



## Vibrational spectrum of 4-fluoraniline

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### Abstract

The Raman spectrum of 4-fluoraniline (4FA) has been recorded, the quadratic force field has been calculated at RHF/6-31 + G\* level of theory and then scaled to reproduce the experimental frequencies, by using Pulay's scaled quantum mechanical force field (SQMFF) methodology. Likewise, DFT force field has been calculated at the B3LYP/6-31 + G\* level. On the basis of all these results, a general assignment of the vibrational spectra of 4FA has been proposed and compared with that of aniline in order to determine the substitution effect of the fluorine atom. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** 4-Fluoraniline; Force field; Raman spectrum

### 1. Introduction

It is a well-known fact that ab initio calculations tend to overestimate the vibrational frequencies with respect to the experimental ones. This is due to several reasons, for instance, the use of finite basis set, the incomplete implementation of the electronic correlation and the neglect of anharmonicity effects in the theoretical treatment. However, the calculated ab initio force field can be improved by using the scaled quantum mechanical force field (SQMFF) methodology [1,2]. Basically, this scaling method consists in multiplying the calculated force constants matrix by the square root of the scale factors of the corresponding internal coordinates [2]. It has been shown that this method allows not only to obtain a

good overall agreement between the theoretical and experimental frequencies, but also to assign the fundamental frequencies in molecules with a large number of atoms [3,4].

In this work the vibrational spectrum of the 4-fluoraniline (4FA) has been studied by scaling the RHF force field with the SQMFF methodology. The scaled frequencies have been fitted to the experimental ones obtained from the Raman spectrum recorded by ourselves, and from the infrared (IR) data found in the literature [5–7]. A description of the normal modes is done on the basis of the potential energy distribution (PED) matrix. Furthermore, a correlation of the 4FA spectrum with that of aniline published in the literature [8] is proposed, in order to determine the substitution effect. Provided the success of density functional theory (DFT) in predicting chemical and physical molecular properties [9] we have also calculated the force field at the B3LYP/6-31 + G\* level without further refinement and compared it with that obtained by RHF/6-31 + G\*/SQMFF method.

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## 2. Experimental

The Raman spectrum of the liquid has been recorded at room temperature in the range 4000–100  $\text{cm}^{-1}$ . The sample of 4FA has been distilled to avoid the fluorescence background in the Raman records. Spectra have been obtained with an HR460 Jobin-Yvon Raman spectrometer with a grating groove density of 1800 G/mm and an ultimate resolving power of about  $3 \times 10^4$  at 550 nm. The detector is a liquid nitrogen-cooled Spectraview 2D CCD head of  $578 \times 375$  pixels which allows for the contemporary recording of a 300  $\text{cm}^{-1}$  wide spectral region. The excitation source is a krypton laser operating on the 647.1 nm line. The laser power used for the measure is 30 mW at the sample and the resolution of the spectra, determined by the width of the monochromator slits (100  $\mu\text{m}$ ), is about 2  $\text{cm}^{-1}$ . A scrambler filter is used to measure accurate relative intensity without polarization effects. A notch filter is set in the optical path between the sample and the spectrometer to enhance the rejection of the exciting radiation. This notch filter limits the spectrum to Raman shifts over 100  $\text{cm}^{-1}$ . The Raman spectrum of 4FA in the wavenumber range 1700–100  $\text{cm}^{-1}$  is shown in Fig. 1.

## 3. Computational details

The optimized structure and the force field of 4FA have been calculated at the RHF level using the 6-31 + G\* basis set which includes diffuse and polarization functions. It has been shown that it is necessary to introduce polarization functions for calculating the non-planar equilibrium structure of aniline due to the presence of the nitrogen lone pair [10,11]. Furthermore, it has been also shown that the above mentioned level of theory reproduces the non-planarity of the amino group in 4FA as well as the barrier height for the inversion motion in the ground electronic state [12]. We have also calculated both the optimized structure and the force field by using DFT calculations with the hybrid method B3LYP [13] and the above mentioned basis set. All the calculations have been carried out by using the GAUSSIAN 94 program package [14].

