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Density Functional Theoretical Studies of the Perfluoroalcohols C_4F_9OH and C_6F_5OH

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Halo organic compounds are widely used in industry. The geometries and frequencies of the stationary point with their minimum-energy paths of optimized perfloroalcohols C_4F_9OH and C_6F_5OH were calculated by using DFT (B3LYP) methods with 6-311G basis sets. The model structure and theoretical study on perfluoroalcohols which could be synthesized to provide X-ray structured crystals were also reported. Furthermore, calculated results were reported for molecular C_4F_9OH and C_6F_5OH.

Key words: Halo organic compounds; electronic structure; calculations; vibrational analysis; Raman analysis; natural bond orbitals

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Many halo organic compounds have been used in theoretical studies [1-2]. Much differing data has been found about the structural properties of halo compounds; however, they are not sufficient and are of opposing characteristics in some areas. Two new primitive synthesized halo compounds are C_4F_9OH and C_6F_5OH which are used for structural chemistry studies and organic synthesis [3–4]. Investigating the structures and properties of these compound and their similarities is interesting [5–8].

In this study we report the optimized geometries, assignments and electronic structure calculations for these compounds. The structure of the compounds was optimized by using the DFT (B3LYP) method with the 6-311G basis sets, using the Gaussian 98 programme [9]. The density functional theoretical method was employed to determine the optimized structures of C_4F_9OH and C_6F_5OH. Calculations were first performed at the DFT level and split-valence plus polarization 6-311G basis sets were used. Local minima were obtained by full geometrical optimization at all positive frequencies [10–11].

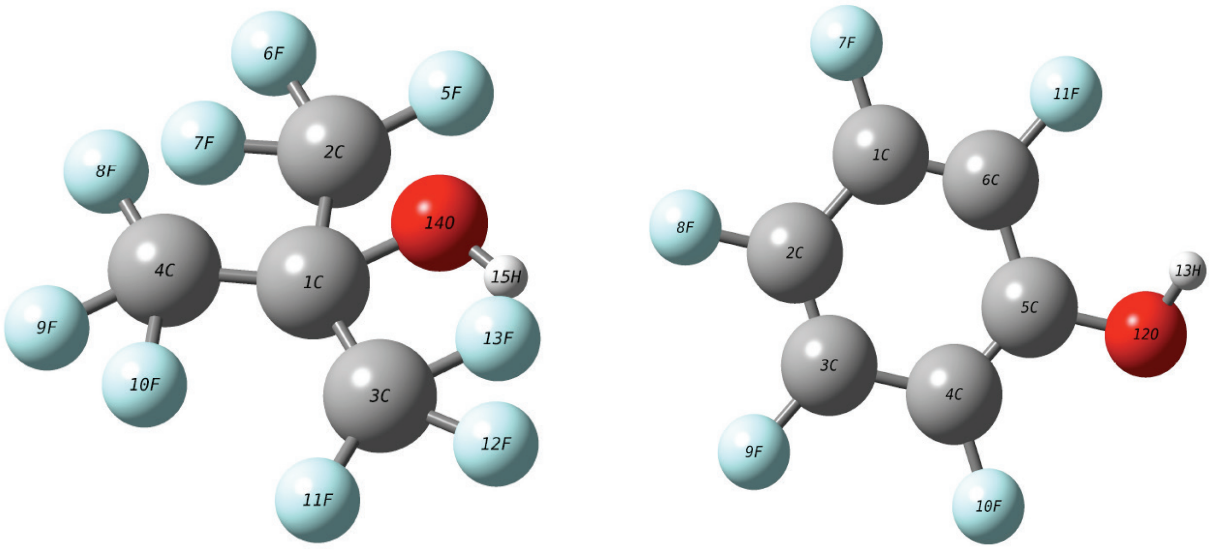
Computational Methods

All computation was carried out using Gaussian 98 programme [9]. The structures of the molecules were optimized without symmetry in all the levels. The optimized structural parameters were used in the vibrational frequency calculations at the DFT levels to characterize all stationary points as minima. Infrared intensities in kilometer per mole of all compounds were applied at the same level on the respective fully optimized geometries.

