

FTIR and Raman spectra of 2,4-difluorobenzonitrile

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FTIR spectra of 2,4-difluorobenzonitrile were recorded in KBr pellet and Nujol mull in the region $200\text{-}4000\text{ cm}^{-1}$ on a Nicolet DX spectrometer and in liquid and vapour phases on a Jasco FTIR/7000 spectrometer. Raman spectrum was recorded in the region $50\text{-}4000\text{ cm}^{-1}$ on a Jasco K-500 spectrophotometer using the 488.0 nm radiation from an argon ion laser. The observed vibrational frequencies were analysed and assigned to different normal modes of the molecule. Ab initio and density functional calculations were performed to support our frequency assignments. Specific scale factors were deduced and employed in the predicted frequencies. The geometry structure was determined and several thermodynamic parameters were also calculated.

1 Introduction

Vibrational spectra of benzonitrile and mono-substituted benzonitriles have been extensively studied¹⁻³. Recently the vibrational spectra of some disubstituted benzonitriles have been reported⁴⁻⁶. Force field calculations have also been made in a few cases using the classical method developed by Wilson et al⁷ to support the vibrational analysis. Studies of several difluorobenzonitriles in the near-UV region have been reported⁸. Other studies on these molecules also appear in the literature⁹⁻¹². However, to the best of our information, the vibrational analysis of 2,4-difluorobenzonitrile has not been completely and rigorously studied yet. Therefore, the present investigation has been undertaken to study the vibrational spectra of this molecule completely and to identify the various normal modes. Ab initio and density functional calculations were performed to support our frequency assignments. Specific scale factors were also deduced and employed in the predicted frequencies.

2 Experimental

2,4-difluorobenzonitrile (2,4-DFBN) of spectral grade was purchased from manufacturers Aldrich Chemical Co. The FTIR spectra were recorded in the region $200\text{-}4000\text{ cm}^{-1}$ in KBr and Nujol on a Nicolet DX spectrometer and in liquid and vapour phases on a Jasco spectrometer model FTIR/7000. The FTIR spectra in the liquid and vapour phases were recorded by heating the compound in a variable T cell (SPECAC) and heating the windows of the cell to avoid condensation of the gas. The temperature was controlled by two thermocouples.

For recording the Raman spectrum, the sample was sealed in a pyrex glass capillary sample tube of internal diameter about 2 mm, which was mounted in a sample illuminator. The Raman spectrum was recorded in the region 50-4000 cm^{-1} on a Jasco K-500 Raman spectrophotometer with the 488.0 nm radiation of an argon ion laser as the source of excitation. The slit width at the entrance was 380 μm , the time constant was 0.5 s and the scanning speed was 5.

The resolution of the IR spectrometer was of the order of 2 cm^{-1} and that of the Raman spectrometer was of the order of 1 cm^{-1} . The wavenumbers reported here are accurate within $\pm 3 \text{ cm}^{-1}$.

3 Computational Methods

The calculations were carried out by using ab initio calculations¹³, including HF at the 6-31G** level and MP2¹⁴, and by using Density Functional methods (DFT)¹⁵, including the Becke's three-parameter exchange functional (B3)¹⁶ in combination with both the correlational functional of Lee, Yang and Parr (LYP)¹⁷, and with the P86¹⁸, and at the 6-31G** level. These procedures are implemented in the GAUSSIAN 94 program package¹⁹.

The optimum geometry was determined by minimizing the energy with respect to all geometrical parameters without imposing molecular symmetry constraints.

4 Results and Discussion

Geometry Optimization

The optimized bond lengths and angles in 2,4-difluorobenzonitrile using ab initio and DFT methods are given in Table I, while the labelling of the atoms is plotted in Fig. 1. For comparison purposes, the experimental data reported by microwave in the molecule of benzonitrile^{20,21} is included in the last column.

In general the values obtained in bond lengths and angles are very similar and they are in accordance with the microwave data of benzonitrile^{20,21}. The differences are in accordance with the average errors reported^{13,25} for these methods. However, several particular differences are seen. Thus it is noted that the benzene ring appears a little distorted with larger C1-C2 and C1-C6 bond lengths and shorter C2-C3 and C5-C6 (and C3-C4 in HF and MP2 levels), and angles out of the regular hexagonal structure. It is due to the effects of substitution of hydrogen with fluorine and cyanogen on the benzene ring. The broad features of the effect of such substitution can be described as: (i) the ring angle at the C2 and C4 sites increases, (ii) the ring angles at the C3, C5 and C6 positions decrease, in special at C3, and (iii) the C-C bond lengths adjacent to the C-C \equiv bond increase. These distortions are explained in terms of the change in hybridization effected by the substituent at the carbon site to which it is appended. In the case of *ortho*- and *meta*-difluorobenzenes²² and in 2,6-difluorobenzonitrile¹¹, the ring angles obtained have been reasonably explained (in the difluorobenzenes) by the superposition of the ring angular distortions of monofluorobenzene and in the case of 2,6-difluorobenzonitrile by the superposition of *meta*-difluorobenzene and benzonitrile.

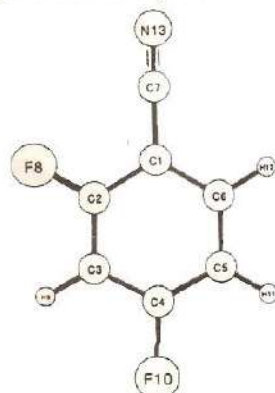


Fig 1. Labeling of the atoms in 2,4-difluorobenzonitrile molecule.

Table 1. Geometrical parameters, bond lengths (in Å) and angles (in degrees) of 2,4-difluorobenzonitrile molecule.

Parameters	ab initio		density functional		Microwave ^a in benzonitrile
	HF/6-31G ^{**}	MP2/6-31G ^{**}	Becke3-P86/6-31G ^{**}	Becke3-LYP/6-31G ^{**}	
Bond lengths					
C1-C2	1.3865	1.3990	1.3998	1.4033	1.3876(20)
C2-C3	1.3767	1.3870	1.3840	1.3870	1.3956(20)
C3-C4	1.3782	1.3896	1.3876	1.3907	1.3974(20)
C4-C5	1.3820	1.3918	1.3903	1.3933	
C5-C6	1.3791	1.3911	1.3860	1.3895	
C1-C6	1.3933	1.4038	1.4028	1.4067	
C1-C7	1.4392	1.4312	1.4250	1.4293	1.4509(20)
C2-F	1.3162	1.3475	1.3311	1.3379	
C4-F	1.3198	1.3504	1.3347	1.3413	
C≡N	1.1358	1.1833	1.1623	1.1630	1.1581(20)
Bond angles					
C-C2-C	122.09	122.04	122.00	122.10	119.00(15)
C-C3-C	117.41	117.47	117.63	117.60	120.06(15)
C-C4-C	122.87	122.69	122.62	122.62	120.05(15)
C-C5-C	118.25	118.60	118.52	118.54	
C2-C1-C6	118.50	118.67	118.37	118.27	121.82
C1-C6-C5	120.88	120.53	120.87	120.88	
C6-C1-C7	120.92	121.34	121.25	121.32	
C2-C1-C7	120.58	119.99	120.38	120.41	
C1-C2-F	119.09	118.86	118.95	118.91	
C3-C2-F	118.82	119.10	119.05	119.00	120.36(50) ^b
C2-C3-H	121.07	121.05	120.95	120.96	120.01(50)
C4-C3-H	121.52	121.48	121.42	121.44	
C3-C4-F	118.33	118.36	118.41	118.42	
C-C≡N	178.76	179.05	178.94	178.99	

