

# Vibrational (IR and Raman) and Computational Tool (HF and DFT) Analysis on 2,4-Difluoro Benzyl Alcohol

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**Abstract:** The solid phase FTIR and FT-Raman spectra of 2,4-difluorobenzyl alcohol (DFBA) have been recorded in the regions 4000 - 50 and 3500 - 100 cm<sup>-1</sup>, respectively. A systematic set of symmetry coordinates has been constructed. A reasonable set of potential constants evaluated for this molecule have been compared with those of related molecules and are in the characteristic range. The potential energy distribution (PED) has been evaluated using the vibrational spectral data and molecular parameters. A satisfactory vibrational band assignment has been made by using the FTIR and FT-Raman spectra of the compound.

## 1.1. Introduction

Benzyl alcohol (Schaefer et al, 1978) and its derivatives, which have vast synthetic utility are frequently found in natural products and play a central role in numerous mechanistic investigations. Amino benzyl alcohols are useful as anti-microbiological agents and herbicides. Alcohols are used in topical ophthalmic pharmaceuticals and are useful against cataracts. In spite of these numerous applications and consequent interest in their qualitative and quantitative characterization, the vibrational spectra of these compounds have not been thoroughly investigated in the mid-infrared spectral region. Though there are few studies on benzyl alcohol compounds, up to our knowledge, the structural characteristics and vibrational spectroscopic analysis of 2-4-difluorobenzyl alcohol (DFBA) by the quantum mechanical *ab initio* and DFT methods have not been studied. Hence, in the present study an extensive, experimental and theoretical *ab initio* and DFT studies on 2-4-difluorobenzyl alcohol to obtain a completely reliable and vibrational assignments, thermodynamic properties and structural characteristics of the compound. *Ab initio* (HF) and density functional theory (B3LYP) calculations have been acceptable and supportable with experimental ones, and the theoretical calculations are valuable for predicting the molecular properties and providing insight into the structural and functional properties of the compound.

## 1.2. Experimental Procedures

The compound DFBA in the solid form were purchased from Lancaster chemical company, UK and they were used as such without further purification. The room temperature Fourier transform infrared (FTIR) spectra of the title compound was measured in the region 4000 - 400 cm<sup>-1</sup> at a resolution of  $\pm 1$  cm<sup>-1</sup> using a BRUKER IFS-66V FTIR spectrometer equipped with an MCT detector, KBr beam splitter and globar source.

The FT-Raman spectra of DFBA has been recorded on a BRUKER IFS-66V model interferometer equipped with an FRA-106 FT-Raman accessory in the region 3500 - 100 cm<sup>-1</sup> using the 1064 nm line of a Nd:YAG laser for excitation operating at 200 mW power. The reported wave numbers are believed to be accurate within  $\pm 1$  cm<sup>-1</sup>.

## 1.3. Method of Calculations

The molecular geometry optimization, energy and vibrational frequency calculations were carried out for DFBA with the GAUSSIAN 09W software package (Frisch et al, 2009) using the HF and B3LYP functionals with the standard 6-311++G(d,p) basis set. The Cartesian representation of the theoretical force constants has been computed at optimized geometry by assuming C<sub>s</sub> point group symmetry. Scaling of the force field was performed according to the SQM procedure (Pulay et al, 1983; Rauhut et al, 1995) using selective scaling in the natural internal coordinate representation (Fogarasi et al, 1985; Zhou et al, 1992). Transformations of the force field and the subsequent normal coordinate analysis including the least square refinement of the scaling factors, calculation of the total energy distribution (TED), and the prediction of IR and Raman intensities were done on a PC with MOLVIB program (version V7.0-G77) written by Sundius (Sundius, 1990; 2002). The symmetry of the molecule was also helpful in making vibrational assignments. The symmetries of the vibrational mode were determined by using the standard procedure (Cotton, 1971) of decomposing the traces of the symmetry operation into the irreducible

representations. The symmetry analysis for the vibrational modes of DFBA are presented in some details in order to describe the basis for the assignments.

By combining the results of the GAUSSVIEW program (Frisch et al, 2004) with symmetry considerations, vibrational frequency assignments were made with a high degree of confidence. There is always some ambiguity in defining internal coordinate form complete set and matches quite well with the motions observed using the GAUSSVIEW program.

### 1.3.1 Prediction of Raman intensities

The Raman activities ( $S_i$ ) calculated with the GAUSSIAN 09 Window program and adjusted during the scaling procedure with MOLVIB were subsequently converted to relative Raman intensities ( $I_i$ ) using the following relationship derived from the basic theory of Raman scattering (Polavarapu, 1990; Keresztury, 2002; Holly et al, 1993)

$$I_i = \frac{f(v_0 - v_i)^4 S_i}{v_i \left[ 1 - \exp\left(\frac{hcv_i}{kT}\right) \right]} \quad \dots (6.1)$$

where  $v_0$  is the exciting frequency (in  $\text{cm}^{-1}$  units),  $v_i$  is the vibrational wavenumber for the  $i^{\text{th}}$  normal modes,  $h$ ,  $c$ ,  $k$  are fundamental constants and  $f$  is a suitable chosen common normalization factor for all peak intensities.

