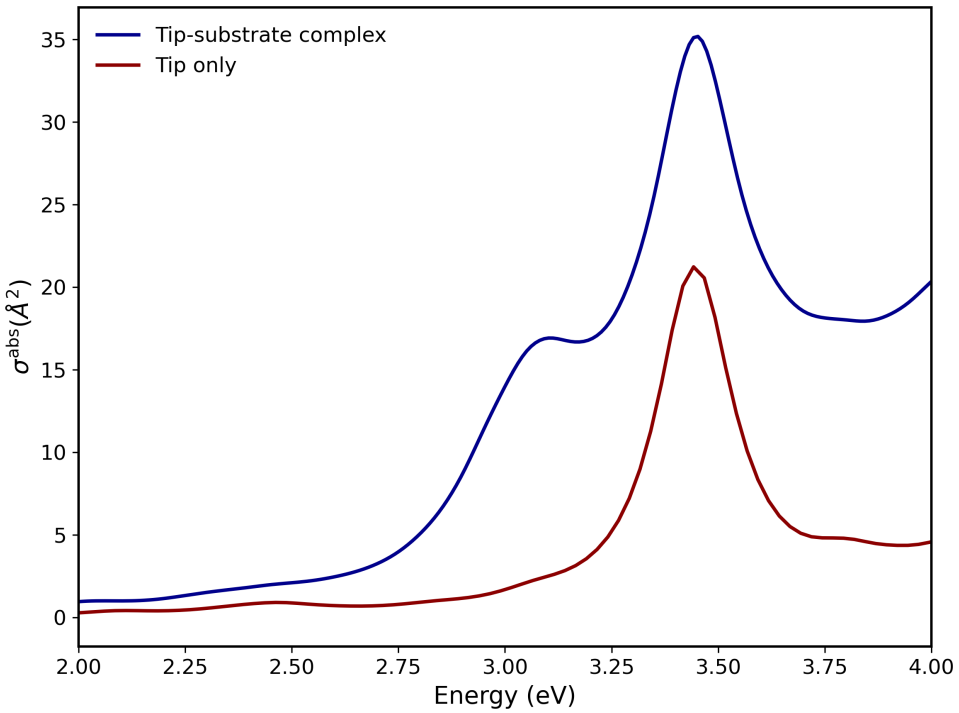

FIG. S5. Absorption spectra of a stand alone Ag_{20} tip and the Ag_{20}-Ag_{40} complex.

IV. SIMPLIFIED RAMAN BOND MODEL OF TERS IMAGES

For the other two modes of the free benzene molecule, the Raman bonds decomposition was also carried out as shown in Figure S6.

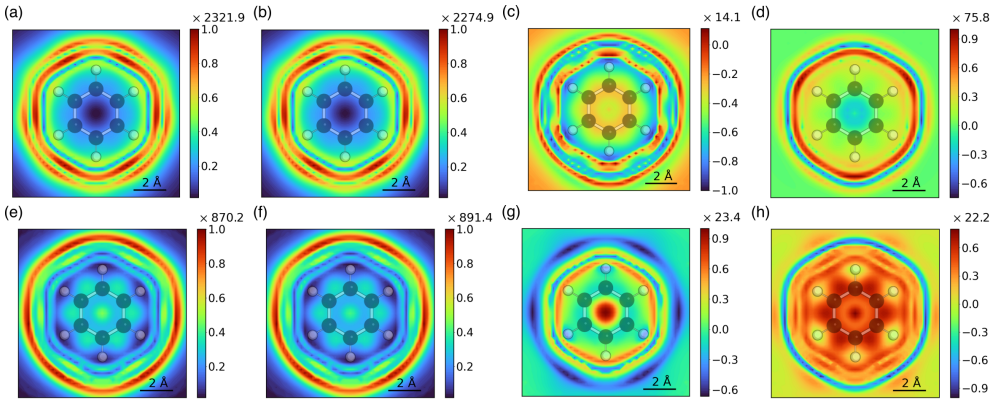

FIG. S6. Raman bond decomposition of mode 662 cm^{-1} (a)-(d) and mode 981 cm^{-1}(e)-(h).

REFERENCES

[1] "The PyMOL Molecular Graphics System, Version 1.2r3pre, Schrödinger, LLC." (2019).