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Theoretical Study of Vibrational Frequencies and Chemical Shifts of Choline Halides (F, Cl, Br)

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Abstract: The vibrational frequencies and ^1H and ^{13}C chemical shifts of choline halides have been calculated using density functional theory (B3LYP) method with 6-311++G(d, p) and 6-31 G(d, p) basis set level in Gaussian 03 and Parallel Quantum Solutions (PQS) ab initio packages programs, respectively. The calculated optimized geometric parameters, vibrational frequencies and chemical shifts were seen to be a very good agreement with the experimental data. The electronegativity influence of the halogen substitutions on the vibrational frequencies and chemical shifts have also been investigated. It was observed that the chemical shifts for H nucleus, especially the most near nucleus to the halogen atom decrease while it increases for C nucleus. The roughly linear variation of the chemical shift with the electronegativity of the halogen, whatever the shielding for C nucleus or deshielding for H nucleus is, has been commented that the local electron density near the halogen atom is affected.

Key words: Choline halides, vibrational spectroscopy, chemical shift, B3LYP, Gaussian, PQS

Kolin Halidlerin (F, Cl, Br) Kimyasal Kaymalarının ve Titreşim Frekanslarının Teorik Çalışması

Özet: Taban setleri 6-311++G(d,p) ve 6-31G(d,p) olan yoğunluk fonksiyon kuramı (B3LYP) yöntemi kullanılarak kolin halojenlerinin (F, Cl, Br), Gaussian 03 programında titreşim frekansları ve Paralel Quantum Solutions (PQS) programında ise, ^1H ve ^{13}C çekirdeklerinin kimyasal kaymaları hesaplandı. Hesaplanan optimize geometrik yapı parametreleri, titreşim frekansları ve kimyasal kaymalar, deneysel verilerle çok iyi uyumaktadırlar. Kimyasal kaymalara ve titreşim frekanslarına, halojen katkılanmalarının, yani elektronegatifliğin etkileri incelendi. Kimyasal kaymaların, H çekirdeği için özellikle halojen atomuna en yakın çekirdekler olmak üzere azalırken, C çekirdeği için aynı sıralamayla arttığını gözledik. Halojenin elektronegatifliği ile kimyasal kaymanın kabaca çizgisel değişimi, C çekirdeği için ekranlanma ya da H çekirdeği için ekranlanmama ne olursa olsun, halojen atomu yakınındaki yerel elektron yoğunluğunun değişimin olarak yorumlandı.

Anahtar kelimeler: Kolin halidleri, titreşim spektroskopisi; kimyasal kayma; B3LYP, Gaussian, PQS

1. Introduction

Choline compounds are interest because of both the unusual radiation sensitivity and the frequent occurrence in biological systems. They are components of complex lipids, and can act as transmethylyng agents [1]. Köksal and Bahçeli, have studied the effect of methyl group reorientation and spin diffusion on spin-lattice relaxation in some choline and acetylcholine halides by NMR spectroscopy [2]. Likewise, Akın and Harmon have

investigated the effects of anesthetics on hydration of choline and acetylcholine halides in aqueous solution using NMR spectroscopy [3]. Harmon and et al. have studied the high-temperature phases of choline bromide and choline iodide by IR spectroscopy [4]. NMR and IR studies of the lower hydrates of choline and acetylcholine halides have been done by some authors [5-7]. The crystal structure of choline chloride was investigated using X-ray diffraction method [8,9].

In the present study we wish to report the vibrational analysis and optimized molecular geometries and chemical shifts of choline halides having a central importance for the study of the pharmacologically active molecules, by means of density functional theory (B3LYP) method in Gaussian and PQS package programs, respectively.