## 4. Results and discussion

The optimized equilibrium structure of 4FA yields a geometry with a symmetry plane perpendicular to the aromatic plane ( $C_s$  symmetry), showing the amino group a pyramidal structure. The inversion angle,

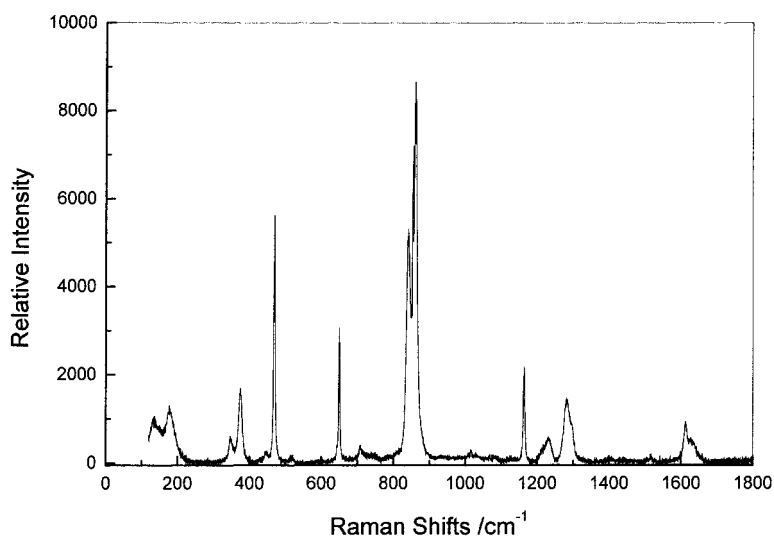


Fig. 1. Raman spectrum of 4FA in the range of 1700–100  $\text{cm}^{-1}$ .

between the NH<sub>2</sub> and ring planes, is 44.7°. This value satisfactorily agrees with that obtained from the microwave spectrum, 46.2° [15].

The force field has been calculated in the space of Cartesian coordinates by analytic differentiation and then transformed to internal coordinates by the FLINT program [16]. The internal coordinates have been defined according to the recommendations of Pulay et al. [17]. Finally, a modified version of the QCPE#576 program [18] has been used to carry out the scaling procedure. A single scale factor is used for each set of internal coordinates with the same vibrational character and only the scale factors involving the diagonal of the force constant matrix were initially adjusted. As it occurs for benzene [1], it is also necessary to introduce an off-diagonal scale factor corresponding to the *ortho*-, *meta*- and *para*-ring stretchings in order to improve the frequency about 1300 cm<sup>-1</sup>. Table 1 collects the values of the refined scale factors and the qualitative description of the internal coordinates.

Table 1  
Character of the internal coordinates and scale factors obtained by the SQMFF method for 4FA

|                       | Character <sup>a</sup>   | Scale factors |
|-----------------------|--|---------------|
| Ring                  | C–C stretching; $\nu(\text{CC})$                                 | 0.82          |
|                       | C–H stretching; $\nu(\text{CH})$                                 | 0.82          |
|                       | C–H rocking (i.p. def.); $\delta(\text{CH})$                     | 0.82          |
|                       | C–H wagging (o.p. def.); $\gamma(\text{CH})$                     | 0.73          |
|                       | Ring i.p. def.; $\delta_{\text{ring}}$ (12, 6a, 6b) <sup>b</sup> | 0.88          |
|                       | Ring o.p. def.; $\tau_{\text{ring}}$ (4, 16a, 16b) <sup>b</sup>  | 0.85          |
|                       | C–C stretchings <i>ortho</i> -, <i>meta</i> -, <i>para</i> -     | 0.69          |
| NH <sub>2</sub> group | N–H stretching; $\nu(\text{NH})$                                 | 0.79          |
|                       | Scissoring; $\delta(\text{NH})_{\text{sciss}}$                   | 0.80          |
|                       | Rocking (i.p. def.); $r(\text{NH})$                              | 0.87          |
|                       | Inversion (o.p. def.); $\gamma(\text{NH})$                       | 1.0           |
| C <sub>ring</sub> –N  | Stretching; $\nu(\text{CN})$                                     | 0.88          |
|                       | Rocking (i.p. def.); $\delta(\text{CN})$                         | 0.96          |
|                       | Wagging (o.p. def.); $\gamma(\text{CN})$                         | 0.82          |
|                       | Torsion; $\tau(\text{CN})$                                       | 0.74          |
| C <sub>ring</sub> –F  | Stretching; $\nu(\text{CF})$                                     | 0.80          |
|                       | Rocking (i.p. def.); $\delta(\text{CF})$                         | 0.77          |
|                       | Wagging (o.p. def.); $\gamma(\text{CF})$                         | 0.82          |

<sup>a</sup> i.p. def., in-plane deformation; o.p. def., out-of-plane deformation.

<sup>b</sup> Varsanyi's nomenclature Ref. [19].

The experimental and calculated frequencies with both the SQMFF and DFT results are shown in Table 2 together with the PED obtained with the SQMFF method. The 36 normal modes of this molecule distribute as 20 A' + 16 A'' according to the C<sub>s</sub> point group. The DFT frequencies are overestimated with respect to the experimental ones in the region between 3500 and 1000 cm<sup>-1</sup> and are accurate enough in the range 1100–100 cm<sup>-1</sup>, giving frequencies in this region similar to those obtained by the SQMFF method. The latter method yields a satisfactory overall agreement between the calculated frequencies and the experimental ones.

