



Adsorption of cystine on copper cluster : A DFT study

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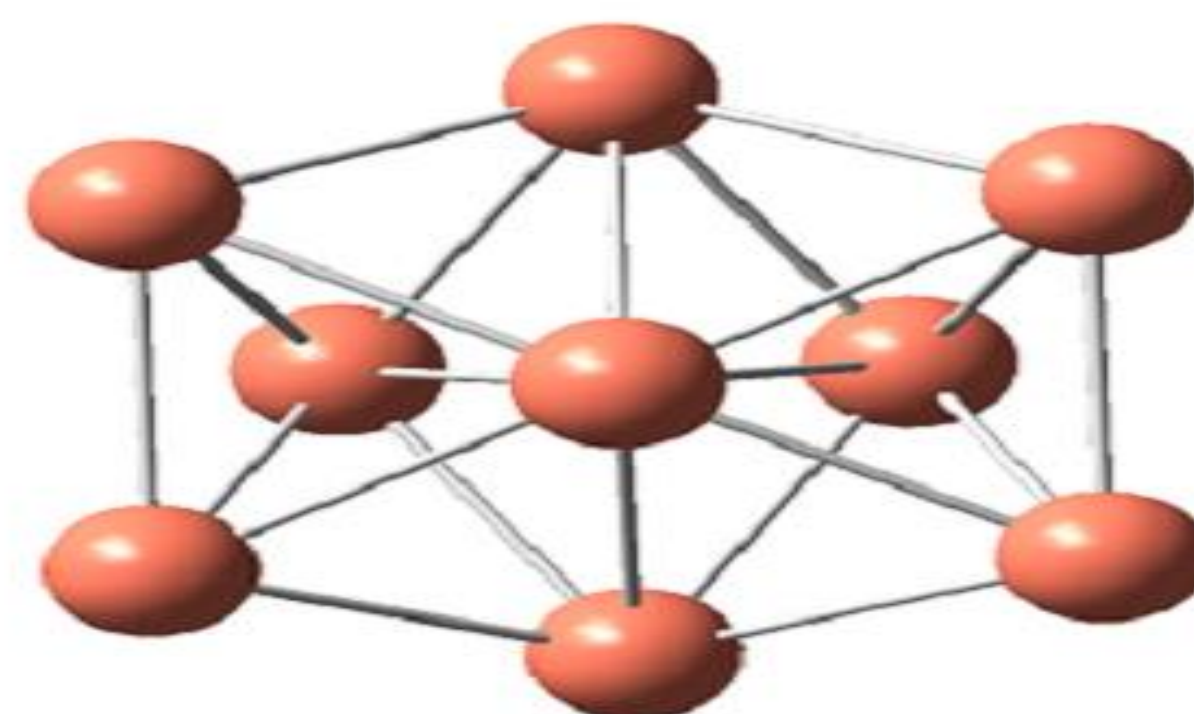