RESULTS AND DISCUSSION

Molecular Properties

The molecules under study are represented in Figure 1. All calculations were carried out using the computer program Gaussian 98. Theoretical calculation of bond and angle of the compound was determined by optimizing the geometry (Table 1). NBO analysis is in Table 1 and the NBO calculated hybridizations are reported in Table 2. We could not compare the calculation results which are given in bond lengths and bond angle values with the experimental data, because the crystal structure of the title compound was



(1) (2)

Figure 1. Optimized geometries of perfluoroalcohols for (1) C_4F_9OH and (2) C_6F_5OH.

Table 1. Geometrical parameters optimized for (1) C_4F_9OH, (2) C_6F_5OH, some selected bond lengths (Å) and angles (◦).

(1) C_4F_9OH		(2) C_6F_5OH	
Bond	Lengths(Å)	Bond	Lengths (Å)
C_1–C_2	1.53	C_2–C_3	1.3885
C_1–C_3	1.53	C_3–C_4	1.3877
C_1–C_4	1.37	C_2–F_8	1.3634
C_1–O_{14}	1.97	C_1–C_2	1.3879
O_{14}–H_{15}	1.34	C_1–F_7	1.3617
Bond	Angles (◦)	Bond	Angles (◦)
C_2–C_1–F_5	121.706	C_2–C_1–F_7	120.3213
C_2–C_1–F_6	113.957	C_2–C_3–F_9	119.6189
C_2–C_1–F_7	134.327	C_2–C_3–F_8	120.1180
C_3–C_1–F_{11}	108.631	C_3–C_4–F_{10}	119.9732
C_3–C_1–F_{12}	142.734	C_4–C_2–C_3	120.7307
C_3–C_1–F_{13}	127.207	C_4–C_5–O_{12}	119.9215
C_4–C_1–F_8	103.948	C_5–C_6–F_{11}	116.8364
C_4–C_1–F_9	102.074	C_1–C_6–F_{11}	121.2723
C_4–C_1–F_{10}	101.153	H_{13}–O_{12}–C_5	107.9006

not available earlier. B3LYP/6-311G calculation results showed that the (C1-C2) and (C2-F5) bond lengths could be values for the C_4F_9OH.

NBO Study of Structures

Natural bond orbitals (NBOs) are localized few-centred orbitals that describe the Lewis-like molecular bonding pattern of electron pairs in optimal compact form. More precisely, NBOs are orthonormal sets of localized 'maximum occupancy' orbitals whose leading *N*/2 members (or *N* members in the open-shell case) give the most accurate possible Lewis-like description of the total *N*-electron density.

The analysis was carried out by looking at all possible interactions between 'filled' (donor) Lewis-type NBOs and 'empty' (acceptor) non-Lewis NBOs, and estimating the energetic importance of the 2nd-order perturbation theory. Since these interactions lead to the donation of occupancy from the localized NBOs of the idealized Lewis structure into the empty non-Lewis orbitals (and thus, to departures from the idealized Lewis structure description), they are referred to as 'delocalization' corrections to the zero-order natural Lewis structure.

Natural charges were computed using the natural bond orbital (NBO) module and were carried out in Gaussian 98. The NBO calculated hybridizations were significant parameters for our investigation. These quantities were derived from the NBO population analysis. The former provided an orbital picture that was closer to the classical Lewis structure. The NBO analysis involving hybridizations of selected bonds were calculated using B3LYP methods and 6-311G level A theory (Table 2). The data showed the hyper conjugation of electrons between ligand atoms with the central metal atom and the conjugations stand on the base of p-d π-bonding.

The NBO calculated hybridization for C_4F_9OH and C_6F_5OH showed that all the complexes had SP^X hybridization and non-planar configurations. Total hybridizing of these molecules was SP^X as confirmed by structural analysis. The amount of bond hybridization showed the inequality between central atom angles (Table 2).

