

An ab initio study of dimethyl sulfoxide and its adducts with H₂O, HCl and OH⁻

Luminița C. Jitariu¹, Craig Wilson, David M. Hirst*

Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK

Received 18 March 1996; accepted 18 July 1996

Abstract

Optimized geometries for dimethyl sulfoxide (DMSO) and its adducts with H₂O, HCl and OH⁻ have been obtained by ab initio HF/6-31G** calculations. HF/6-31 + G** calculations for the anion [CH₃SOCH₂]⁻ (DSN) have also been carried out. Vibrational frequencies have been calculated at the equilibrium geometries for DMSO, DMSO··H₂O, DMSO··HCl and DSN and compared with experimental data. Solvation effects have been taken into account by self-consistent reaction field calculations.

Keywords: Ab initio; Dimethyl sulfoxide adduct; Vibrational frequency; Solvation effect

1. Introduction

The vibrational spectra of dimethyl sulfoxide (DMSO) in the gas phase, in the liquid phase and in water, concentrated hydrochloric acid and aqueous sodium hydroxide have been reported by Dozmorov [1]. Both infrared and Raman spectra were obtained and analyzed to provide information about the nature of the vibrational modes. In aqueous solution the vibrational frequency of the SO bond was observed to decrease by 55 cm⁻¹. This was interpreted in terms of the formation of a hydrogen bond with the oxygen atom of the SO group. In HCl solution the SO stretching frequency decreased further and protonation of the oxygen atom and the formation of an SCl bond were proposed. In alkaline solution it was suggested that

two processes could occur, namely ionization to form the anion [CH₃SOCH₂]⁻ (DSN) and the formation of an adduct (CH₃)₂S(OH)O⁻. From the analysis of the observed spectra it was concluded that in alkaline solution, addition of the hydroxyl ion was more probable. Early work on the solvent properties of DMSO has been reviewed by Martin et al. [2]. The majority of previous experimental studies on DMSO have been concerned with the DMSO–water system. In addition to the spectroscopic studies of Dozmorov [1], measurements have been made of its thermodynamic [3], dielectric [4] and viscometric properties [5,6], and there have been neutron diffraction [7] and NMR studies [8,9]. The work of LeBel and Goring [5] and Linderberg and Lauren [6] shows that there is a strong interaction between DMSO and water and it has been suggested that one molecule of DMSO preferentially associates with two molecules of water [6]. This view is supported by molecular dynamics simulations of the liquid phase [10].

* Corresponding author.

¹ Permanent address: University of Bucharest, Faculty of Chemistry, Bdul Republicii 13, R70034, Sector 5, Bucharest, Romania.

There has been relatively little theoretical work on these systems. A geometry optimization for DMSO with a 3-21G* basis set was reported by Pietro et al. [11]. An optimized geometry for a DMSO–Cl⁻ complex has been obtained with a 4-31G basis set by Maguera et al. [12]. Slivko et al. [13] have carried out MNDO/H calculations for DMSO, DSN and adducts of DMSO with H₂O, HCl and OH⁻ in which they calculated optimized geometries. The optimized structure for the DSN anion was consistent with that suggested by Dozmorov [1] on the basis of the polarization of the Raman bands. Slivko et al. [13] report a calculated geometry for an adduct of DMSO with OH⁻. Their paper does not report any calculated vibrational frequencies and the discussion is based on calculated charges and bond orders. A variety of theoretical methods has been applied by Alkorta [14] to 22 sulfur compounds, including DMSO. The highest level used for geometry optimization was a Hartree–Fock calculation with a 6-31G* basis set. For DMSO this yielded a calculated geometry in good agreement with experiment [15]. An MP2 calculation at this geometry yielded a dipole moment in

good agreement with experiment. More recently, Torii and Tasumi [16] reported optimized MP2 geometries for DMSO with a variety of basis sets. Expansion of the basis set beyond 6-31G* was found to result in relatively small changes in the geometrical parameters. They also reported vibrational frequencies for DMSO obtained in an MP2 calculation with a large basis set.