Due to the low symmetry of the molecule, several internal coordinates contribute to each normal modes. The frequencies of the amino group appear within the range of experimental frequencies found in the literature [8,19]: the NH<sub>2</sub> stretchings around 3500–3300 cm<sup>-1</sup>, the scissoring deformation around 1610–1630 cm<sup>-1</sup> and the rocking deformation around 1050–1070 cm<sup>-1</sup>, respectively. The calculated inversion frequency of this group is estimated at about 590 cm<sup>-1</sup> but it is well known that this mode is strongly anharmonic and its motion is described by a symmetrical one-dimensional double-minimum potential function. Far infrared spectrum indicates an inversion frequency about 31 cm<sup>-1</sup> [6]. Given that the inversion mode shows a large amplitude motion, the way Gaussian calculates this wavenumber is not acceptable and the scaling process is not done.

Though the scaled ring stretching frequencies (1600–1400 cm<sup>-1</sup>) are slightly overestimated with respect to the experimental ones, they have similar frequencies to those found for aniline [8]. This indicates that not only the RHF/6-31 + G\* calculations underestimate the electronic delocalization in the aromatic ring but also that these vibrations are not affected by the fluorine substitution as occurred with the 12 mode. This mode is observed in the IR spectrum at 1028 and 1008 cm<sup>-1</sup> for aniline and 4FA, respectively.

The theoretical calculations have allowed to assign definitively the vibrational spectrum in the low frequency region. In this region there are several modes affected for the fluorine substitution of the aromatic ring of aniline, such as the breathing vibration 1, the in-plane ring deformation 6a and the out-of-plane torsion 16b. The 1

Table 2  
Experimental and calculated vibrational frequencies ( $\text{cm}^{-1}$ ) of 4FA