## 1.4. Results and Discussion

### 1.4.1. Molecular geometry

The optimized molecular structure of DFBA is shown in Fig.1, respectively. The global minimum energy obtained for DFBA are calculated as -542.43977611 and -545.41007466 Hartrees, by HF and B3LYP functionals with the standard 6-311++G(d,p) basis set, respectively. The calculated optimized geometrical parameters obtained in this study are presented in Table 1 respectively. Definitions of internal coordinates of DFBA are tabulated in Table 2. The local symmetry coordinates are summarized in Table 3 for the title compound.

### 1.4.2. Vibrational Spectra

From the structural point of view, the molecule is assumed to have  $C_1$  point group symmetry and hence, all the calculated frequency transforming to the same symmetry species (A). The molecule DFBA consists of 16 atoms and 42 normal modes of vibrations. All the vibrations are active both in the Raman Scattering and infrared absorption.

The observed and calculated frequencies of DFBA are compared for HF/6-311++G(d,p) and

B3LYP/6-311++G(d,p) are summarized in Table 4. The detailed vibrational assignments of fundamental modes of DFBA along with the calculated IR and Raman intensities, Reduced mass, force constants and normal mode descriptions (characterized by TED) are also reported in Table 4. The FTIR and FT-Raman spectra of DFBA are shown in Figs. 2–3.

### O–H Vibrations

The O–H group gives rise to three vibrations (Stretching, in-plane bending and out-of-plane bending vibrations). The O–H group vibrations are likely to be the most sensitive to the environment. So, they show pronounced shifts in the spectra of the hydrogen bonded species. The hydroxy stretching vibrations are generally (Sajan et al, 2006) observed in the region around  $3500 \text{ cm}^{-1}$ . The O–H in-plane bending vibrations occur in the region  $1150 - 1250 \text{ cm}^{-1}$  and is not much affected due to hydrogen bonding unlike to stretching and out-of-plane bending frequencies (Michalska et al, 1996). The O–H out-of-plane bending mode generally observed in the region below  $300 \text{ cm}^{-1}$  (Sathyanarayana, 2004).

In this study, the bands observed at  $3618 \text{ cm}^{-1}$  in FTIR have been designated to O–H stretching vibrations of DFBA respectively. The bands appeared at  $1318 \text{ cm}^{-1}$  in FTIR and  $1180 \text{ cm}^{-1}$  in FT-Raman have been assigned to O–H in-plane bending vibrations of DFBA. Similarly, the FT-Raman bands appeared at  $152 \text{ cm}^{-1}$  and  $103 \text{ cm}^{-1}$  are assigned to O–H out-of-plane bending vibrations of DFBA respectively.

### C–H Vibrations

The molecular structure of DFBA shows the presence of C–H stretching vibrations in the region  $3100 - 3000 \text{ cm}^{-1}$  and these vibrations are not found to be affected due to the nature and position of the substituent (Peesole et al, 1976; Sharma, 1994).

Accordingly, in the title compound, C–H stretching vibrations are observed at  $3138, 3126, 3086 \text{ cm}^{-1}$  in the FTIR spectrum whereas, in the FT-Raman, it is at  $3100, 2960 \text{ cm}^{-1}$  for DFBA respectively.

The C–H in-plane bending vibrations usually occur in the region  $1400-990 \text{ cm}^{-1}$  and are very useful for characterization purposes (Pagannone et al, 1986). In the present work, the FTIR bands observed at  $1140, 1098, 1046, 1014 \text{ cm}^{-1}$  for DFBA whereas in the Raman, the peaks observed at  $1136, 1090, 1018 \text{ cm}^{-1}$  for DFBA respectively.

The C–H out-of-plane bending vibrations are generally occurring in the region  $900-667 \text{ cm}^{-1}$  (Sathyanarayana, 2004). In this current work, the FTIR peaks at  $716, 699, 629, 589 \text{ cm}^{-1}$  and  $620, 502 \text{ cm}^{-1}$  in

FT-Raman confirms the C–H out-of-plane bending vibrations for DFBA respectively.