2. Material and Method

2.1. Computational methods

The optimized structure parameters and vibrational frequencies for choline halides (ChF, ChCl, ChBr) have been calculated by B3LYP methods at 6-311++G(d,p) basis set level in Gaussian [10]. The vibrational modes were assigned on the basis of visual inspection of each of the vibrational modes by Gauss-View molecular visualization program [11]. The calculated vibrations were multiplied with a scale factor of 0.9614 [12]. By using PQS ab initio package program [13], ^1H and ^{13}C NMR chemical shifts of all the compounds have been calculated within GIAO approach applying B3LYP method with 6-31 G(d,p) basis set. Since the NMR spectra of the compounds studied in this work are taken in aqueous solutions we have carried out the calculations in solutions by using the conductor-like screening model (COSMO) [14,15] as implemented in PQS by using water as solvent. These calculations produce absolute shielding values that are converted into chemical shifts by subtraction from the shielding value for TMS (^{13}C and ^1H chemical shifts are 192.6365 ppm and 31.7099 ppm; respectively).

3. Results and Discussion

3.1. Ground State Conformations

After having a few different conformation calculations we have decided the ground state conformations of the choline halides which have minimum energy and do not cause imaginary frequencies. These conformations can be seen in Fig. 1. The sum of electronic and zero-point energies of the ground state conformations of the compounds are -428.66 hartree/par for ChF, -789.04 hartree/par for ChCl and -2902.96 hartree/par for ChBr, respectively.

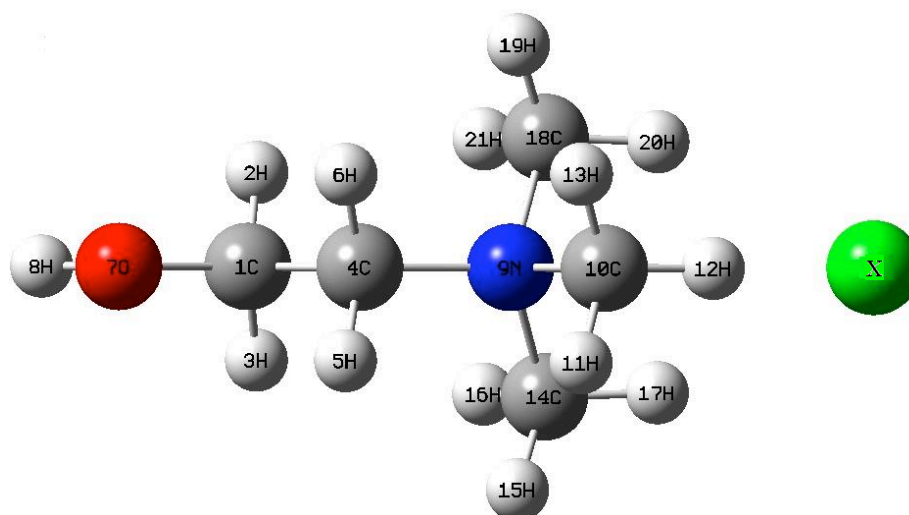


Figure 1. Optimized molecular structures of choline halides (X= F, Cl, Br).

3.2. Vibrational symmetries

As seen from Fig. 1 the choline halides belong to the point group C_s . For an N-atomic molecule the three Cartesian displacements of the N-atoms provide 3N internal modes, namely;

$$\Gamma_{inter.} = 3N.$$

From the following character table for the C_s point group,

C_s	E	σ_h	
A'	1	1	x, y, R_z ; x^2 , y^2 , z^2 , xy
A''	1	-1	z, R_x , R_y ; yz, xz
χ	66	14	

since $\Gamma_{trans.} = 2A' + A''$ and $\Gamma_{rot.} = A' + 2A''$, we obtain

$$\Gamma_{vib.} = \Gamma_{inter.} - \Gamma_{trans.} - \Gamma_{rot.} = \Gamma_{inter.} - 3A' - 3A''$$

normal modes of vibration. All the vibrations are active both infrared (IR) and Raman (R). Since the molecules are in the C_s group, the vibrations being anti-symmetric through the mirror plane σ_h will belong to the species A'' and the ones being symmetric through σ_h to the species A' . So, the numbers of vibration modes for all the choline halides are as follows:

$$\Gamma_{vib.} = 34A' + 26A''.$$

This was corrected by the inspection of each of the vibrational mode on Gauss-View molecular visual program.