In C_4F_9OH, the lone pair was found on chlorine atoms and was significantly delocalized in the hybrid orbitals C-F bonds. Indeed, the interaction energy from the charge transfers of complex confirms the above point and the maximum interaction energy was predicted in the average for C_4F_9OH. Second order perturbation theory, analysis of Fock matrix in NBO basis for (1) C_4F_9OH (2) C_6F_5OH $E^{(2)a}$ meant the energy of hyper conjugative interaction (stabilization energy); ^{b} energy difference between donor and acceptor, *i* and *j* NBO orbitals; $^c F(i, j)$ has the Fock matrix part between *i* and *j* NBO orbitals (Table 3).

Frontier Molecular Orbital

Both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the main orbitals which take part in chemical stability. The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. The HOMO and LUMO energy were calculated by the B3LYP/6-311G method [12]. This electronic

Table 2. The NBO calculated hybridizations for (1) C_4F_9OH and (2) C_6F_5OH.

(1) C4F9OH			(2) C6F5OH		
Bond	ATOM	B3LYP	Bond	ATOM	B3LYP
C–C	C_1–C_2	$S^1P^{2.08}$	C–C	C_3–C_2	$S^1P^{1.91}$
C–F	C_2–F_5	$S^1P^{2.86}$	C–F	C_3–F_9	$S^1P^{3.57}$
C–F	C_4–F_{10}	$S^1P^{99.99}$	C–F	F_8–C_2	$S^1P^{99.88}$
C–O	C_3–F_{11}	S^1P^1d	C–O	O_{12}–C_5	$S^1P^{99.77}$
O–H	O_{14}–H_{15}	$S^1P^{99.99}$	O–H	H_{13}–O_{12}	$S^1P^{99.33}$

Table 3. Second order perturbation theory analysis of Fock matrix in NBO basis for (1) C_4F_9OH and (2) C_6F_5OH.

Donor (*i*)	Type	ED/^{e}	Acceptor (*j*)	Type	ED/^{e}	$E(2)^a$ (kJ/mol)	$E(j)–E(i)^b$ (a.u.)	$F(i,j)^c$ (a.u.)
(1) C_4F_9 OH								
C_1C_2	σ	1.98887	$C_1–C_2$	σ*	1.78982	0.70	0.91	0.022
$C_1–C_3$	σ	1.99119	$C_1–C_3$	σ*	1.78982	2.05	1.16	0.043
$C_1–C_4$	n	1.92956	$C_1–C_4$	σ*	1.78985	1.53	0.36	0.022
$C_1–O_{14}$	n	1.79180	$C_1–O_{14}$	σ*	1.68883	24.65	0.55	0.104
(2) C_6F_5OH								
$C_3–C_2$	σ	1.97964	$C_1–C_2$	σ*	1.98076	0.63	1.04	0.023
$C_3–F_9$	σ	1.99181	$C_1–F_9$	σ*	1.99092	2.01	1.18	0.045
$F_8–C_2$	n	1.93516	$F_{10}–C_2$	σ*	1.97964	8.82	0.66	0.069
$O_{12}–C_5$	n	1.72110	$O_7–C_4$	σ*	1.98076	2.54	1.04	0.047
$H_{13}–O_{12}$	n	1.54637	$H_8–O_7$	σ*	1.99790	4.47	0.81	0.054

absorption corresponds to the transition from the ground to the first excited state and is mainly described by a single electron excitation from the highest occupied molecular or orbital (LUMO). So, while the energy of the HOMO is directly related on the ionization potential, LUMO energy is directly related on the electron affinity. The energy difference between HOMO and LUMO orbitals is called as energy gap which has an important stability for structures. The 3D plots of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and their energies were also calculated at the 6-311G and the values are listed in Figure 2, respectively.

