

## FTIR and FT-RAMAN Spectral Investigation of Fluorobenzene

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### Abstract

Normal coordinate calculations of Fluorobenzene have been carried out using Wilson's FG matrix mechanism on the basis of general valence force field (GVFF) for both in-plane and out-of-plane vibrations. The potential energy constants obtained in this study are refined using numerical methods.

**Keywords:** FTIR, FT-Raman, fluorobenzene, normal coordinate analysis, potential energy distribution.

### 1. INTRODUCTION

Fluorobenzene is the chemical compound often abbreviated as PhF. This species is a derivative of benzene, with a single fluorine atom attached. The other names are phenyl fluorine, monofluorobenzene. PhF is a relatively inert compound because the C-F bond is very strong. PhF is a useful solvent for highly reactive species, but a metal complex has been crystallised [1]. PhF and its derivatives are used to control carbon content in steel manufacturing. Normal coordinate analysis of fluorobenzene compound was carried out to obtain a more complete description of the molecular vibrations involved in the fundamental vibrations of fluorobenzene.

In the present paper, an effort has been made to record spectra and to assign the observed fundamental modes of vibrations. The evaluation of potential energy constants has been made on the basis of general valence force field (GVFF) by applying Wilson's FG matrix mechanism [2].

### 2. EXPERIMENTAL METHODS

Pure chemical of fluorobenzene is obtained from Lancaster chemical company, England and used as such without any further purification. The FT-IR spectrum of

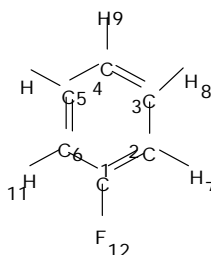
fluorobenzene was recorded in the region 4000-400  $\text{cm}^{-1}$  using KBr pellet. The Bruker IFS 66V model FT-IR spectrometer was used for the spectral measurements. The globar and mercury arc sources, KBr beam splitters are used while recording FTIR spectra of the title compound.

The FT-Raman spectrum was recorded on a Bruker IFS 66V model interferometer equipped with an FRA-106 FT-Raman accessory the spectrum was recorded in the Stokes region (4000-100  $\text{cm}^{-1}$ ) using the 1064 nm line of a Nd:YAG laser for excitation operating at 200 mw of power.

### 3. RESULTS AND DISCUSSION

#### 3.1. STRUCTURE AND SYMMETRY

The molecular structure of fluorobenzene is shown in Fig. 1. From the structural point of view the molecule is assumed to have  $C_s$  point group symmetry. The 30 fundamental modes of vibrations arising for this molecule are distributed into 21  $A'$  and 9  $A''$  species. The  $A'$  and  $A''$  species represent the in-plane and out-of-plane vibrations.



**Fig. 1** – Molecular Structure of Fluorobenzene

#### 3.2. NORMAL COORDINATE ANALYSIS

The evaluation of potential energy constants are made on the basis of GVFF by applying Wilson's FG matrix mechanism. The structural parameters were taken from the Sutton's table [3]. The vibrational secular determinants have been solved using the computer programmes with the SIMPLEX optimization procedure [4]. The initial set of force constants and the vibrational frequencies required for the calculations were taken from the literature [5]. All the force constants have been refined via a non-linear square fit analysis between the calculated and observed frequencies. The refinement converged smoothly in three cycles.

#### 3.3. SYMMETRY COORDINATES

Detailed description of vibrational modes can be given by means of normal coordinates analysis. For this purpose, the full set of 42 standard internal valence coordinates (containing 12 redundancies) were defined as given in Table 1. From there a non-redundant set of local internal coordinates were constructed (Table 2) much like the natural internal coordinates recommended by IUPAC [6,7]. Theoretically calculated force fields were transformed to the latter set of vibrational co-ordinates and used in all subsequent calculations.

