



A Theoretical Study of Spectroscopic Properties of a Hemiacetal by TDDFT Method

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ABSTRACT

Hemiacetals being unstable compounds are difficult to isolate and it is difficult to establish their structure and spectroscopic properties by experiment. IR and NMR experimental data are available in the literature only for the hemiacetal 1-methoxy ethanol in a reaction mixture. The objective of the present work is to investigate how the methods based on density functional theory (DFT) and its time dependant version (TDDFT) can predict structural and spectroscopic properties of this unstable compound. Geometry optimization and frequency calculations have been carried out by DFT method at 6-31+G(d) and 6-31++G(d,p) levels. The UV-Vis spectra in a number of solvents have been calculated by the TDDFT method under the polarizable continuum model and the variation of the calculated UV-vis absorption peak with two solvent polarity indices (namely, $E_T(30)$ and Z-values) has been studied in these solvents; electronic transition energies at the λ_{max} values in the theoretically calculated spectra increase with solvent polarity. The calculated infrared absorption bands and NMR chemical shifts (¹H and ¹³C) are in good agreement with reported experimental data. In case of IR, consideration of anharmonicity effect yields better agreement with experiment.

Key words: Hemiacetal, 1-Methoxy ethanol, Solvent polarity indices, TDDFT, Anharmonicity.

INTRODUCTION

The formation of acetals as a result of reaction between aldehydes and alcohols is known to proceed through the formation of the corresponding hemiacetals (Structure 1, Fig. 1). These hemiacetals are highly unstable and difficult to isolate and therefore it is not possible to record the spectra of pure hemiacetals. Their existence in reasonable concentration in solutions, however, has been postulated in a number of cases¹⁻³ and spectroscopic data of some of such compounds in

reaction medium have been reported.^{2, 3} The proposed hemiacetal structure and the reported spectra in reaction mixture can only be justified by theoretical calculation. The density functional theory (DFT)^{4, 5} is currently being applied for carrying out a variety of quantum chemical calculations ranging from geometry optimization of large clusters⁶ to the study of reaction rates.^{7, 8} For theoretical prediction of spectroscopic properties (transition energy, oscillator strength etc.), the time dependent density functional theory (TDDFT) has been developed⁹⁻¹¹ and is now being widely used.¹²⁻¹³ The objective of

the present work is to calculate the infrared absorption frequencies, UV-vis absorption maxima and NMR chemical shifts of the unstable molecule, 1-methoxy ethanol (Structure 2, Fig. 1) by applying the computational method of TDDFT and comparing them with available experimental data.^{2, 3} Effect of change in solvent polarity on the UV-vis spectrum has also been studied theoretically and the results are expected to have some predictive value for spectroscopic investigations of similar compounds which may be formed *in situ* during chemical reactions.

Computational details

All computations were performed on a Pentium computer with Gaussian 03 Revision D.01 suite of programmes.¹⁴ DFT calculations were done by using the Becke's three parameter hybrid¹⁵ exchange potential with the correlation function of Lee, Yang and Parr¹⁶ (B3LYP). The basis sets 6-31+G(d), 6-31++G(d,p) and 6-311+G(d,p) were used. Optimization of the ground state geometry of the molecule at B3LYP level was carried out in vacuum and also in Tetrahydrofuran (THF), Chloroform (CHCl₃), acetonitrile (CH₃CN), dimethylsulfoxide (DMSO) and methanol (MeOH) solutions by the polarizable continuum model^{17, 18} (PCM). Using the ground state optimized geometry, the vibrational frequencies, ¹H and ¹³C NMR chemical shifts and electronic transition energies were calculated. Similarly by using the TDDFT method under the

PCM formalism the electronic transition energies in THF, CHCl₃, CH₃CN, DMSO and MeOH medium were calculated. In the PCM, the solute is placed in the solvent reaction field cavity created by a series of overlapping spheres initially devised by Tomasi *et. al.*^{17, 18} and implemented by Barone *et. al.*¹⁹⁻²⁰ also by Tomasi and co-workers^{21, 22}.

