

Supporting Information

Raman Scattering and DFT Calculations Used for Analyzing the Structural Features of DMSO in Water and Methanol

Shweta Singh^a, Sunil K. Srivastava^b, Dheeraj K. Singh^{a*}

^a*Laser and Spectroscopy Laboratory, Department of Physics, Banaras Hindu University, Varanasi-221 005, India.*

^b*Department of Pure and Applied Physics, Guru Ghasidas Vishwavidyalaya, Main Campus, Koni, Bilaspur-495009, India.*

Table 1: Observed and calculated structural parameters: bond lengths and bond angle for neat DMSO in gas phase using DFT method employing B3LYP functional, and MP2 method

	DMSO _{gas}		
Experimental	B3LYP	MP2	
Ref.27	6-311++G(d,p)	6-311++G(d,p)	
<u>Bond length (Å)</u>			
r(S=O)	1.485	1.514	1.508
r(S-C ₁)	1.799	1.835	1.807
r(S-C ₂)	1.799	1.835	1.807
r(C ₁ -H ₁)	1.096	1.090	1.091
r(C ₁ -H ₂)	1.097	1.091	1.093
r(C ₁ -H ₃)	1.093	1.092	1.093
r(C ₂ -H ₄)	1.096	1.090	1.091
r(C ₂ -H ₅)	1.097	1.091	1.093
r(C ₂ -H ₆)	1.093	1.092	1.093
<u>Bond angles (°)</u>			
∠(C ₁ SC ₂)	96.56	96.56	95.92
∠(SC ₁ H ₁)	106.03	106.54	107.06
∠(SC ₁ H ₂)	108.16	109.05	108.74
∠(SC ₁ H ₃)	109.49	109.66	109.93
∠(H ₁ C ₁ H ₂)	112.11	109.97	109.67
∠(H ₁ C ₁ H ₃)	110.06	110.04	109.87
∠(H ₂ C ₁ H ₃)	110.84	111.46	111.46

Dihedral angles

C ₂ SC ₁ H ₁	178.01	176.82	177.48
C ₂ SC ₁ H ₂	57.59	58.17	59.06
C ₂ SC ₁ H ₃	-63.29	-64.12	-63.22

The atom numbering is shown in Fig. 1.

Table 2: Calculated binding energy (BE) and bond lengths for different possible clusters of DMSO in water (W) and methanol (M) using DFT method employing B3LYP functional

System	BE (kcal / mol)	Bond length (Å)								
		(S=O)	(S-C ₁)	(S-C ₂)	(C ₁ -H ₁)	(C ₁ -H ₂)	(C ₁ -H ₃)	(C ₂ -H ₄)	(C ₂ -H ₅)	(C ₂ -H ₆)
DMSO	---	1.514	1.835	1.835	1.089	1.091	1.092	1.089	1.091	1.092
Dimer	7.02	1.525	1.832	1.826	1.089	1.091	1.092	1.092	1.091	1.092
Trimer	13.49	1.527	1.833	1.823	1.089	1.091	1.092	1.092	1.091	1.092
2DMSO+1W	15.94	1.528 (1.522)	1.833 (1.830)	1.833 (1.830)	1.090 (1.089)	1.091 (1.091)	1.092 (1.092)	1.090 (1.089)	1.091 (1.091)	1.092 (1.091)
DMSO+1W	8.47	1.529	1.831	1.831	1.090	1.091	1.091	1.090	1.091	1.091
DMSO+2W	16.69	1.543	1.826	1.826	1.090	1.090	1.091	1.089	1.090	1.091
DMSO+3W	28.68	1.541	1.828	1.824	1.090	1.091	1.092	1.090	1.092	1.092
DMSO+4W	38.09	1.544	1.826	1.822	1.090	1.091	1.092	1.089	1.092	1.092
Dimer+2W	---	1.535 (1.535)	1.828 (1.824)	1.820 (1.826)	1.089 (1.090)	1.091 (1.090)	1.091 (1.091)	1.093 (1.090)	1.091 (1.090)	1.092 (1.091)
Trimer+3W	---	1.527 (1.542) [1.534]	1.830 (1.823) [1.828]	1.823 (1.824) [1.818]	1.089 (1.090) [1.089]	1.091 (1.091) [1.091]	1.091 (1.092) [1.091]	1.093 (1.089) [1.094]	1.091 (1.091) [1.091]	1.092 (1.092) [1.092]
2DMSO+1M	15.53	1.529 1.529	1.829 1.823	1.829 1.832	1.090 1.092	1.092 1.091	1.092 1.092	1.090 1.089	1.091 1.091	1.091 1.092
DMSO+1M	8.16	1.529	1.831	1.831	1.090	1.091	1.091	1.090	1.091	1.091
DMSO+2M	16.25	1.543	1.827	1.825	1.090	1.090	1.091	1.090	1.091	1.091

Dimer+2M --- 1.531 1.821 1.829 1.090 1.091 1.092 1.089 1.091 1.091

The values presented in parenthesis () and [] shows the bond lengths of 2nd and 3rd DMSO respectively.

