Theoretical and experimental study of dimethyl sulfoxide and N-substituted DMSO

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Infrared spectrum of dimethylsulfoxide (DMSO) has been studied using quantum chemical calculations and FTIR spectroscopy. Theoretical infrared and electronic absorption spectra for the ions of DMSO, DMSO in water solvent and nitrogen substituted DMSO (N-DMSO) have also been obtained using second order Møller-Plesset and 6-311++g(d,p) basis set. The IEFPCM model has been used to study the solvation effect for DMSO. The geometrical parameters and dipole moments for the neutral DMSO have been compared with the available experimental determinations. Calculated vibrational frequencies have been compared with the experimental frequencies for the DMSO obtained using FTIR spectrometer. Rotational and centrifugal distortional constants for these molecules have been reported. The electronic absorption spectra of DMSO, its ions, and N-DMSO have been obtained using time dependent density functional theory (TDDFT) approach. Almost all the vibrational modes in the vibrational spectrum of DMSO anion are intense whereas fewer intense modes have been observed in the vibrational spectra of DMSO, its cation, DMSO in water solvent and N-DMSO. The most intense mode is different for DMSO, its ions and N-DMSO. The S=O stretching mode is the most intense mode for DMSO as well as DMSO in water solvent and it is red shifted by 62 cm^{-1} in latter than the former.

Keywords: interstellar molecule, DMSO, N-substituted DMSO, Vibrational spectra, Electronic absorption spectra, Rotational and distortional constants

1 Introduction

Dimethylsulfoxide (DMSO) is one of the important solvents and has several applications in industry as well as in chemistry and biochemistry. During past few years DMSO has received a great deal of attention from researchers in medicine and chemistry because of its usefulness as a solvent. Dimethyl sulfoxide is a highly associated liquid[1-3] with high dipole moment (μ= 3.96 D) and permittivity (ε= 46.4). It is extensively used in organic synthesis. In the ocean atmosphere, DMSO is naturally emitted from the oxidation of dimethylsulfide produced by the marine phytoplankton and plays a significant role in the atmospheric chemistry of sulphur[4]. Its chemical reactivity has been reviewed earlier[5-7]. First spectroscopic analysis of microwave transitions in the ground state of DMSO which allowed quartic centrifugal distortion constants determination was reported earlier in 1969 and 1976 [8,9] and later again in 2010[10].

High resolution gas phase study of parallel band of DMSO associated with the ν_{11} bending vibrational mode at 380 cm^{-1} has been carried out by Cuisset

et al.[11]. They have analysed the resolved rotational transitions and obtained the rotational constants and centrifugal corrections to reproduce the spectrum of experimental accuracy. Following the first successful high-resolution study of the perpendicular band of DMSO at 324 cm^{-1}, associated with twenty-three bending vibration, they discovered a sequence of fourfold degenerate cluster of rotational levels at high angular momenta J > 40. The millimeter-wave and submillimeter-wave spectra of DMSO have been measured up to 660 GHz, corresponding to maximum values of J = 70 and Kc = 68[12].

Chemical activity and relatively high abundance of sulfur in space demands detailed spectroscopic study of sulfur containing molecules in order to identify these molecules in space[13]. Some sulfur containing molecules and their ions have already been detected in interstellar medium. The dimethylsulfoxide molecule is one of the sulphur containing molecules that may be present in space. Depending upon the astrophysical environment, there is also possibility of presence of its ions and DMSO in astrophysical ice. In order to detect DMSO and its ions in interstellar medium prediction of their vibrational and electronic

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absorption spectra using quantum chemical methods will be helpful. Due to high abundance of nitrogen than sulfur in interstellar medium, there is possibility of existence of nitrogen substituted DMSO (N-DMSO) in space which may be the precursor of DMSO. Also the amount of energy required for the formation of C–N bond is less as compared to that for the C–S bond. Similar to N-substituted PAH, nitrogen substituted molecules may also be one of the possible interstellar emission features. In order to detect DMSO, its ions and N-DMSO in interstellar medium, their thorough spectroscopic study is necessary.

The aim of this work is to study vibrational and electronic absorption spectra of DMSO molecule, its ions, N-DMSO and DMSO in water solvent using quantum chemical method. A comparative study of spectra of these molecules has been carried out. Theoretical infrared spectrum of DMSO is also compared with the measured experimental spectrum using FTIR spectroscopy. The present paper is organized as follows. Next section gives the computational and experimental details. Results are presented and compared in section Results and Discussion section. Conclusions are given in the final section.