3.3. Molecular geometries

The calculated optimized structure parameters of all the title compounds are summarized in Table 1. The experimental data [8,9] for ChCl are also given in the table. Taking into account that the molecular geometry in the vapour phase may be different from the one in the solid phase, owing to extended hydrogen bonding and stacking interactions there is reasonable agreement between the calculated and experimental geometric parameters. The differences are also attributed to that the experimental data taken X-ray crystallographic analysis have been obtained the averaged geometries of the structures of ChCl. The correlation values between experimental and calculated parameters can be seen in the last line of the table.

3.4. Vibrational frequencies

The resulting vibrational frequencies for the optimized geometries of the choline halides are given in Table 2. For comparison the table also show the experimental vibrational frequencies for ChCl [16,17]. From the table we can see that the largest variation between the calculated and experimental frequencies is for the OH stretching vibration. This may partially be attributed to the anharmonicity of the OH group. The proposed vibrational assignments are given in the second column of Table 2. They are made by the inspection of each of the vibrational mode by Gauss-View molecular visualization program. The symmetry species of all the vibrations are written in the first column of the table.

As seen from Table 2 the calculated frequencies in the higher frequency region increase while the electronegativity of the halide decrease in the order $F < Cl < Br$. From the table this can clearly be seen for especially the CH_2 and CH_3 groups. But, for the lattice vibrations in the lower frequency region this situation is vice versa. In Fig. 2 are drawn the deviations of the calculated frequencies of ChCl and ChBr relative to ChF. Mean vibrational deviation is 12.21 for ChCl and 14.75 for ChBr.

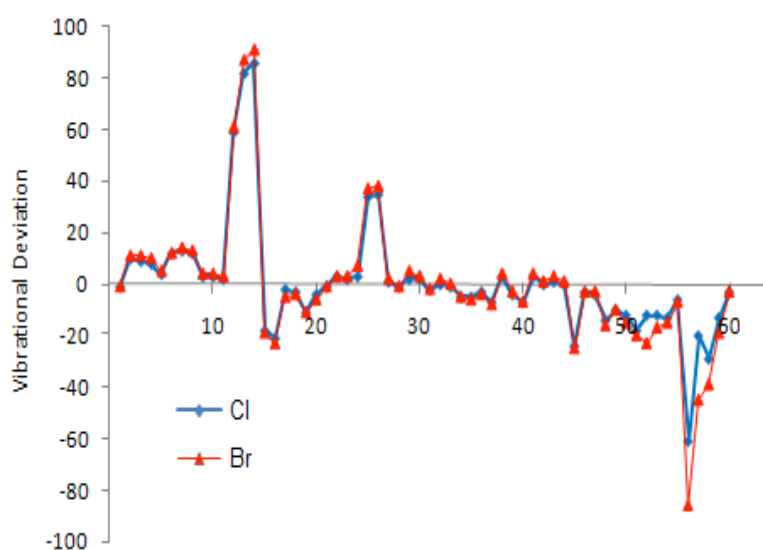


Figure 2. Calculated vibrational deviations of ChCl and ChBr relative to ChF.

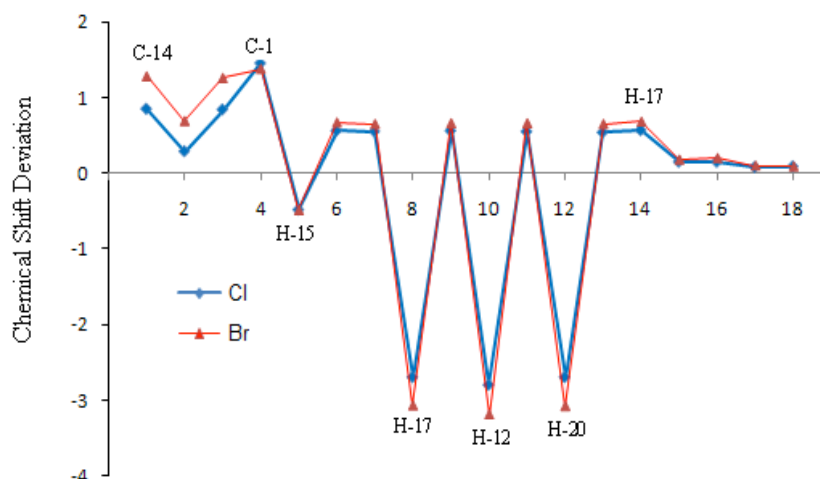


Figure 3. Calculated chemical shift deviations of ChCl and ChBr relative to ChF.