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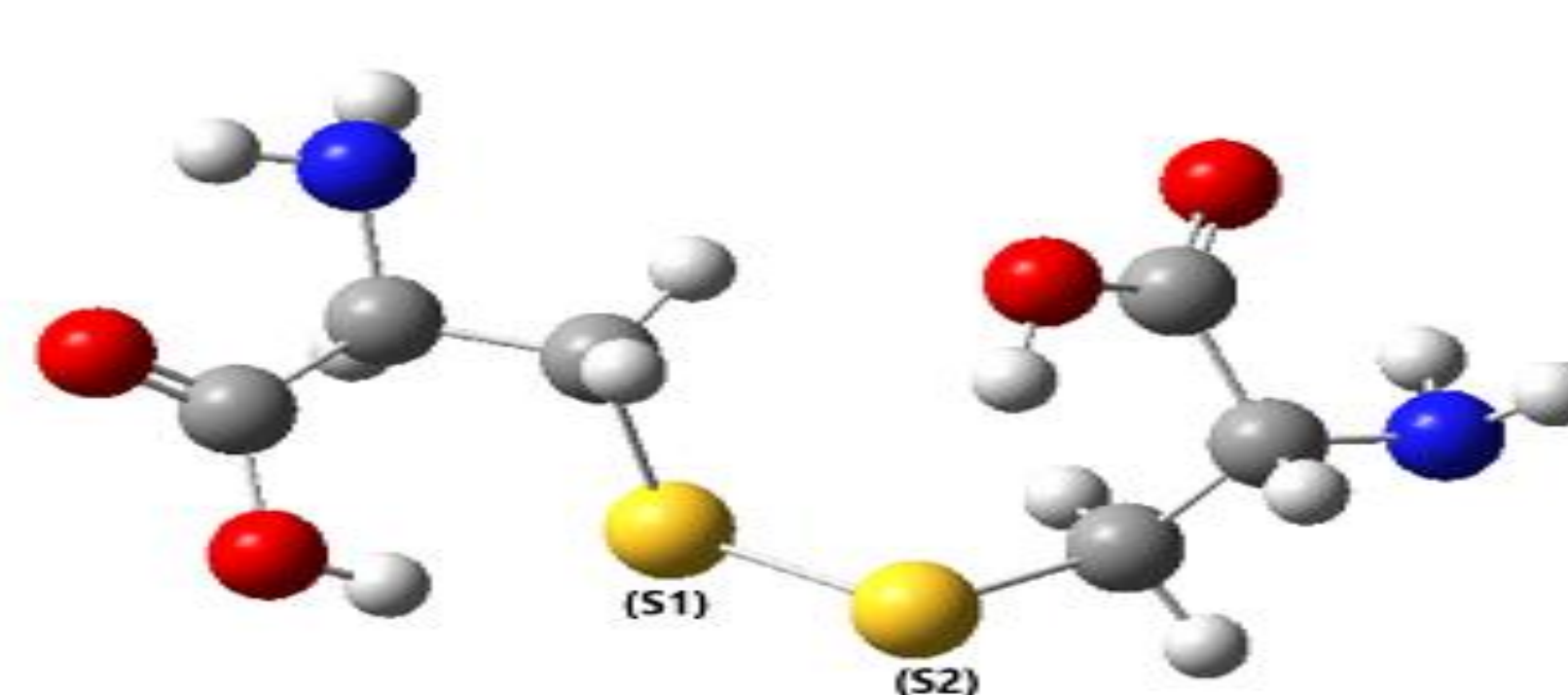
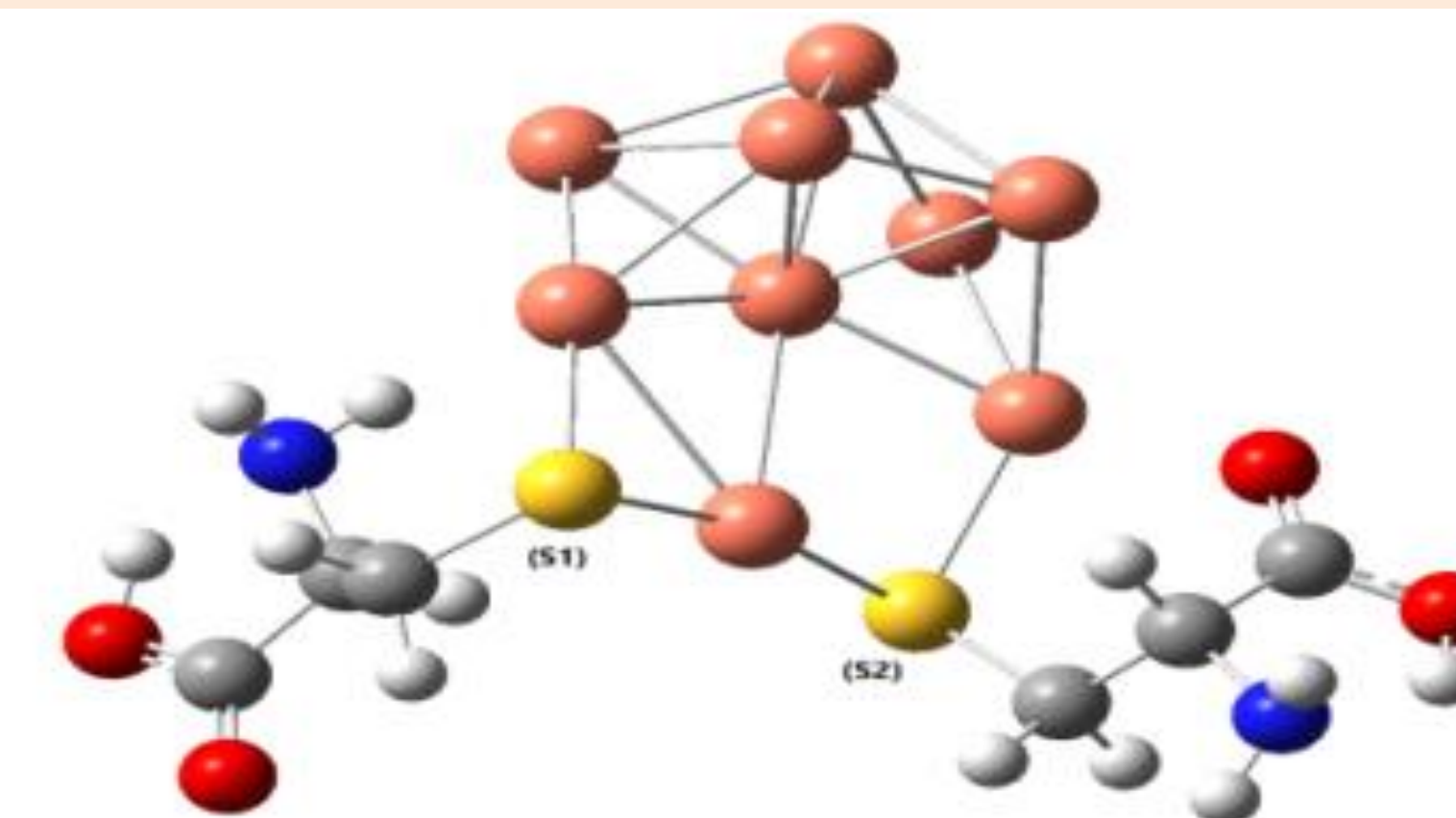
Background