^aFrom refs. 20, 21. ^bWith a hydrogen atom instead of a fluorine atom.

Using this superposition principle, the angles obtained in our molecule of 2,4-DFBN

can be explained as follows: starting from the symmetrical structure of benzene, the ring angle increases by nearly 3.4° at the site of fluorine substitution and decreases by 2.1° at adjacent positions, as it is observed in fluorobenzene²³. This is because of shortening of the nearest C–C bonds as a result of highly electronegative fluorine substitution. A similar but to some extent lesser change of 1.8° and 1° takes place due to C≡N substitution, as it is observed in benzonitrile²¹. When two fluorines are substituted at 2,4 positions, the meta-difluorobenzene molecule²⁴, a pronounced reduction in angle takes place at position 3, the angle value going down to 115.74° , and lower at 1,5 positions to the value of 118.5° . When a C≡N bond is added at position 1, the angle on position 2 is very little affected, only is reduced in ca. 0.7° , but this change give rise to an opening of the angle on position 3 by ca. 2° , to the value of ca. 117.5° . Due to the stronger effect of the fluorine atom than the cyanogen group in the opening of the ring angle to which they are bonded, the angle on position 1 is lower than 120° and only ca. 1° higher than in the position 3. Consequently, the angle on position 6, instead of be lower than 120° , as the C≡N substitution produces on the ring, it is a little higher, ca. 120.9° .

Vibrational Frequencies

The present molecule belongs to C_s point group with the normal mode distribution as: $23 a' + 10 a''$. According the selection rules both a' and a'' vibrations are allowed in Raman as well as in IR spectra. a' vibrations are totally symmetric and give rise to polarised Raman lines, whereas a'' vibrations are antisymmetric and give rise to depolarised Raman lines.

The theoretical vibrational bands are shown in Table 2. The second column lists their wavenumbers, their absolute infrared intensities (the sixth column), their Raman activities (the eighth column), the reduced masses and force constant of each vibration (the 11th and 12th columns), and the characterization established at HF/6-31G** level (the last column). The relative intensities (and activities) were obtained by dividing the computed value by the intensity of the strongest line, line no. 5 (and 4 respectively). To improve the computed wavenumbers, in the third column appears the scaled wavenumbers obtained with an uniform scale factor²⁶, $v^{\text{exp}}/v^{\text{calc}}$, of 0.8992. For wavenumbers lower than 800 cm^{-1} we used the scale factor²⁶ of 0.9089. With these predicted scaled wavenumbers the error obtained is in general lower than 5%. However, if specific scale factors are used for each mode (the fifth column), instead of an overall scale factor, a better accuracy is obtained in the predicted wavenumbers (the fourth column). These specific scale factors were determined from benzene molecule.

The predicted infrared spectrum at HF/6-31G** is shown in Fig 2. Only the bands with a relative intensity higher than 1% are plotted. As scaled wavenumbers were considered those listed in the sixth column of Table 4. In Fig. 3 is plotted the experimental infrared spectra in Nujol. The predicted Raman spectrum is shown in Fig. 4, while the corresponding experimental one appears in Fig. 5.

Table 3 shows the calculated wavenumbers at the Becke3-P86/6-31G** level. In the last column of this Table is included, at difference of the Table 2, the % contribution of the different modes to a computed wavenumber. Contributions lower than 10% were not considered.

Table 2. Vibrational wavenumbers (in cm^{-1}) obtained in 2,4-difluorobenzonitrile molecule at HF/6-31G⁺⁺ level

No	Wavenumbers		specific scale factors ^d	IR intensity		Raman activity		Depolarization ratios		Force constant (mDyne/Å)	Characterization ^f
	Calc scaled ^a	scaled ^c		Absolute	Relative	Absolute	Relative	Absolute	Relative		
1	3409	3065	3107	0.9113	1.5	1	101.2	39	0.29	7.50	2, ν (C3-H)
2	3402	3059	3102	0.9117	0.5	0	125.1	48	0.19	7.48	20a, ν (C5-H, C6-H) mainly in C5-H
3	3384	3043	3085	0.9117	0.8	0	44.9	17	0.67	7.36	20b, ν (C6-H, C5-H) mainly in C6-H
4	2612	2349			49.0	23	258.4	100	0.31	51.05	ν (C=N) + ν (C1-C7) ^e
5	1824	1640	1627	0.8919	211.9	100	60.8	24	0.55	13.00	8a, ν (C=C)
6	1787	1607	1594	0.8919	98.1	46	4.9	2	0.65	16.52	8b, ν (C=C)
7	1685	1515	1519	0.9016	130.7	62	6.4	2	0.46	5.56	19a, ν (C=C)
8	1605	1443	1447	0.9016	50.7	24	1.0	0	0.42	8.35	19b, ν (C=C) + ν (C-F8) ^e
9	1451	1305	1327	0.9147	63.2	30	10.8	4	0.11	4.99	7a, ν (C-X) mainly in C5-H, C-F
10	1384	1244	1245	0.8994	2.7	1	11.6	4	0.21	1.80	3, ν (C-H) mainly in C6-H
11	1321	1188	1212	0.9178	67.3	32	0.5	0	0.57	2.92	13, ν (C-X) mainly in C-F
12	1296	1165	1181	0.9116	3.3	2	16.6	6	0.25	3.36	18a, δ (C-H) + ν (C-C \equiv)
13	1251	1125	1213	0.9699	51.8	24	3.5	1	0.68	3.01	14, ν (C=C)
14	1202	1081	1096	0.9116	15.1	7	4.0	2	0.46	1.51	18b, δ (C-H)
15	1094	984	960	0.8775	0.9	0	0.8	0	0.75	0.94	17b, γ (C-H) in C5-H, C6-H

(contd...)