3.5. Chemical shifts

An important factor influencing on chemical shift is electron density expected to be altered by the substitution of a halogen. Table 3 and Table 4 indicate the ^1H and ^{13}C chemical shifts of the choline halides given as group and atomic, respectively. They were calculated within GIAO approach applying B3LYP method with 6-31G(d,p) basis set by using PQS ab initio package program which gives generally better agreement with experimental results for chemical shifts calculations than Gaussian. The experimental chemical shifts for ChCl in the table are taken from the references [18,19]. The chemical shifts given as group in Table 3 are the mean values of the chemical shifts of the single atoms in any group. As seen the experimental and calculated values are very close to each other. The correlation values between experimental and calculated chemical shifts for ChCl can be seen in the last line of the table.

In Fig.3 are drawn the deviations of the atomic chemical shifts of ChCl and ChBr relative to ChF. From Fig. 3 and Table 4 we see the ^1H chemical shifts are in the order $\delta(\text{F}) > \delta(\text{Cl}) > \delta(\text{Br})$ while those of ^{13}C have the opposite order ($\delta(\text{Br}) > \delta(\text{Cl}) > \delta(\text{F})$). As expected the effect of the halogen substitution on the chemical shifts of the nearest H nucleus (H-17, H-12 and H-20) are highest (see Fig. 1). The variation of the chemical shift with the electronegativity of the halogen, whether shielding for C nucleus or deshielding for H nucleus, indicates that the local electron density is affected due to the halogen substitution at the X position. As shown in Fig.3, the ^{13}C chemical shifts are also correlated with the electronegativity of the substituent at the position X. The highly electronegative fluoride substituent leads to a strong electron-density-withdrawing effect on the resonance of ^{13}C . Therefore the ordering of the halogen-substitution effect for C nucleus is $\delta(\text{Br}) > \delta(\text{Cl}) > \delta(\text{F})$ which is vice versa for H nucleus.

Table 1. Calculated optimized structure parameters for choline halides.