**Table – 1** Definition of internal coordinates of fluorobenzene

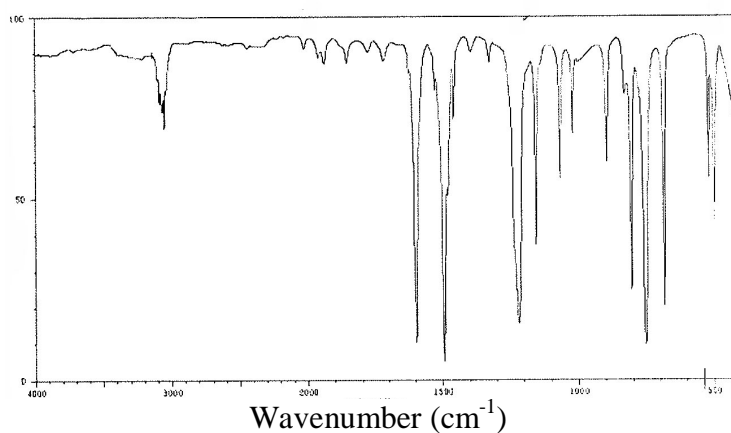
| No. (i)                     | Symbol     | Type        | Definition   |
|-----------------------------|------------|-------------|--|
| <b>Stretching</b>           |            |             |  |
| 1-6                         | $r_i$      | C-C         | C1-C2, C2-C3, C3-C4, C4-C5, C5-C6, C6-C1   |
| 7-11                        | $R_i$      | C-H         | C2-H7, C3-H8, C4-H9, C5-H10, C6-H11  |
| 12                          | $q_i$      | C-F         | C1-F12   |
| <b>In-plane bending</b>     |            |             |  |
| 13-22                       | $\alpha_i$ | C-C-H       | C1-C2-H7, C3-C2-H7, C2-C3-H8, C4-C3-H8, C3-C4-H9, C5-C4-H9, C4-C5-H10, C6-C5-H10, C5-C6-H11, C1-C6-H11 |
| 23-24                       | $\beta_i$  | C-C-F       | C2-C1-F12, C6-C1-F12   |
| 25-30                       | $\gamma_i$ | Ring        | C1-C2-C3, C2-C3-C4, C3-C4-C5, C4-C5-C6, C5-C6-C1, C6-C1-C2   |
| <b>Out-of-plane bending</b> |            |             |  |
| 31-35                       | $\omega_i$ | C-H         | H7-C2-C1-C3, H8-C3-C2-C4, H9-C4-C3-C5, H10-C5-C4-C6, H11-C6-C5-C1                                      |
| 36                          | $\sigma_i$ | C-F         | F12-C1-C6-C2   |
| <b>Torsion</b>              |            |             |  |
| 37-42                       | $t_i$      | $\tau$ 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                           |

**Table – 2** Definition of local symmetry coordinates of fluorobenzene

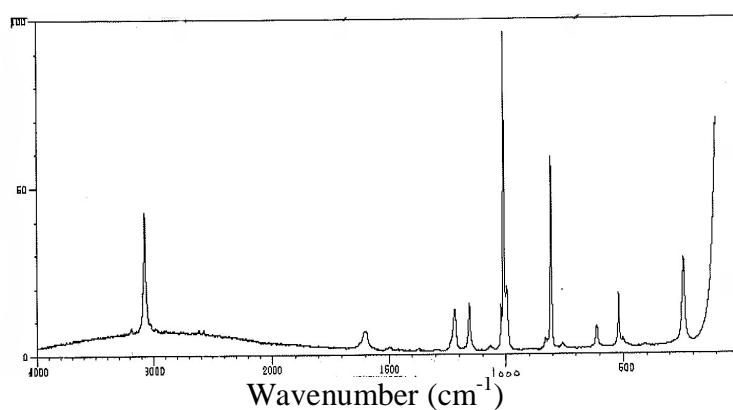
| No(i) | Type        | Definition   |
|-------|-------------|--|
| 1-6   | CC          | $r_1, r_2, r_3, r_4, r_5, r_6$   |
| 7-11  | CH          | $R_7, R_8, R_9, R_{10}, R_{11}$  |
| 12    | CF          | $q_{12}$   |
| 13-17 | bCH         | $(\alpha_{13} - \alpha_{14})/\sqrt{2}, (\alpha_{15} - \alpha_{16})/\sqrt{2}, (\alpha_{17} - \alpha_{18})/\sqrt{2}, (\alpha_{19} - \alpha_{20})/\sqrt{2}, (\alpha_{21} - \alpha_{22})/\sqrt{2}$ |
| 18    | bCF         | $(\beta_{23} - \beta_{24})/\sqrt{2}$   |
| 19    | R trig d    | $(\gamma_{25} - \gamma_{26} + \gamma_{27} - \gamma_{28} + \gamma_{29} - \gamma_{30})/\sqrt{6}$   |
| 20    | R sym d     | $(-\gamma_{25} - \gamma_{26} + 2\gamma_{27} - \gamma_{28} - \gamma_{29} + 2\gamma_{30})/\sqrt{12}$   |
| 21    | R asym d    | $(\gamma_{25} - \gamma_{26} + \gamma_{27} - \gamma_{28})/\sqrt{2}$   |
| 22-26 | $\omega$ CH | $\omega_{31}, \omega_{32}, \omega_{33}, \omega_{34}, \omega_{35}$  |
| 27    | $\sigma$ CF | $\sigma_{36}$  |
| 28    | t R trig    | $(\tau_{37} - \tau_{38} + \tau_{39} - \tau_{40} + \tau_{41} - \tau_{42})/\sqrt{6}$   |
| 29    | t R sym     | $(\tau_{37} - \tau_{39} + \tau_{40} - \tau_{42})/\sqrt{2}$   |
| 30    | t R asy     | $(-\tau_{37} + 2\tau_{38} - \tau_{39} - \tau_{40} + 2\tau_{41} - \tau_{42})/\sqrt{12}$   |

### 3.4. VIBRATIONAL BAND ASSIGNMENTS

The FTIR and FT-Raman spectra of the title compound are shown in Figs. 2-3.