We are not aware of any ab initio investigations of the adducts of DMSO with H₂O, HCl and OH⁻ nor of any calculation of vibrational frequencies for these species. In this paper we report preliminary calculations made with the GAUSSIAN94 suite of programs [17] in which we have optimized geometries for DMSO, DSN and the adducts of DMSO with H₂O, HCl and OH⁻. Optimization of the structure of a possible adduct of DMSO with two water molecules would be much more computationally demanding and we have not considered such structures. Vibrational frequencies have been calculated at the equilibrium geometries from analytic second derivatives of the energy. The vibrational modes have been analyzed with the help of the MOLDEN [18] program. In order to

Table 1

Optimized geometries from HF/6-31G(d,p) calculations for DMSO (A) and its adducts with H₂O (B), HCl (C) and OH⁻ (D). (Labelling on atoms is defined in Fig. 1.)

	Calculated ^a								Experimental DMSO
	A	B		C		D			
r(SO)	1.485	1.522	1.498	1.523	1.655	1.652	1.506	1.521	1.485
r(CS)	1.795	1.791	1.793	1.831	1.798	1.793	1.789	1.842	1.799
r(CH ₁)	1.084	1.103	1.084	1.101	1.076	1.103	1.104	1.102	1.054
r(CH ₂)	1.082		1.082		1.081		1.085		1.097
r(CH ₃)	1.083		1.083		1.081		1.086		1.093
r(OH ^a)			0.951	0.995	0.947	0.944	0.951	0.938	
r(OH ^b)			0.943	0.941					
r(O⋯H)			1.98	1.591					
r(SCl)					2.743	2.12			
r(SO)							3.506	1.742	
∠CSC	97.82	103.0							96.6
∠OSC	106.7	105.6	106.5	109.8	95.54	103.1	108.6	108.8	106.7
∠SCH ¹	109.6	107.6	109.4	109.3	107.5	111.3	105.9	111.9	108.3
∠SCH ²	107.4	106.7	107.5	106.5	106.9	108.6	108.0	107.7	108.2
∠SCH ³	110.2	112.8	109.9	110.3	108.1	107.0	108.2	109.9	109.6
∠H ^a OH ^b			106.0	111.6					
∠O⋯HO			154.0	172.3					
∠SOH			106.3	131.9	109.2	111.7	120.8	116.9	
∠OSO,OSCl					178.2	129.3	155.1	101.8	

^a Values in right-hand column for A, B, C and D are MNDO/H calculations from [13].

account for solvation effects, further calculations have been made with the self-consistent reaction field method [19].

2. Results and discussion

Table 1 contains details of the geometrical parameters obtained in optimizations at the HF/6-31G** level for DMSO (A) and its adducts with H₂O (B), HCl (C) and OH⁻ (D). The structures are shown in Fig. 1. For DMSO our results are in excellent agreement with those obtained by Alkorta [14] with a 6-31G* basis set. Experimental data for DMSO [15] and the results of the MNDO/H calculations of Slivko et al. [13] are also given in Table 1. There is very good agreement between the HF/6-31G** calculations and

the experimental geometry for DMSO. The agreement between our geometries for the adducts with H₂O, HCl and OH⁻ and those calculated by the MNDO/H method is reasonable except that for the adducts we obtain significantly longer distances for the S...HOH, S...Cl and S...OH bonds than those reported by Slivko et al [13]. A 6-31G** basis set is not adequate for a satisfactory description of an anion and the lack of diffuse functions may be the reason for the very long S...OH bond length in the OH⁻ adduct.

In Table 2 we report vibrational frequencies for DMSO and the DMSO...HOH and DMSO...HCl adducts. The calculated vibrational frequencies have been scaled by a factor of 0.89. In the table we have used the notation CH₃⁺ to denote a symmetric stretching mode and CH₃⁻ for an asymmetric stretching mode. Vibrational frequencies for the DMSO...OH⁻ adduct are not reported because we are not confident that the structure obtained in our optimization is sufficiently realistic. For DMSO there is very good agreement with the experimental vibrational frequencies reported by Dozmorov [1] for gas-phase DMSO. For the DMSO...H₂O adduct Dozmorov reported that in the Raman spectrum the vibrational frequency for the SO bond decreased from 1102 to 1044 cm⁻¹ due to the formation of a hydrogen bond. The calculated frequencies also indicate a decrease in frequency in the H₂O adduct. Formation of an adduct with two water molecules might be expected to result in a further decrease in the SO vibrational frequency. No other experimental data for the H₂O adduct were reported.