			Calculated B3LYP [6-311++G(d,p)]		
Parameters	Exp. ^a	Exp. ^b	ChF	ChCl	ChBr
Bond lengths(Å)					
N(9)-C(18)	1.506	1.52	1.513	1.512	1.511
N(9)-C(10)	1.509	1.50	1.516	1.514	1.513
N(9)-C(14)	1.491	1.53	1.513	1.512	1.511
N(9)-C(4)	1.559	1.60	1.503	1.507	1.508
C(1)-C(4)	1.461	1.56	1.526	1.527	1.527
C(1)-O(7)	1.440	1.39	1.425	1.424	1.423
O(7)-N(9)	3.237		3.730	3.730	3.729
O(7)-C(14)	3.028		4.346	4.333	4.330
C(10)-H(11)	1.120		1.090	1.090	1.090
C(10)-H(12)	1.100		1.103	1.097	1.096
C(10)-H(13)	1.100		1.090	1.090	1.090
C(14)-H(15)	1.000		1.091	1.090	1.090
C(14)-H(16)	1.040		1.089	1.088	1.088
C(14)-H(17)	1.090		1.101	1.098	1.097
C(18)-H(19)	1.050		1.090	1.090	1.090
C(18)-H(20)	1.150		1.105	1.098	1.097
C(18)-H(21)	0.970		1.089	1.088	1.088
C(1)-H(2)	1.040		1.095	1.095	1.095
C(1)-H(3)	1.000		1.095	1.095	1.095
C(4)-H(5)	1.100		1.091	1.091	1.091
C(4)-H(6)	1.090		1.091	1.091	1.091
X(22)-H(12)			1.848	2.390	2.556
X(22)-H(17)			1.839	2.376	2.537
X(22)-H(20)			1.839	2.376	2.536
X(22)-C(14)			2.794	3.367	3.538
			R ² =0.956	R ² =0.957	R ² =0.957
Bond angles (°)					
C(18)-N(9)-C(10)	106.8		107.4	108.0	108.0
C(18)-N(9)-C(14)	109.6		108.3	109.0	109.1
C(4)-N(9)-C(14)	110.9		112.4	111.8	111.7
C(4)-N(9)- C(10)	104.2		108.7	108.1	108.2
C(4)-N(9)- C(18)	115.2		112.4	111.8	111.7
N(9)-C(4)-C(1)	114.6		116.3	116.3	116.3
N(9)-C(10)-H(12)			105.1	107.2	107.4
C(1)-O(7)-H(8)			109.2	109.3	109.3
C(4)-N(9)-C(10)			108.7	108.1	108.2
C(14)-N(9)-C(10)			107.4	108.0	108.0
H(2)-C(1)-H(3)			108.7	108.7	108.7
H(6)-C(4)-H(5)			108.1	108.1	108.1
H(6)-C(4)-N(9)			107.2	107.1	107.2
H(21)-C(18)-N(9)			109.0	109.1	109.1
H(20)-C(18)-N(9)			104.6	106.9	107.1
H(19)-C(18)-H(21)			110.3	110.4	110.5
H(19)-C(18)-H(20)			112.9	111.6	111.4
H(19)-C(18)-N(9)			108.2	108.3	108.2
H(20)-C(18)-H(21)			111.5	110.4	110.3
H(13)-C(10)-H(12)			112.5	111.4	111.2
H(13)-C(10)-N(9)			108.2	108.3	108.4
X(22)-C(10)-N(9)			80.8	85.5	86.6
			R ² =0.652	R ² =0.685	R ² =0.672

^a Taken from Ref [7], ^b Ref [8].

Table 2. Experimental and calculated vibrational frequencies of choline halides. ν shows stretching, δ bending, γ out of plane bending, ρ_r rocking, w wagging and τ torsion modes.