- Cystine has a disulfide linkage which is responsible for stabilization of secondary & tertiary structure of proteins.
- Probing stability of disulfide in cystine using Cu metal as SERS substrate by means of DFT calculation.

Cu9 Cluster



Cystine

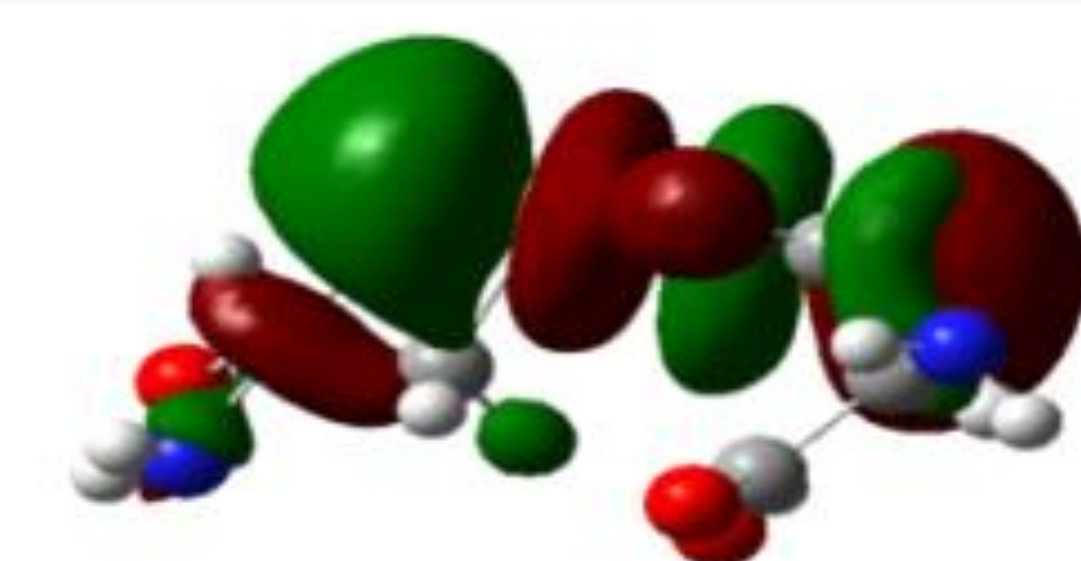


Optimized structure of Cystine-Cu9 system with highest interaction energy -78.9 kcal/mol.

