Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION:

Enhance Raman scattering based on a ZnO/Ag nanostructured substrate: an in-depth study of the SERS mechanism

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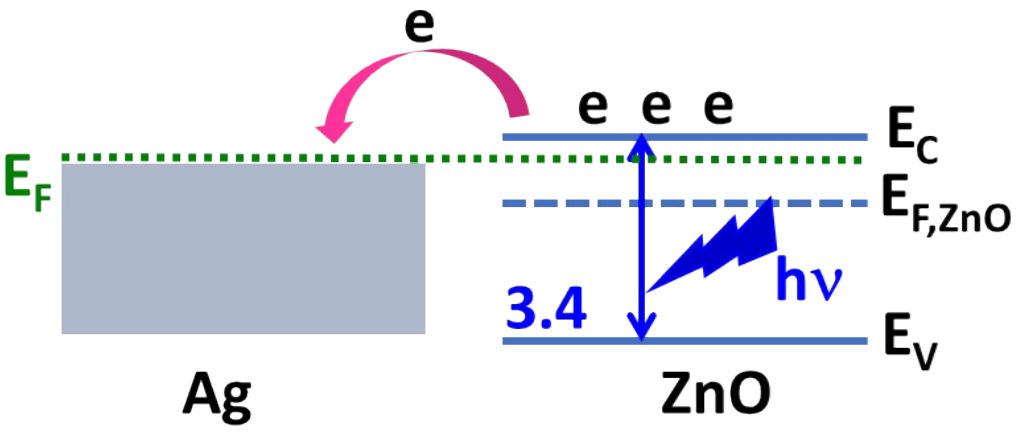


Figure S1. Schematic energy band diagram of ZnO-Ag interface of charge transfer from E_C of ZnO to E_F under 305 nm laser excitation, causing fluorescence quenching of ZnO.

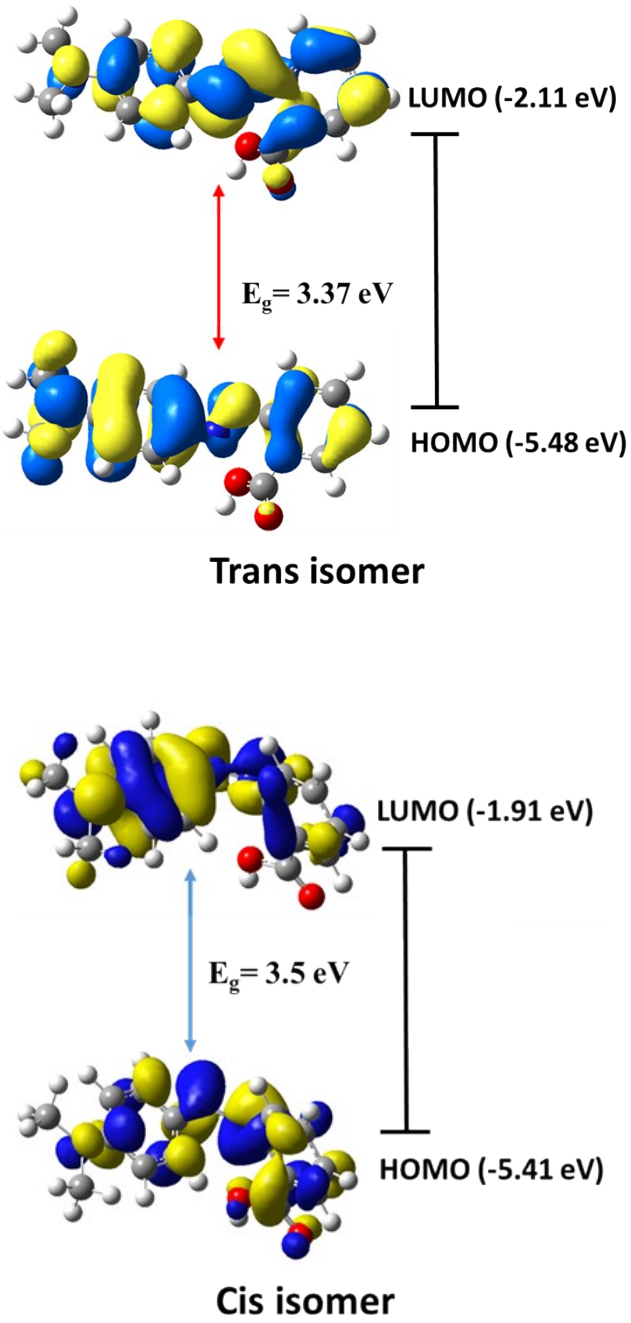


Figure S2: The frontier molecular orbitals (highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)) of two trans and cis isomers of MR molecule.