2 Experimental and Computational Details

DMSO of AR grade (assay ≥ 99.5%) was purchased from S. D. Fine Chem. Ltd. and used as such without any further purification. An infrared spectrum of pure DMSO was recorded using Perkin-Elmer spectrum two spectrometer. Second order Møller–Plesset perturbation method (MP2) with 6-311++g(d,p) basis set has been used to optimize geometries of DMSO, its ions and N-DMSO[14,15]. DMSO in water solvent is studied using IEFPCM model at MP2/6-311++G(d,p) level of theory with dielectric constant of 78.5[16]. The scaling factor of 0.967 has been used for the vibrational frequencies[17]. The electronic absorption spectra for DMSO, its ions,

N-DMSO and DMSO in water solvent have been obtained using Time dependent density functional theory (TDDFT)[18-23]. The percent contribution from each electronic transition was obtained using the SWizard program[24]. All the calculations were performed by Gaussian 03 program package[25].

3 Results and Discussion

3.1 Geometrical parameters

The geometries of DMSO, its ions, N-DMSO and DMSO in water solvent are optimized at MP2/6-311++g(d,p) level of theory and are shown in Fig. 1. Table 1 shows the geometrical parameters such as bond length, angle, and dihedral angle along with dipole moment of DMSO, DMSO in water solvent, its ions, and N-DMSO. Significant change in structural parameters of DMSO has been observed upon ionization. DMSO is higher in energy by 8.2 eV and 0.02 eV than its cation and anion respectively. Calculated geometrical parameters and dipole moment are compared with the available experimental values[26,27] in Table 1. Calculated dipole moment and geometrical parameters such as bond length and angles are in agreement with the experimental determinations. A change in bond length and dihedral angle upon ionization is found to be large. The bond angles CSC and CSO for neutral DMSO are 95.92° and 106.76° respectively which are 109.8° and 115.5° for the DMSO cation. The highest change in
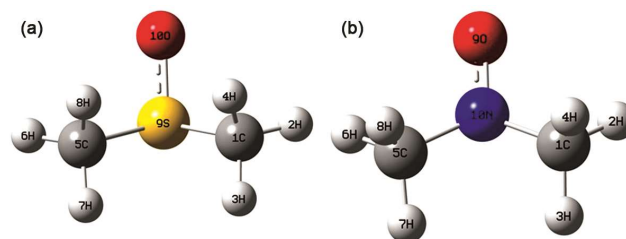

Fig. 1 – Optimized geometries A) DMSO and B) N-DMSO at MP2/6-311++g(d,p) level of theory.

Table 1 – Geometrical parameters for the DMSO, its ions, N-DMSO and DMSO in water solvent at MP2/6-311++g(d,p) level of theory

Parameters	DMSO	DMSO Expt.	Cation	Anion	N-DMSO	DMSO in water
C-H (1CH$_3$)	1.091	1.093[a]	1.091	1.092	1.092	1.091
C-H (5CH$_3$)	1.091	1.097[a]	1.091	1.092	1.092	1.091
C-S/C-N	1.806	1.799[a]	1.783	1.801	1.459	1.796
S-O/N-O	1.507	1.485[a]	1.440	1.519	1.269	1.529
∠ C-S-C/C-N-C	95.92	96.6[a]	109.8	96.43	118.2	97.32
∠ C-S-O/C-N-O	106.76	106.5[a]	115.5	107.4	118.5	106.1
Ψ CSOC/CNOC	101.72	-------	130.2	102.8	154.5	102.7
Diploe (Debye)	4.427	3.96[b]	3.715	6.818	3.964	6.09

[a]Ref [26] and [b]Ref [27].

dihedral angle has been observed in cation by 28.48° than the DMSO.

3.2 Infrared spectra

Calculated and experimental vibrational frequencies for the DMSO, its ions, N-DMSO and DMSO in water solvent are tabulated in Table 2 and vibrational spectra are shown in Fig. 2. DMSO, its ions, N-DMSO and DMSO in water solvent are having 24 vibrational modes. Out of 24 modes we could identify 21 modes successfully. Experimental

values of vibrational modes from this work are also reported here for comparison. Of these 21 modes, DMSO shows the S=O stretching mode as the most intense mode and peaks at 1034 cm^{-1} which is in agreement with the experimental peak at 1044 cm^{-1}. It is also the most intense mode for the DMSO in water solvent. This peak is red, blue and red shifted by 168, 30 and 62 cm^{-1} in its cation, anion and DMSO in water solvent respectively than that for the DMSO. This mode is equally intense in anion and very weak