### C–C Vibrations

The bands 1430 - 1650  $\text{cm}^{-1}$  were assigned to C–C stretching modes (Sathyanarayana, 2004). Socrates (Socrates, 2001) mentioned that the presence of conjugate substituent such as C = C causes a heavy doublet formation around the region 1625 - 1575  $\text{cm}^{-1}$ . The six ring carbon atoms undergo coupled vibrations called skeletal vibrations and give a maximum of four bands in the region 1660 - 1420  $\text{cm}^{-1}$  (Dani, 1995). As predicted in the earlier references, in this work, the C–C stretching vibrations observed in DFBA the FTIR peaks observed at 1621, 1606, 1505, 1465, 1431  $\text{cm}^{-1}$  and in FT-Raman 1610, 1510, 1470, 1440, 1380  $\text{cm}^{-1}$  are assigned for C–C stretching vibrations. The C–C in-plane and out-of-plane bending modes are summarized in Table 4.

### C–F Vibrations

In the vibrational spectra of related compounds the bands due to C–F stretching vibrations (Gunasekaran et al, 2006) may be found over a wide frequency range 1360 - 1000  $\text{cm}^{-1}$  since the vibration is easily affected by adjacent atoms or groups. In the present investigation, the FTIR bands observed at 1225, 1189  $\text{cm}^{-1}$  for DFBA respectively. The in-plane and out-of-plane bending vibrations of C–F are presented in Table 4 for the title compound.

### C–O Vibrations

The interaction of carbonyl group with other groups present in the system does not produce such a drastic and characteristic changes in the frequency of C–O stretch as did by interaction of N–H stretch. (Jeyavijayan et al, 2010). In the present study, the FTIR bands observed at 1276  $\text{cm}^{-1}$  in DFBA

compound and the FT-Raman band found at 1280  $\text{cm}^{-1}$  in DFBA. The in-plane and out-of-plane bending vibrations of C–O group are also found well within the characteristic region (Arivazhagan, 2010).

## 1.5. Other Molecular Properties

In addition to the vibrational assignments, several thermodynamic parameters are also calculated on the basis of vibrational analysis at HF/6-311++G(d,p) and B3LYP/6-311++G(d,p). The calculated thermodynamic properties are presented in the Table 5. The self-consistent field (SCF) energy, zero point vibrational energies (ZPVE), rotational constants, dipole moment and entropy  $S_{\text{vib}}(T)$  are calculated to the extent of accuracy and the variations in the ZPVEs seem to be insignificant. The total energies and change in total entropy of DFBA at room temperature are only marginal.

## 1.6. Conclusion

In this present study, the SQM force field method based on ab initio and DFT calculations at the HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels have been carried out to analyze the vibrational frequencies of 2,4-difluorobenzyl alcohol. The close agreement established between the experimental and scaled frequencies obtained by B3LYP using the large basis set (6-311++G(d,p)) calculation is proved to be more reliable and accurate than the calculations of semi-empirical methods or lower basis sets. This accuracy is desirable for resolving disputes in vibrational assignments and provides valuable insight for understanding the observed spectral features. In addition, thermodynamic functions of DFBA are also presented. The results confirm the ability of the methodology applied for interpretation of the vibrational spectra of the title compound

Table 1 : Optimized geometrical parameters of 2,4-difluorobenzyl alcohol obtained by HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) calculations

Parameter	Value (Å)		Bond angle	Value (°)		Dihedral Angle	Value (°)	
	HF	B3LYP		HF	B3LYP		HF	B3LYP
C1–C2	1.3827	1.3935	C2–C1–C6	116.5159	116.8336	C6–C1–C2–C3	0.0806	-0.3247
C1–C6	1.3864	1.3975	C2–C1–C7	120.8453	121.4072	C6–C1–C2–F12	-179.7674	-179.7674
C1–C7	1.5129	1.5036	C6–C1–C7	122.6388	121.7335	C7–C1–C2–C3	-179.8855	-178.5113
C2–C3	1.374	1.386	C1–C2–C3	123.8988	123.3856	C7–C1–C2–F12	0.4623	2.0461
C2–F12	1.3314	1.3533	C1–C2–F12	118.0694	118.9677	C2–C1–C6–C5	-0.2528	0.1756
C3–C4	1.3785	1.3861	C3–C2–F12	118.0309	117.6445	C2–C1–C6–H16	179.6392	-179.646
C3–H13	1.0728	1.0816	C2–C3–C4	116.9843	117.1288	C7–C1–C6–C5	179.7127	178.3558
C4–C5	1.3747	1.386	C2–C3–H13	121.4241	121.2972	C7–C1–C6–H16	-0.3953	-1.4658