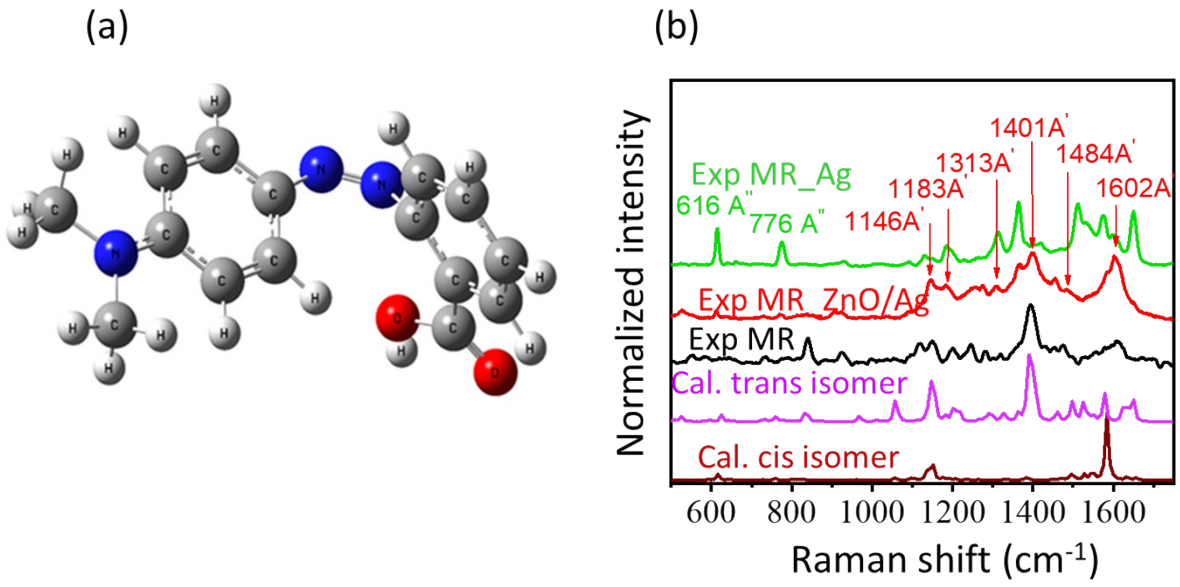


Figure S3: (a) The Optimized molecular structure of the cis isomer; (b) Normalized Raman spectra of Methyl Red in comparison between theoretical calculation study for neutral cis- and trans isomers.

Table S1: Bands assignment of MR molecule in comparison between theoretical calculation (neutral cis isomer), typical Raman spectrum, and SERS substrates of ZnO/Ag and Ag.

Raman $_{calculation}$ (cm^{-1}) Cis-	Raman $_{experiment}$ (cm^{-1})	Frequency (cm^{-1}) On SERS surfaces		Band assignments Cis form
		ZnO/Ag	Ag	
616	-	612	616	C-H in CH3 Out of plane (A'')
760	-	770	776	C-H Out of plane bending (A'')
1148	-	1146	1132	(C-H in CH_3 In plane bending) (A')
1176	-	1183	1185	C-H in Benzen; In plane bending (A')
1328	1320	1313	1314	C=C; Stretching (A')
1386	1394	1401	1364	C-H in CH_3 ; Stretching (A')
1496	1475	1484	1512	C-H; in plane bending (A')
1592	1608	1602	1576	(N=N ; C=C; Stretching) (A')
1634	-	1650(sh)	1650	C=C; streching (A')