Symmetry	Assignments	Experimental Frequencies (cm ⁻¹)		Calculated Frequencies (cm ⁻¹)		
		ChCl		B3LYP 6-311++G(d,p)		
		IR ^a	R ^b	ChF	ChCl	ChBr
A'	$\nu(\text{OH})$	3367	3229	3701	3700	3700
A'	$\nu(\text{CH}_3)_{\text{asym}}$	3264	3028	3027	3037	3038
A''	$\nu(\text{CH}_3)_{\text{asym}}$	3017	3019	3024	3033	3035
A''	$\nu(\text{CH}_3)_{\text{asym}}$	-	-	3018	3026	3028
A''	$\nu(\text{CH}_2)_{\text{asym}}$	-	-	3002	3006	3007
A'	$\nu(\text{CH}_3)_{\text{asym}}$	-	-	2982	2994	2994
A''	$\nu(\text{CH}_3)_{\text{asym}}$	-	2969	2972	2985	2986
A'	$\nu(\text{CH}_3)_{\text{asym}}$	2956	2956	2972	2984	2985
A'	$\nu(\text{CH}_2)_{\text{sym}}$	-	2927	2952	2955	2956
A''	$\nu(\text{CH}_2)_{\text{asym}}$	2905	-	2933	2936	2937
A'	$\nu(\text{CH}_2)_{\text{sym}}$	-	2891	2897	2899	2900
A'	$\nu(\text{CH}_3)_{\text{sym}}$	2848	2860	2810	2869	2871
A'	$\nu(\text{CH}_3)_{\text{sym}}$	2744	2833	2761	2843	2848
A''	$\nu(\text{CH}_3)_{\text{sym}}$	2539	2815	2752	2838	2843
A'	$\delta(\text{CH}_2) + \delta(\text{CH}_3)$	1642	-	1493	1475	1474
A'	$\delta(\text{CH}_2) + \delta(\text{CH}_3)$	-	-	1493	1472	1470
A''	$\gamma(\text{CH}_3)$	-	-	1472	1470	1467
A'	$\gamma(\text{CH}_3) + \delta(\text{CH}_2)$	-	1491	1462	1459	1458
A'	$\delta(\text{CH}_3) + \delta(\text{CH}_2)$	-	-	1459	1448	1448
A''	$\gamma(\text{CH}_3)$	1476	-	1448	1444	1442
A'	$\delta(\text{CH}_2) + \delta(\text{CH}_3)$	-	1470	1433	1432	1432
A''	$\gamma(\text{CH}_3)$	1461	1461	1416	1419	1419
A'	$\delta(\text{CH}_3) + \delta(\text{CH}_2)$	-	-	1415	1417	1418
A'	$\delta(\text{C-CH}_2) + \delta(\text{OH}) + \delta(\text{CH}_3)$	-	1438	1403	1406	1410
A''	$\delta(\text{CH}_3)$	-	1427	1351	1385	1388
A'	$\delta(\text{CH}_3)$	1407	1416	1347	1382	1385
A'	$\delta(\text{C-CH}_2) + \delta(\text{OH})$	-	1383	1332	1333	1334
A''	$\delta(\text{C-CH}_2) + \delta(\text{CH}_3)$	1349	1352	1306	1305	1305
A''	$\delta(\text{C-CH}_2) + \gamma(\text{N-CH}_3)$	1318	1338	1249	1251	1254
A'	$\delta(\text{CH}_3) + \nu(\text{N-CH}_2)$	-	1275	1245	1247	1248
A'	$\nu(\text{N-CH}_3) + \delta(\text{N-CH}_3) + \delta(\text{OH}) + \delta(\text{C-CH}_2)$	1268	1243	1227	1225	1225
A'	$\delta(\text{OH}) + \delta(\text{C-CH}_2) + \delta(\text{N-CH}_3)$	1241	1224	1187	1187	1189
A''	$\delta(\text{N-CH}_3) + \gamma(\text{C-CH}_2)$	-	1206	1183	1182	1183
A''	$\delta(\text{N-CH}_3) + \gamma(\text{C-CH}_2)$	-	1154	1142	1137	1137
A'	$\delta(\text{N-CH}_3) + \delta(\text{OH}) + \delta(\text{C-CH}_2)$	1137	1146	1118	1113	1112
A''	$\delta(\text{N-CH}_3) + \gamma(\text{C-CH}_2)$	1095	1087	1057	1054	1053
A''	$\delta(\text{N-CH}_3)$	-	-	1054	1047	1046
A'	$\nu(\text{C-OH}) + \delta(\text{N-CH}_3)$	-	1057	1022	1025	1026
A'	$\delta(\text{OH}) + \nu(\text{C-CH}_2) + \delta(\text{N-CH}_3)$	1006	1015	1003	999	1000
A'	$\nu(\text{N-CH}_3) + \delta(\text{N-CH}_3) + \delta(\text{OH})$	952	968	940	933	933
A''	$\nu(\text{N-CH}_3) + \delta(\text{N-CH}_3) + \delta(\text{C-CH}_2)$	-	956	895	898	899
A'	$\nu(\text{N-CH}_3) + \delta(\text{N-CH}_3) + \delta(\text{OH})$	871	898	883	883	884
A''	$\gamma(\text{CH}_2)$	-	-	781	782	784
A'	Breathing	621	723	731	731	732
A'	$\delta(\text{N-CH}_3)$	563	535	540	516	515
A'	Torsion	459	469	443	440	440

Table 2. (Continued)