16	1068	960	977	0.9147	29.0	14	6.0	2	0.11	1.99	7b, ν (C-X)
17	959	862	836	0.8715	72.1	34	1.8	1	0.75	0.82	5, γ (C-H) mainly in C3-H
18	931	837	821	0.8821	27.5	13	1.9	1	0.75	0.74	11, γ (C-H) in C5-H, C6-H
19	815	733	747	0.9169	4.3	2	20.9	8	0.13	2.86	1 or 12, δ (CCC) + δ (C \equiv N)
20	794	722 ^b	722	0.9088	6.3	3	1.2	0	0.75	1.53	4, γ (CCC)
21	760	691 ^b	700	0.9216	20.4	10	0.4	0	0.66	2.31	12 or 1, δ (CCC) + δ (C \equiv N)
22	705	641 ^b	619	0.8786	5.3	3	0.0	0	0.75	1.13	16a, γ (CCC)
23	687	624 ^b			1.4	1	0.9	0	0.20	1.93	δ (C \equiv N) + 12 ^c , δ (CCC)
24	585	532 ^b			8.7	4	9.2	4	0.75	1.40	γ (C \equiv N) + 16b ^c , γ (CCC)
25	559	508 ^b	511	0.9145	6.1	3	6.3	2	0.49	1.52	6a or 6b, δ (CCC)
26	497	452 ^b	437	0.8786	0.1	0	2.2	1	0.75	0.49	16b, γ (CCC)
27	489	444 ^b	447	0.9144	0.9	0	3.0	1	0.75	1.43	9b, δ (C-X) mainly in C-F + δ (C \equiv N)
28	438	398 ^b	401	0.9145	2.1	1	3.3	1	0.39	1.20	6b or 6a, δ (CCC) + δ (C \equiv N)
29	351	319 ^b	321	0.9144	5.8	3	0.2	0	0.35	1.05	9a, δ (C-X) mainly in C-F + δ (C \equiv N) ^c
30	300	273 ^b	264	0.8814	0.4	0	0.3	0	0.75	0.43	10a, γ (C-X) mainly in C4-F + γ (C \equiv N) ^c
31	257	234 ^b	227	0.8814	1.3	1	2.5	1	0.75	0.27	10b, γ (C-X) mainly in C2-F
32	156	142 ^b	150	0.9637	5.8	3	3.4	1	0.75	0.17	15, δ (C-F) mainly in C2-F + δ (C \equiv N)
33	112	102 ^b	98	0.8775	5.4	3	0.8	0	0.75	0.08	17a, γ (C-X) mainly in C4-F + γ (C \equiv N)

^aWith the scale factor of 0.8992 from ref 26. ^bWith the scale factor of 0.9089 recommended for the prediction of low-wavenumber vibrations, ref 26. ^cWith the scale factors of the fifth column. ^d $\nu_{\text{exp}}/\nu_{\text{cal}}$ from benzene molecule. ^eLow contribution of this mode. ^fX = substituent.

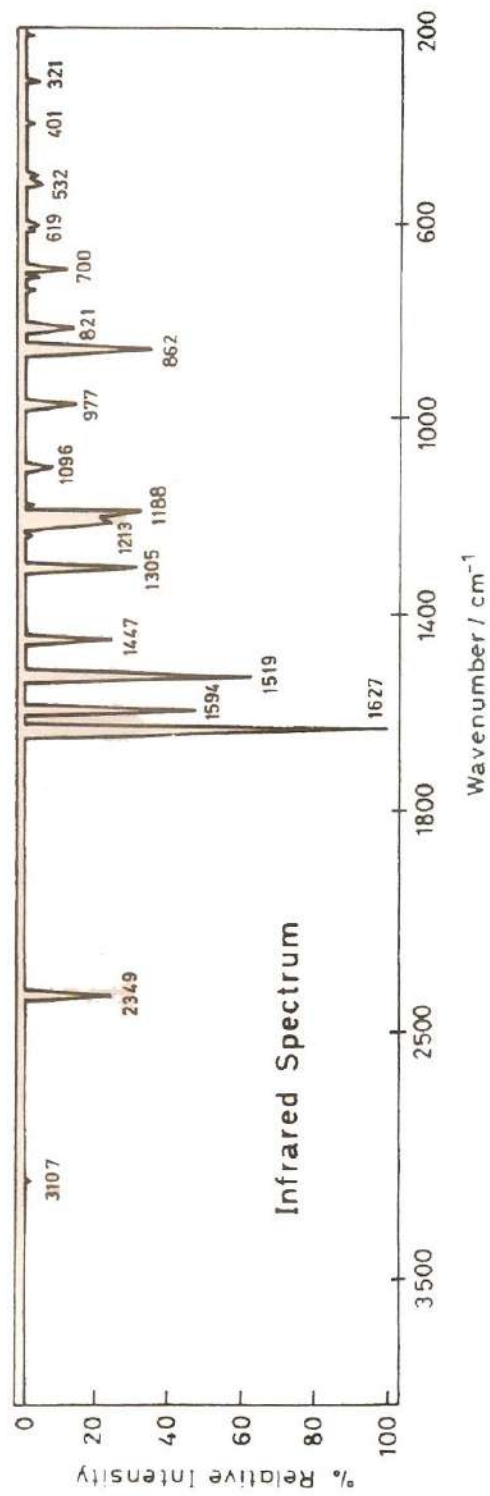


Fig 2. Predicted infrared spectrum of 2,4-difluorobenzonitrile molecule at HF/6-31G** level with scaled wavenumbers.

