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Table 3.13: Comparison of experimental and simulated ^{1}H NMR peaks of DTT Conformer (G'TG'1/G'TT)

^{1}H NMR peaks [ppm]			Assignment[#]
Reported in literature[36,37] [in $CDCl_3$] with TSP, δ	Simulated peaks, δ [in CH_3OH with TMS]		
	G'TG'1	G'TT	
3.6-3.7	3.7	3.4	H5, m
3.3	3.0	1.9	H18, s
2.5-2.9	3.6	3.1	H3, m
2.5-2.9	2.8	2.6	H2, m

[#]: s and m denote multiplicity of the peaks namely singlet and multiplet respectively, number after atoms represent the label of the proton atom shown in figure 3.2.

3.4 Conclusion

The conformational space of DTT has several local minima and among them, the lowest iso-energic conformers were identified as G'TG'1 and G'TT. Analysis of AIM and NCI calculations revealed that there is intra-molecular H-bond formation not only by OH groups but by SH groups as well which provides stability to the titled molecule. NBO results, besides reiterating these intramolecular H-bond interactions, revealed other hyperconjugative interactions which further imparts the stability to DTT molecule. ESP charge analysis supports these observations very well. The calculated vibrational spectra too were found in good agreement with the observed experimental data.

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4.4 Conclusion

The conformational space of TGA was explored using the CCSD/cc-pVDZ level of theory. The most energetically favorable structure, referred to as GGC, was found as global minimum, in good agreement with the experimentally observed conformer. The second most stable conformer was also observed known as GAC conformer. The SH flipping barrier in TGA was found to be in good agreement with experimental observation suggesting low energy barrier. To examine sulfur-centered intermolecular hydrogen bonding, dimers and trimers of TGA were examined. Five stable dimers and seven stable trimers were optimized and evaluated using BSSE corrected interaction energy calculations. Among these structures, the D1 dimer and T1 trimer were found to be the most stable, displaying interaction energies of -14.64 kcal/mol and -22.87 kcal/mol, respectively, surpassing the other dimers and trimers in stability. And LED analysis using DLPNO-CCSD(T)/cc-pVTZ method revealed that the electrostatic correlation energy is the most significant contributor in interaction energy across all TGA clusters followed by exchange and dispersion correlation energy. These clusters exhibited intermolecular hydrogen bonding involving both oxygen and sulfur atoms, which contributed to their overall stability and cooperativity. The presence of these intermolecular hydrogen bond interactions in the dimers and trimers was confirmed through various analyses, including AIM (Atom in Molecules), RDG (Reduced Density Gradient), NBO (Natural Bond Orbital), and charge analysis. Furthermore, the existence of HBs was supported by the observation of a Red shift in the S-H stretching modes, as well as in O-H and C=O stretching modes, as determined by infrared (IR) frequency calculations.

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5.4 Conclusion

Structural, electronic, and spectral properties of cystine and its complex with Cu9 cluster were investigated using DFT method. The interaction energy between cystine and Cu cluster was observed to be −88.34 kcal/mol in Cys-Cu(A) system where disulfide linkage got cleaved completely. In calculated SERS of cystine on Cu9 cluster, the cleavage of disulfide linkage was confirmed by the disappearance of the S–S stretching vibrational mode and the blue shift in C–S stretching mode suggest the strong interaction between cystine and copper cluster. Involvement of the carboxyl moiety in interacting with the Cu9 cluster was also significant. These observations are in good agreement with earlier reported experimental findings. NBO and PDOS analysis revealed that electron density got transferred from cystine molecule to copper cluster along with a back donation from cluster to molecule, thereby contributing to the overall stability of the system. AIM analysis revealed the partial covalent and partial electrostatic nature of the Cu–S bond. Results of FMO and MK[ESP] charge calculations supported the above mentioned results exceedingly well. Thus, from the present computational study, it is reinforced that cystine got chemisorbed on copper cluster via the cleavage of its disulfide linkage.