Charge and Electron Density Distribution

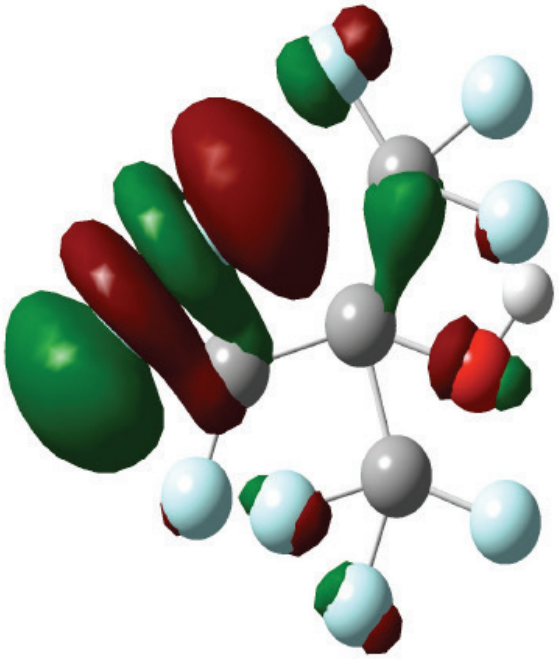
The total electron density distribution is a physical property of molecules. The electron density is usually shown as a comparison of the identified electron density with that predictable by spherical models of the atoms and is called deformation electron density. The total electron density was calculated by DFT/ 6-311G using ESP type with SCF density matrix and the structure, atomic Mulliken charges are displayed in Figure 3 that fixes colour range and references. Thus, Table 4 shows the charge of C_4F_9OH and C_6F_5OH.

IR Spectrum

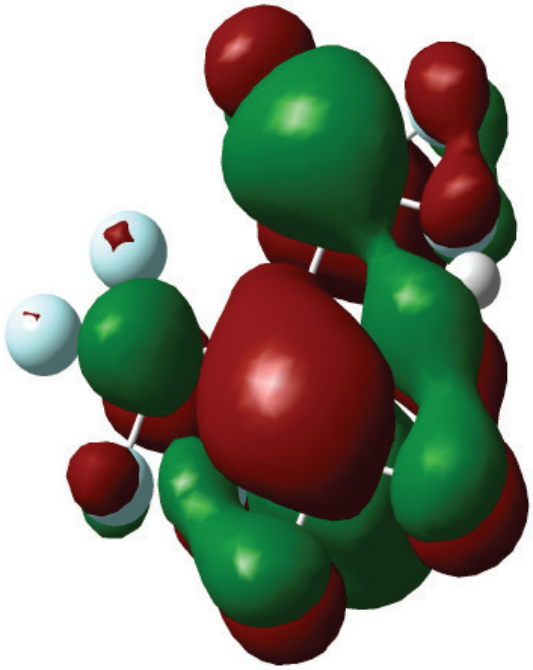
Vibrational spectroscopy is widely used in organic chemistry for identification of functional groups of organic compounds, the study of molecular conformations and reaction kinetics. The IR spectrum and vibration information for the highest peak for (A) C_4F_9OH are Frequency: 4381.04; Infrared: 8820.9568; Raman activity: 490735; while for (B) C_6F_5OH they are Frequency: 868.92; Infrared: 141.4411; Raman activity: 0.3746; as shown in Figures 4 and 5.

Raman Analysis

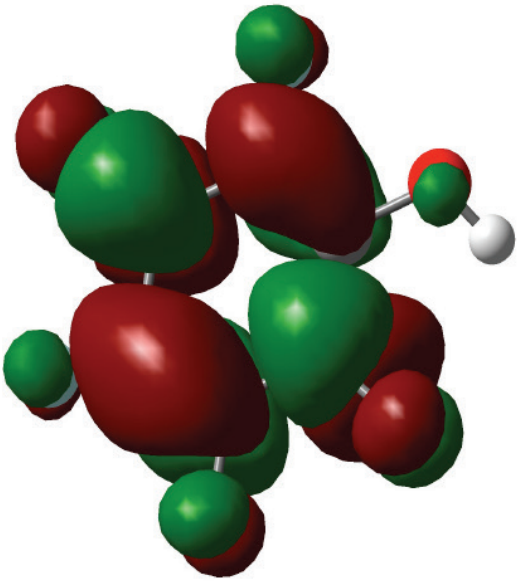
The Raman Effect happens when light impinges on a molecule with interdependence with the electron cloud and the bonds of that molecule. For the extemporary Raman Effect, which is a form of light scattering, a photon motivates the molecule from the ground state to a suitable energy state. When the molecule moderates it emits a photon and it comes to a different rotational or vibrational state. The difference in energy between the original state and this novel state hints to a shift in the emitted photon's frequency away from the excitation wavelength. The Raman Effect, which is a light scattering phenomenon, should not be misled as absorption where the molecule is



