

Spectroscopic investigations of dimethyl sulfoxide

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ABSTRACT

The vibrational wavenumbers of dimethyl sulfoxide molecule were calculated using Gaussian03 software package at different levels and the fundamental modes are assigned. The predicted infrared and Raman activities are reported. The first hyperpolarizability is calculated and the dimethyl sulfoxide molecule is an attractive object for future studies of non linear optics. The calculated wavenumbers and geometrical parameters are in agreement with the reported experimental values.

Key words: HF, DFT, sulfoxide, hyperpolarizability.

INTRODUCTION

Dimethyl sulfoxide (DMSO) is a colorless liquid which is an important polar aprotic solvent that dissolves both polar and nonpolar compounds and is miscible in a wide range of organic solvents as well as water. It has the distinctive property of penetrating the skin very readily, so that one can taste it soon after it comes in contact with the skin. DMSO is used in the polymerase chain reaction to inhibit the formation of secondary structures in the DNA template or DNA primers. It is added to the polymerase chain reaction mix before reacting, where it intereferes with the self complementarity of the DNA, preventing the occurrence of interfering reactions.¹ However, use of DMSO in polymerase chain reaction increases the mutation rate. DMSO is also used as a cryoprotectant, added to cell media in order to prevent the cells from dying as they are being frozen² dimethyl sulfide is an important sulfur containing trace gas produced by some classes of

marine phytoplankton³. Dimethyl sulfide is the most abundant naturally occurring sulfur species emitted from oceans⁴. The oxidation of dimethyl sulfide is of particular interest since it may result in the formation of aerosols, and eventually cloud condensation nuclei⁵. The effects of aerosols and clouds remain as the largest uncertainty in climate forecasting today.⁶ Microbial degradation of dimethyl sulfide however, appears to be the main sink for DMS in the marine environment, often leading to oxidation of 90% or more of dimethyl sulfide in the surface ocean.^{7,8} Bacterial degradation of dimethyl sulfide therefore significantly reduces the amount of dimethyl sulfide in the mixed surface layer that is available for sea-to-air transfer. Growth on dimethyl sulfide as a carbon source has been described for a range of prokaryotes, including anaerobic degradation by methanogens⁹ and sulfate-reducing bacteria.¹⁰ In the present study, the wavenumbers of the title molecule and geometrical parameters are calculated theoretically at various computational levels.

Computational details

The vibrational wavenumbers were calculated using the Gaussian03 software package on a personal computer.¹¹ The computations were performed at HF/6-31G*, HF/6-311G* and B3LYP/6-31G* levels of theory to get the optimized geometry (Fig. 1) and vibrational wavenumbers of the normal modes of the title compound. DFT calculations were carried out with Becke's three-parameter hybrid model using the Lee-Yang-Parr correlation functional (B3LYP) method. Molecular geometries were fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibrational wavenumbers were calculated using analytic second derivatives to confirm the convergence to minima in the potential surface. The DFT hybrid B3LYP functional tends also to overestimate the fundamental modes; therefore scaling factors have to be used for obtaining a considerably better agreement with experimental data. Thus, a scaling factor of 0.9613 has been uniformly applied to the B3LYP and 0.8929 for HF methods calculated wavenumbers.¹² The observed disagreement between theory and experiment could be a consequence of the anharmonicity and of the general tendency of the quantum chemical methods to overestimate the force constants at the exact equilibrium geometry. The obtained geometrical parameters are given in Tables 1-3.

RESULTS AND DISCUSSION

The calculated (scaled) wavenumbers and assignments are given in Table 4. In the spectra of methyl esters, the CH vibrations¹³ are expected in the region 3050-2840 cm⁻¹. The asymmetric and symmetric deformations of the methyl group^{13,14} are

expected in the region 1485-1435 cm⁻¹ and 1450-1420 cm⁻¹, respectively. The methyl rock νCH_3 has been observed¹³ at 1185 ± 35 cm⁻¹ and at 1155 ± 35 cm⁻¹. In the present work, all the methyl modes are found in this regions and assigned (table 4).