**Fig. 2 – FT-IR Spectrum of Fluorobenzene**



**Fig. 3 – FT-Raman Spectrum of Fluorobenzene**

The observed frequencies of the title compound together with relative intensities, probable assignment, calculated frequencies and PEDS are presented in Table 3.

**Table – 3** Vibrational frequencies and assignments of fluorobenzene

| S. No. | Species | Observed frequency (cm <sup>-1</sup> ) |          | Calculated frequency (cm <sup>-1</sup> ) | Assignment (% PED)  |
|--------|---------|--|----------|--|---------------------|
|        |         | FTIR                                   | FT-Raman |  |                     |
| 1      | A'      | 3097                                   | -        | 3086                                     | C-H stretching (99) |
| 2      | A'      | -                                      | 3077     | 3061                                     | C-H stretching(98)  |
| 3      | A'      | 3064                                   | -        | 3054                                     | C-H stretching(97)  |
| 4      | A'      | 3051                                   | -        | 3039                                     | C-H stretching((96) |
| 5      | A'      | 3033                                   | -        | 3021                                     | C-H stretching(98)  |
| 6      | A'      | 1716                                   | -        | 1705                                     | C-C stretching(72)  |
| 7      | A'      | 1696                                   | -        | 1684                                     | C-C stretching(73)  |
| 8      | A'      | 1527                                   | --       | 1517                                     | C-C stretching(72)  |
| 9      | A'      | 1495                                   | -        | 1482                                     | C-C stretching(71)  |
| 10     | A'      | 1480                                   | -        | 1469                                     | C-C stretching(70)  |

|    |     |      |      |      |   |
|----|-----|------|------|------|---|
| 11 | A'  | 1459 | -    | 1448 | C-C stretching(72)                        |
| 12 | A'  | 1328 | -    | 1315 | C-F stretching(89)                        |
| 13 | A'  | 1220 | 1220 | 1213 | C-H in-plane bending(71)                  |
| 14 | A'  | 1166 | -    | 1157 | C-H in-plane bending(70)                  |
| 15 | A'  | 1144 | -    | 1133 | C-H in-plane bending(72)                  |
| 16 | A'  | -    | 1128 | 1116 | Ring deformation in-plane bending(52)     |
| 17 | A'  | 1066 | -    | 1055 | Ring deformation in-plane bending(52)     |
| 18 | A'  | 1021 | 1022 | 1013 | Ring deformation in-plane bending(53)     |
| 19 | A'  | -    | 1011 | 1002 | C-H in-plane bending(71)                  |
| 20 | A'  | -    | 998  | 987  | C-H in-plane bending(72)                  |
| 21 | A'' | 896  | -    | 884  | C-H out-of-plane bending(66)              |
| 22 | A'' | 831  | -    | 820  | C-H out-of-plane bending(65)              |
| 23 | A'' | 763  | -    | 751  | C-H out-of-plane bending(66)              |
| 24 | A'' | 685  | -    | 673  | C-H out-of-plane bending(64)              |
| 25 | A'' | -    | 634  | 622  | Ring deformation out-of-plane bending(58) |
| 26 | A'' | 519  | 520  | 529  | C-H out-of-plane bending(65)              |
| 27 | A'  | 511  | -    | 522  | C-F in-plane bending(56)                  |
| 28 | A'' | 489  | -    | 498  | C-F out-of-plane bending(56)              |
| 29 | A'' | 470  | -    | 462  | Ring deformation out-of-plane bending(59) |
| 30 | A'' | -    | 448  | 455  | Ring deformation out-of-plane bending(58) |

### 3.4.1. C-H Vibrations

The molecular structure shows the presence of C-H stretching vibrations in the region 3000-3100  $\text{cm}^{-1}$  which is the characteristic region for the ready identification of C-H stretching vibrations [8,9]. In this region, the bands are not affected appreciably by the nature of the substituents. Hence, in the present investigation, the C-H vibrations have been found at 3097, 3064, 3051, 3033  $\text{cm}^{-1}$  in IR and 3077  $\text{cm}^{-1}$  in Raman.

### 3.4.2. C-C Vibrations

The bands between 1400 and 1650  $\text{cm}^{-1}$  in benzene derivatives are due to C-C stretching vibrations [10]. Therefore, the C-C stretching vibrations of the title compound are observed at 1716, 1696, 1527, 1495, 1480 and 1459  $\text{cm}^{-1}$  in the FTIR spectrum.

### 3.4.3. C-F Vibrations

In the vibrational spectra of related compounds, the bands due to C-F stretching vibrations [11] 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 study the FTIR bands observed at 1328  $\text{cm}^{-1}$  has been assigned to C-F stretching mode of vibration.

## 4. CONCLUSION

Based on the normal coordinate analysis a complete vibrational analysis was performed for Fluorobenzene. A systematic set of symmetry coordinates have been constructed. The closer agreement obtained between the calculated and the observed frequencies and the PED calculations are also supporting the assignments made for various functional groups presents in the molecule.

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