Table 2 – The vibrational modes (ω in cm^{-1}) and intensities (km mol^{-1}) for DMSO, its ions, N-DMSO and DMSO in water solvent optimized at MP2/6-311++g(d,p) level of theory along with experimental vibrational frequencies. The values in parenthesis are intensities.

| Modes	DMSO	DMSO Expt	Cation	Anion	N-DMSO	DMSO in water
CH$_3$asymm str	3014 (2.2)		3013 (27)	2976 (0.1)	2977 (30)	3021 (1.5)
	3013 (0.8)		3012 (3)	2968 (0.3)	2975 (0.8)	3019 (1.3)
CH$_2$asymm str	3005 (6.8)		3029 (22)	2995 (288)	3030 (6)	3013 (6.8)
	3002 (0.01)	2996	3026 (14)	2992 (98)	3028 (1.7)	3008 (0.1)
CH$_3$symm str	2897 (8)	2912	2899 (14)	2868 (363)	2888 (24)	2904 (6)
	2896 (4)		2897 (30)	2866 (42)	2883 (17)	2901 (5.4)
CH$_3$ scissor	1394 (23)	1438	1374 (47)	1393 (255)	1418 (4)	1386 (37)
	1379 (5)	1414	1366 (15)	1361(1539)	1414 (46)	1371 (9)
	1366 (10)		1351 (15)	1345 (2033)	1401 (2)	1359(17)
CH$_3$ umbrella	1296 (10)		1308 (3.6)	1286 (316)	1372 (6)	1303 (12)
	1273 (3)		1281 (0.08)	1253 (3868)	1355 (0.5)	1278 (1.5)
S=O/N-O str	1034 (172)	1044	1202 (22)	1004 (178)	1526 (125)	972 (209)
CH$_3$ rocking	985 (14)	954	1001 (11)	991 (9.5)	1072 (28)	920 (132)
	925 (14)		921 (14)	919 (157)	1016 (0.9)	903 (12)
	891 (7)		904 (26)	864 (117)	973 (1)	875 (2)
CS/CN asymm str	674 (18)	698	706 (3.3)	682 (125)	1233(0.01)	694 (19)
CS/CN symm str	651 (9)	670	607 (1.3)	655 (34)	791 (10)	666 (6)
Molecule bending	343 (10)		317 (24)	287 (293)	488 (18)	343 (18)
	292 (9.8)		278 (13)	271 (3)	301 (0.4)	296 (23)
CH$_3$ torsion	223 (0.4)		161 (0.9)	233 (0.09)	160 (2)	224 (0.8)
	160 (0.02)		127 (0.003)	117 (10)	127 (0.2)	137 (0.001)
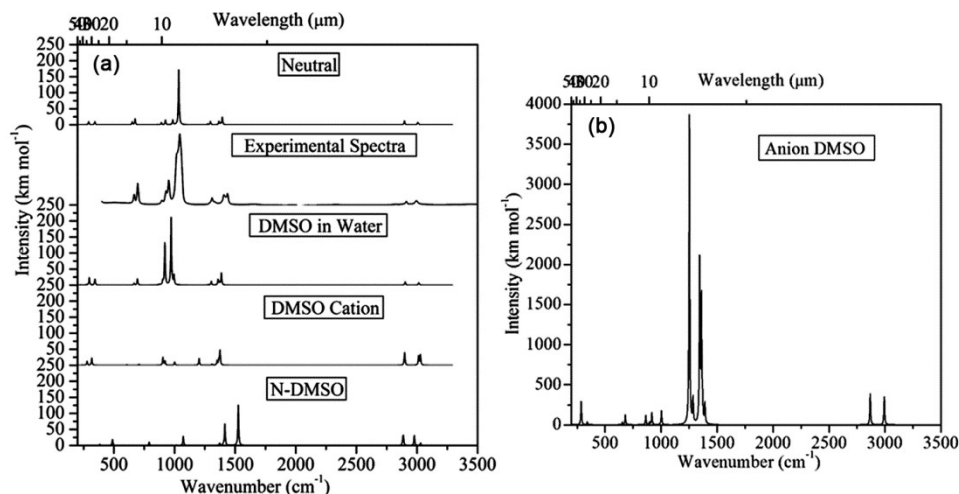
Fig. 2 – (A) Theoretical and experimental infrared spectra of DMSO, its cation, N-DMSO and DMSO in water solvent at MP2/6-311++g(d,p) level of theory and (B) theoretical infrared spectra of DMSO anion at MP2/6-311++g(d,p) level of theory.

in cation. The N=O stretching mode is the most intense mode in N-DMSO that appears at 1526 cm^{-1}. It is as intense as the S=O mode for DMSO.