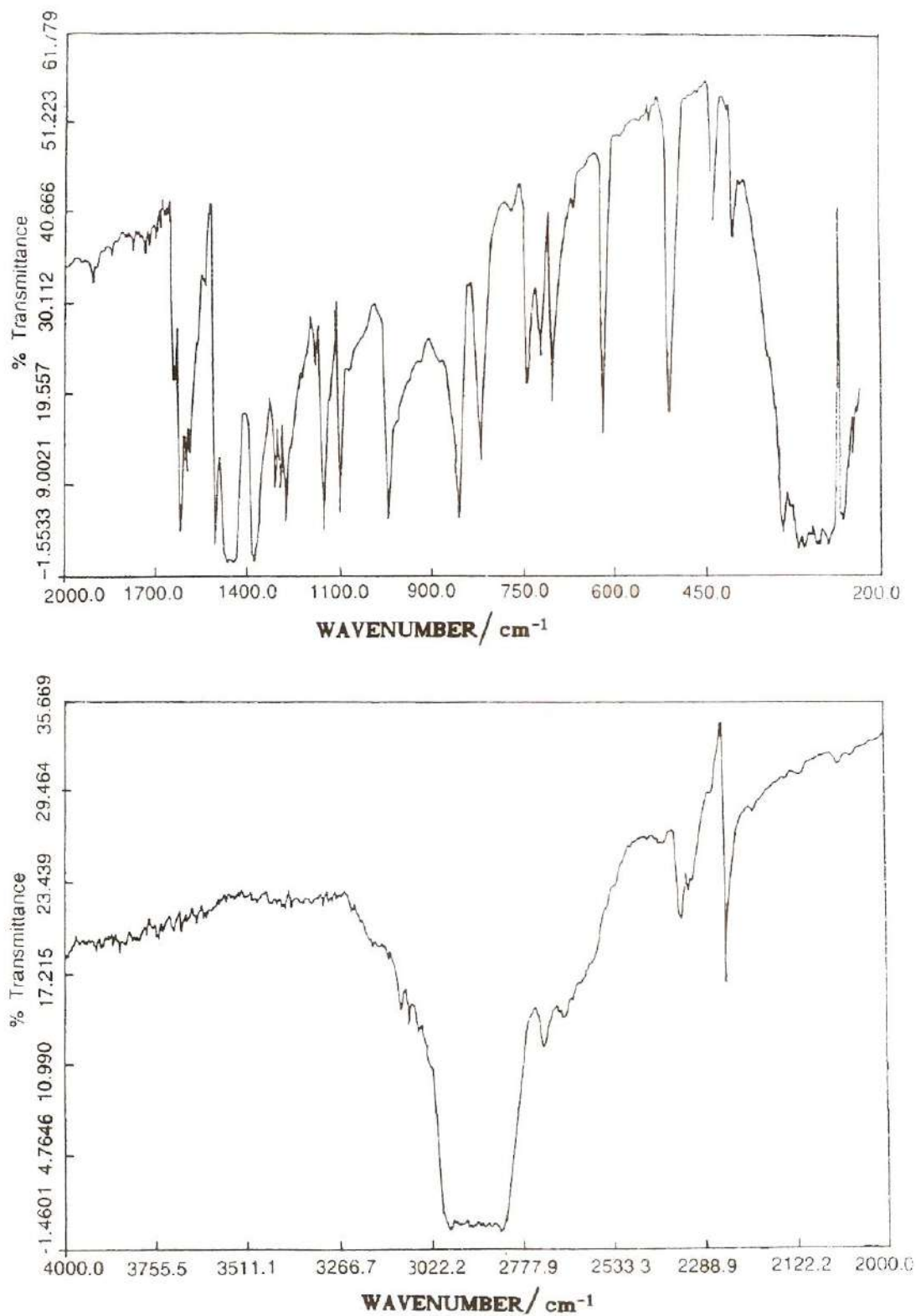


Fig 3. FTIR spectrum of 2,4-difluorobenzonitrile (Nujol).

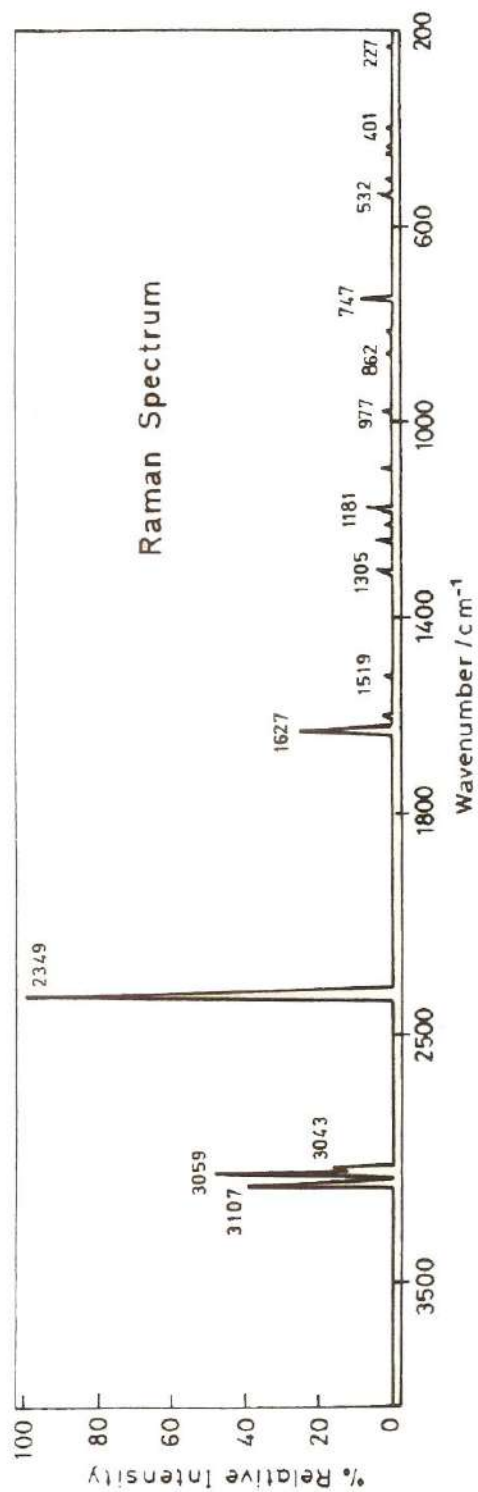


Fig 4. Predicted Raman spectrum of 2,4-difluorobenzonitrile molecule at HF/6-31G** level with scaled wavenumbers.