| Symm. | IR <sup>a</sup>  | Ra   | Calc.<br>(DFT) | Calc.<br>(SQM) | PED<br>(%) <sup>b</sup>  |
|-------|------------------|------|----------------|----------------|--|
| A''   | 3425             | –    | 3643           | 3445           | 100 $\nu(\text{NH})$   |
| A'    | 3370             | 3368 | 3548           | 3360           | 100 $\nu(\text{NH})$   |
| A'    | 3053             | 3069 | 3218           | 3072           | 100 $\nu(\text{CH})$   |
| A''   | –                | –    | 3217           | 3072           | 98 $\nu(\text{CH})$  |
| A'    | 3025             | 3010 | 3180           | 3040           | 98 $\nu(\text{CH})$  |
| A''   | –                | –    | 3180           | 3040           | 100 $\nu(\text{CH})$   |
| A'    | 1630             | 1627 | 1696           | 1660           | 50 $\delta(\text{NH})_{\text{sciss}}$ , 24 $\nu(\text{CC})$                    |
| A'    | 1620             | 1612 | 1665           | 1640           | 36 $\nu(\text{CC})$ , 40 $\delta(\text{NH})_{\text{sciss}}$                    |
| A''   | –                | –    | 1649           | 1633           | 70 $\nu(\text{CC})$  |
| A'    | 1500             | 1510 | 1554           | 1524           | 48 $\delta(\text{CH})$ , 34 $\nu(\text{CC})$                                   |
| A''   | –                | –    | 1476           | 1452           | 38 $\delta(\text{CH})$ , 40 $\nu(\text{CC})$                                   |
| A''   | 1325             | –    | 1365           | 1324           | 78 $\delta(\text{CH})$ , 18 $\nu(\text{CC})$                                   |
| A''   | 1275             | 1274 | 1332           | 1275           | 52 $\nu(\text{CN})$ , 16 $\nu(\text{CC})$                                      |
| A'    | –                | –    | 1303           | 1256           | 66 $\nu(\text{CC})$ , 18 $\delta(\text{CH})$                                   |
| A'    | 1225             | 1223 | 1241           | 1228           | 51 $\nu(\text{CF})$ , 20 $\nu(\text{CC})$ ,<br>20 $\delta(\text{CH})$          |
| A'    | 1155             | 1155 | 1185           | 1156           | 76 $\delta(\text{CH})$ , 18 $\nu(\text{CC})$                                   |
| A''   | 1115             | –    | 1150           | 1113           | 60 $\nu(\text{CC})$ , 20 $\tau(\text{NH})$ ,<br>18 $\delta(\text{CH})$         |
| A''   | 1072             | –    | 1089           | 1075           | 38 $\nu(\text{CC})$ , 22 $\tau(\text{NH})$ ,<br>34 $\delta(\text{CH})$         |
| A'    | 1008             | –    | 1028           | 1013           | 45 $\delta_{\text{ring}}:12$ , 36 $\nu(\text{CC})$                             |
| A''   | 940              | –    | 943            | 947            | 62 $\gamma(\text{CH})$ , 37 $\tau_{\text{ring}}:16a$                           |
| A'    | 916              | –    | 932            | 921            | 70 $\gamma(\text{CH})$ , 26 $\tau_{\text{ring}}:4$                             |
| A'    | –                | 852  | 860            | 834            | 54 $\nu(\text{CC})$ , 21 $\delta_{\text{ring}}:12$                             |
| A'    | 835              | 832  | 836            | 823            | 62 $\gamma(\text{CH})$ , 15 $\gamma(\text{CN})$                                |
| A''   | 820              | –    | 808            | 783            | 98 $\gamma(\text{CH})$   |
| A'    | 745              | –    | 759            | 743            | 32 $\delta_{\text{ring}}:12$ , 20 $\nu(\text{CC})$ ,<br>25 $\nu(\text{CF})$    |
| A'    | –                | 700  | 698            | 703            | 33 $\tau_{\text{ring}}:4$ , 30 $\gamma(\text{CN})$ ,<br>24 $\gamma(\text{CF})$ |
| A''   | 635 <sup>c</sup> | 641  | 652            | 654            | 76 $\delta_{\text{ring}}:6b$ , 12 $\nu(\text{CC})$                             |
| A'    | –                | –    | 621            | 591            | 73 $\gamma(\text{NH}_2)$   |
| A'    | 502 <sup>c</sup> | 500  | 509            | 506            | 36 $\gamma(\text{CF})$ , 30 $\gamma(\text{CN})$                                |
| A'    | 452 <sup>d</sup> | 461  | 462            | 461            | 74 $\delta_{\text{ring}}:6a$   |
| A''   | –                | 438  | 436            | 437            | 40 $\delta(\text{CN})$ , 31 $\delta(\text{CF})$                                |
| A''   | –                | –    | 426            | 420            | 66 $\tau_{\text{ring}}:16a$ , 34 $\gamma(\text{CH})$                           |
| A'    | 352 <sup>c</sup> | 366  | 358            | 357            | 38 $\tau_{\text{ring}}:4$ , 25 $\gamma(\text{CF})$ ,<br>16 $\gamma(\text{CN})$ |
| A''   | –                | 338  | 329            | 328            | 47 $\delta(\text{CF})$ , 36 $\delta(\text{CN})$                                |
| A''   | –                | 171  | 246            | 170            | 83 $\tau(\text{CN})$   |
| A'    | –                | 125  | 152            | 152            | 73 $\tau_{\text{ring}}:16b$  |

<sup>a</sup> Ref. [5].

<sup>b</sup> PED corresponding to the SQM force field.

<sup>c</sup> Ref. [6].

<sup>d</sup> Ref. [7].

mode shifts from  $990\text{ cm}^{-1}$  observed in aniline to  $860\text{ cm}^{-1}$  in 4FA and corresponds to the strongest band of the Raman spectrum. Moreover, two bands with strong intensity appear in the  $800\text{ cm}^{-1}$  region. We assign the band at  $860\text{ cm}^{-1}$  to the breathing mode while the band of  $840\text{ cm}^{-1}$  is assigned to an out-of-plane CH bending. The latter band was assigned by Smentanine and Etchepare [7] to the 1 mode at  $844\text{ cm}^{-1}$  Raman frequency. The 6a ring deformation assigned at about  $520\text{ cm}^{-1}$  in the Raman spectrum of aniline [8] appears in 4FA at  $469\text{ cm}^{-1}$  (Raman) and  $452\text{ cm}^{-1}$  (IR) while the 16b ring torsion downshifts from  $233\text{ cm}^{-1}$  in aniline [8] to  $133\text{ cm}^{-1}$  in 4FA.

The CN normal modes in 4FA do not change with respect to those assigned in aniline [8]. The stretching, the in-plane deformation and the out-of-plane deformation appear near to  $1275$ ,  $350$  and  $500\text{ cm}^{-1}$ , respectively. The CF normal modes appear in the same range of frequencies: stretching,  $1225\text{ cm}^{-1}$ ; in-plane deformation,  $445\text{ cm}^{-1}$  while the out-of-plane deformation appears at  $374\text{ cm}^{-1}$ . All these frequencies agree with those obtained for di-substituted benzenes [19]. Finally, the remaining vibrations correlate quite well with those reported for aniline [8].

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