C4-F14	1.3231	1.3525	C4-C3-H13	121.5915	121.574	C2-C1-C7-H8	55.8655	-34.5789
C5-C6	1.3864	1.3925	C3-C4-C5	122.3559	122.5702	C2-C1-C7-H9	173.5741	-153.3946
C5-H15	1.0734	1.0821	C3-C4-F14	118.3641	118.3271	C2-C1-C7-O10	-68.1326	86.3074
C6-H16	1.0753	1.0843	C5-C4-F14	119.2799	119.1025	C6-C1-C7-H8	-124.0986	147.3238
C7-H8	1.0865	1.0946	C4-C5-C6	118.2751	118.0891	C6-C1-C7 - H9	-6.3899	28.508
C7-H9	1.0811	1.0968	C4-C5-H15	119.9903	120.0107	C6-C1-C7-O10	111.9033	-91.79
C7-O10	1.4007	1.4342	C6-C5-H15	121.7343	121.9002	C1-C2-C3-C4	0.1242	0.3132
O10 - H11	0.9411	0.9628	C1-C6-C5	121.9692	121.992	C1-C2-C3-H13	-179.9263	-179.7538
			C1-C6-H16	119.0313	118.6858	F12-C2-C3-C4	179.7765	179.7628
			C5-C6-H16	118.9993	119.322	F12-C2-C3-H13	-0.274	-0.3043
			C1-C7-H8	109.7894	109.9832	C2-C3-C4-C5	-0.1699	-0.1514
			C1-C7-H9	109.045	109.1993	C2-C3-C4-F14	179.9199	-179.9992
			C1-C7-O10	113.4535	108.4392	H13-C3-C4-F14	179.9199	-179.9992
			H8-C7-H9	107.6434	108.3848	H13-C3-C4-F14	-0.0296	0.0681
			H8-C7-O10	110.3604	110.4609	C3-C4-C5-C6	0.0086	0.0172
			H9-C7-O10	106.3289	110.3627	C3-C4-C5-H15	-179.8158	-179.9623
			C7-O10-H11	109.9729	108.4825	F14-C4-C5-C6	179.918	179.8638
						F14-C4-C5-H15	0.0936	-0.1156
						C4-C5-C6-C1	0.2126	-0.0304
						C4-C5-C6-H16	-179.6794	179.7901
						H15-C5-C6 - C1	-179.9662	179.9487
						H15-C5-C6-H16	0.1417	-0.2308
						C1-C7-O10-H11	70.0014	-169.6829
						H8-C7-O10-H11	-53.6855	-49.0926
						H9-C7-O10-H11	-170.1473	70.7457

For numbering of atoms refer Fig.1.

**Table 2**  
Definition of Internal Coordinates of 2,4-difluorobenzyl alcohol

No(i)	Symbol	Type	Definition <sup>a</sup>
<b>Stretching</b>			
1-5	ri	C - H	C3 - H13, C5 - H15, C6 - H16, C7 - H8, C7 - H9, C7 - O10
7	Qi	C - O	C7 - O10
8 - 9	Ti	C - F	C2 - F12, C4 - F14
10 - 16	Ri	C - C	C1 - C2, C2 - C3, C3 - C4, C4 - C5, C5 - C6, C6 - C1, C1 - C7
<b>In-plane bending</b>			
17 - 22	$\beta_i$	Ring	C1 - C2 - C3, C2 - C3 - C4, C3 - C4 - C5, C4 - C5 - C6, C5 - C6 - C1, C6 - C1 - C2
23 - 30	$\alpha_i$	C - C - H	C2 - C3 - H13, C4 - C3 - H13, C4 - C5 - H15, C6 - C5 - H15, C5 - C6 - H16, C1 - C6 - H16
31 - 32	$\delta_i$	C - C - C	C2 - C1 - C7, C6 - C1 - C7
33	$\xi_i$	C - O - H	C7 - O10 - H11
34 - 35	$\sigma_i$	H - C - O	H8 - C7 - O10, H9 - C7 - O10
36	$\gamma_i$	H - C - H	H8 - C7 - H9

37 – 40	$\theta_i$	C – C – F	C1 – C2 – F12, C3 – C2 – F12, C3 – C4 – F14, C5 – C4 – F14
<b>Out-of-plane bending</b>			
41 – 45	$\omega_i$	C – H	H13 – C3 – C2 – C4, H15 – C5 – C4 – C6, H16 – C6 – C5 – C1, H9 – C7 – C1 – (C6, C2), H8 – C7 – C1, (C6, C2)
46	$\pi_i$	O – C	O10 – C7 – C1 – (C6, C2)
47	$\rho_i$	O – H	H11 – O10 – C7 – C1
48	$\gamma_i$	C – C	C7 – C1 – C2 – C6
49 – 50	$\psi_i$	C – F	F12 – C2 – C1 – C3, F14 – C4 – C3 – C5
<b>Torsion</b>			
51 – 56	$t_i$	t Ring	C1 – C2 – C3 – C4, C2 – C3 – C4 – C5, C3 – C4 – C5 – C6, C4 – C5 – C6 – C1, C5 – C6 – C1 – C2, C6 – C1 – C2 – C3