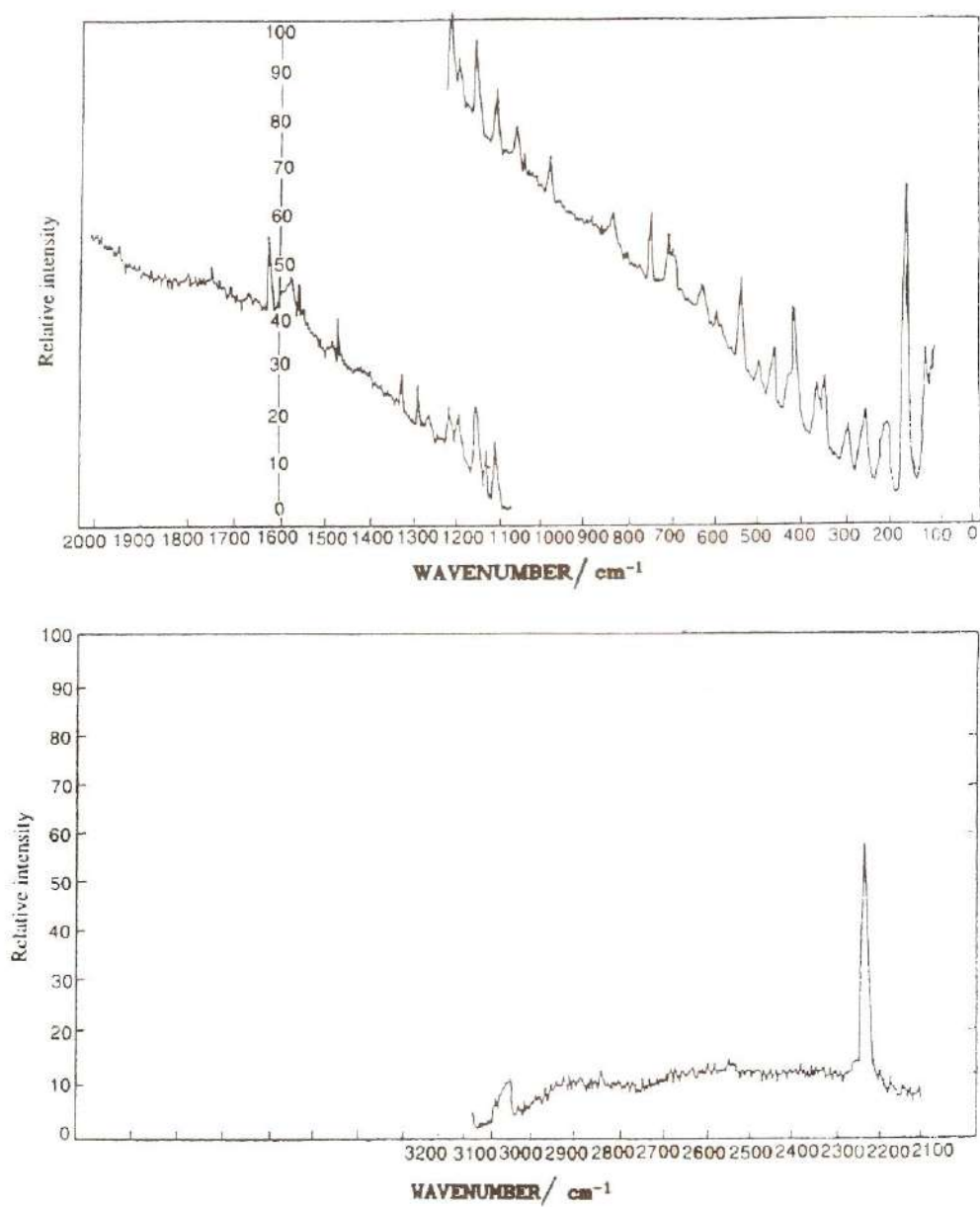


Fig 5. Raman spectrum of 2,4-difluorobenzonitrile molecule in the solid state.

Table 3. Vibrational wavenumbers (in cm^{-1}) obtained in 2,4-difluorobenzonitrile molecule at Becke3-LYP/6-31G** level.

o	Wavenumbers		specific scale factors	IR intensity		reduced masses (amu)	Force constant (mDync/Å)	Characterization
	Calc scaled ^a	scaled ^c		Absolute	Relative			
1	3244	3119	0.9582	1.6	1	1.09	6.78	(100%) 2, v (C3-H)
2	3236	3111	0.9585	0.4	0	1.10	6.76	(100%) 20a, v (C5-H, C6-H) mainly in C5-H
3	3221	3097	0.9585	0.5	0	1.09	6.66	(100%) 20b, v (C6-H, C5-H) mainly in C6-H
4	2356	2265		27.0	17	12.67	41.44	(86%) v (C≡N) + (14%) v (C1-C7)
5	1672	1607	0.9685	154.4	100	7.00	11.53	(95%) 8a, v (C=C)
6	1635	1572	0.9685	60.6	39	8.80	13.87	(97%) 8b, v (C=C)
7	1547	1487	0.9731	99.5	64	3.38	4.76	(94%) 19a, v (C=C)
8	1482	1425	0.9731	40.3	26	5.49	7.10	(98%) 19b, v (C=C)
9	1363	1310	0.9656	13.3	9	8.13	8.90	(95%) 14?, v (C=C)
0	1323	1272	0.9609	64.9	42	5.78	5.96	(96%) 7a, v (C-X) mainly in C-F
1	1281	1232	0.9775	2.8	2	1.60	1.55	(94%) 3, v (C-H) mainly in C6-H
2	1216	1169	0.9730	7.5	5	3.48	3.03	(57%) 18a, δ (C-H)+(27%) v (C-F)+(16%) (C-C≡)
3	1187	1141	0.9638	58.2	38	1.76	1.46	(96%) 13, v (C-X) mainly in C-H, CCC
4	1127	1083	0.9730	29.9	19	1.60	1.20	(94%) 18b, δ (C-H)
5	993	955	0.9609	26.5	17	2.98	1.73	(97%) 7b, v (C-X)

(contd...)

16	962	925	955	0.9929	0.9	1	1.29	0.71	(100%) 17b, γ (C-H) in C5-H, C6-H
17	851	818	832	0.9773	44.3	29	1.39	0.59	(100%) 5, γ (C-H) mainly in C3-H
18	831	799	807	0.9712	17.1	11	1.42	0.58	(98%) 11, γ (C-H) in C5-H, C6-H
19	760	731	740	0.9736	3.6	2	7.01	2.39	(85%) 1 or 12, δ (CCC) + (15%) δ (C \equiv N)
20	713	714 ^b	707	0.9922	14.8	10	6.85	2.05	(65%) 12 or 1, δ (CCC) + (35%) δ (C \equiv N)
21	703	704 ^b	692	0.9846	3.0	2	5.13	1.49	(95%) 4, γ (CCC)
22	632	633 ^b	606	0.9590	3.8	2	4.18	0.98	(97%) 16a, γ (CCC)
23	630	631 ^b			1.4	1	6.97	1.63	(40%) δ (C \equiv N) + (60%) 12?, δ (CCC)
24	525	526 ^b			5.9	4	7.16	1.16	(40%) γ (C \equiv N) + (60%) 16b?, γ (CCC)
25	518	518 ^b	507	0.9792	4.2	3	8.03	1.27	(92%) 6a or 6b, δ (CCC)
26	454	455 ^b	435	0.9590	0.2	0	3.48	0.42	(94%) 16b, γ (CCC)
27	445	446 ^b	436	0.9790	0.7	0	10.89	1.27	(65%) 9b, δ (C-X) mainly in C-F + (35%) δ (C \equiv N)
28	408	409 ^b	400	0.9792	1.8	1	10.25	1.00	(57%) 6b or 6a, δ (CCC) + (43%) δ (C \equiv N)
29	322	322 ^b	315	0.9790	3.8	2	14.48	0.89	(70%) 9a, δ (C-X) mainly in C-F + (30%) δ (C \equiv N)
30	273	273 ^b	267	0.9793	0.5	0	8.14	0.36	(58%) 10a?, γ (C-F) mainly in C4-F + (42%) γ (C \equiv N)
31	232	232 ^b	227	0.9793	0.7	0	7.08	0.22	(98%) 10b, γ (C-X) mainly in C2-F
32	141	141 ^b	137	0.9743	4.4	3	12.13	0.14	(35%) 15, δ (C-F) mainly in C2-F + (65%) δ (C \equiv N)
33	102	102 ^b	101	0.9929	4.2	3	10.54	0.06	(55%) 17a, γ (C-F) mainly in C4-F + (45%) γ (C \equiv N)

^aWith the scale factor of 0.9614 reported at Becke3-LYP/6-31G^{*} level, ref. 26. ^bWith the scale factor of 1.0013 recommended for the prediction of low-wavenumber vibrations at Becke3-LYP/6-31G^{*} level, ref. 26. ^cWith the scale factors of the fifth column.