The $\nu\text{S-O}$ mode is reported at 1026 cm⁻¹ for sulfamic acid,¹⁴ at around 1020 cm⁻¹ for amino benzenesulfonic acids¹⁵ and at 1040 cm⁻¹ for p-toluene sulfonic acid.¹⁶ For the title compound, the $\nu\text{S-O}$ is assigned at 1059 cm⁻¹ theoretically.¹⁷ The C-S stretching vibration appears moderately to strongly in the region 500-700 cm⁻¹ for majority of investigated molecules.¹³ The bands calculated (DFT) at 639 and 610 cm⁻¹ are assigned to C-S stretching vibration.

According to literature, the S-O bond lengths are 1.386 Å for pyridine sulfuric acid complex,¹⁸ 1.446-1.448 Å for sulfuric acid,¹⁹ 1.448-1.472 Å for some monohydrated sulfuric acid.²⁰ In

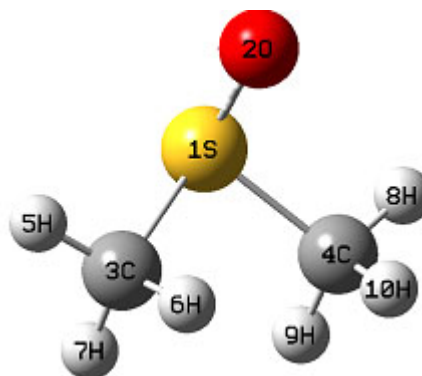


Fig. 1: Optimized geometry

Table 1: Bond lengths (Å)

	HF/6-31G*	HF/6-311G*	B3LYP/6-31G*
S1-O2	1.7259	1.4828	1.5117
S1- C3	1.8522	1.7965	1.8376
S1-C4	1.8522	1.7965	1.8376
C3-H5	1.0773	1.0807	1.0927
C3-H6	1.0781	1.0817	1.0941
C3-H7	1.0782	1.0825	1.0945
C4-H8	1.0773	1.0807	1.0927
C4-H9	1.0782	1.0825	1.0945
C4-H10	1.0781	1.0817	1.0941

present case, from DFT calculations, the S-O bond length as 1.5117 Å. The reported values of C-S bond lengths are 1.8807, 1.8316 Å (DFT calculations)²¹ and in the present case, the DFT calculations give the CS bond lengths as 1.8376 Å.

The first hyperpolarizability ($\hat{\alpha}_0$) of this novel molecular system is calculated using theoretically, based on the finite field approach. In the presence of an applied electric field, the energy

of a system is a function of the electric field. First hyperpolarizability is a third rank tensor that can be described by a $3 \times 3 \times 3$ matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry.²² The calculated first hyperpolarizability of the title compound is 0.810^{-30} , 1.510^{-30} , 1.1210^{-30} , 0.410^{-30} esu for HF/6-31G*, HF/6-311G* and B3LYP/6-31G* methods. We conclude that the title compound is an attractive object for future studies of non linear optical properties.

Table 2. Bond angles (°)

	HF/6-31G*	HF/6-311G*	B3LYP/6-31G*
A(2,1,3)	102.6	106.1	107.5
A(2,1,4)	102.6	106.1	107.5
A(3,1,4)	100.3	98.0	95.8
A(1,3,5)	106.7	107.2	107.0
A(1,3,6)	108.1	109.0	109.5
A(1,3,7)	109.8	110.5	110.0
A(5,3,6)	109.7	109.3	109.5
A(5,3,7)	110.6	109.7	109.8
A(6,3,7)	111.8	111.1	111.0
A(1,4,8)	106.6	107.2	107.0
A(1,4,9)	109.8	110.5	110.0
A(1,4,10)	108.1	109.1	109.5
A(8,4,9)	110.6	109.6	109.8
A(8,4,10)	109.7	109.3	109.5
A(9,4,10)	111.8	111.1	111.0

Table 3. Dihedral Angles (°)