<sup>a</sup> For numbering of atoms refer Fig. 1

**Table 3**  
**Definition of Local Symmetry coordinates of 2,4-difluorobenzyl alcohol**

No(i)	Symbol <sup>a</sup>	Definition <sup>b</sup>
1 – 5	CH	$r_1, r_2, r_3, r_4, r_5$
6	CO	$Q_6$
7	OH	$S_7$
8 – 9	CCl	$T_8, T_9$
10 – 16	CC	$R_{10}, R_{11}, R_{12}, R_{13}, R_{14}, R_{15}, R_{16}$
17	R trigd	$(\beta_{17} - \beta_{18} + \beta_{19} - \beta_{20} + \beta_{20} + \beta_{21} - \beta_{22}) / \sqrt{6}$
18	R symd	$(-\beta_{17} - \beta_{18} + 2\beta_{19} - \beta_{20} - \beta_{21} + 2\beta_{22}) / \sqrt{12}$
19	R asymd	$(\beta_{17} - \beta_{18} + \beta_{20} - \beta_{21}) / 2$
20 – 23	bCH	$(\alpha_{23} - \alpha_{24}) / \sqrt{2}, (\alpha_{25} - \alpha_{26}) / \sqrt{2}, (\alpha_{27} - \alpha_{28}) / \sqrt{2},$ $(\alpha_{29} - \alpha_{30}) / \sqrt{2}$
24	bCC	$(\delta_{31} - \delta_{32}) / \sqrt{2}$
25	bOH	$\xi_{33}$
26	bCO	$(\sigma_{34} - \sigma_{35}) / \sqrt{2}$
27	bCH	$\gamma_{36}$
28 – 29	bCF	$(\theta_{37} - \theta_{38}) / \sqrt{2}, (\theta_{39} - \theta_{40}) / \sqrt{2}$
30 – 34	$\omega$ CH	$\omega_{41}, \omega_{42}, \omega_{43}, \omega_{44}, \omega_{45}$
35	$\omega$ OC	$\pi_{46}$
36	$\omega$ OH	$\rho_{47}$
37	$\omega$ CC	$\gamma_{48}$
38 – 39	$\omega$ CF	$\psi_{49}, \psi_{50}$
40	t R trigd	$(\tau_{51} - \tau_{52} - \tau_{53} - \tau_{54} + \tau_{55} - \tau_{56}) / \sqrt{6}$
41	t R symd	$(\tau_{51} - \tau_{53} + \tau_{54} - \tau_{56}) / \sqrt{2}$
42	t R asymd	$(-\tau_{51} + 2\tau_{52} - \tau_{53} - \tau_{54} + 2\tau_{55} - \tau_{56}) / \sqrt{12}$

<sup>a</sup> These symbols are used for description of normal modes by TED in Table 4

<sup>b</sup> The internal coordinates used here are defined in Table 2

Table 4

The observed FTIR, FT-Raman and calculated (Unscaled and Scaled) frequencies ( $\text{cm}^{-1}$ ), IR intensity ( $\text{Km mol}^{-1}$ ), Raman Activity ( $\text{\AA}^4 \text{amu}^{-1}$ ), Reduced masses (amu) and force constant ( $\text{m dyne \AA}^{-1}$ ) and probable assignments (characterized by TED) of 2,4-difluorobenzyl alcohol using HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) calculations