The CH$_3$ scissoring mode in DMSO vibrational spectrum appears at three frequencies 1394, 1379 and 1366 cm^{-1}. Out of these three, vibration appearing at 1394 is more intense than the remaining two. The CH$_3$ scissoring mode appearing at 1394 cm^{-1} is the second intense mode in the vibrational spectrum of DMSO. The theoretical calculations are in good agreement with experimental determinations for this mode. Two experimental peaks for the CH$_3$ scissoring mode appear at 1438 and 1414 cm$^{-1.}$ This mode is red, red, blue and red shifted by 20, 1, 24 and 8 cm^{-1} in cation, anion, N-DMSO and DMSO in water solvent respectively than that for the DMSO. It is twice and more than ten times intense in cation and anion respectively whereas it is very weak in N-DMSO. It is more intense for DMSO in water solvent as well than DMSO.

Third intense mode in DMSO vibrational spectrum is the C-S asymmetric stretching mode which appears at 674 cm^{-1}. Experimentally this peak is observed at 698 cm^{-1}. This mode is very weak in cation and ten times more intense in anion. It is blue shifted by 32 and 8 cm^{-1} in cation and anion respectively than DMSO. It is blue shifted by 20 cm^{-1} for the DMSO in water solvent and equal intense to that for the DMSO. There are three peaks for the CH$_3$ rocking mode appeared at 985, 925 and 891 cm^{-1}. The experimental peak for this vibration is appeared at 954 cm^{-1}. There is no large difference in the intensity for DMSO and its ions for this mode whereas it is twice intense in N-DMSO. This mode is ten times more intense for DMSO in water solvent. Peaks for the CH$_2$ asymmetric stretching (3002 cm^{-1}), CH$_3$ symmetric stretching (2897 cm^{-1}) and C-S symmetric stretching (651 cm^{-1}) are also comparable with the experimental peaks at 2996, 2912 and 670 cm^{-1}, respectively.

The S=O stretching mode which is the most intense vibrational mode for the DMSO, does not remain most intense for its cation. The most intense mode for the cation is the CH$_3$ scissoring mode appearing at 1374 cm^{-1}. There are three peaks observed for this mode in vibrational spectrum of cation at 1374, 1366 and 1351 cm^{-1}. The latter two are equally intense whereas the first is three times more intense than the remaining two. This mode was the second intense mode for the DMSO. Second intense mode for DMSO cation is the CH$_3$ symmetric stretching mode appearing at 2897 cm^{-1}. This mode is very weak in

DMSO. There is no significant blue shift for cation than the DMSO for this mode. The third intense mode in vibrational spectrum of cation is the CH$_3$ asymmetric stretching mode appeared at 3013 cm^{-1} which is very weak for the DMSO. There is no large shift in the vibrational frequency for this mode in cation than the DMSO. Other intense mode for the DMSO cation are CH$_3$ rocking, molecule bending, CH$_2$ asymmetric stretching, S=O stretching appeared at 904, 317, 3029 and 1202 cm^{-1}, respectively.

Almost all the modes are intense in the vibrational spectrum of DMSO anion. Most of the vibrational modes for DMSO anion are more intense than that for the DMSO and its cation. Their intensities are 10 to 100 times more than that for the DMSO and its cation. The most intense mode for the DMSO anion is the CH$_3$ umbrella mode appeared at 1253 cm^{-1}. There are two peaks for the CH$_3$ umbrella mode. The peak at 1286 cm^{-1} is about twelve times less intense than that at 1253 cm^{-1}. Second intense peak represents the CH$_3$ scissoring mode and appeared at 1345 cm^{-1}. Similar to DMSO and its cation, DMSO anion also has three peaks for the CH$_3$ scissoring mode appeared at 1393, 1361 and 1345 cm^{-1}. Third peak for the CH$_3$ scissoring mode at 1345 cm^{-1} is more intense than the remaining two. Third intense peak in the vibrational spectrum of DMSO anion is the CH$_3$ symmetric stretching mode appeared at 2868 cm^{-1}. There are several other intense peaks in the vibrational spectrum of DMSO anion. These are CH$_2$ asymmetric stretching (2995 cm^{-1}), S=O stretching (1004 cm^{-1}), CH$_3$ rocking (919 and 864 cm^{-1}), C-S asymmetric stretching (682 cm^{-1}) and molecule bending (287 cm^{-1}). There are few weak intense peaks as well in the vibrational spectrum of DMSO anion which are the CH$_3$ asymmetric stretching, C-S symmetric stretching and CH$_3$ torsion.

