

## Supplementary Materials

### 1. Raman spectra of (a) transformer oil and (b) methanol

In the experimental Raman spectrum of methanol, there are two obvious Raman peaks with wavenumbers between 2800 and 3000  $\text{cm}^{-1}$ ; these are caused by the C-H stretching vibration. This paper aims to study the enhancement of methanol Raman peaks in transformer oil by applying SERS. However, there are many C-H bonds in transformer oil, resulting in high-intensity Raman peaks at 2800 ~ 3000  $\text{cm}^{-1}$ , completely obscuring the Raman peaks of the methanol. In addition, the simulation results show that the Raman peak caused by the C-O stretching vibration mode is most affected by surface enhanced Raman scattering. This paper only studies the methanol Raman peaks located between 500 and 1800  $\text{cm}^{-1}$ .

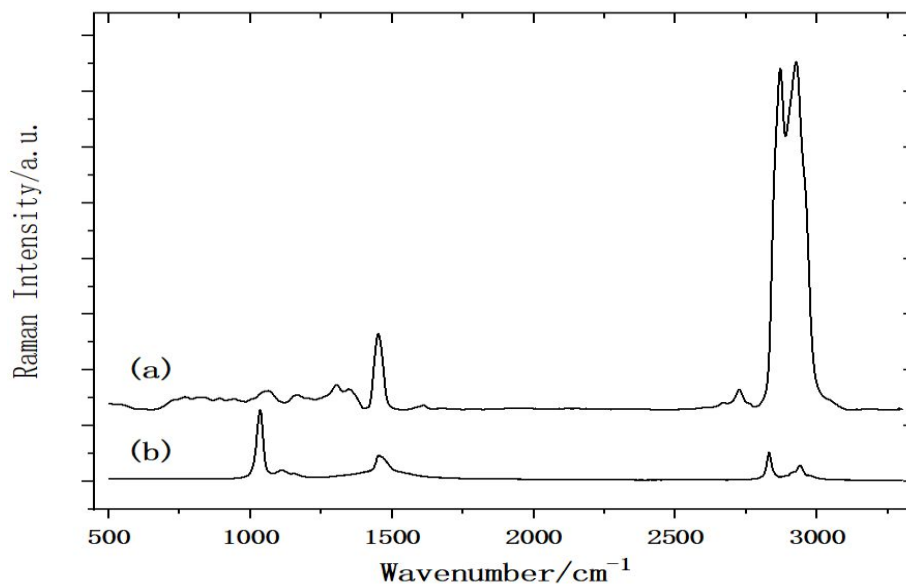


Figure S1 Raman spectra of (a) transformer oil and (b) methanol

### 2. Raman Spectra of (a) 3-21G, (b) 6-31G, (c) 6-311G and (d) experiments

The construction of the  $\text{Ag}_{19}$  geometry is based on the LANL2DZ basis set. The B3LYP method was selected to calculate the Raman spectra of the methanol molecules. Comparing the Raman spectra calculated by 3-21G, 6-31G, and 6-311G with pure methanol, the 6-311G basis set is more suitable for the experimental data. In our earlier research,[35] the 6-311G basis set was used to calculate the Raman spectrum of the methanol molecule.

The calculated methanol Raman spectra of different basis sets are shown in Figure S2.