Species	Observed wave numbers ( $\text{cm}^{-1}$ )		HF/6-311++G(d,p)						B3LYP/6-311++G(d,p)						TED% among types of coordinates
	FTIR	FT Raman	Unscaled	Scaled	Reduced mass	Force Constants	IR intensity	Raman active	Unscaled	Scaled	Reduced mass	Force Constants	IR intensity	Raman active	
A	3618 (s)	-	4176	3702	1.0670	10.9663	65.2925	35.7143	3829	3625	1.0666	9.2161	28.0522	262.7674	vOH (98)
A	3138 (w)	-	3376	3390	1.0955	7.3563	0.2709	97.5723	3217	3345	1.0933	6.6679	0.7274	112.7081	vCH (97)
A	3126 (w)	-	3366	3359	1.0962	7.3203	2.2338	112.8971	3208	3324	1.0941	6.6345	1.1061	133.5885	vCH (95)
A	-	3100 (s)	3337	3125	1.0912	7.1607	6.8446	57.6053	3177	3103	1.0897	6.4823	4.4224	62.8356	vCH (96)
A	3086 (ms)	-	3260	3098	1.0976	6.8751	24.5968	53.2805	3051	3084	1.1026	6.0484	23.5804	73.4879	vCH (94)
A	-	2960 (w)	3182	3003	1.0697	6.3846	50.6297	119.6458	3005	2967	1.0610	5.6455	55.8393	123.1607	vCH (92)
A	1621 (s)	-	1814	1654	7.0645	13.7018	145.8548	16.6518	1657	1625	7.4414	12.0414	116.6359	28.1965	vCC (89)
A	1606 (w)	1610 (ms)	1783	1619	7.7159	14.4543	79.7387	9.6948	1637	1605	7.8669	12.4280	64.0338	7.1219	vCC (88)
A	1505 (s)	1510 (w)	1670	1518	3.2277	5.3064	110.4907	0.7510	1534	1508	3.0599	4.2440	94.5116	2.9007	vCC (86)
A	1465 (ms)	1470 (w)	1631	1498	1.1056	1.7344	3.1574	6.7724	1516	1468	1.1355	1.5396	6.1563	6.8496	vCC (85)
A	-	1440 (w)	1583	1465	3.4610	5.1123	38.8272	1.9491	1458	1445	2.9260	3.6685	34.7300	2.2249	vCC (84)
A	1431 (s)	-	1540	1439	1.3656	1.9097	65.1913	2.8762	1439	1430	1.5860	1.9358	20.2941	5.1245	vCC (82)
A	-	1380 (ms)	1496	1399	1.2036	1.5886	7.3477	3.9973	1351	1381	3.9536	4.2577	0.3785	1.2780	vCC (81)
A	1276 (w)	1280 (w)	1410	1296	3.0175	3.5368	75.5989	13.6042	1295	1276	3.2622	3.2276	57.9818	27.4003	vCO (80)
A	1225 (s)	-	1397	1238	1.8622	2.1439	18.8408	9.5929	1284	1224	1.8080	1.7588	32.8644	3.4831	vCF (78)
A	1189 (w)	-	1329	1198	1.5892	1.6556	12.0503	3.1462	1263	1185	1.2589	1.1846	18.9551	5.5975	vCF (77)
A	-	1180 (w)	1294	1189	2.7164	2.6823	24.2308	5.7646	1223	1176	1.3058	1.1508	30.0439	2.8285	bOH (76)
A	1140 (vw)	1136 (ms)	1261	1153	1.5256	1.4301	163.4105	1.2876	1191	1137	2.0410	1.7068	42.3155	9.3486	bCH (72)
A	1098 (s)	-	1217	1099	2.3330	2.0386	33.3390	2.9010	1157	1097	1.5495	1.2235	42.0174	0.8703	bCH (73)
A	-	1090 (w)	1186	1094	2.1460	1.7807	28.0795	1.4244	1114	1089	1.7967	1.3155	1.3155	3.7788	bCH (70)
A	1046 (s)	-	1171	1059	6.6822	5.4019	81.1204	6.7253	1022	1048	7.2207	4.4504	4.4504	13.1226	bCH (72)



A	1014 (vw)	1018 (ms)	1075	1024	1.4175	0.9669	6.8367	0.0726	1007	1016	1.9891	1.1889	1.1889	2.2295	bCH (71)
A	981 (w)	980 (s)	1061	998	2.4108	1.6007	28.8399	4.9362	966	980	2.5517	1.4040	1.4040	8.0069	R trigd (70)
A	961 (w)	960 (vs)	1032	969	1.8481	1.1611	45.5444	6.1155	954	961	1.3441	0.7212	0.7212	0.1990	R symd (69)
A	861 (ms)	-	968	875	1.5916	0.8804	54.6332	0.0613	864	863	1.5550	0.6855	0.6855	20.0602	R asymd (68)
A	826 (s)	-	927	838	1.5057	0.7627	16.7171	0.3114	832	830	1.6821	0.6868	0.6868	0.3038	bCC (69)
A	813 (ms)	-	855	820	3.2640	1.4079	14.5172	6.1860	783	812	2.9207	1.0556	1.0556	10.9479	bCO (66)
A	764 (w)	-	805	772	6.5922	2.5189	4.2120	18.7961	745	765	5.8887	1.9272	1.9272	12.6658	bCF (65)
A	735 (w)	740 (w)	774	745	4.1141	1.4523	3.8044	0.8110	720	732	4.3257	1.3237	1.3237	0.6691	bCF (68)
A	716 (w)	620 (w)	696	625	3.6951	1.0554	10.5004	1.3402	630	618	3.6782	0.8607	0.8607	0.8265	ωCH (64)
A	699 (ms)	-	611	605	6.0936	1.3436	7.7415	5.1724	562	600	6.4673	1.2051	1.2051	5.2954	ωCH (62)
A	629 (w)	-	580	536	6.8613	1.3626	24.7632	1.8942	533	530	5.3200	0.8918	0.8918	0.8061	ωCH (63)
A	-	502 (vw)	538	515	4.8347	0.8275	9.0999	1.4323	503	501	5.2899	0.7909	0.7909	2.1471	ωCH (62)
A	589 (ms)	-	503	495	3.2885	0.4912	8.3087	0.5480	461	490	3.4133	0.4277	0.4277	0.5913	ωCH (61)
A	-	410 (ms)	427	421	6.7416	0.7260	1.2057	4.7349	403	412	6.2609	0.6006	0.6006	3.5826	t R trigd (60)
A	-	340 (ms)	371	354	1.3110	0.1067	137.8143	1.2497	330	342	11.1961	0.7202	0.7202	0.2249	t R symd (59)
A	-	258 (s)	355	265	5.3684	0.4001	18.5235	0.3924	286	256	2.7482	0.1327	0.1327	0.2794	t R asymd (59)
A	599 (w)	240 (ms)	300	248	3.6213	0.1932	16.7198	1.7310	241	242	6.4295	0.2201	0.2201	1.7733	ωCC (62)
A	-	231 (w)	261	242	6.2705	0.2535	1.2094	1.3647	232	230	1.1833	0.0376	116.6357	1.7520	ωCO (61)
A	529 (w)	218 (ms)	236	225	3.7841	0.1248	3.7599	1.2539	223	217	6.1090	0.1790	0.9567	1.6597	ωCF (62)
A	-	150 (w)	115	175	7.5105	0.0586	1.9520	0.7996	99	158	6.9274	0.0400	0.1831	0.8998	ωCF (60)
A	-	103 (w)	64	116	4.0136	0.0100	3.3436	0.3089	47	108	4.2360	0.0055	0.4574	1.3063	ωOH (58)