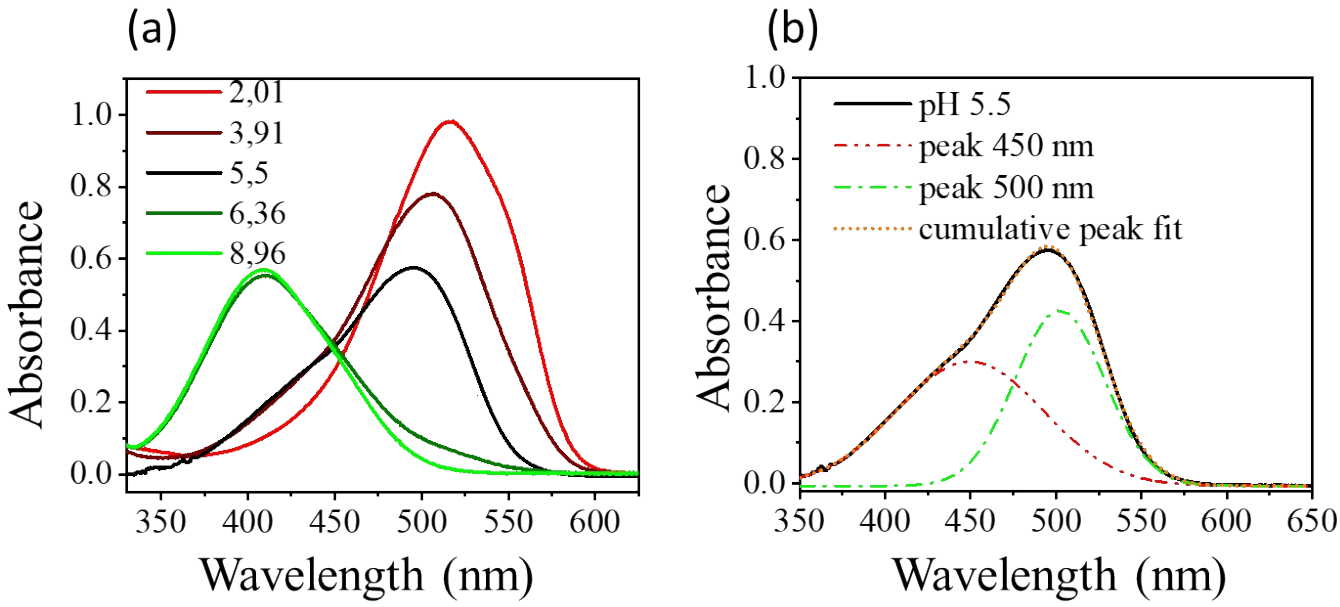


Figure S4: Absorption spectra of MR in ethanol under different pH. The spectrum at pH 5.5 was obtained without needing any pH adjustment.

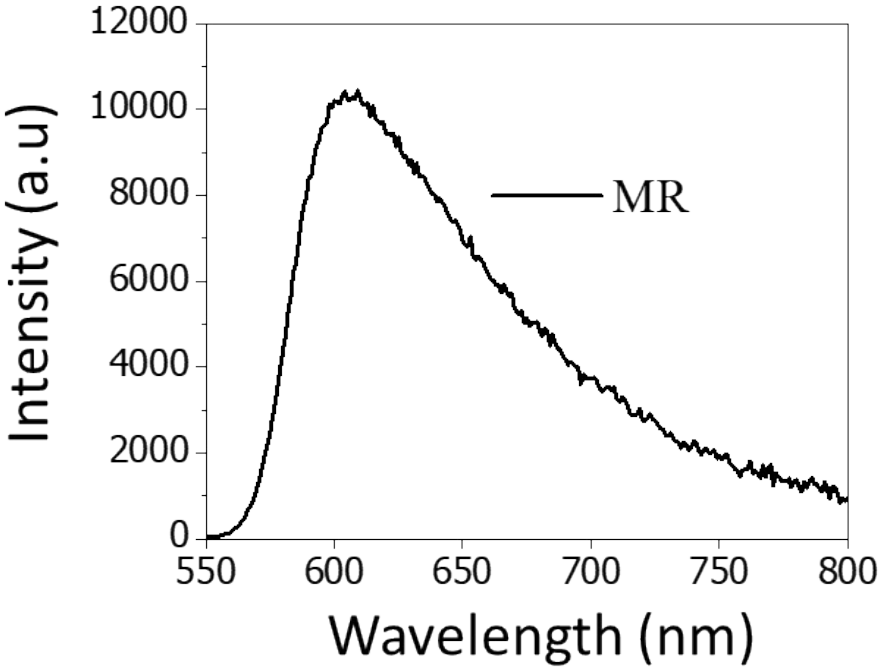


Figure S5. Fluorescence spectrum of MR under excitation wavelength at 500 nm.