818 s	822 vs	820 m	818 m	–	821	13	1	807	11	a'	11, γ (C–H)	807 vs
743 m	742 s	743 w	742 w	742 m	747	2	8	740	2	a''	1', δ (CCC)	727
720 m	–	–	–	710 m	722	3	0	692	2	a'	4, γ (CCC)	692
700 s	702 vs	699 m	699 m	–	700	10	0	707	10	a''	12', δ (CCC) + δ (C≡N)	764 s
615 s	615 vs	620 m	620 m	620 w	624 ^c	1	0	631 ^d	1	a'	δ (C≡N) + 12', δ (CCC)	605 s
–	585 w	–	–	–	619	3	0	606	2	–	16a, γ (CCC)	–
–	–	–	–	–	532 ^c	4	4	526 ^d	4	a'	δ (C≡N)	–
510 vs	507 vs	507 s	506 m	515 m	511	3	2	507	3	a'	γ (C≡N) + 16b', γ (CCC)	–
434 w	435 m	439 m	440 w	443 w	447	0	1	436	0	a'	6a', δ (CCC)	560 s
401 w	402 m	406 s	417 m	408 s	437	0	1	435	0	a'	9b, δ (C–X) + δ (C≡N)	445 s
325 vs	328 s	–	–	329 vw	401	1	1	400	1	a''	16b, γ (CCC)	456 s
298 vs	305 w	–	–	–	321	3	0	322 ^c	2	a'	6b', δ (CCC) + δ (C≡N)	501 m
285 vs	288 w	–	–	–	264	0	0	267	0	a'	9a, δ (C–X) + δ (C≡N)	332 s
262 vs	267 w	–	–	269 vw	264	0	0	267	0	a''	δ (C–X)	–
245 vs	245 m	–	–	240 w	227	1	1	227	0	a''	γ (C–X)	283 vw
220 vs	230 s	–	–	–	227	1	1	227	0	a''	10a, γ (C–X) + γ (C≡N)	–
205 s	208 s	–	–	–	–	–	–	–	–	a''	γ (C–C≡)	235
–	–	–	–	–	–	–	–	–	–	a''	10b', γ (C–X)	–
–	–	–	–	–	–	–	–	–	–	a''	γ (CCC)	–

^aFrom the fourth column of Table 2. ^bFrom the fourth column of Table 3. ^cFrom the third column of Table 2. ^dFrom the third column of Table 3. ^eWith no scaling. ^fFrom ref. 28.

Fig. 6 displays the atomic displacements corresponding to the ring normal modes with each computed wavenumber observed at Becke3-LYP/6-31G** level. These displacements are represented as xyz coordinates, in the standard orientation, which have been plotted to identify each vibration. No significant difference in the plot has been observed at the other levels of computations. In this Fig 6 is only drawn the motion when the sum of the displacements on the X, Y and Z axis is higher than 0.07 on the carbon and nitrogen atoms, 0.06 on the fluorine atoms, and higher than 0.15 on hydrogen atoms. The larger circles or arrows represent particularly large displacements.

In the columns first to fifth of Table 4 is collected the observed FTIR and Raman lines with their intensity. The columns sixth to eighth list the scaled wavenumbers calculated at the HF/6-31G**, from Table 2, with their relative % infrared intensities and Raman activities. The columns ninth to tenth collect the scaled wavenumbers at Becke3-LYP/6-31G** level, from Table 3, with their infrared intensities. The column 12 shows the tentative assignment carried out for the vibrational bands. For comparison, in the last column of this Table we have included the IR wavenumbers of 2,4-difluorotoluene.

The errors obtained in the predicted wavenumbers were very small, the mean deviation was 7 cm^{-1} (0.3%). These values being close to other benzene derivatives studied by us²⁷. It demonstrates the good agreement between the scaled theoretical and the experimental wavenumbers.

An analysis of the vibrations is as follows:

Normal vibrations of the ring

Table 4 shows that assignments for several of the phenyl ring modes are obvious and require no further discussion, therefore a brief analysis is given here. Theoretically the normal modes of the benzene ring change for the 2,4-tri-"light" (a substituent is said to be light one if the atom directly attached to the phenyl ring has mass less than 25 amu) substituted benzene. Thus the $\nu(\text{C-X})$ stretching vibrations correspond to the normal modes 7a, 13 and 7b, that lie at ca. 1280, 1210 and 950 cm^{-1} , respectively. At the Becke3-LYP/6-31G** level they were characterized and scaled at 1271, 1144 and 954 cm^{-1} , respectively, which were tentatively related to the IR bands, in KBr pellets, observed at 1310 (or 1290), 1152 and 975 cm^{-1} . The strong and very strong infrared intensity of these modes is in accordance with the theoretically predicted ones. Some bending $\delta(\text{C-H})$ contribution is associated with these modes. The computed wavenumbers at 1363 and 1216 cm^{-1} by Becke3-LYP also contain some contribution of the $\nu(\text{C-X})$ mode. At HF/6-31G** level, the scale factors from the benzene molecule are inadequate for the 7a and 13 modes; thus these wavenumbers were scaled at 1305 and 1188 cm^{-1} using the overall scale factor of 0.8992, and included in the sixth column of Table 4. These scaled wavenumbers at 1305 and 1188 cm^{-1} for the modes 7a and 13, respectively, are far from the DFT calculations. It is due to that the specific scale factors used for these modes were from benzene, which change remarkably on substitution and give rise to bad scaled wavenumbers.

The C-X in-plane vibrations, modes 9b, 9a and 15, were characterized at Becke3-LYP/6-31G** level at 445, 322 and 141 cm^{-1} , respectively. Their scaled wavenumbers at 436 and 315 cm^{-1} for the 9b and 9a mode, respectively, are very close to the scaled HF wavenumbers at 447 and 321 cm^{-1} , and they were assigned to the IR bands at 435 and 328 cm^{-1} , respectively. Mode 15 is characterized as an in-plane rocking motion of the ring.