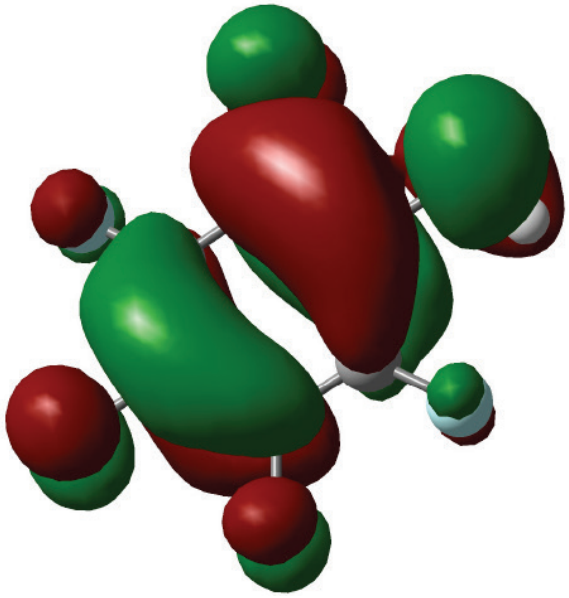
E. LOMO (C4F9OH) = –0.00243 a.u.



E. HOMO (C4F9OH) = –0.19433 a.u.

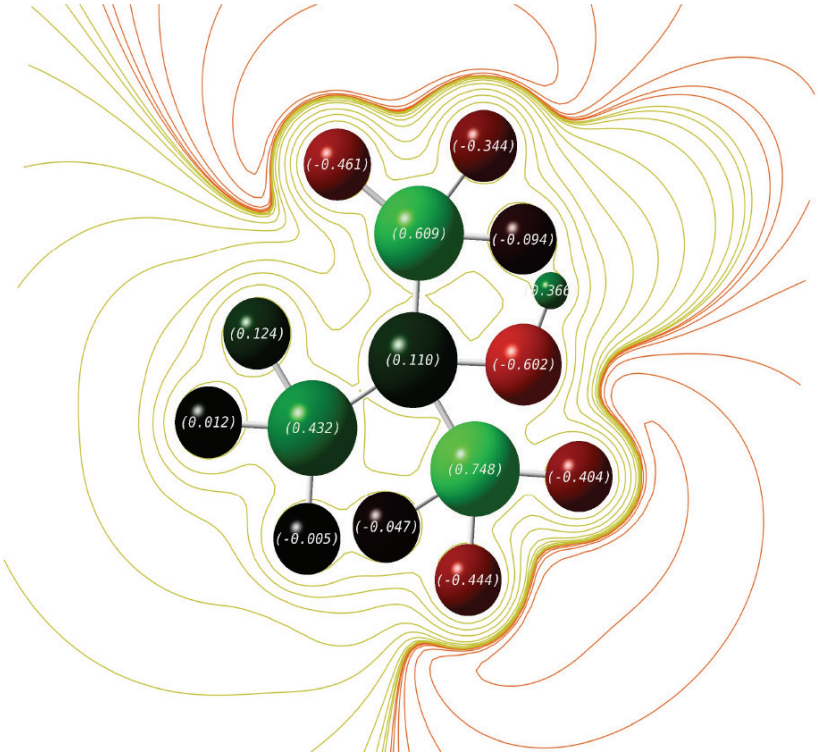


E. LOMO (C6F5OH) = –0.03260 a.u.



E. HOMO (C6F5OH) = -0.25134 a.u

Figure 2. The frontier molecular orbital with energy level for (1) C_4F_9OH and (2) C_6F_5OH.