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in gaining an insight into the interaction between PATP and the BOC cluster. An interaction energy of -54.87 kcal/mol suggests the strong interaction between these moieties. FMO analysis revealed the stability of this (PATP@BOC) system. Also from the analysis of the projected density of states it can be inferred that there is charge transfer from the PATP molecule to the BOC cluster which further supports the experimentally observed chemical enhancement effect. The simulated SERS spectrum of PATP@BOC is in good agreement with the currently reported experimental SERS spectrum. Thus this study validates the experimental observation where the genuine SERS spectrum of PATP can be obtained using β-Bi_2O_3/$Bi_2O_2CO_3$ nanoparticles. Moreover, these nanoparticles can also be taken into consideration in the future to obtain the genuine SERS spectra of other molecules where there is a possibility for dimerization.

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APPENDIX

Vibrational modes analysis of main group alkaline earth metals (Ba and Ca) carbonyl compounds at different computational methods

Wu and colleagues initiated their research by synthesizing alkaline earth metal carbonyl complexes. Initially, they generated both cationic and anionic monocarbonyl complexes of barium using the matrix isolation method.[1] Following this, they went on to synthesize di, tri, tetra, and octacarbonyls of alkaline earth metals like barium (Ba), calcium (Ca), and strontium (Sr).[2] Their findings suggested that these alkaline earth metal carbonyl complexes exhibited a similar phenomenon of back bonding, akin to what is observed in transition metal carbonyl complexes. Additionally, they conducted computational analyses on select systems within this context.

I got introduced to computational chemistry with work on these types of systems. Observing a significant disparity between the calculated frequencies and the actual experimental carbonyl frequencies, efforts were undertaken to identify the most effective method for accurately reproducing experimental frequencies. This involved exploring various methods, including combinations of different functionals and basis sets, in the quest for a more accurate match. Figure A1 illustrates the optimized structures of the $Ba(CO)^+$, $Ba(CO)^-$, $Ba(CO)_2$, and $Ca(CO)_2$ complexes. While Tables A1 and A2 provide a comparison between the carbonyl stretching frequencies obtained at various theoretical levels and the vibrational wave numbers reported in experiments. Additionally, the calculated values reported by Wu et al.[1] and Frenking et al.[3] are also included for reference.

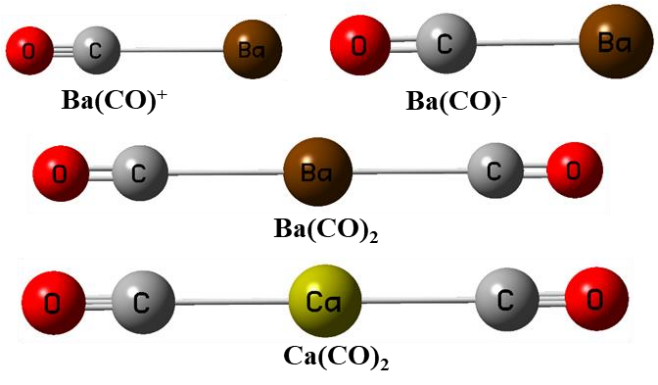

Figure A1: Optimized structure of $Ba(CO)^+$, $Ba(CO)^-$, $Ba(CO)_2$ and $Ca(CO)_2$ complexes

Table A1: Comparison of calculated CO stretching vibrational frequency with experimentally reported frequency in alkaline earth metal carbonyl complexes [$Ba(CO)^+$, $Ba(CO)^-$ and $Ba(CO)_2$]