RESULTS AND DISCUSSION

Optimized Geometry

The optimized geometry of the hemiacetal of acetaldehyde (compound II, Figure 1) computed at B3LYP/6-31++G(d,p) level in vacuo and in dimethyl sulfoxide (DMSO) is shown in Figure 2 along with the necessary atom labels. The calculated structural details are summarized in Table 1. Such optimization has also been carried out in four other solvents of varying polarity and also using the 6-31+G(d) basis set; these results are given as supplementary material.

Results of thermo-chemical calculation, as given in Table 2, indicate that in going from vacuum to solution phase the stability of the hemiacetal increases and that too, with increase in solvent polarity (dielectric constant, ξ). This suggests that the hemiacetal molecule should be polar, and this is substantiated by the calculated dipole moment of about 3.2 D (Table 1 and also in supplementary material). It is also to be noted that change of basis set from 6-31+G(d) to 6-31++G(d,p) brings about

Table 1. Main structural features (bond length, bond angle, dipole moment) of the optimized geometries in vacuum and in DMSO solvent calculated with 6-31+G(d) and 6-31++G(d,p) basis set. Atom labels refer to Fig. 2

Geometrical Parameter	B3LYP/6-31+G(d)		B3LYP/6-31++G(d,p)	
	Vacuum	DMSO	Vacuum	DMSO
R(C1-O5) / Å	1.426	1.433	1.426	1.434
R(O5-C10) / Å	1.419	1.425	1.419	1.426
R(O3-H4) / Å	0.972	0.988	0.968	0.984
A(O3-C1-O5) / deg	107.1	107.3	107.1	107.3
A(O3-C1-C6) / deg	107.7	108.1	107.7	108.1
A(O5-C1-C6) / deg	113.0	112.1	113.0	112.0
A(C1-O3-H4) / deg	107.7	108.6	107.7	108.7
A(C1-O5-C10) / deg	114.9	114.5	114.9	114.4
Dipole moment / Debye	2.3164	3.2535	2.2908	3.2386

an increase in stabilization energy of about 9.5 kcal mol⁻¹ (Table – 2).

UV-vis spectra

The electronic transitions were calculated by the TDDFT method in vacuum and in five different solvents, namely, tetrahydrofuran (THF), chloroform (CHCl₃), acetonitrile (CH₃CN), methanol (MeOH)

and dimethylsulfoxide (DMSO) at the B3LYP level of theory with basis sets 6-31+G(d) and 6-31++G(d,p), using 30 singlet states in each case. The PCM formalism was used for calculation in solution phase and the respective optimized ground state geometries in the above mentioned solvents were used as input. Five absorption bands were found to have reasonable oscillator strength within

Table 2: Variation of ground state energy of the hemiacetal with solvent polarity calculated at DFT /B3LYP level using two basis sets; the absolute energies include zero-point correction

Medium	Dielectric constant of solvent	Absolute energy / Ha		Energy relative to vacuum (kcal mol ⁻¹)	
		6-31+G(d)	6-31++G(d,p)	6-31+G(d)	6-31++G(d,p)
Vacuum	-	-269.465167	-269.480562	0.00	0.00
CHCl ₃	4.9	-269.475150	-269.490404	-6.26443	-6.17595
THF	7.58	-269.476783	-269.492023	-7.28915	-7.19189
MeOH	32.63	-269.479858	-269.495075	-9.21874	-9.10705
CH ₃ CN	36.64	-269.479918	-269.495133	-9.25640	-9.14344
DMSO	46.70	-269.480087	-269.495292	-9.36244	-9.34222

Table 3: Transition energies (eV), wave lengths of absorption maxima (nm) and oscillator strengths (f) of electronic transitions of 1-Methoxy ethanol in different media calculated by TDDFT method using two basis sets