Symmetry	Assignments	Experimental Frequencies (cm ⁻¹) ChCl		Calculated Frequencies (cm ⁻¹) B3LYP 6-311++G(d,p)		
		IR ^a	R ^b	ChF	ChCl	ChBr
A''	δ (N-CH ₃) + γ (N-CH ₂)	451	429	434	430	431
A'	δ (N-CH ₃) + ρ_r (CH ₃) out of plane γ (N-CH ₃) + [ρ_r (CH ₂) + ρ_r (CH ₃)]	-	378	373	359	357
A''	out of plane	-	335	364	354	354
A'	w(CH ₃) + ρ_r (OH) + ρ_r (CH ₂)	-	324	354	342	339
A''	[ρ_r (CH ₃) + ρ_r (CH ₂)] out of plane	-	-	333	315	313
A'	ρ_r (CH ₃) out of plane	-	-	324	312	301
A''	ρ_r (CH ₃) out of plane	-	-	287	275	270
A''	w(OH)	-	-	237	224	222
A'	ρ_r (CH ₃) + ρ_r (OH) + ρ_r (CH ₂)	-	-	226	220	219
A'	ν (X-N)	-	-	221	160	135
A''	w(CH ₃) + w(CH ₂)	-	-	162	142	117
A'	ρ_r (Molecule)	-	-	113	84	74
A''	w(CH ₂) + w(OH) + w(CH ₃)	-	-	85	72	66
A''	w(CH ₂)	-	-	39	36	36

R²=0.9920 R²=0.9906 R²=0.9905^a Taken from Ref. [15]; ^b Ref. [16].**Table 3.** Calculated and experimental ¹H and ¹³C NMR chemical shifts of choline halides given as group.

Groups	Calculated chemical shifts (ppm) B3LYP 6-31G(d,p)							
	ChF		ChCl				ChBr	
	$\delta_{\text{calc}}(^{13}\text{C})$	$\delta_{\text{calc}}(^1\text{H})$	$\delta_{\text{exp}}(^{13}\text{C})$	$\delta_{\text{exp}}(^1\text{H})$	$\delta_{\text{calc}}(^{13}\text{C})$	$\delta_{\text{calc}}(^1\text{H})$	$\delta_{\text{calc}}(^{13}\text{C})$	$\delta_{\text{calc}}(^1\text{H})$
Methyl	51.34	3.77	55.20	3.22	52.00	3.23	52.41	3.12
Hydroxymethyl	56.98	4.00	57.00	4.07	56.50	4.09	56.49	4.10
N-Methylene	66.62	2.88	68.60	3.54	68.07	3.02	68.00	3.05
R ²					0.9774	0.7104		

Table 4. Calculated ¹H and ¹³C NMR chemical shifts of choline halides given as atomic.

Atom	Calculated chemical shifts (ppm) B3LYP 6-31G(d,p)		
	ChF	ChCl	ChBr
C-14	49.24	50.09	50.52
C-10	55.42	55.71	56.11
C-18	49.36	50.20	50.62
C-4	66.62	68.07	68.00
C-1	56.98	56.50	56.49
H-15	2.03	2.59	2.70
H-16	2.22	2.77	2.87
H-17	6.99	4.30	3.92
H-11	2.17	2.73	2.83
H-12	7.22	4.43	4.03
H-13	2.16	2.71	2.82
H-20	6.96	4.27	3.88
H-21	2.19	2.73	2.84
H-19	1.97	2.54	2.65
H-5	2.95	3.10	3.13
H-6	2.78	2.93	2.98
H-2	4.08	4.16	4.18
H-3	3.92	4.01	4.01

4. Summary and Conclusion

The optimized structure parameters, vibrational frequencies and chemical shifts of choline halides were theoretically examined using ab initio B3LYP methods at 6-311++G(d,p) and 6-31G(d,p) basis set levels in Gaussian and PQS package programs. The comparison of the experimental and calculated results showed a well agreement with the each other. The electronegativity influence of the halogen substitution on the vibrational frequencies and chemical shifts have also been investigated. It was seen that the calculated frequencies generally increase in the order $F < Cl < Br$ while the chemical shifts decreases in the same trend for H nucleus although the situation is vice versa for C nucleus. These were attributed the variation of the force constants, the molecular weight and the local electron density on the H and C nucleus which is affected due to the halogen substitution at the X position.

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