**Abbreviations:**  $\gamma$ -stretching; b-bending;  $\omega$ -out-of-plane bending; R-ring; trigd-trigonal deformation; symd-symmetric deformation; asymd-antisymmetric deformation; t-torsion; s-strong; vs-very strong; ms-medium strong; w-weak; vw-very weak.

**Table 5**  
Thermodynamic properties of 2,4-difluorobenzyl alcohol

Parameters	DFBA	
	HF/6-311++G(d,p)	B3LYP/6-311++G(d,p)
Energy	-542.4397	-545.4100 a.u

Zero point vibrational energy	78.70751 (Kcal/Mol)	73.00373 (Kcal/Mol)
Rotational constants	2.82065 GHz	2.59447 GHz
	0.89087 GHz	0.88957 GHz
	0.70727 GHz	0.70047 GHz
Entropy	89.632 Cal/Mol-Kelvin	92.961 Cal/Mol-Kelvin
Specific heat capacity at constant volume	30.259 Cal/Mol-Kelvin	32.712 Cal/Mol-Kelvin
Translational energy	0.889 KCal/Mol-Kelvin	0.889 KCal/Mol-Kelvin
Rotational energy	0.889 Cal/Mol-Kelvin	0.889 Cal/Mol-Kelvin
Vibrational energy	82.012 Cal/Mol-Kelvin	76.945 Cal/Mol-Kelvin
Dipole moment	1.3206 Debye	2.6059 Debye