Medium	B3LYP/6-31+G(d)			B3LYP/6-31++G(d,p)		
	eV	nm	f	eV	nm	f
Vacuum	6.901	179.66	0.0137	6.6189	187.32	0.0136
	7.2611	170.75	0.0326	6.9064	179.52	0.0305
	7.4144	167.22	0.0424	7.041	176.09	0.0416
CHCl ₃	7.0542	175.76	0.0144	6.7551	183.54	0.0139
	7.3004	169.83	0.0536	6.9499	178.4	0.0434
	7.5102	165.09	0.0247	7.1042	174.52	0.0405
THF	7.0787	175.15	0.0142	6.7781	182.92	0.0136
	7.3027	169.78	0.055	6.9537	178.3	0.0438
	7.5365	164.51	0.0228	7.1117	174.34	0.0382
MeOH	7.1276	173.95	0.0141	6.8265	181.62	0.0132
	7.3164	169.46	0.0559	6.9729	177.81	0.0437
	7.5945	163.25	0.0228	7.1326	173.83	0.0339
CH ₃ CN	7.1292	173.91	0.0145	6.8271	181.61	0.0134
	7.3142	169.51	0.0565	6.9719	177.84	0.0441
	7.596	163.22	0.0227	7.1319	173.84	0.0338
DMSO	7.128	173.94	0.0149	6.8277	181.59	0.0139
	7.3124	169.55	0.0593	6.971	177.86	0.0463
	7.594	163.27	0.0245	7.1312	173.86	0.035

Table 4: Variation of transition energy of UV absorption maximum of 1-methoxy ethanol with solvent polarity

Solvent	$E_T(30) / \text{kcal-mol}^{-1}$	$Z / \text{kcal-mol}^{-1}$	$E / \text{kcal-mol}^{-1}$
THF	37.4	-	160.35
CHCl_3	39.1	63.2	160.26
DMSO	45.1	71.1	160.74
CH_3CN	45.6	71.3	160.76
MeOH	55.4	83.6	160.79

the region of 150 nm. Some more absorption bands with strong oscillator strength were observed below 150 nm, but such bands fall deep within the vacuum UV region and were discarded as they might not be observed experimentally. Changing the medium from vacuum to different solvents causes a blue shift for all the calculated absorption bands. Some important transitions are shown in Table 3. A representative UV-vis spectrum of 1-Methoxy

Table 5: Vibrational frequency data of 1-Methoxy ethanol calculated at 6-31+G(d) and 6-31++G(d,p) basis sets with and without connection for anharmonicity

Medium	Frequency (cm^{-1})				Experimental (in MeOH)
	B3LYP/6-31+G(d)		B3LYP/6-31++G(d,p)		
	Harmonic	Anharmonic	Harmonic	Anharmonic	
Vacuum	939	921	935	917	920,1100 – 1150 (with a peak at 1140), 1210
	1119	1093	1112	1087	
	1125	1140	1121	1150	
	1169	1157	1164	1136	
	1233	1204	1227	1250	
	3734	3556	3810	3637	
CHCl_3	840	943	929	978	
	1105	972	1028	1080	
	1111	1042	1100	1117	
	1155	1038	1104	1147	
	1280	1061	1149	1254	
	3508	3244	3569	3321	
THF	931	931	927	911	
	1103	1160	1148	1173	
	1153	1133	1173	1200	
	1230	1198	1223	1232	
MeOH	3464	3146	3531	3220	
	1098	931	1030	917	
	1106	999	1110	953	
	1118	1229	1143	1222	
	1149	1082	1174	1178	
	1276	1235	1265	1216	
CH_3CN	3382	3019	3447	3083	
	928	985	1030	1010	
	1099	1077	1095	1110	
	1105	1149	1096	1033	
	1148	1139	1143	952	
	1228	1206	1222	1167	
DMSO	3380	3016	3444	3092	
	838	937	924	1040	
	1036	947	1094	1052	
	1098	916	1143	1120	
	1103	1017	1173	1140	
	1149	1047	1222	1215	
	3374	3194	3439	3293	

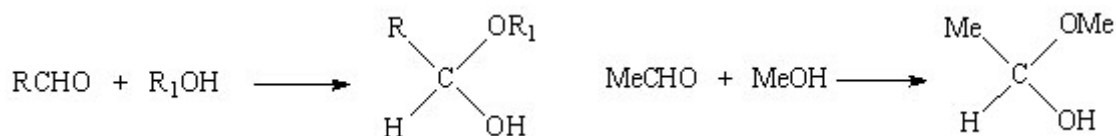


Fig. 1: Formation of (I) hemiacetal by reaction between an aldehyde (RCHO) and an alcohol (R₁OH); hemiacetal (II) formation by reaction between acetaldehyde and methanol