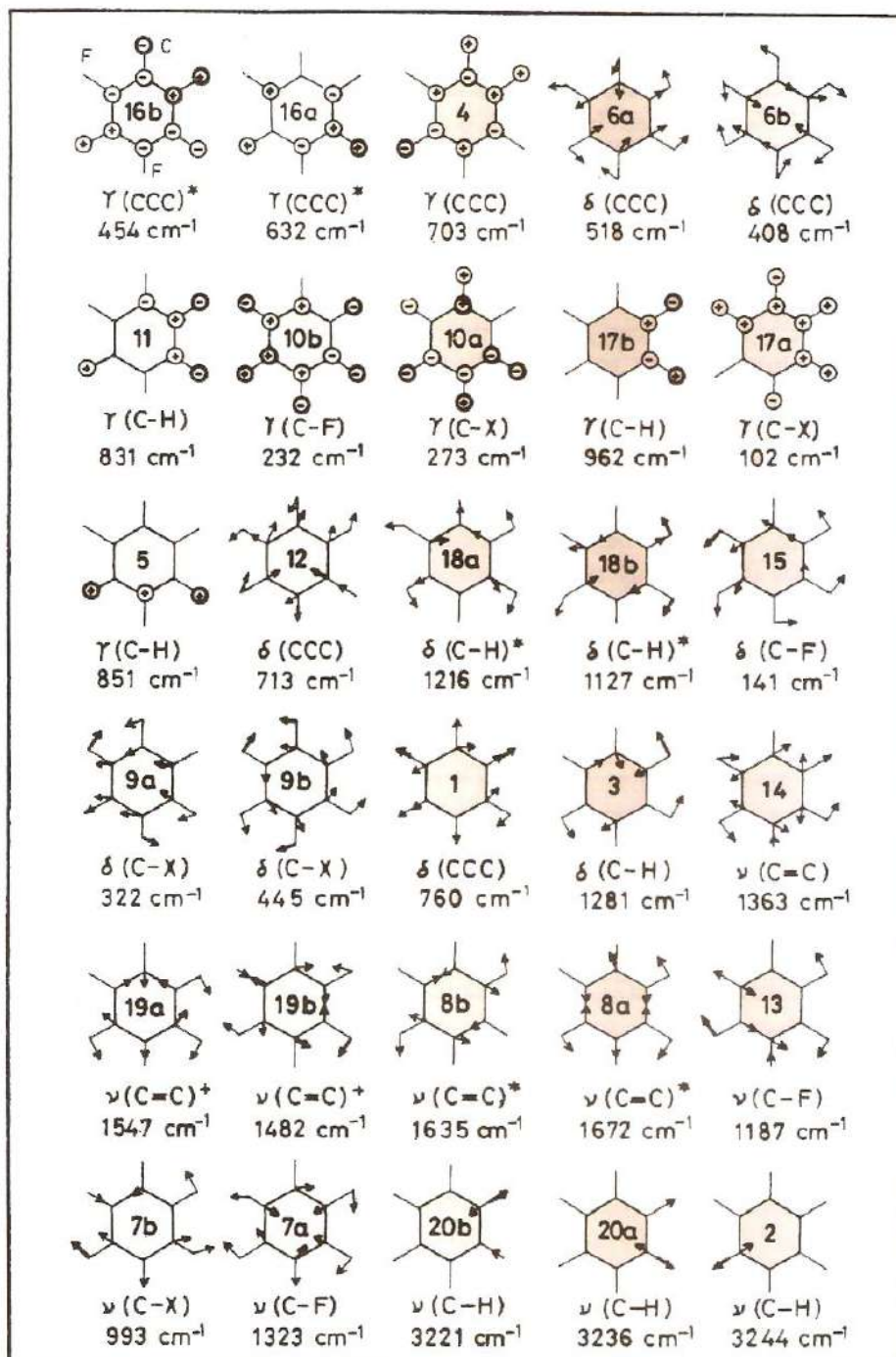


Fig. 6. Characterization of the normal modes computed in 2,4-difluorobenzonitrile molecule at Becke3-LYP/6-31G** level, with the main assignment and the wavenumber in which they were computed.

The C–X out-of-plane vibrations, modes 10, 10b and 17a, lie in the range 300–150 cm^{-1} . In this low wavenumber range, it was not possible to observe the characteristic motions of these modes clearly, due to they are coupled with other $\gamma(\text{C–H})$ and $\gamma(\text{CCC})$ vibrations. However, the accurate scale factor used, permit to assign the infrared bands at 267 and 230 cm^{-1} to the 10a and 10b modes. The other infrared wavenumbers observed were tentatively assigned to $\gamma(\text{CCC})$ and $\gamma(\text{C–X})$ modes.

In the tangential vibrations, the carbon–carbon stretchings, normal modes 8a, 8b, 19a, 19b and 14, involve by HF and DFT methods more or less strong $\delta(\text{C–H})$ bendings, $\nu(\text{C–F})$ stretchings (specially in modes 14 and 19b), and ring deformations, Fig 6, which make difficult their clear characterization. The modes 8a and 19a are identified at higher wavenumber than their corresponding counterpart 8b and 19b modes, but this assignment is inverse of that reported in difluorotoluene²⁸, with higher wavenumber in the b modes. Vibration 19 (a and b) appears strongly coupled with the vibrational pair 18 (a and b), in agreement with Scherer³⁵, with similar directions of the motions of the hydrogen atoms in both modes.

The Kekule C–C stretching (mode 14) appears coupled by Becke3-LYP/6-31G** with the mode 7a which gives rise to an increase in the computed wavenumber until 1363 cm^{-1} (scaled at 1316 cm^{-1}), out of the range 1235–1290 cm^{-1} established for this mode²⁸, and a decrease in the wavenumber of mode 7a. However this coupling is not observed by HF/6-31G** and this mode 14 is calculated at 1251 cm^{-1} (scaled at 1213 cm^{-1}), and thus assigned to the infrared band detected in the solid state at 1220 cm^{-1} , in accordance with the reported²⁸ in 2,4-difluorotoluene at 1237 cm^{-1} . The corresponding Raman band appears at 1218 cm^{-1} .

The C–H stretching modes, 2, 20a and 20b, were related to the C–H9, C–H11 and C–H12 bonds, respectively. These modes are not coupled with other vibrations and thus are easily identified by HF and DFT methods (Table 4).