Method

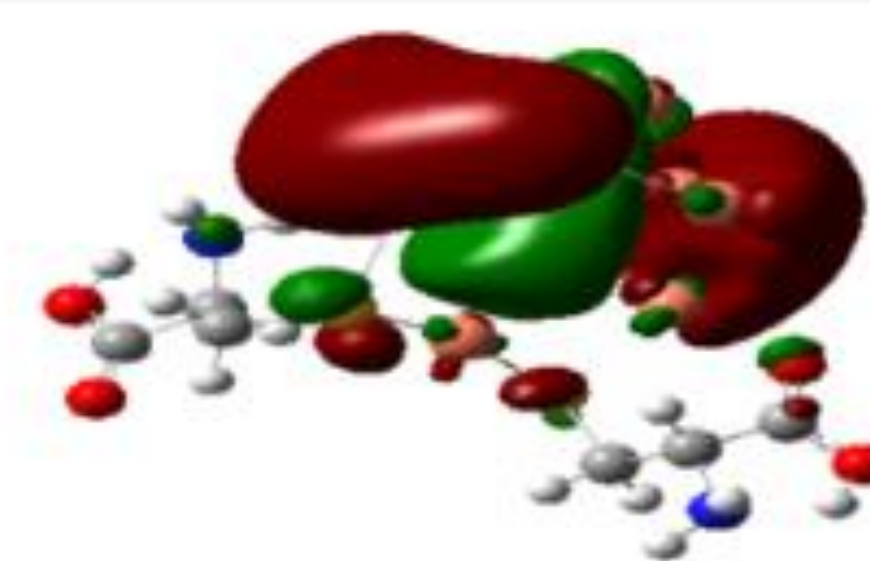
B3LYP functional and LANL2DZ basis set with relativistic effective core potential for Cu and 6-31G* basis set for C,H,O,N and S atoms.