Similar to DMSO, N-DMSO also shows few intense peaks in its vibrational spectrum. The first intense mode is the N=O stretching mode appeared at 1526 cm^{-1}. Out of three peaks for the CH$_3$ scissoring mode, the peaks at 1414 cm^{-1} is more intense than that at 1418 and 1401 cm^{-1}. The peak at 1414 cm^{-1} for the CH$_3$ scissoring mode is the second intense mode in the vibrational spectrum of N-DMSO. The CH$_3$ asymmetric stretching mode is the third intense peak and appeared at 2977 cm^{-1}. The CH$_3$ rocking and CH$_3$ symmetric stretching modes are the fourth and fifth intense modes appeared at 1072 cm^{-1} and 2888 cm^{-1} respectively. The Watson's A-reduced form of centrifugal and distortional constants for DMSO, its

ions, and N-DMSO alongwith experimental values are presented in Table 3.

As observed for the DMSO, the S=O stretching mode is the most intense mode for the DMSO in water solvent also. It is little more intense for DMSO in water solvent and red shifted by 62 cm^{-1} than that for the DMSO. The second intense peak in the vibrational spectrum of DMSO in water solvent represents the CH_3 rocking vibration appeared at 920 cm^{-1}. This mode is red shifted by 65 cm^{-1} in water solvent and approximately ten times more intense than that for the DMSO. Apart from these modes, peaks representing for the CH_3 scissoring, molecule bending, and C-S asymmetric stretching vibrations are quite intense appearing at 1386, 296 and 343 cm^{-1}, respectively.

3.3 Electronic absorption spectra

The electronic absorption spectra of DMSO, its ions, N-DMSO and DMSO in water solvent are shown in Fig. 3 and the wavelength of transitions, symmetry, oscillator strength and HOMO-LUMO gap are tabulated in Table 4. DMSO shows seven electronic transitions at 54.38, 57.8, 61.68, 72.8, 76.03, 98.2, and 124.4 nm with major contribution from H-3→L+33, H→L+36, H-7→L+21, H-3→L+21, H→L+30, H-3→L+2 and H-1→L+6 transition respectively. Here H and L respresent highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), respectively. The HOMO-LUMO gap for the DMSO is 10.97 eV. The DMSO in water solvent shows five

Table 3 – Rotational and centrifugal distortional constants for DMSO, its ions, and N-DMSO optimized at MP2/6-311++g(d,p) level of theory with experimental determinations.

			Molecule		
Parameters	DMSO	Expt*	Cation	Anion	N-DMSO
A (MHz)	6917.76	7036.57	7535.8	6934.6	10401.48
B (MHz)	6888.57	6910.83	6572.8	6832.4	8888.99
C (MHz)	4183.32	4218.77	3867.1	4145.9	5140.07
Δ_J(kHz)	3.329	4.050	4.546	3.352	6.089
Δ_K(kHz)	6.408	6.706	13.38	6.672	16.102
Δ_{JK}(kHz)	-2.868	-4.452	-8.802	-2.882	-9.296
δ_J(kHz)	1.245	1.454	1.905	1.267	2.523
δ_K(kHz)	-1.375	1.285	0.163	-1.392	1.167
Φ_J (mHz)	-1.189	2.580	6.703	-0.823	8.198
Φ_K (mHz)	-22.58	80.893	-36.49	-19.38	-110.5
Φ_{JK} (mHz)	-18.06	17.3	-56.74	-62.04	-213.4
Φ_{KJ} (mHz)	42.06	-83.46	71.92	137.6	-352.5
Φ_J (mHz)	-0.506	1.145	3.386	-0.296	4.05
Φ_K (mHz)	8.667	4.977	63.65	12.63	90.49
Φ_{JK} (mHz)	-12.02	8.209	-21.52	-13.15	-58.52
ρ (Hz)	411.17	---	285.6	394.5	275.5
μ(Hz)	$0.708*10^{-2}$	--	$0.903*10^{-2}$	$0.739*10^{-2}$	$2.05*10^{-2}$
ν(Hz)	$1.402*10^{-3}$	--	$1.235*10^{-3}$	$1.371*10^{-3}$	$1.562*10^{-3}$
λ(Hz)	$2.860*10^{-3}$	---	$-3.665*10^{-3}$	$2.994*10^{-3}$	$1.337*10^{-2}$

*Ref [12].