	HF/6-31G*	HF/6-311G*	B3LYP/6-31G*
D(2,1,3,5)	70.7	68.3	66.9
D(2,1,3,6)	-47.3	-49.9	-51.7
D(2,1,3,7)	-169.4	-172.2	-173.9
D(4,1,3,5)	176.2	177.7	177.4
D(4,1,3,6)	58.3	59.5	58.7
D(4,1,3,7)	-63.9	-62.9	-63.4
D(2,1,4,8)	-70.7	-68.3	-66.9
D(2,1,4,9)	169.4	172.3	173.9
D(2,1,4,10)	47.3	49.9	51.7
D(3,1,4,8)	-176.2	-177.7	-177.4
D(3,1,4,9)	63.9	62.9	63.4
D(3,1,4,10)	-58.2	-59.5	-58.7

The theoretically calculated thermal energy (KCal/Mol), specific heat capacity at constant volume (Cal/Mol-Kelvin), entropy (Cal/Mol-Kelvin) are respectively, 56.770, 17.578, 71.962 for HF/6-31G*, 56.770, 17.578, 71.962 for HF/6-311G* and 53.670, 18.930, 73.521 for B3LYP/6-31G* methods.

Table 4: Calculated (scaled) wavenumbers and assignments

$\nu(\text{cm}^{-1})$	HF/6-31G*		HF/6-311G*			B3LYP/6-31G*			Assignments
	IR intensity	Raman activity	$\nu(\text{cm}^{-1})$	IR intensity	Raman activity	$\nu(\text{cm}^{-1})$	IR intensity	Raman activity	
3003	0.77	101.48	2949	9.58	102.73	3046	4.75	107.52	$\nu_{\text{as}}\text{Me}$
3003	0.19	46.47	2948	5.94	43.70	3046	3.32	39.86	$\nu_{\text{as}}\text{Me}$
2997	5.90	110.89	2945	25.39	110.27	3038	14.37	104.01	$\nu_{\text{as}}\text{Me}$
2996	0.06	12.03	2940	0.33	10.91	3034	0.04	8.32	$\nu_{\text{as}}\text{Me}$
2895	14.90	212.39	2860	14.54	216.62	2944	7.26	206.03	$\nu_{\text{s}}\text{Me}$
2893	11.69	1.39	2856	12.49	0.37	2942	4.63	0.13	$\delta_{\text{s}}\text{Me}$
1455	35.58	3.55	1442	23.14	1.35	1449	19.97	2.73	$\delta_{\text{as}}\text{Me}$
1444	2.89	33.16	1425	0.28	22.50	1431	0.47	32.50	$\delta_{\text{as}}\text{Me}$
1442	7.21	27.46	1421	3.69	18.45	1427	3.07	26.60	$\delta_{\text{as}}\text{Me}$
1432	13.98	4.76	1409	9.69	2.34	1414	9.37	3.95	$\delta_{\text{as}}\text{Me}$
1365	1.43	0.95	1345	7.84	3.28	1318	6.49	0.62	$\delta_{\text{s}}\text{Me}$
1342	1.01	0.08	1323	1.18	0.16	1295	0.77	1.33	$\delta_{\text{s}}\text{Me}$
1048	20.55	9.34	1023	100.88	3.29	1059	111.2	6.69	νSO
1005	5.97	6.99	1020	38.68	3.07	999	22.87	7.00	ρMe
970	0.49	9.85	948	50.48	6.05	934	13.01	9.03	ρMe
936	0.73	0.76	933	9.08	3.72	908	5.86	6.47	ρMe
671	0.01	38.70	888	1.02	0.35	870	2.15	1.02	ρMe
637	3.40	38.70	694	11.80	18.09	639	20.40	15.81	νCS
568	8.02	29.43	659	2.77	31.83	610	10.04	26.69	νCS
267	3.39	2.39	358	13.92	1.41	346	7.52	1.51	tMe
219	6.32	3.41	310	17.08	2.99	284	7.11	3.47	δCSO
211	11.80	6.28	277	0.56	1.83	273	0.62	1.67	δCSC
165	0.90	0.01	228	0.816	0.05	222	0.49	0.07	tMe
141	0.25	0.00	188	0.00	0.13	177	0.00	0.06	tSCMe

ν -stretching; δ -bending; ρ -rocking; t-torsion; subscripts: as-asymmetric; s-symmetric; Me-methyl.

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