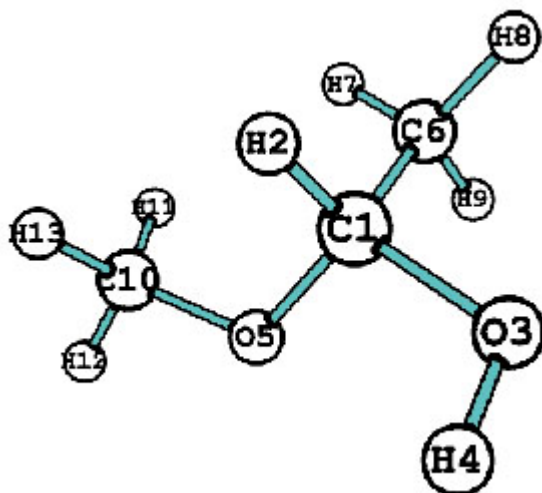


Fig. 2: The optimized geometry of the hemiacetal of acetaldehyde (compound II, Figure 1) computed at B3LYP/6-31++G(d,p) level in vacuum

ethanol in CHCl₃ medium calculated at TDDFT/B3LYP/6-31++G(d,p) level is given in Figure 3.

Electronic transitions in the long wavelength region (above 150 nm) with the maximum oscillator strengths are found to follow a certain trend with change in solvent polarity. For example, the transition energies shown in Table 4 increase with two important solvent polarity indices, namely, $E_T(30)$ and Z-value of the solvents (introduced by Reichardt²³ and Kosower²⁴ respectively) with an exception in case of chloroform. The variation of electronic transition energy (Kcal mol⁻¹) with two solvent polarity indices, $E_T(30)$ and Z is shown in Figure 4. This indicates a specific type of interaction between molecule II and chloroform. However, the slow overall increase of transition energy with solvent polarity hints at an

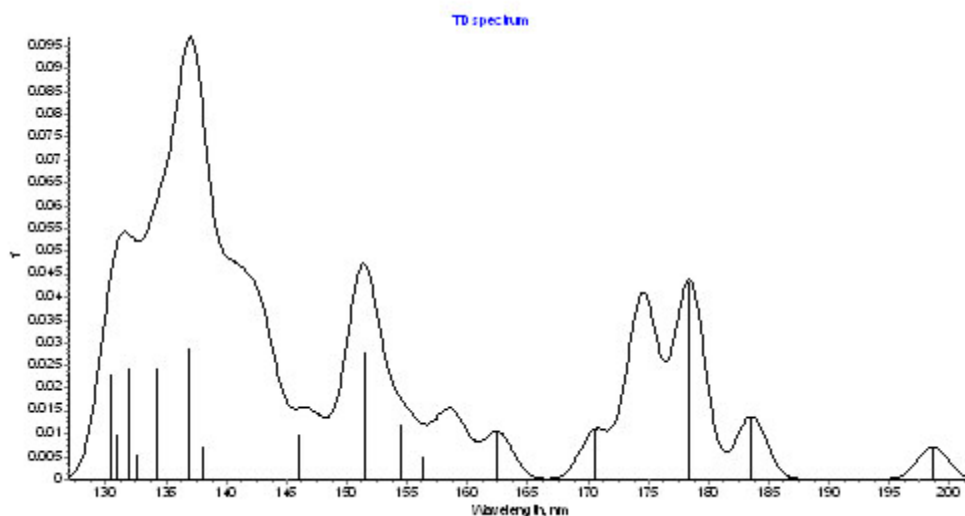


Fig. 3: UV-vis spectrum of 1-Methoxy ethanol in CHCl₃ medium calculated by TDDFT method at B3LYP/6-31++G(d,p) level