In the case of the formation of the HCl adduct there is a significant increase in the length of the SO bond from 1.485 Å in DMSO to 1.655 Å in the adduct. This reflects the greater change in the SO bond on protonation in the HCl adduct than in hydrogen bond formation in the H₂O adduct. However, the calculated SO stretching frequency shows very little change from that in DMSO. The calculated CS stretching frequencies do show an increase as was observed experimentally. Some low frequency modes due to the newly formed S...Cl fragment are obtained. The ab initio calculations yield a long S...Cl bond. Further calculations were made with the 6-31 + G* basis set which should give a better description of a negatively charged chlorine atom. This did not result in any significant change in the S...Cl bond length.

For the DSN anion we have used the 6-31 + G**

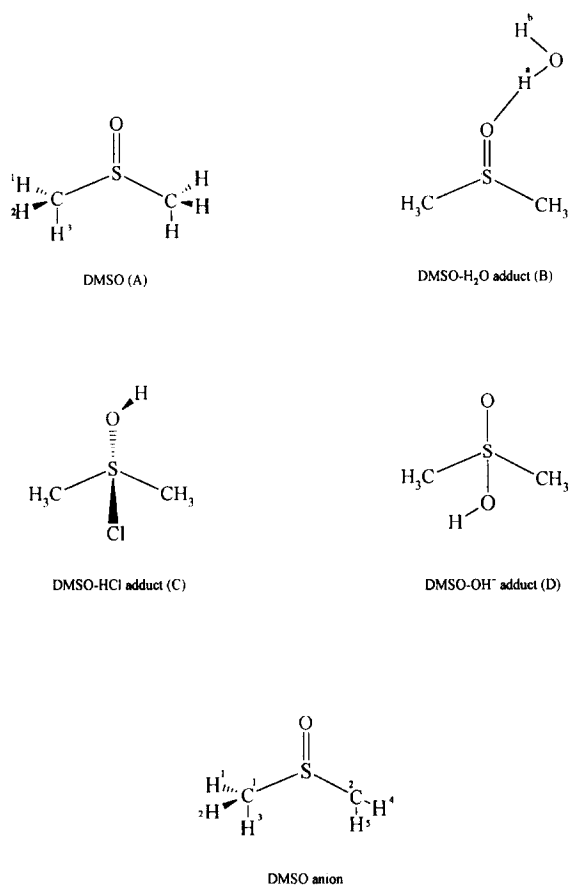


Fig. 1. Structures of DMSO, DMSO anion and DMSO adducts with HCl, H₂O and HCl.

Table 2

Calculated and experimental vibrational frequencies/cm⁻¹ for DMSO and its adducts with H₂O and HCl

DMSO		DMSO···HOH		DMSO···HCl		
ν_{calc}	$\nu_{\text{exp}}[1]$	ν_{calc}		ν_{calc}	$\nu_{\text{exp}}[1]$	
				3694		OH stretch
2945		2936		3013		CH ₃ ⁺ stretch
2944		2853	CH ₃ ⁺ stretch	3012		CH ₃ ⁻ stretch
2938		2849	CH ₃ ⁻ stretch	2968		CH ₃ ⁺ stretch
2934		1604	HOH sym stretch	2967		CH ₃ ⁻ stretch
2851		1436		2877		CH ₃ ⁺ stretch
2845		1418	CH ₃ ⁻ bend	2877		CH ₃ ⁻ stretch
1430	1435	1410	CH ₃ ⁺ bend	1426	1418	CH ₃ ⁺ bend
1414	1420	1399	CH ₃ ⁻ bend	1412	1416	CH ₃ ⁻ bend
1411	1410	1343	CH ₃ ⁺ bend	1411	1410	
1399	1400	1322	CH ₃ ⁻ bend	1395		SCH bend
1339	1310	1026	CH ₃ ⁻ bend	1341		HCH bend, CH ₃ ⁺
1318	1300			1319	1289	HCH bend, CH ₃ ⁻
1043	1102	1021	SO ⁺ stretch	1152	1380	S–OH deformation
		946	SO ⁻ stretch	1050	1010	SO stretch
1015	955	939	SCH ⁻ rock	999		
949	935	895	SCH ⁺ rock	976	946	SCH rocking
930	900	712	SC ⁻ stretch	938	875	SCH rocking
884	820	669	SC ⁺ stretch	735	712	CS stretch
706	697	606	O–H out-of-plane	717	675	CS stretch
667	667	358	CSO bend	647	506	SOH deformation
355	384	330	O···H stretch	345	330	CH ₃ ,SOH bend
304	334	313	O···H stretch	343		S–OH bend
278	305	280	CSC bend	278	305	CSC bend
225	258	233	CH ₃ ⁻ torsion	218		S–OH out of plane
183	178	191	CH ₃ ⁺ torsion	190	122	CISO bend
		152	OH stretch	180	222	S–Cl stretch
		143	HOH rock	157	153	CISC bend
		84	O···H–O twisting	109		CH ₃ ⁻ torsion
		30		59		CH ₃ ⁺ torsion