The ring breathing (mode 1) and the trigonal planar ring bending (mode 12) are the most widely discussed modes in the literature. These modes are drastically affected in magnitudes upon substitution. The radial vibrations are usually strongly coupled in benzene derivatives, in our case with the $\delta(\text{C}\equiv\text{N})$, and correspond to the $\delta(\text{CCC})$ skeletal modes 1, 12, 6a and 6b. The wavenumber of the ring breathing, mode 1, is computed at a higher wavenumber than the mode 12, but this assignment is inverse of that reported in difluorotoluene²⁸ and 1,2,4-tri-"light" benzene derivatives with a higher wavenumber in the mode 12 than in the mode 1. Due to the coupling, which produce a change in the directions of several atoms, modes 6a and 6b are not recognized clearly, and in our assignment they can be interchanged.

The C–H in-plane bending vibrations, modes 3, 18a and 18b were computed by Becke3-LYP at 1281 (scaled at 1252), 1216 (1183) and 1127 (1097) cm^{-1} , respectively, and related to the infrared bands (in KBr) at 1276, 1172 and 1100 cm^{-1} . Mode 3 is associated with C–H12 bond, while mode 18b corresponds mainly to C–H11 bond. Mode 18a appears coupled with $\nu(\text{C–F})$ and $\nu(\text{C–C}\equiv)$ stretching vibrations, increasing therefore its wavenumber to ca. 1180 cm^{-1} , out of the range established for this vibration²⁸, 1130–1175 cm^{-1} , and also differing of the wavenumber reported in difluorotoluene at 1138 cm^{-1} .

In the out-of-plane vibrations, the skeletal modes 4, 16a and 16b are rather insensitive to substitution, which facilitate their characterization by HF and DFT methods.

However they appear with low wavenumber, which make difficult their identification in the infrared spectra.

As the skeletal modes, the C–H out-of-plane vibrations 5, 11 and 17b, are insensitive to substitution, specially mode 5 which requires no scale factor, and thus can be easily characterized and assigned with low error. Mode 5 corresponds to C–H9, while modes 11 and 17b are associated with both C–H11 and C–H12 bonds.

Cyanogen group vibrations

The nitrile stretching frequency is highly localised within the C≡N group because the potential energy distribution (PED) for this wavenumber contains contributions from the C–CN and C≡N stretching force constants only. The characteristic wavenumber of C≡N stretching vibrations of benzonitriles falls³⁰⁻³² in the range of 2220-2240 cm⁻¹, with an IR intensity which varies from medium-weak to strong depending of the substituent. In benzonitrile this band has been identified at 2230 cm⁻¹. Their vibrational wavenumber and IR intensity have been correlated to the Hammett-type substitution parameters both experimentally and theoretically³³. Electron-withdrawing groups, as –F, –NO₂, –OH, or –CF₃, decrease the IR band intensity and increase the wavenumber to the higher limit of the characteristic spectral region, whereas electron-donating groups, such as the amino group, increase the IR intensity and decrease the wavenumber³⁴. Successive substitution of electron-withdrawing or -donating groups can also shift the C≡N stretching wavenumber beyond the characteristic wavenumber region mentioned above, e.g. 2,3,5,6-tetrafluoro-4-cyanobenzonitrile at 2253 cm⁻¹. It is apparent from Table 4 that this characteristic wavenumber appears in the expected range in all the phases. The corresponding Raman band appears at 2236 cm⁻¹ very strongly. This assignment is in accordance with the literature values.

The Raman intensity of the C≡N band is enhanced by the conjugation of the aromatic ring. Nevertheless, the aromatic ring stretching and deformation modes often exhibit stronger Raman intensities than the CN stretching vibration³².

Thus it is apparent from Table 4 that all the 33 expected fundamentals could be observed in this case. Most of the modes have magnitudes in the expected ranges suggested in the literature. As the difference in the observed and theoretical values of most of the fundamentals is very small, therefore the assignments seems to be correct.

Other molecular properties

The values of the charge obtained with the theoretical methods used, are listed in Table 5. Close values are obtained between HF and MP2 ab initio methods. However, they differ remarkably with the density functional results. Appreciable differences are also noted between the Becke3-P86 and Becke3-LYP methods.

Several thermodynamic parameters were also calculated and collected in Table 6. Scale factors have been recommended²⁶ for an accurate prediction in determining the ZPVE (Zero-Point Vibrational Energies), the enthalpy $\Delta H_{\text{vib}}(T)$, and the entropy $S_{\text{vib}}(T)$.

Table 5. Total atomic charges on the atoms.

Atoms	ab initio		Density functional	
	HF/6-31G**	MP2/6-31G**	Becke-3P86/6-31G**	Becke-3L.YP/6-31G**
C1	-0.1411	-0.1264	-0.0014	0.0379
C2	0.5119	0.5074	0.376	0.3585
C3	-0.2957	-0.2794	-0.2418	-0.1978
C4	0.4871	0.4815	0.3829	0.3775
C5	-0.2363	-0.2284	-0.1844	-0.1431
C6	-0.0717	-0.0711	-0.0962	-0.0734
C7	0.3002	0.3081	0.2836	0.2604
F8	-0.3530	-0.3695	-0.2611	-0.2625
H9	0.2089	0.2138	0.1739	0.1353
F10	-0.3691	-0.3846	-0.2789	-0.2799
H11	0.1936	0.1971	0.1604	0.1232
H12	0.2056	0.2098	0.1680	0.1316
N13	-0.4403	-0.4584	-0.4808	-0.4676

Table 6. Theoretical computed total energies (A.U.), zero-point energies (KJ mol⁻¹), rotational constants (GHz), entropies (J mol⁻¹ K⁻¹) and dipole moments (Debyes) in 2,4-difluorobenzonitrile molecule.

Parameters	ab initio		Density functional	
	HF/6-31G**	MP2/6-31G**	Becke3-P86/6-31G**	Becke3-LYP/6-31G**
Total energy (RH)	-520.141529	-520.133052	-524.198653	-522.959448
(MP2)		-521.527891		
Zero-point energy	234.07			217.41
Rotational constants	2.98	2.92	2.94	2.92
	0.95	0.92	0.93	0.93
	0.72	0.70	0.71	0.70
Entropy				
Total	356.34			365.12
Translational	170.13			170.13
Rotational	123.10			123.35
Vibrational	63.12			71.60
Dipole moments	4.13	4.21	4.00	3.95

Because of some symmetry of the molecule, the dipole moment is mainly along the H-C...C-C≡N axis. Its value is in accordance with the experimental dipole moment reported²⁹ in benzonitrile is 4.53 D, and in 2,6-difluorobenzonitrile¹¹, ca. 4 D.

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[Received 6.6.98; revised recd 17.6.98; accepted 21.6.98]