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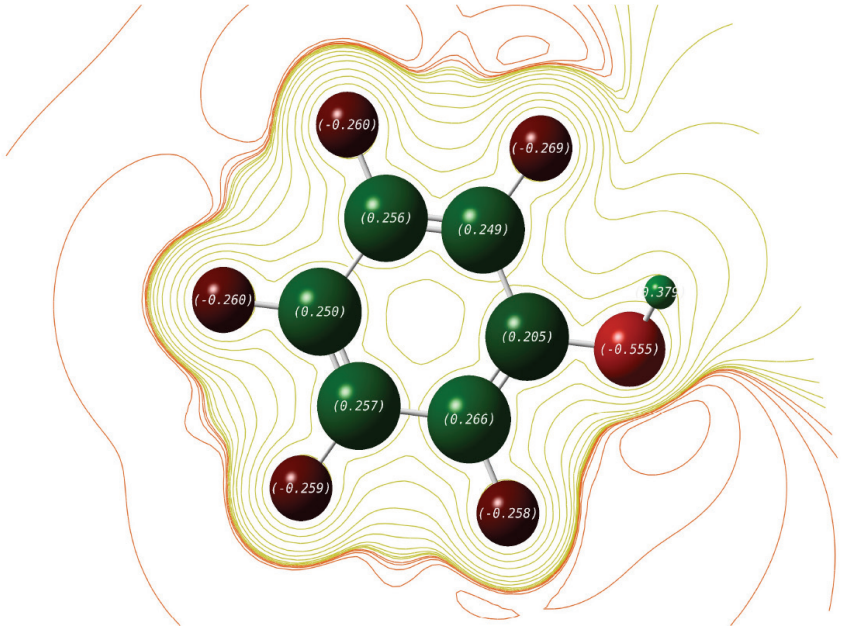

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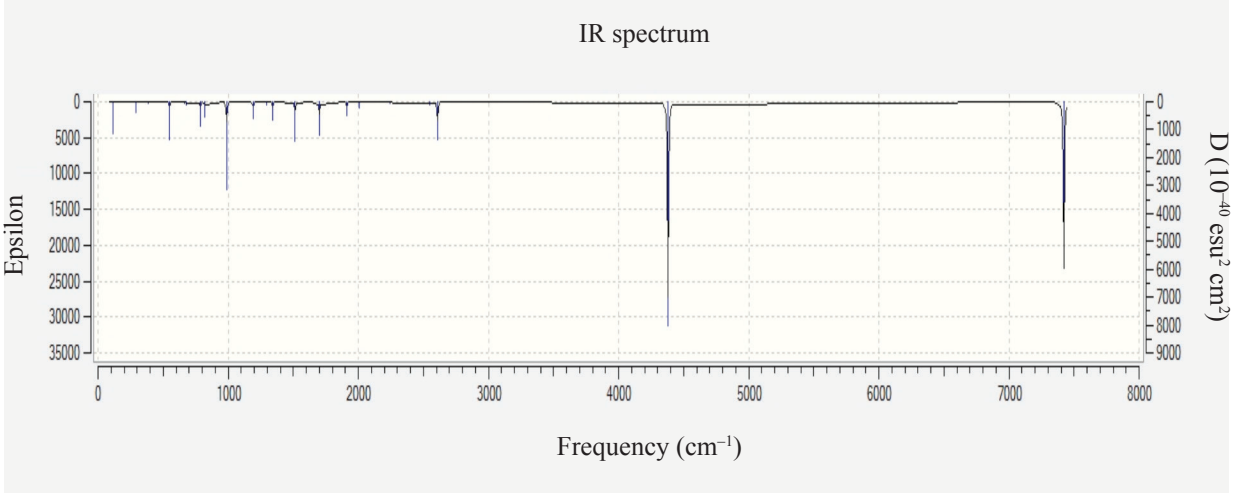
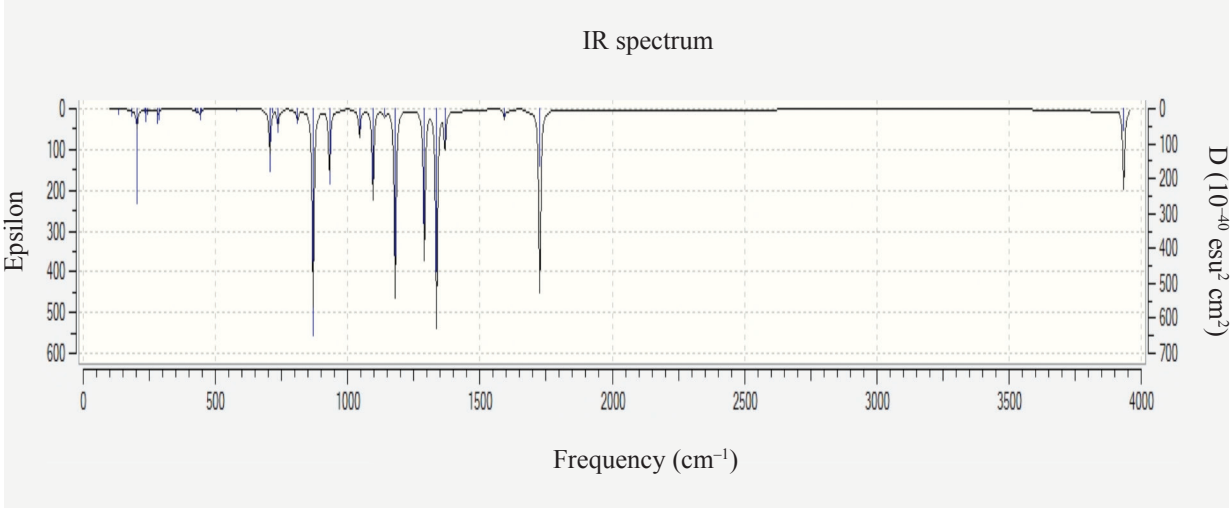
Figure 3. Contour map of electron density and the structure atomic charges with wan der Waals radii for (1) C_4F_9OH and (2) C_6F_5OH.