basis set which includes diffuse functions appropriate for calculations on anions. Table 3 compares the geometry obtained in optimization at the Hartree–Fock level with the results of the MNDO/H calculations of Slivko et al. [13]. Comparison with the structure of DMSO shows that on removal of a proton the SO bond lengthens from 1.485 to 1.529 Å and that the CS bonds become unequal in length. There is a significant shortening of the bond between S and the CH₂ group. In Table 4 we report vibrational frequencies calculated at our optimized geometry. Since these frequencies refer to an isolated gas-phase molecular ion they are not directly comparable with the results obtained by Dozmorov [1]. In order to take into account solvent effects we have calculated the

vibrational frequencies with the Onsager model [20] in a self-consistent reaction field (SCRf) calculation [19]. The calculated vibrational frequencies differ from the experimental values by up to 60 cm⁻¹. Dozmorov considered three possible structures for the DSN anion and concluded on the basis of the polarization of the Raman bands that the C₁ structure was the more probable. Our optimized structure is consistent with this structure in which the C–(SO)–C skeleton is non-planar.

The calculations reported above for DMSO and its adducts are for isolated molecules and are therefore relevant to gas-phase spectra. Dozmorov [1] obtained spectra for DMSO in the liquid phase and in solution in water, concentrated hydrochloric acid and aqueous

Table 3
Optimized geometries for the DSN⁻ anion

	This work	MNDO/H ^a
r(SO)	1.529	1.541
r(C ¹ S)	1.803	1.830
r(C ² S)	1.719	1.635
r(CH ¹)	1.081	1.103
r(CH ²)	1.084	1.103
r(CH ³)	1.086	1.103
r(C ² H ⁴)	1.086	1.074
r(C ² H ⁵)	1.090	1.078
∠OSC ¹	101.2	104.8
∠OSC ²	117.2	109.1
∠SCH ¹	108.4	112.5
∠SCH ²	108.2	107.7
∠SCH ³	110.0	108.0
∠SCH ⁴	109.1	123.5
∠SCH ⁵	111.8	117.0

^a From [13].

sodium hydroxide. We have performed SCRF calculations [19] as implemented in GAUSSIAN94. A value of 3.2 Å was used for the radius of the cavity, a_0 . This value was obtained by adding 0.5 Å to the radius given by a molecular volume calculation. Atomic charges obtained from a Mulliken population analysis for the SCRF/HF/6-31G** calculations are compared with the gas-phase values in Table 5. There is a significant increase in the negative charge on the oxygen atom in going from the gas phase to liquid or solution. However, there is very little change in geometry on including reaction field theory with the SO bond length increasing by 0.01 Å. Inclusion of solvation effects results in the SO bond vibrational frequency decreasing by about 20 cm⁻¹ but otherwise there is very little effect on the calculated vibrational frequencies.

