Supplementary Information

Molecular Resonant Dissociation of Surface-Adsorbed Molecules by Plasmonic Nanoscissors

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4 Figures

3 Tables

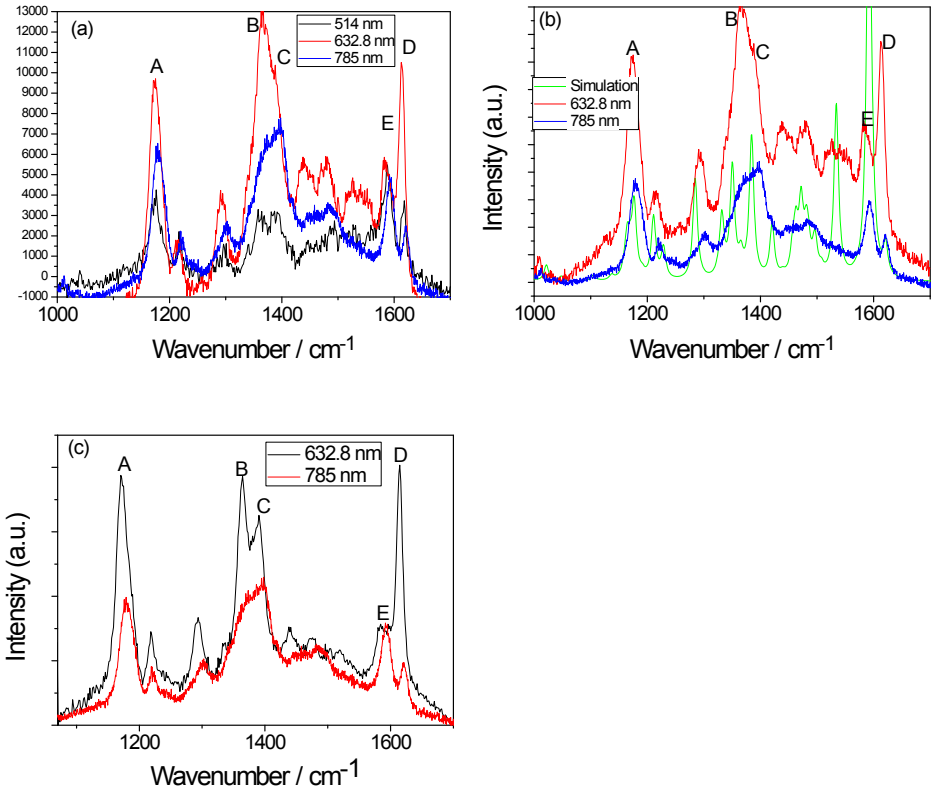

Figure S1. (a) The SERS spectra of MG in Ag sol excited at different frequencies, and (b) the comparison between the simulated normal Raman spectrum and experimental SERS spectra, where the simulated normal Raman frequencies were scaled by 0.965, and (c) the comparison between TERRS excited at 632.8 nm and SERS excited at 785 nm.

a_{39}	1176
a_{41}	1211
b_{44}	1284
a_{45}	1350
b_{49}	1385
a_{47}	1420
b_{55}	1471
a_{66}	1534
b_{61}	1591
a_{58}	1620

Table S1. The calculated vibration frequencies (cm^{-1}) and vibrational modes of MG, according to the simulated spectrum (green line) in Fig. S1(b).

b_{31}	1180
b_{32}	1196
a_{31}	1204
a_{32}	1284
a_{33}	1302
b_{36}	1344
b_{37}	1356
a_{34}	1402
a_{39}	1472
b_{41}	1482
b_{42}	1555
b_{43}	1572
a_{40}	1600

Table S2. The calculated vibration frequencies (cm^{-1}) and vibration modes of large fragment in Fig. 3(d).

$^{2}a_{2}$	1097
$^{1}b_{3}$	1161
$^{2}b_{2}$	1183
$^{1}a_{3}$	1262
$^{2}b_{4}$	1442
$^{2}b_{5}$	1489
$^{1}a_{5}$	1521

Table S3. The calculated vibration frequencies (cm^{-1}) and vibration modes of small fragment in Fig. 3(e).

According to our experimental condition, it is monolayer, and the effective size is about

$\pi R^2 \approx 78.5$ nm^2, where R=5 nm is the effective tip-enhanced region, because when R=5 nm, the intensity of surface Plasmon is decreased to the half of the strongest Plasmon at the central gap (the below Figure was calculated using FDTD Solusions, where all of parameters in calculations were based on experimental conditions). From the calculation, the size of one molecule is around 0.5 nm^2, and then there are less than 157 molecules in the effective region.

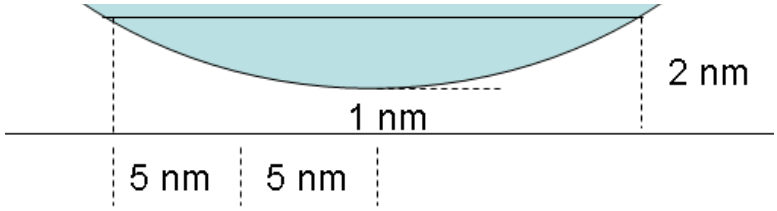

Figure S2. | Plamson intensity in the nanogap in HV-TERS.

By comparing the intensity of peak C in Fig. 2 (a) and (c), more than 80% of 157 molecules have been dissociated. Also, by comparing the ratio of intensities of experimental and theoretical Raman peaks of G and I in Fig. 2(c), more than 40% molecules of $N(CH_3)_2$ are still present.