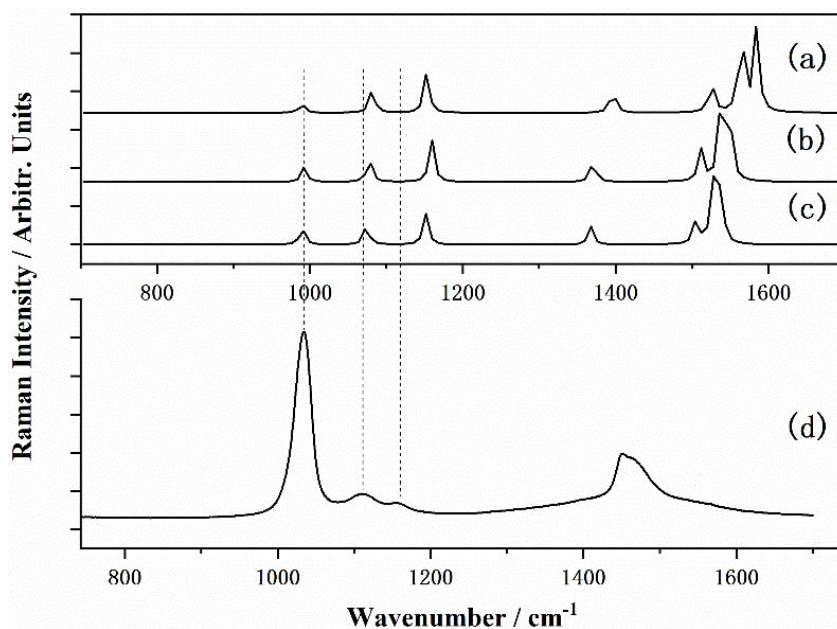


Figure S2 Raman spectra of (a) 3-21G, (b) 6-31G, (c) 6-311G and (d) experiments

### 3. Raman spectra affected by diffusion and polarization basis sets

The effects of the diffuse and polarization functions are mainly concentrated in the range of wavenumbers between 960 and 1200  $\text{cm}^{-1}$  (the Raman peaks of methanol are at 1034, 1110 and 1156  $\text{cm}^{-1}$ ). Figure S3 calculates some basis sets with diffuse and/or polarization functions. This usually leads to a decrease in the Raman peak intensity caused by the C-O stretching vibration, except for 6-311+G (Figure S3 (d)). The distance between this Raman peak and its adjacent Raman peak is shortened.

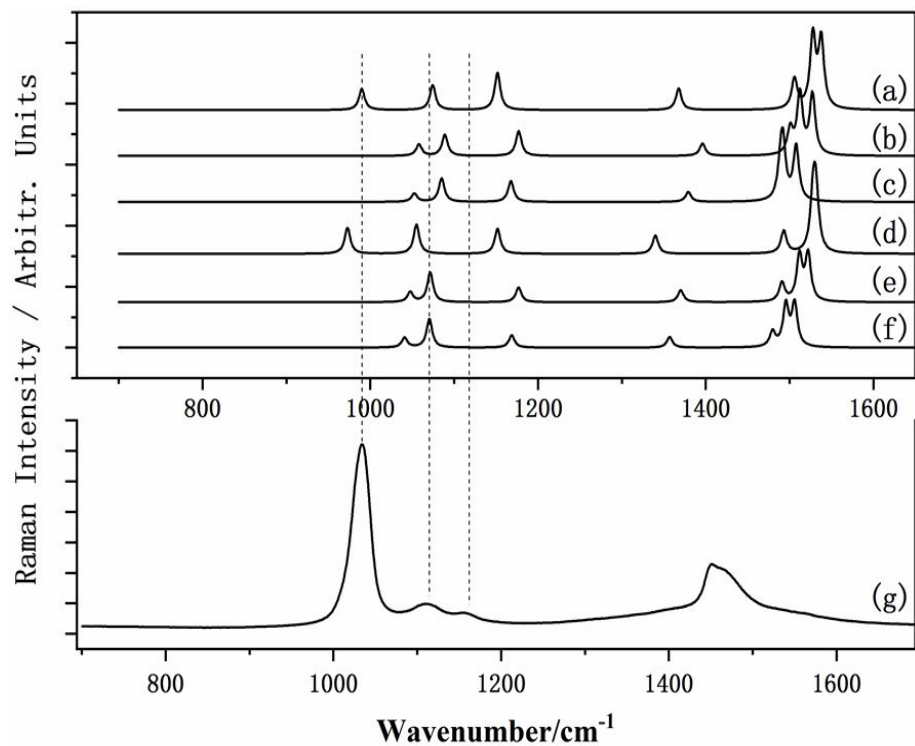


Figure S3 Raman spectra of (a) 6-311G, (b) 6-311G(d), (c) 6-311G(d,p), (d) 6-311+G, (e) 6-311+G(d), (f) 6-311+G(d,p) and (g) experiments