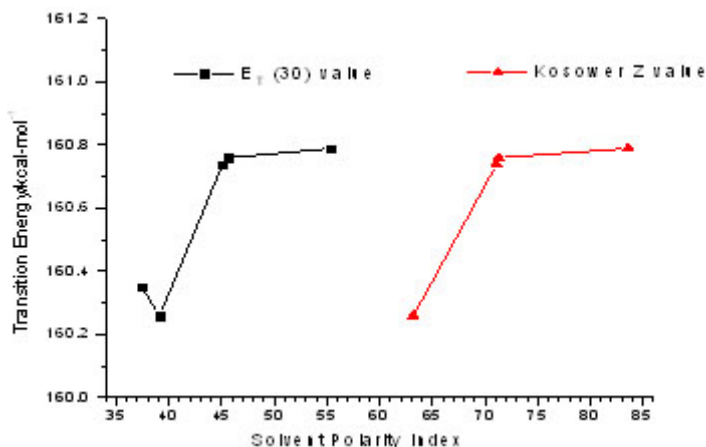


Fig. 4: Variation of electronic transition energy with two solvent polarity indices, $E_T(30)$ and Z

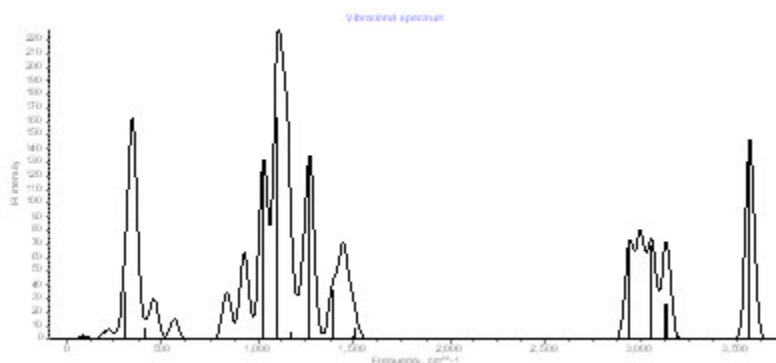


Fig. 5: Theoretically predicted infra red spectrum of 1-Methoxy ethanol in CHCl_3 medium calculated at B3LYP/6-31++G(d,p) level

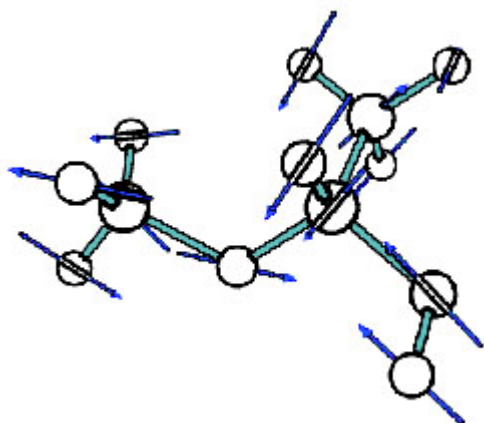


Fig. 6: Displacement vectors of the vibrational mode at 1104 cm^{-1} of 1-Methoxy ethanol in CHCl_3 medium calculated at B3LYP/PCM/ 6-31++G(d,p) level

uneven distribution of electronic charge in the ground state which gives rise to an appreciable dipole moment of the hemiacetal molecule.

Infrared spectra

With the optimized geometries obtained at B3LYP level in vacuum, THF, CHCl_3 , CH_3CN , DMSO and MeOH the vibrational frequencies were calculated with 6-31+G(d) and at 6-31++G(d,p) basis sets and compared with the reported experimental results of the IR absorption bands of the hemiacetal of acetaldehyde. Anharmonicity effects were also taken into account at five different temperatures and the thermochemical results are given in the supplementary materials. Both harmonic and anharmonic frequencies are given in Table 5