HOMO-LUMO gap for (a) Cystine (b) Cystine-Cu9



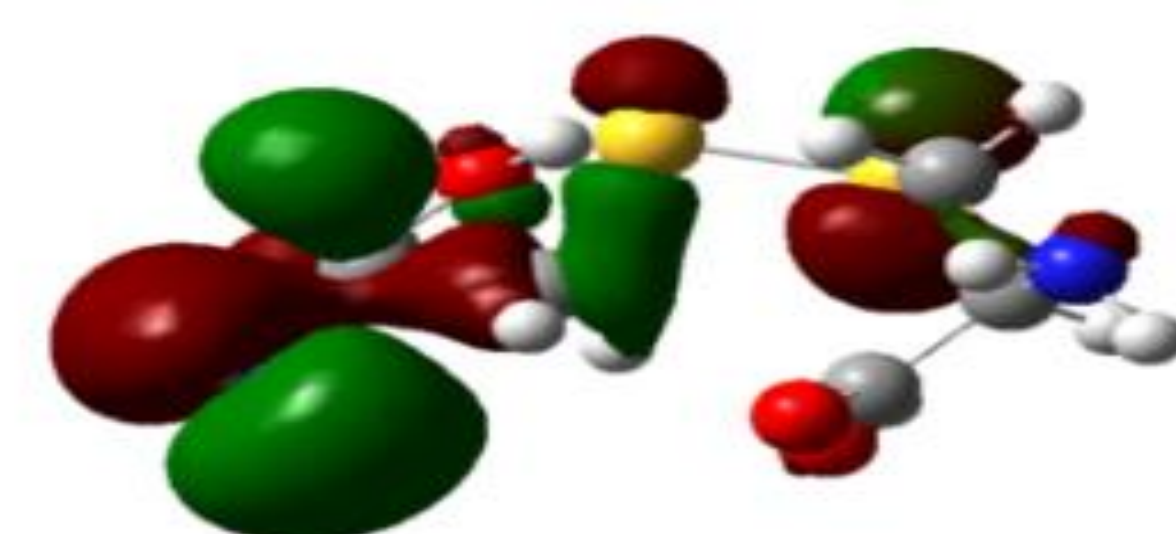
LUMO = -1.883 eV

$\Delta E = 4.933$ eV



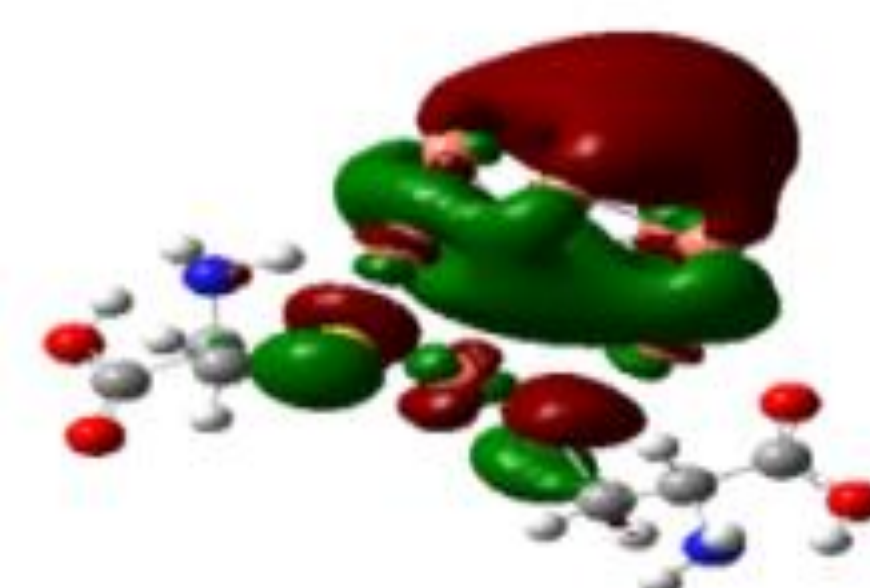
LUMO = -2.351 eV

$\Delta E = 2.292$ eV