Table 4 – Orbitals involved for the electronic transitions, state of symmetry, absorbance, oscillator strength and HOMO-LUMO gap for the DMSO, DMSO in water solvent, its ions and N-DMSO. H and L represent HOMO and LUMO, respectively.

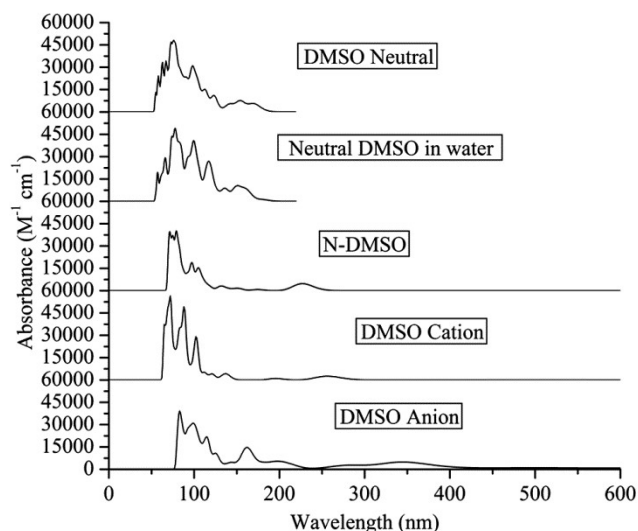| Wavelength (nm)	Symmetry	Absorbance (esu^{2}cm^2)	Oscillation strength	Transitions	HOMO-LUMO gap (eV)
DMSO					
76.03	1A"	48123	0.1696	H→L+30	10.97
DMSO in Water Solvent					
76.23	1A"	48297	0.113	H-1→L+23	11.55
DMSO Cation					
72.44	A"	56423	0.2193	H-1→L+15	14.88
DMSO Anion					
83.56	A'	39156	0.1081	H-1→L+16	8.16
N-DMSO					
79.58	A'	40094	0.2775	H-1→L+22	11.12

Fig. 3 – Electronic absorption spectra of DMSO, its ions, N-DMSO and DMSO in water solvent at MP2/6-311++g(d,p) level of theory.

electronic transitions at 57.13, 65.59, 76.23, 100.96, and 114.55 nm with major contributions from H→L+36, H-1→L+32, H-2→L+11, H-2→L+16, and H-1→L+17, respectively. The HOMO to LUMO gap for the DMSO in water solvent is found to be 11.55 eV. The cation of DMSO shows three electronic transitions at 72.44, 87.01 and 102.58 nm with major contribution from H-1→L+15, H-1→L+6, and H-2→L+4 transitions, respectively. The HOMO-LUMO gap for the cation of DSMO is 14.8 eV. The anion of DMSO shows four electronic trnasitions at 83.56, 104.12, 114.25 and 161.33 nm with major contribution from H-1→L+15, H-5→L, H-1→L+16 and H-1→ L+6 respectively. The HOMO-LUMO gap for the DMSO anion is 8.16 eV. The N-DMSO shows five electronic transitions at 70.9, 79.58, 97.71, 103.7, and 227.1 nm with major contribution from H-1→L+27, H-1→L+22, H-5→L+0, H-1→L+11, and H-1→L+6, respectively. The HOMO - LUMO gap from the N-DMSO is 14.88 eV.

4 Conclusions

Theoretical infrared, electronic absorption spectra, rotational and distortional constants for the DMSO, its ions, and N-DMSO are reported using MP2/6-311++g(d,p) level. Theoretical vibrational modes for the DMSO are in good agreement with our experimental modes. The intense peaks for the neutral DMSO represent the S=O stretching, CH_3 scissoring and C-S asymmetric stretching vibrations observed at 1034, 1394, and 674 cm^{-1}, respectively. After substitution of nitrogen in place of sulfur in DMSO

the first three intense modes are observed at 1526, 1414 and 2977 cm^{-1} representing the N=O stretching, CH_3 scissoring and CH_3 asymmetric stretching vibration, respectively. Number of intense modes in vibration spectrum of DMSO anion is more than that for the DMSO, its cation, N-DMSO and DMSO in water solvent. The most intense peaks are different for these molecules which will help in detecting these molecules in space.

Acknowledgement

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