Level of theory		IR active vibrational wave numbers of CO stretching mode (cm^{-1})					
		In $Ba(CO)^+$		In $Ba(CO)^-$		In $Ba(CO)_2$	
		Harmonic	Anharmonic	Harmonic	Anharmonic	Harmonic	Anharmonic
B3LYP	cc-pVTZ-DK3	2092.18	2084.15	CF	CF	1940.60	1855.23
	cc-pVTZ-X2C	2102.95	2162.06	1740.14	1727.36	1946.15	1766.93
	Def2-TZVPP	2029.70	1956.92	1835.35	1809.49	1916.10	1951.87
CAM-B3LYP	cc-pVTZ-DK3	2145.99	2148.69	1730.50	1719.05	1989.52	1937.03
	cc-pVTZ-X2C	2158.83	2121.05	1803.53	1733.46	1995.20	1894.66
	Def2-TZVPP	2053.11	2025.57	1853.87	1829.05	CF	CF
M06	cc-pVTZ-DK3	2146.08	2107.42	CF	CF	1987.44	1996.02
	cc-pVTZ-X2C	2156.06	2050.75	CF	CF	2098.35	2020.72
	Def2-TZVPP	2062.84	Con Fail	1884.16	1398.90	1955.80	2139.66
M062X	cc-pVTZ-DK3	2164.63	2149.87	1795.33	1744.56	2005.62	2032.54
	cc-pVTZ-X2C	2176.64	2091.37	1822.76	2082.91	2105.55	2149.41
	Def2-TZVPP	2098.11	2065.25	1894.03	2010.78	1988.71	1976.04
MN12L	cc-pVTZ-DK3	2183.70	2147.83	CF	CF	2011.12	1921.64
	cc-pVTZ-X2C	2194.03	2175.84	1846.57	1991.87	2017.66	1805.61
	Def2-TZVPP	2112.48	CF	1939.35	1896.86	1998.77	1954.45
MN15	cc-pVTZ-DK3	2157.26	2187.56	1755.10	1892.09	1985.26	1922.88
	cc-pVTZ-X2C	2168.85	2167.15	1832.38	1804.89	1991.21	1885.66
	Def2-TZVPP	2065.64	2033.52	1907.15	1818.91	1956.55	1609.41
MN15L	cc-pVTZ-DK3	2129.63	2107.01	CF	CF	1967.92	1985.76
	cc-pVTZ-X2C	2140.15	2141.19	CF	CF	1969.83	2218.83
	Def2-TZVPP	2064.35	2048.11	1902.93	1913.29	1956.55	1609.41
PBE1PBE	cc-pVTZ-DK3	2124.00	2098.53	1727.25	1732.66	1972.80	1797.82
	cc-pVTZ-X2C	2135.07	2088.59	1771.75	1727.11	1978.18	1816.28
	Def2-TZVPP	2056.49	CF	1872.17	CF	1949.13	1924.01
MP2	cc-pVTZ-DK3	2037.57	1994.18	1674.61	1655.41	1790.03	1957.98
	cc-pVTZ-X2C	2051.58	2053.85	1685.98	1668.53	1799.62	1711.83
	Def2-TZVPP	1876.31	2357.55	1804.71	1788.98	1782.38	1771.23
Experimental Value (cm^{-1})		1911.2		1758.2		1792	
Calculated CO stretching frequency by Wu et al.[1] and Frenking et al.[3]		1970.3 (CCSD/Def2-TZVPP)		1819.7 (CCSD/Def2-TZVPP) 1851.5 (CASSCF/Def2-TZVPD)		1926 (M06-D3/Def2-TZVPP)	

CF represents convergence failure for that particular method.

Table A2: Comparison of calculated CO stretching vibrational frequency with experimentally reported frequency in alkaline earth metal carbonyl complexes [$Ca(CO)_2$]