HOMO = -6.816 eV

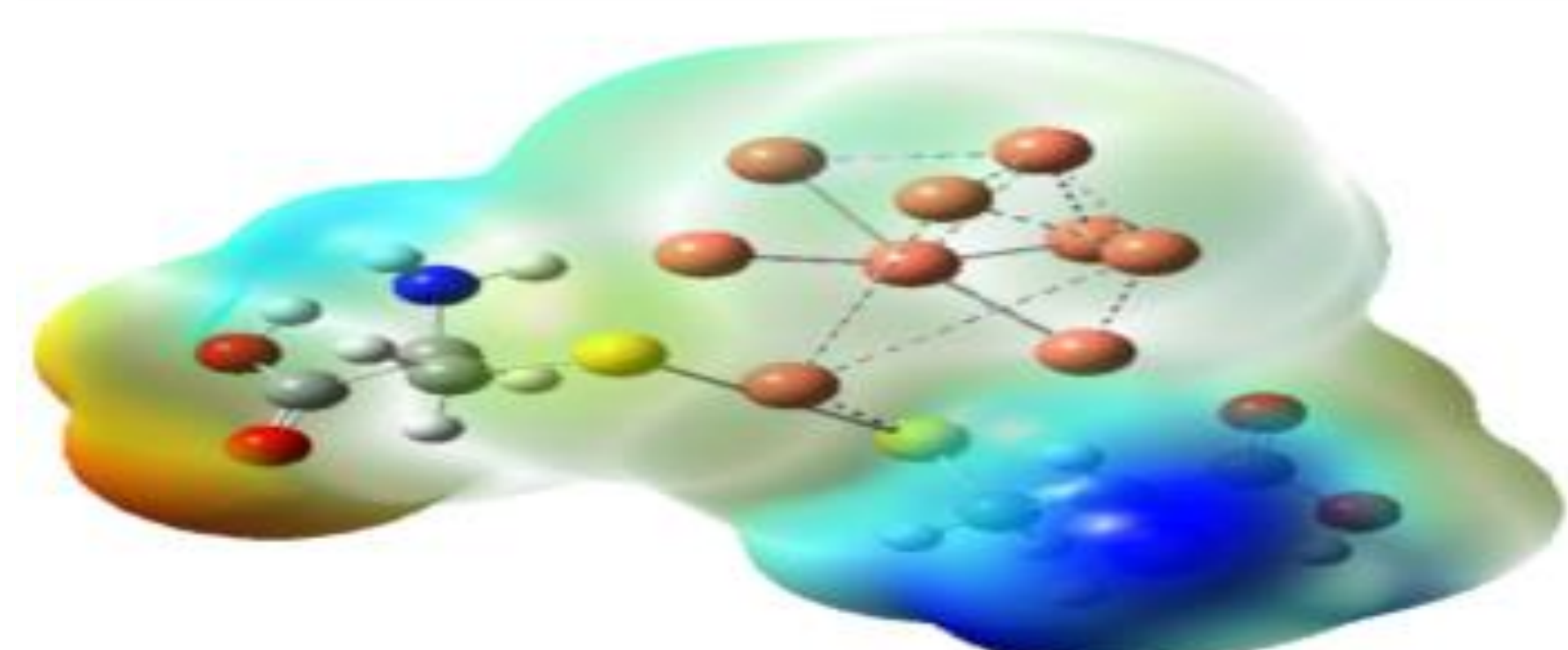
(a)



HOMO = -4.644 eV

(b)

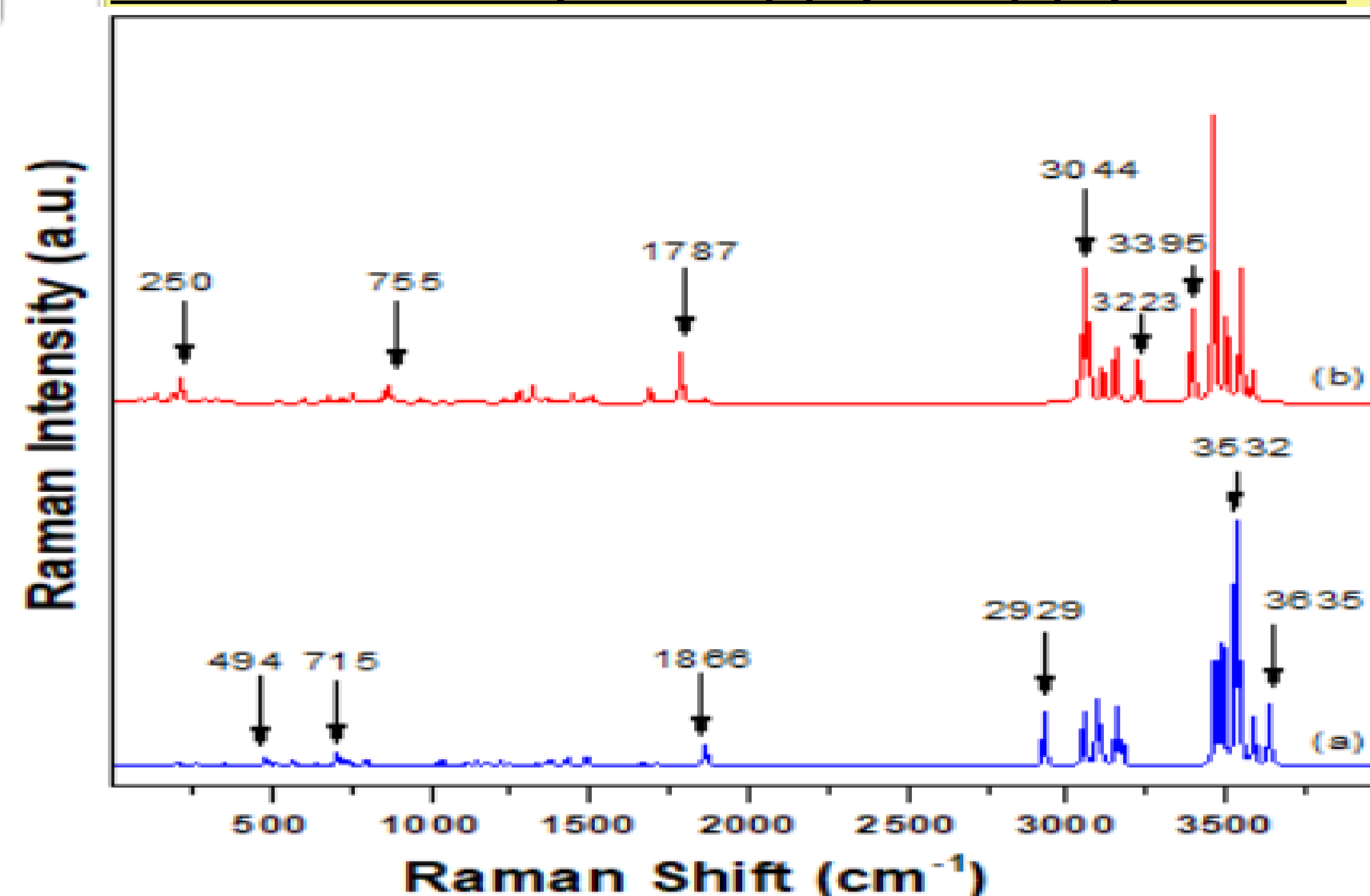
Electrostatic potential (ESP) charge distribution on cystine-Cu9 system