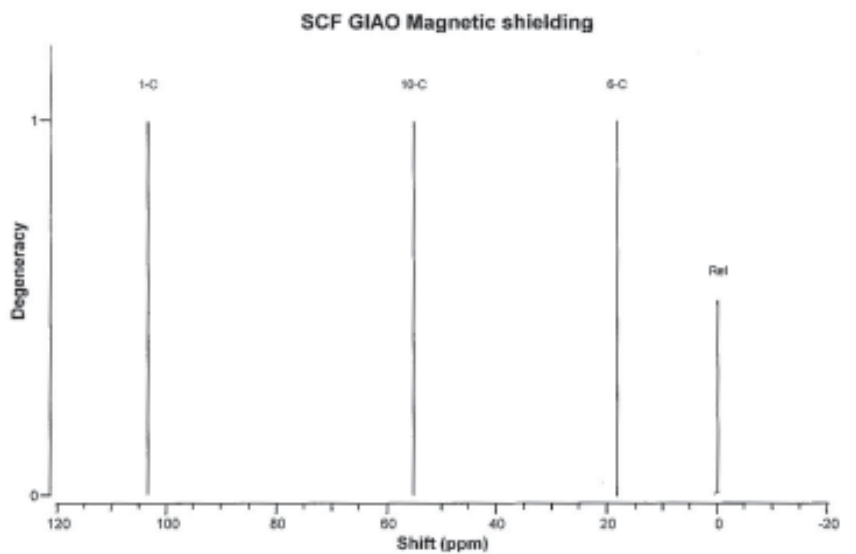


Fig. 7: ^1H NMR spectrum of 1-Methoxy ethanol in CHCl_3 medium calculated at TDDFT/B3LYP/6-31++G(d,p) level

along with reported experimental values^{5, 6} in methanol medium. The theoretical calculated frequencies are in good agreement with the experimentally observed values, particularly if anharmonicity effect is considered.

The absorption around the region of 345 cm^{-1} is due to various bending vibrations present in the molecule, the absorption within the region between 1150 cm^{-1} to 1000 cm^{-1} is due to different O-C stretching and bending of the ether linkage present in the molecule, the absorption region around 3100 cm^{-1} is due to C-H stretching vibrations, and the absorption region in between 3800 cm^{-1} and 3300 cm^{-1} is due to O-H stretching. Table 5 lists the important vibrations observed in the hemiacetal molecule in different media. One calculated IR spectrum of 1-methoxy ethanol is also shown in Fig. 5. The displacement vectors corresponding to the predicted vibrational mode at 1104 cm^{-1} in CHCl_3 medium, calculated at TDDFT/B3LYP/6-31++G(d,p) level, is represented in Fig. 6.

^1H and ^{13}C NMR spectra

For calculation of NMR chemical shifts the structure was optimized at B3LYP/6-311G(2d,p) level in CHCl_3 medium by the PCM formalism^{16- 18}

and the optimized geometry was subjected to NMR calculations by the gauge-independent atomic orbital method. Results are given in Table 6 where the atom labels refer to Fig.1. The ^{13}C NMR

Table 6: ^1H and ^{13}C NMR chemical shifts (δ , ppm) and electronic charge distribution of 1-methoxy ethanol calculated at DFT/B3LYP/6-311+G(2d,p) level in CHCl_3 solvent. Atom labels are in accordance with Fig. 2

Atom type	GIAO NMR Isotropic shielding with respect to TMS (δ , ppm)	Electronic Charge distribution
H2	5.02	0.13943
H4	2.29	0.49775
H7	1.35	0.20429
H8	1.19	0.21238
H9	0.80	0.21024
H11	3.29	0.16282
H12	3.60	0.18792
H13	3.21	0.16274
C1	103.40	0.43955
C6	18.21	-0.61136
C10	55.16	-0.20759

spectrum is represented in Fig. 7. The calculated ^{13}C NMR spectrum shows three distinct signals (Fig. 7), corresponding to three different carbon environments in the hemiacetal molecule as evident from the optimized structure (Fig. 2); the theoretically obtained chemical shifts are in accordance with the electronic charge distribution obtained by natural population analysis. The calculated chemical shifts for ^1H NMR are clustered in the region 0.8 – 5.02 δ as shown in Table 6. The reported experimental values² are also in this range. Moreover, it is noteworthy (Table 6) that the ^1H NMR shifts vary in accordance with the natural charges on the H-atoms – higher electronic charge resulting in upfield resonance

Conclusion

Attempts have been made to circumvent the difficulty in experimental detection and

characterization of unstable hemiacetals by DFT- and TDDFT-based computational predictions. One such hemiacetal of interest, namely, 1-methoxy ethanol has been considered. Its structural and spectroscopic properties (UV-vis, IR, ^1H and ^{13}C NMR) in vacuum and in a series of solvents with varying solvent polarity have been calculated. The computed results are in good agreement with reported experimental data. In case of IR, consideration of anharmonicity effect yields better agreement with experiment. The UV-vis spectra are predicted to show somewhat regular blue shift with increase in solvent polarity.

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