Table 5
Atomic charges for DMSO in different solvents

Solvent	Dielectric constant	O	S	C	H ₁	H ₂	H ₃
Vapour	1.0	-0.786	0.944	-0.558	0.140	0.172	0.166
Pure liquid	46.45	-0.832	0.926	-0.556	0.184	0.158	0.167
HCl	4.6	-0.817	0.932	-0.557	0.171	0.163	0.166
Aq. NaOH	73.0	-0.833	0.925	-0.556	0.185	0.158	0.167
Water	78.54	-0.833	0.925	-0.556	0.185	0.158	0.167

Table 4
Calculated vibrational frequencies (cm⁻¹) for the DSN⁻ anion

HF	SCRF		
ν_{calc}	ν_{calc}	$\nu_{\text{exp}}^{\text{a}}$	
213	218		
263	228		
326	277	245	CSO bend
358	356		CSC bend
397	408	438	CH ₂ twist
606	603	630	HCH out-of-plane
682	667	765	CS ⁺ stretch
816	768		CS ⁻ stretch
902	891	862	SO stretch
907	913	992	CH ₃ torsion
959	948	1019	SCH bend
1023	1028	1087	SCH bend
1299	1304		
1372	1363	1356	CH ₂ bend
1407	1402	1411	CH ₃ ⁺ bend
1415	1412	1455	CH ₃ ⁻ bend
2805	2794		CH ₂ symm stretch
2832	2833		CH ₃ symm stretch
2876	2864		CH ₂ asymm stretch
2902	2913		CH ₃ asymm stretch
2930	2922		CH ₃ asymm stretch

^a From [1].

Acknowledgements

We are grateful to the European Commission for a TEMPUS grant to L.C.J. to enable her to visit Warwick and to EPSRC for a studentship for C.W. and for the provision of computing equipment.

References

- [1] S.V. Dozmorov, Zh. Prikl. Spektrosk., 45 (1986) 438.
- [2] D. Martin, A. Weise and H.-J. Niclas, Angew. Chem., Int. Ed. Engl, 6 (1967) 318.

- [3] M.F. Fox and K.P. Whittingham, *J. Chem. Soc., Faraday Trans. 1*, 71 (1975) 1407.
- [4] R.L. Amey, *J. Phys. Chem.*, 72 (1968) 3358.
- [5] R.G. LeBel and D.A.I. Goring, *J. Chem. Eng. Data*, 7 (1962) 100.
- [6] J.J. Lindberg and R. Lauren, *Fin. Kemistamf. Medd.*, 71 (1962) 37.
- [7] A. Luzar, A.K. Soper and D. Chandler, *J. Chem. Phys.*, 99 (1993) 6836.
- [8] E.S. Baker and J. Jonas, *J. Phys. Chem.*, 89 (1985) 1730.
- [9] T. Tokuhiro, L. Menafra and H.H. Szmant, *J. Chem. Phys.*, 61 (1974) 2275.
- [10] I.I. Vaisman and M.L. Berkowitz, *J. Am. Chem. Soc.*, 114 (1992) 7889.
- [11] W.J. Pietro, M.M. Francl, W.J. Hehre, D.J. DeFrees, J.A. Pople and J.S. Binkley, *J. Am. Chem. Soc.*, 104 (1982) 5039.
- [12] T.F. Maguera, G. Caldwell, J. Sunner, S. Ikuta and P. Kebarle, *J. Am. Chem. Soc.*, 106 (1984) 6140.
- [13] S.A. Slivko, M.A. Sarukhanov and N.N. Kulikova, *Zh. Strukt. Khim.*, 34 (1993) 363.
- [14] I. Alkorta, *Theor. Chim. Acta*, 89 (1994) 1.
- [15] J. Calloman, E. Hirota, K. Kuchitsu, W.J. Lafferty, A.G. Maki and C.S. Pote, in K.H. Hellwege and A.M. Hellwege (Eds.), *Structure Data on Free Polyatomic Molecules*, Landolt-Börnstein, New Series Group II, Vol. 7, Springer-Verlag, Berlin, 1976.
- [16] H. Torii and M. Tasumi, *Bull. Chem. Soc. Jpn.*, 68 (1995) 128.
- [17] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T.A. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez and J.A. Pople, *GAUSSIAN94*, Gaussian Inc., Pittsburgh, PA, 1995.
- [18] G. Schaftenaar, *MOLDEN 2.9*, CAOS/Camm Center, Toernooiveld, Nijmegen, The Netherlands, 1996.
- [19] M.W. Wong, M.J. Frisch and K.B. Wiberg, *J. Am. Chem. Soc.*, 113 (1991) 4776.
- [20] L. Onsager, *J. Am. Chem. Soc.*, 58 (1936) 1486.