-6.953×10^{-2} 6.953×10^{-2}

Less electron density on COOH moiety which is towards the cluster and on disulfide confirms that electron density is transferred to Cu cluster.

Calculated Raman spectrum (a) cystine (b) cystine-Cu9



Disappearance of vibrational $\nu_{\text{S-S}}$ mode (494 cm^{-1}) and appearance of $\nu_{\text{Cu-S}}$ (250 cm^{-1}) confirms the chemisorption of cystine through its disulfide linkage which is in good agreement with experimental study [1].

[1] P. J. Arathi, et al., *Spectrochim Acta A Mol Biomol Spectrosc.* 196, 229 (2018).

Conclusion

- The interaction between Cu9 cluster and cystine is chemisorption as there is formation of bond between sulfur and Cu and between oxygen and Cu atom.
- After interaction the disulfide bond gets cleaved which suggests its interaction majorly through sulfur atoms and this corroborates well with the earlier reported experimental findings.
- Disappearance of $\nu_{\text{S-S}}$ mode (494 cm^{-1}) confirms the interaction through disulfide linkage by means of its cleavage.
- Red shift in Raman frequencies of $\nu_{\text{C=O}}$ and $\nu_{\text{O-H}}$ reveals a strong interaction with Cu cluster through its COOH moiety as well.

Some significant donor-acceptor NBO interactions in Cu cluster and cystine moiety with calculated second-order stabilization energies $E(2)$ (kcal/mol)

Donor NBO (i)	Acceptor NBO (j)	$E(2)$ for interaction (kcal/mol)
LP (2) S	LP*(7)Cu	16.20
LP (1) N	BD*(1) O – H	7.75
LP (2) S	LP*(7)Cu	17.69
LP (1) N	BD*(1) O – H	10.54
BD (1) C – O	LP* (8)Cu	3.13
LP (1) O	LP* (8)Cu	10.57

Here, BD denotes Bonding orbital, BD*; antibonding orbital, LP; lone pair of electrons, LP*; $d\pi$ -orbital of Cu atom.

- Major contribution through sulfur atoms towards Cu cluster.
- Carboxylic group also interacts with cluster.

Acknowledgement

Computer Centre, IIT(BHU) is acknowledged for providing the computational facility.