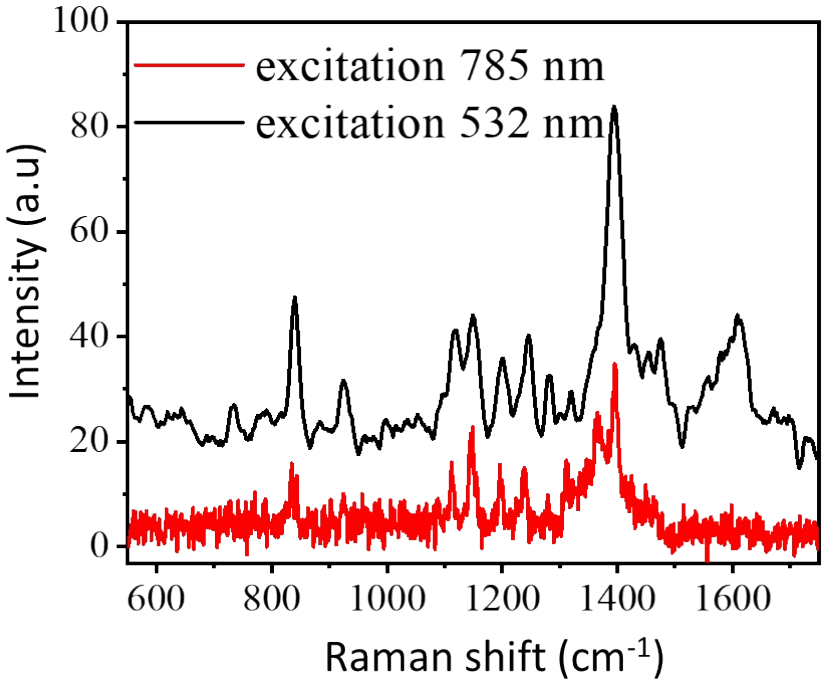


Figure S6: Raman spectra of MR (10^{-2} M) under two different lasers excitation 532 nm and 785 nm.