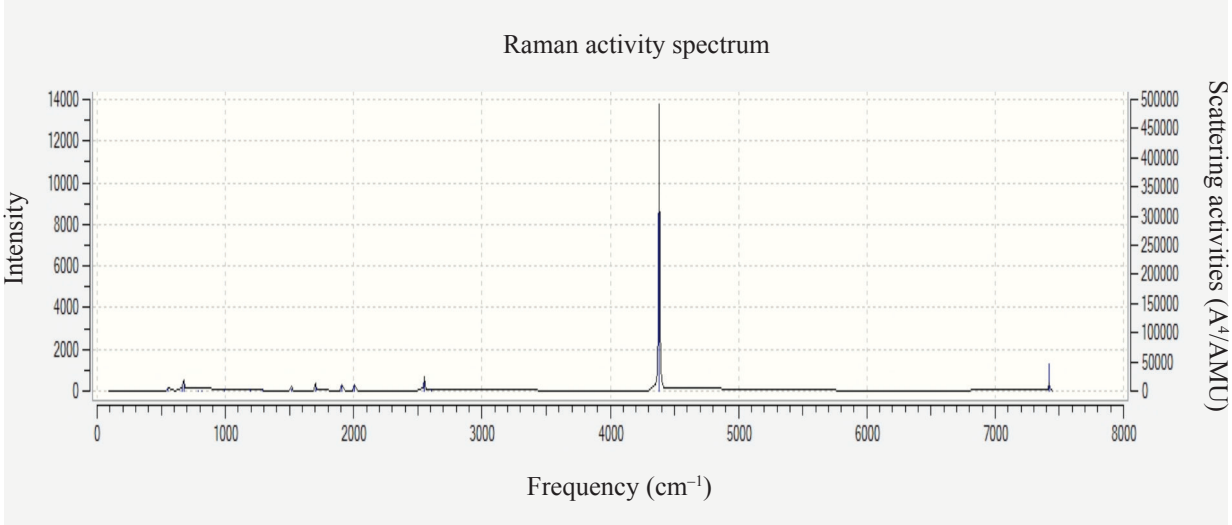


(1)