Level of theory		CO stretching IR active vibrational wave numbers in $Ca(CO)_2$ complex (cm^{-1})	
		Harmonic	Anharmonic
B3LYP	cc-pVTZ-DK2	1889.31	1919.82
	cc-pVTZ-X2C	1888.38	1910.65
	Def2-TZVPP	1885.50	CF
CAM-B3LYP	cc-pVTZ-DK2	CF	CF
	cc-pVTZ-X2C	CF	CF
	Def2-TZVPP	CF	CF
M06	cc-pVTZ-DK2	1922.61	1871.98
	cc-pVTZ-X2C	1922.57	1872.85
	Def2-TZVPP	1920.19	1862.96
M062X	cc-pVTZ-DK2	1934.95	1913.99
	cc-pVTZ-X2C	1935.22	1926.75
	Def2-TZVPP	1935.91	1938.91
MN12L	cc-pVTZ-DK2	1949.86	2143.63
	cc-pVTZ-X2C	1949.87	2102.40
	Def2-TZVPP	1956.779	1927.903
MN15	cc-pVTZ-DK2	1912.65	1809.15
	cc-pVTZ-X2C	1912.66	1862.65
	Def2-TZVPP	1910.19	1888.26
MN15L	cc-pVTZ-DK2	1910.95	1908.71
	cc-pVTZ-X2C	1911.00	1905.16
	Def2-TZVPP	1902.50	1872.25
PBE1PBE	cc-pVTZ-DK2	1918.15	1890.13
	cc-pVTZ-X2C	1918.19	1890.02
	Def2-TZVPP	1916.15	1905.97
MP2	cc-pVTZ-DK2	1804.45	1786.13
	cc-pVTZ-X2C	1803.19	1787.07
	Def2-TZVPP	1809.30	1798.02
Experimental Value (cm^{-1})		1922	
Calculated CO stretching frequency by Frenking et al.[3]		1911 (M06-D3/Def2-TZVPP)	

CF represents convergence failure for that particular method.

Thus from table A1 and A2 it is inferred that after conducting harmonic and anharmonic IR vibrational frequency calculations for alkaline earth metal carbonyl complexes, including $Ba(CO)^{+}$, $Ba(CO)^{-}$, $Ba(CO)_2$, and $Ca(CO)_2$, using various DFT functionals and methods in combination with different basis sets, divergent results were obtained for these systems. A specific method exhibited lower error (i.e., the difference between calculated vibrational frequencies and experimental values) for one system, while the same method displayed substantial error for another system. However, certain methods yielded results remarkably close to the experimental data for individual systems.

This study underscores the ongoing need for a comprehensive understanding of these newly synthesized carbonyl complexes and the development of a benchmark method that can effectively address the vibrational frequencies of all these systems.

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List of Publications

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1. **Poonam Bhadoria**, and Venkatnarayan Ramanathan, Conformational Landscape and Properties of Psilocybin: A Computational Approach, ChemistrySelect, **2022**, 7(37), e202203026.
2. **Poonam Bhadoria**, and Venkatnarayan Ramanathan, Conformational Landscape and Hydrogen Bonding Pattern of Psilocin: Computational Insights. ChemistrySelect, **2023**, 8(1), e202203994.
3. **Poonam Bhadoria**, and Venkatnarayan Ramanathan, Computational underpinnings for the dimerization of para-aminothiophenol to dimercaptoazobenzene on copper surface. Chemical Physics, **2023**, 571, 111910.
4. **Poonam Bhadoria**, Manish Kumar Tripathi and Venkatnarayan Ramanathan, To cleave or not—disulfide bond of cystine on nanocopper: a computational approach. Journal of Nanoparticle Research, **2023**, 25(1), 2.
5. **Poonam Bhadoria**, Arti Saroj and Venkatnarayan Ramanathan, To dimerize or not: para-aminothiophenol on a bismuth heterostructure. Physical Chemistry Chemical Physics, **2023**, 25(13), 9569-9575.
6. **Poonam Bhadoria**, and Venkatnarayan Ramanathan, Combined FTIR/Raman spectroscopic studies and ab initio electronic structure calculations of Dithiothreitol. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, **2023**, 123399.
7. **Poonam Bhadoria**, and Venkatnarayan Ramanathan, Sulfur Centered Hydrogen Bonding in Thioglycolic Acid and Its Clusters: A Computational Exploration. The Journal of Physical Chemistry A, **2023**, 127(39), 8095-8109.
8. **Poonam Bhadoria**, and Venkatnarayan Ramanathan, Exploring the Conformational Landscape and Properties of Mescaline Through ab initio Electronic Structure Calculations. **(Submitted)**
9. **Poonam Bhadoria**, and Venkatnarayan Ramanathan, Testing contemporary functionals and basis sets for their accuracy in predicting vibrational modes of newly discovered alkaline earth metals-carbonyl complexes. Indian Journal of Pure & Applied Physics, **(Under Revision)**