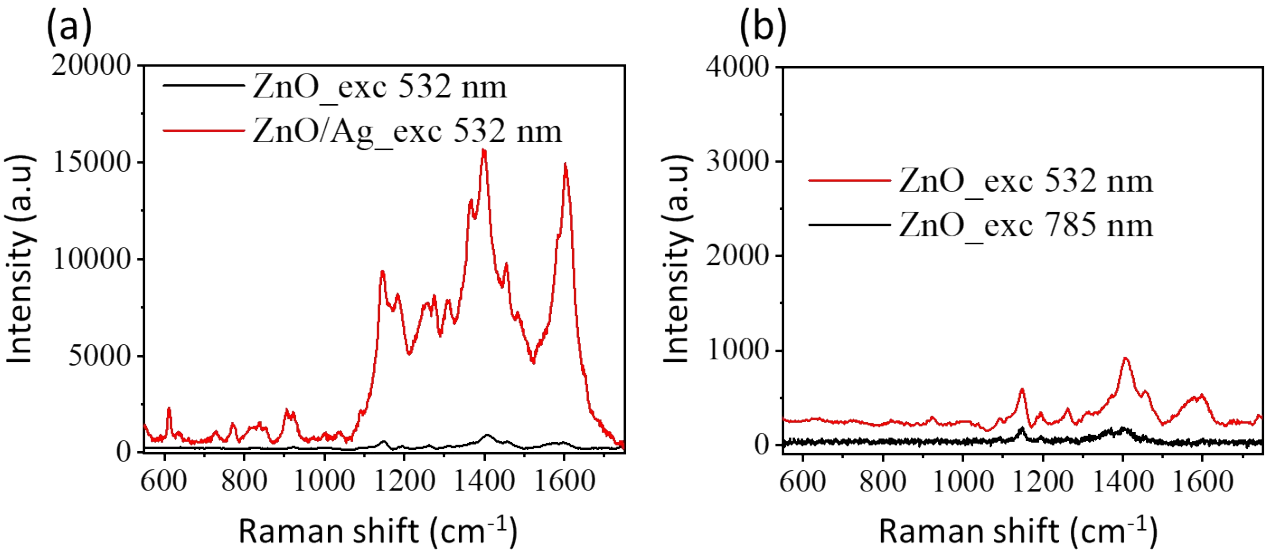
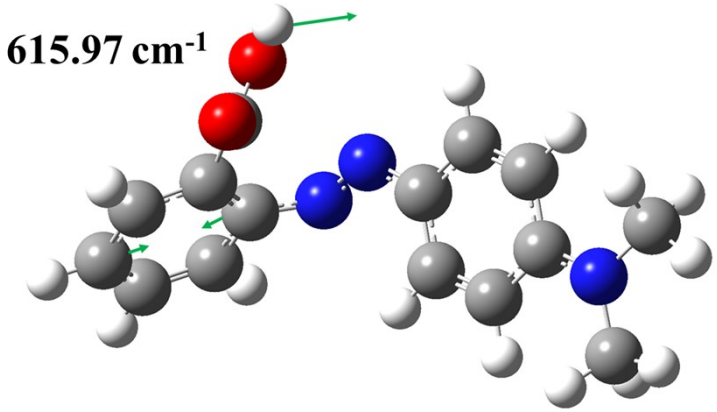
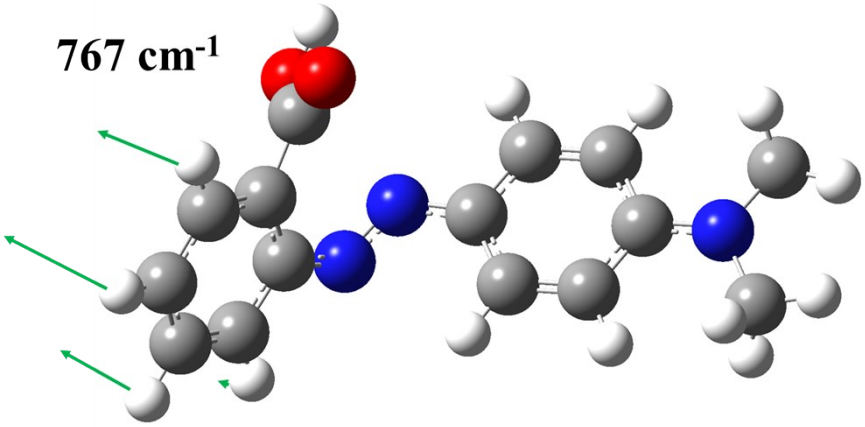
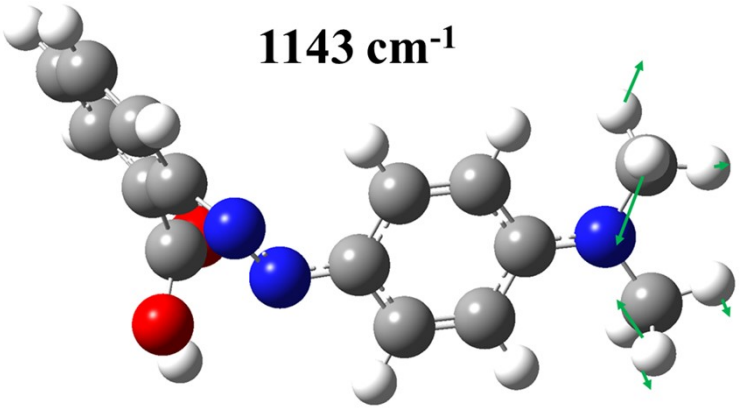


Figure S7: SERS spectra of MR adsorbed on ZnO surface (a) in comparison with ZnO/Ag surface; and (b) under different excitation wavelengths.

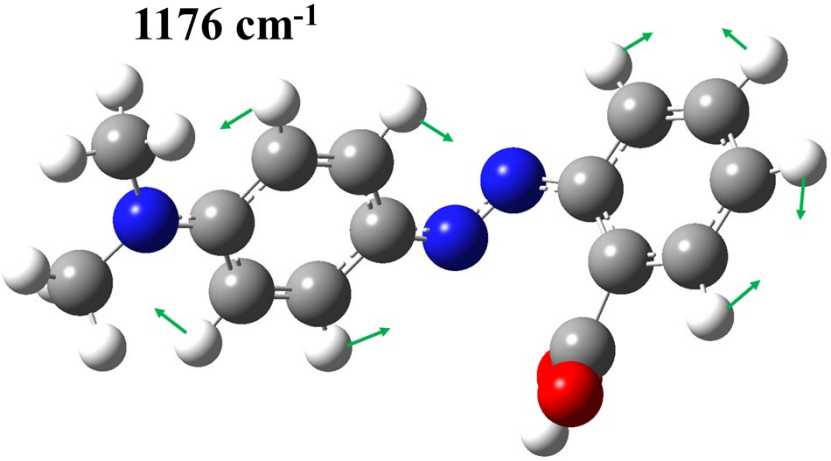
Displacement vectors of neutral trans-isomer at some basic vibration modes:



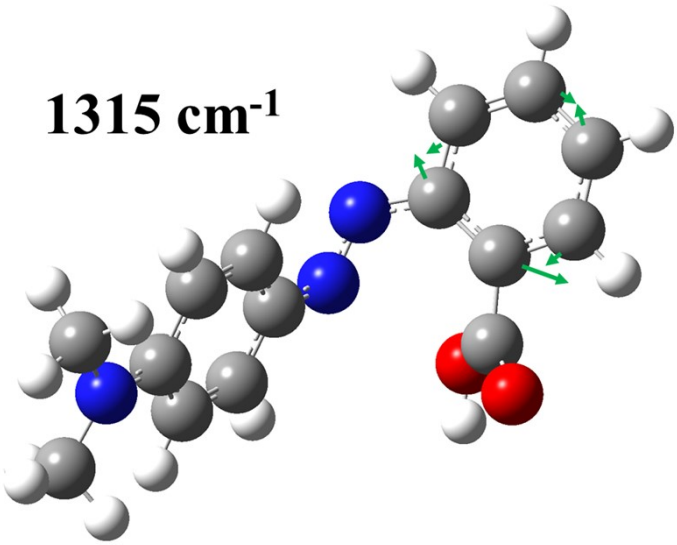




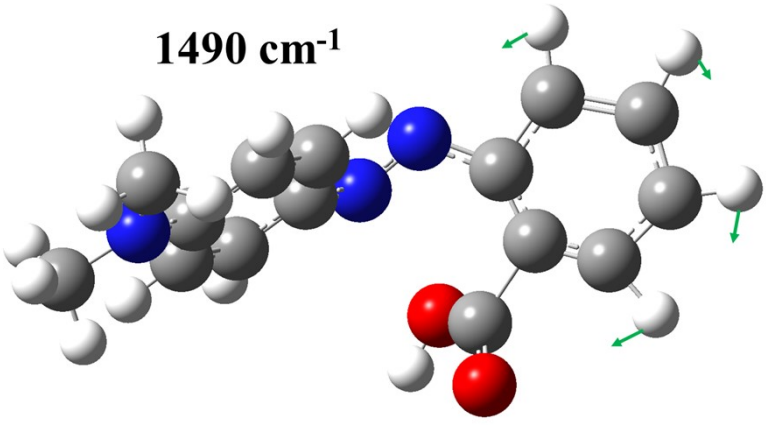
1176 cm^{-1}



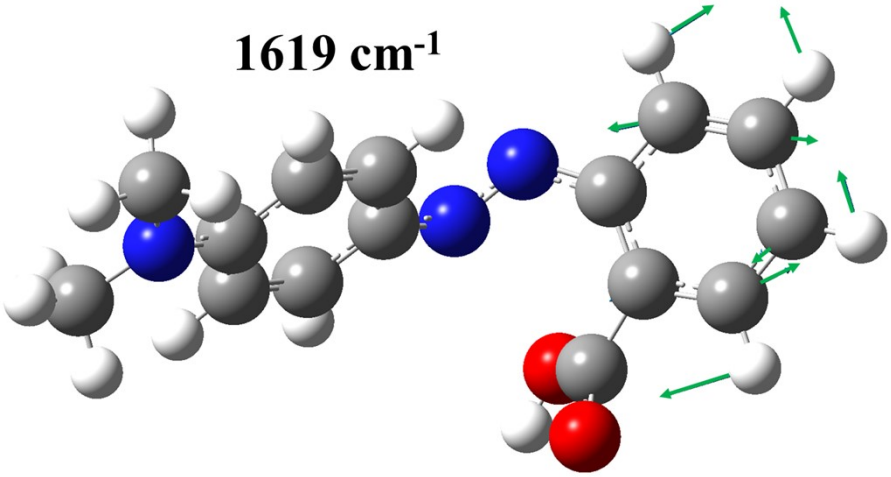
1315 cm^{-1}



1490 cm^{-1}



1619 cm^{-1}



1639 cm^{-1}