Binding Energy Calculations:

The binding energy (BE) between A and B was calculated as:

$$BE = \text{total energy (AB)} - [\text{total energy (A)} + \text{total energy (B)}] + E_{\text{BSSE}}$$

In studies of weakly bound clusters, one often encounters an artificial shortening of intermolecular distances and concomitant artificial strengthening of the intermolecular interaction. Such problems are ascribed to “basis set superposition errors” (BSSEs),^{1, 2} and they are more pronounced for smaller basis sets. As monomer A approaches monomer B, the dimer can be artificially stabilized as monomer A utilizes the extra basis functions from monomer B to describe its electron distribution, and vice versa. The inconsistent treatment of the basis set for each monomer as the intermolecular distance is varied is the source of the basis set superposition error.

For more detail (see the references below):

1 H. B. Jansen and P. Ros, *Chem. Phys. Lett.* **3**, 1969, 140.

2 B. Liu and A. D. McLean, *J. Chem. Phys.* **59**, 1973 4557.

Thus, for BE calculation the term E_{BSSE} are also introduced. Using the equation, we calculated the BE of all the complexes and presented above in Table 4.

Figure 1: Raman spectra of neat methanol

1034 cm^{-1} = O-H Bending vibration of methanol

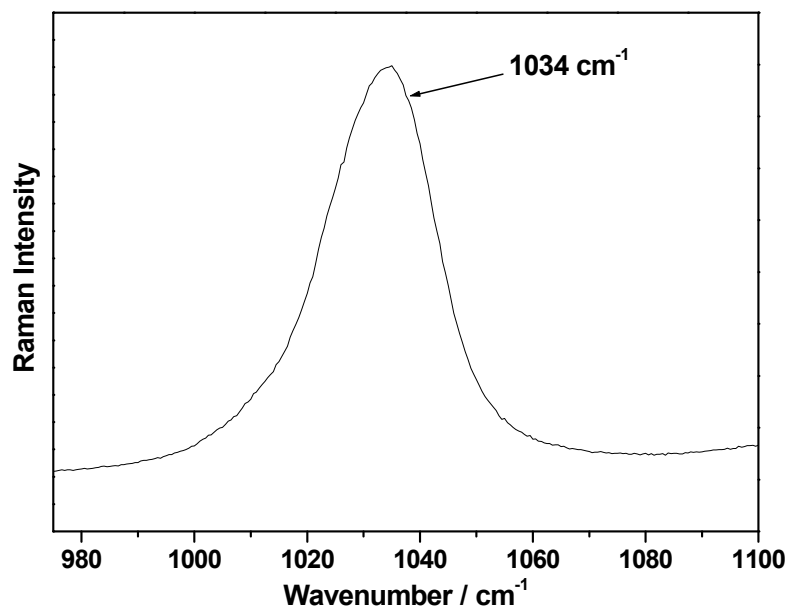


Fig.2: Optimized geometry of neat DMSO in gas phase having the Mulliken charges at each atom.

(Red, yellow, gray and white color of atom shows the oxygen, sulfur, carbon and hydrogen atom, respectively).