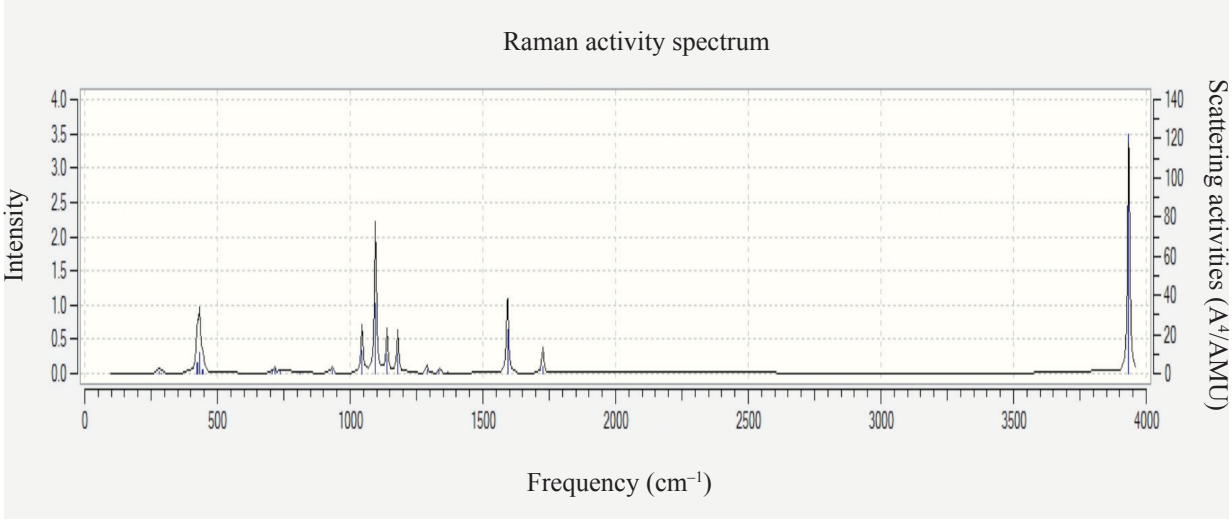


(2)

Figure 4. IR spectrum calculated for (1) C_4F_9OH and (2) C_6F_5OH.



(1)



(2)

Figure 5. Raman spectra calculated for (1) C_4F_9OH and (2) C_6F_5OH.

Table 4. Charge of (1) C_4F_9OH and (2) C_6F_5OH.

(1) C_4F_9OH

Atom	Charge	Atom	Charge
C_1	0.110	F_8	–0.005
C_2	0.748	F_9	0.012
C_3	0.609	F_{10}	0.124
C_4	0.432	F_{11}	–0.461
F_5	–0.404	F_{12}	–0.344
F_6	–0.444	F_{13}	–0.094
F_7	–0.047	O_{14}	–0.604

(2) C_6F_5OH

Atom	Charge	Atom	Charge
C_1	0.256	F_7	−0.260
C_2	0.250	F_8	−0.260
C_3	0.257	F_9	−0.259
C_4	0.266	F_{10}	−0.258
C_5	0.205	O_{12}	−0.604
C_6	0.249	H_{13}	0.379

motivated to a discrete energy level. In this study we have carried out computed chemical shift calculations of molecule and the Raman spectrum of (A) C_4F_9OH and (B) C_6F_5OH as shown in Figure 5. So the comparison among IR and Raman spectra displays of these titled compounds did not show a symmetric structure.

CONCLUSION

In this research, we were interested in studying two compounds usually chosen for theoretical studies. In this study, the optimized geometries and frequencies of the stationary point and the minimum-energy gaps were calculated by using DFT (B3LYP) methods with 6-311G basis sets and the group point of compounds were Cs. The comparison between IR and Raman spectra showed that these compounds did not have a symmetric structure. This work is only a theoretical study of the mentioned compounds which could be given an X-ray structure.

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