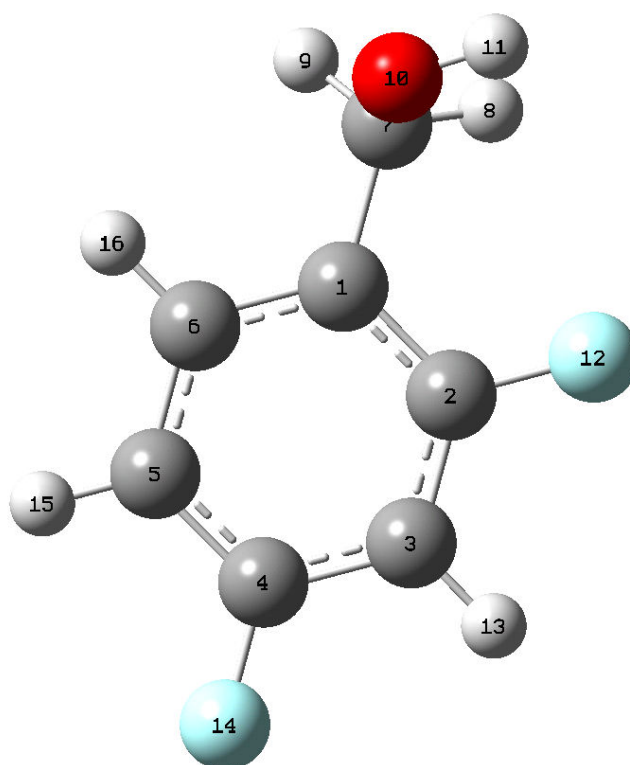


Figure. 1 - Molecular structure of 2-4-difluorobenzyl alcohol



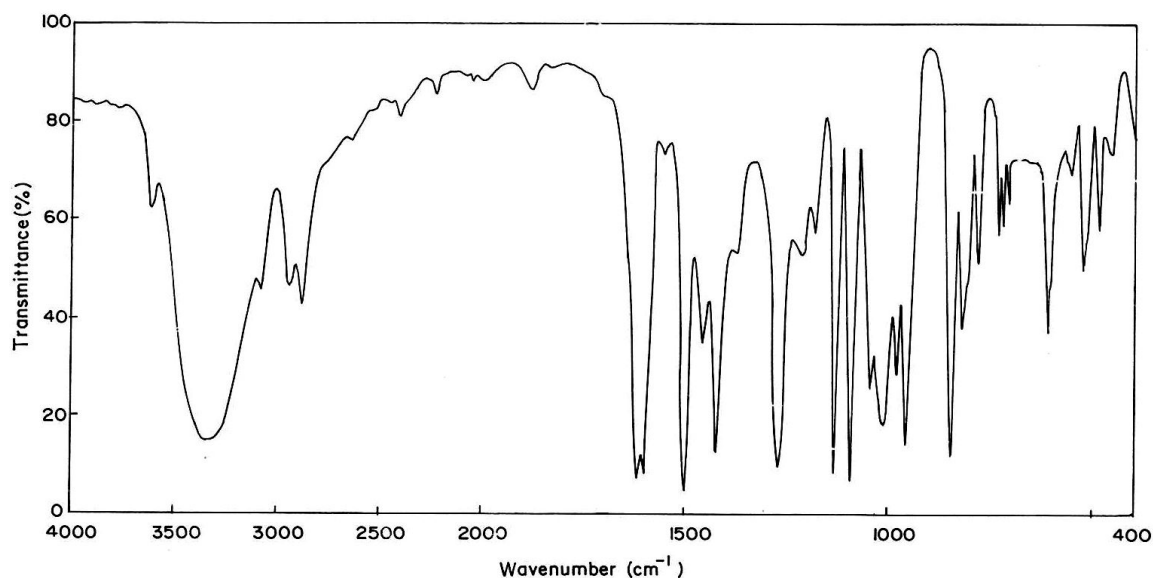


Figure. 2 - FTIR spectrum of 2-4-difluorobenzyl alcohol

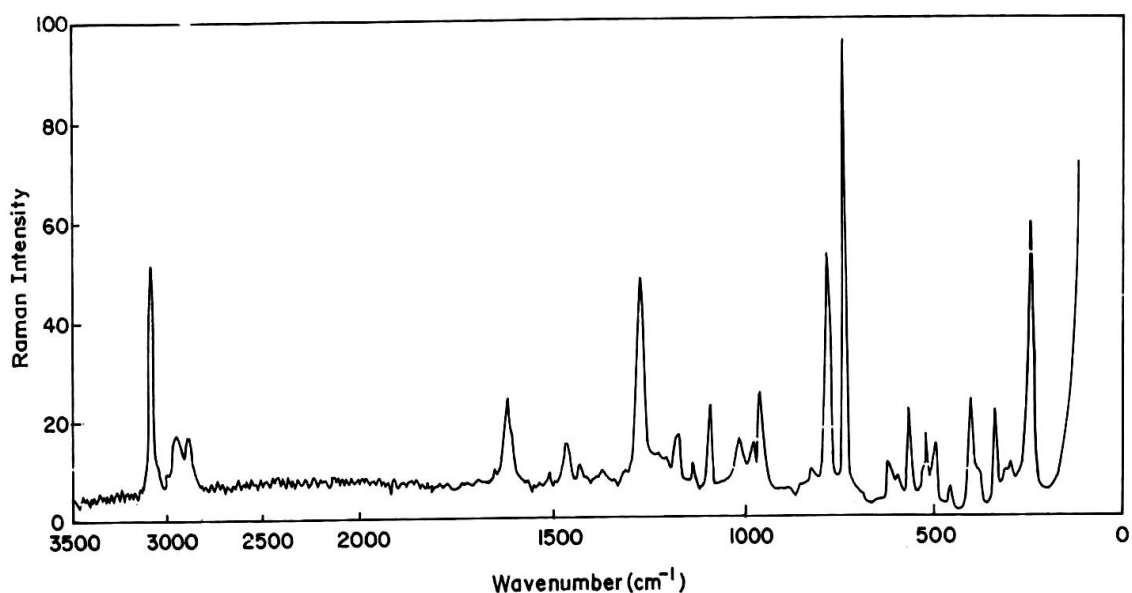


Figure. 3 - FT-Raman spectrum of 2-4-difluorobenzyl alcohol

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