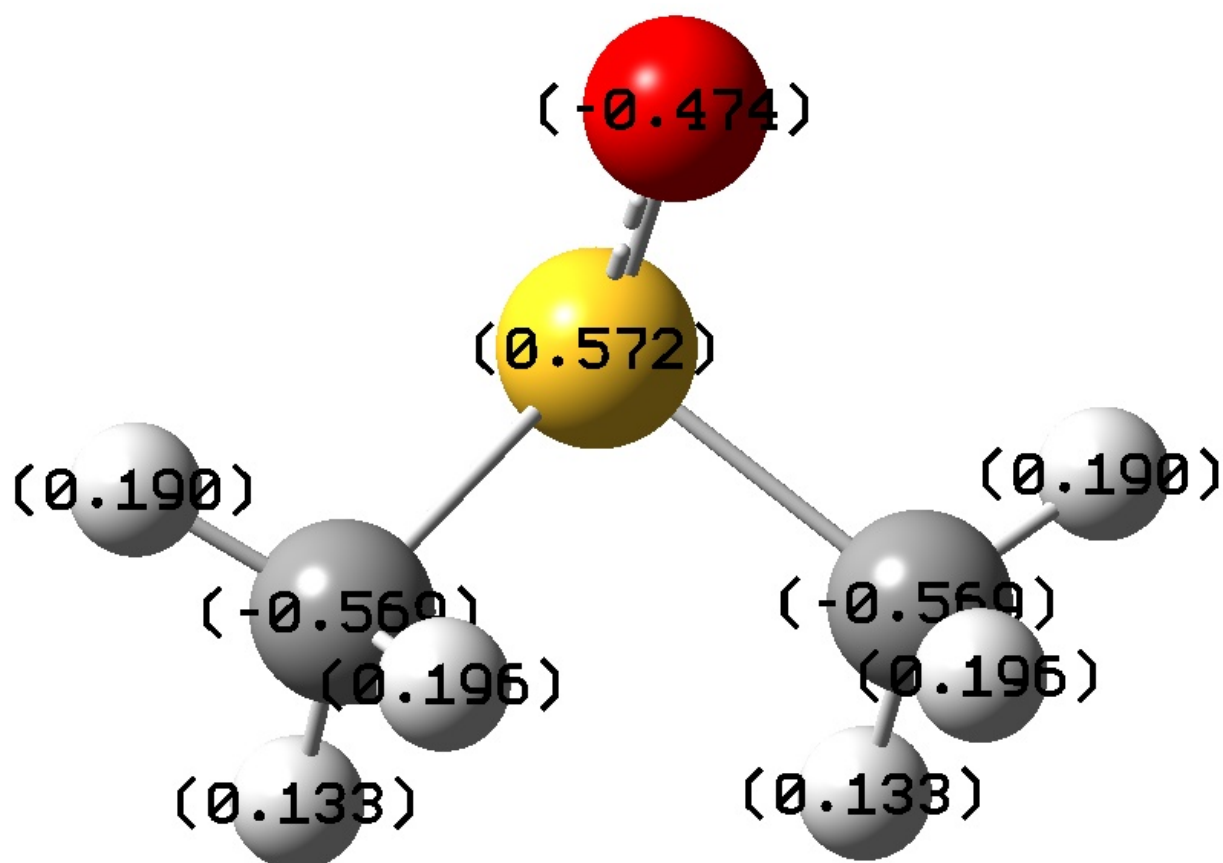


Fig.3: Optimized geometry of DMSO +1 W having the Mulliken charges at each atom.

(Red, yellow, gray and white color of atom shows the oxygen, sulfur, carbon and hydrogen atom, respectively).

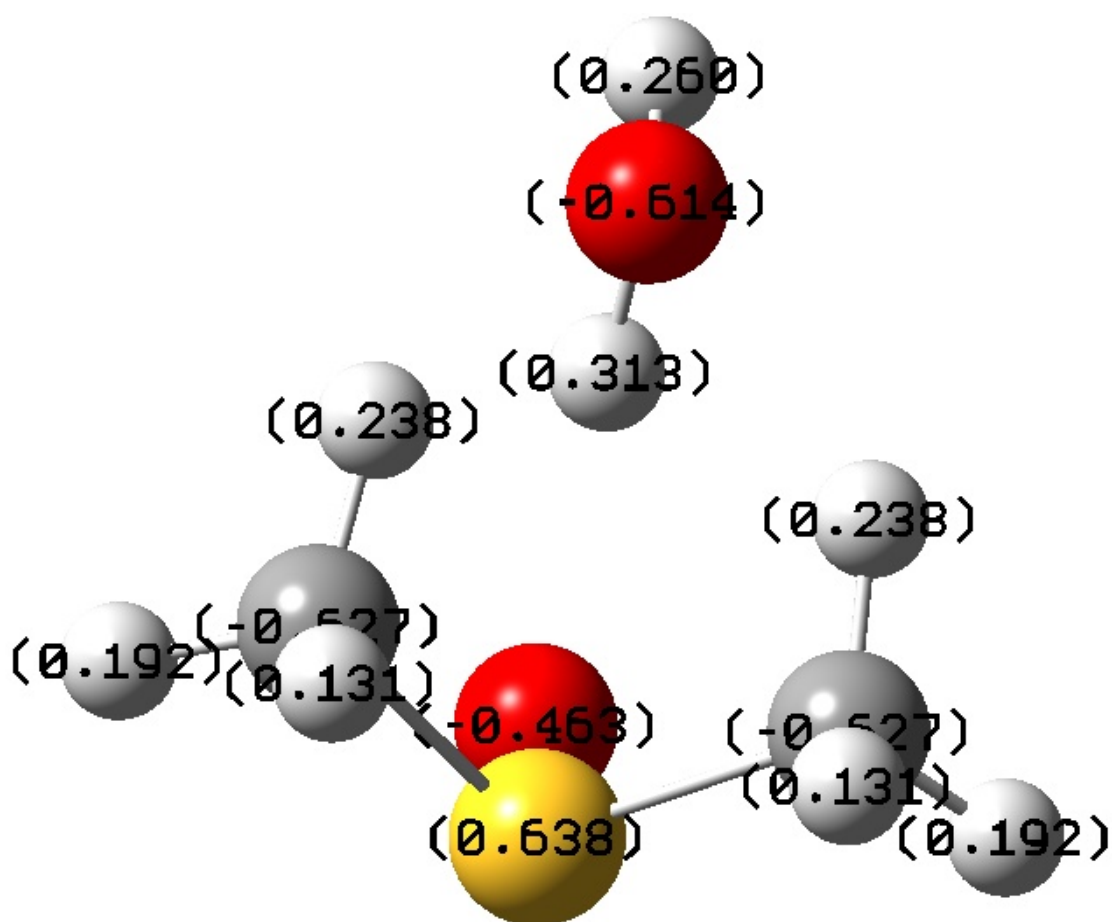


Fig.4: Optimized geometry of DMSO +1 M having the Mulliken charges at each atom.

(Red, yellow, gray and white color of atom shows the oxygen, sulfur, carbon and hydrogen atom, respectively).

