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## **Derivation of an accurate geometry of 2-fluoroaniline from rotational spectroscopy and computational chemistry**

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**ABSTRACT**

The ground state rotational spectrum of 2-fluoroaniline was investigated using Fourier transform microwave spectroscopy in the 6-19 GHz range. The spectrum reveals hyperfine structure due to the  $^{14}\text{N}$  quadrupole moment and additional transitions due to the six  $^{13}\text{C}$  and one  $^{15}\text{N}$  minor isotopologues which were detected in natural abundance. The rotational constants derived from analysis of the observed spectral patterns for the eight isotopologues were used to derive accurate experimental geometries including the substitution ( $r_s$ ), ground state effective ( $r_0$ ) and mass dependence ( $r_m^{(1)}$ ) structures of 2-fluoroaniline. These show excellent agreement with the equilibrium ( $r_e$ ) geometry derived from quantum chemical calculations at the B3LYP/aug-cc-pVTZ level of theory. The geometry of the heavy atom backbone of 2-fluoroaniline, in comparison to the parent aniline, is consistent with effects from the electron withdrawing fluorine atom and from the presence of a weak non-covalent interaction between the neighbouring  $\text{NH}_2$  and F groups as supported by natural bond orbital and non-covalent interaction analyses, respectively.

## INTRODUCTION

The chemical history of aniline and its derivatives is fascinating from their first use as dyes in the textile industry in the second half of the nineteenth century [1]. Since then, the large-scale manufacture of aryl amines has played a critical role in driving research and development on multiple continents that have served to diversify modern chemical industry. This is seen by the use of aniline derivatives in the production of numerous goods such as synthetic colorants, pharmaceuticals (sulfa drugs), rubber, molded plastics (melamine), polymers (polyanilines) and agrochemicals [1].

The structure and dynamics of aniline are also of considerable academic interest owing to some particularly unique features. The pyramidal nitrogen centre (with a relatively low inversion barrier of 6.58 kJ/mol)[2] in the ground electronic state becomes planar in the  $S_1$  electronic state [3–5]. The  $S_0$  state has been well-characterized by various techniques including far infrared studies which provided estimates of the barrier to planarity and mapped out the inversion vibration manifold starting at 40.8  $\text{cm}^{-1}$  [2,6]. The halogen-substituted anilines have also been explored in an effort to deduce the effects on the inversion potential when X=F, Cl or Br is added in the *ortho*, *meta* or *para* positions of the benzene backbone [6,7]. In all cases except *p*-fluoroaniline, the inversion barrier is lowered relative to that of the parent when X is added. This is explained by the electron withdrawing effects of the halogen and mesomeric contributions from the lone pair on nitrogen into the  $\pi$  system of ring. The halogen identity seems to be most important when the substituent is in the *ortho* position as the barrier increases from 4.62 kJ/mol in *o*-bromoaniline to 6.25 kJ/mol in *o*-fluoroaniline which was attributed to formation of an intramolecular hydrogen bond between the neighbouring groups. For comparison, for F, Cl or Br substitution in the *meta* position, the barriers were identical (5.42-5.47 kJ/mol) within experimental accuracy ( $\pm 0.06$

kJ/mol).

The structures of the halogen containing derivatives of aniline have been explored using microwave spectroscopy in order to ascertain whether inductive and mesomeric effects of the substituents alter the geometry of the amine subunit. In *o*-fluoroaniline [8,9] and *o*-chloroaniline [10], substitution structures derived using rotational constants of the NH<sub>2</sub>, NHD and ND<sub>2</sub> containing species suggest that the C-N bond is twisted to bring the amine hydrogen closest to the halogen atom toward the molecular ab-plane. This was interpreted as evidence of a hydrogen bonding interaction of type N-H...X. The dihedral angle  $\phi$  between the plane of the NH<sub>2</sub> group and the benzene ring, however, is nearly identical in *o*-fluoro (36.7°)[9] and *m*-fluoroaniline (36.2°)[11] and similar to that of the aniline parent (37.5°)[12] which seems inconsistent with this assertion. It is also interesting to note that the double-well nature of aniline's inversion potential gives rise to a tunnelling splitting in the microwave spectrum [12–15] which was confirmed by measurements of its deuterated and partially deuterated analogues. The rotational spectra of the *ortho*, *meta* and *para* variants of fluoro-[8,9,11,16] and chloroaniline [10,17,18] also reveal a tunnelling splitting attributed to amine inversion from measurements at ambient or cooled (-15°C) temperatures. The Stark modulated microwave spectra did not, however, offer sufficient resolution to characterize the <sup>14</sup>N quadrupole hyperfine structure and centrifugal distortion effects in these molecules nor the required sensitivity to assign transitions due to other heavy atom isotopologues to facilitate a more comprehensive structural analysis.

In this paper, we investigate whether there is an intramolecular hydrogen bond between the NH<sub>2</sub> and F substituents when substituted in the *ortho* arrangement on a benzene ring using Fourier transform microwave (FTMW) spectroscopy and quantum chemical calculations. We report here the first FTMW spectrum of 2-fluoroaniline (2-FAN or *o*-fluoroaniline) and its <sup>13</sup>C and <sup>15</sup>N minor

isotopologues observed in natural abundance. The  $^{14}\text{N}$  quadrupole hyperfine structure was resolved for the first time and combined with data from large number of isotopic species, has allowed derivation of accurate experimental  $r_s$ ,  $r_0$  and  $r_m^{(1)}$  geometries of 2-FAN. These compare well with the equilibrium geometry ( $r_e$ ) calculated at the B3LYP/aug-cc-pVTZ level. The interpretation of the experimental results was guided by natural bond orbital(NBO), quantum theory of atoms in molecules (QTAIM) and non-covalent interaction (NCI) calculations.

## EXPERIMENTAL DETAILS

A commercially available sample of 2-FAN (99%) from Sigma-Aldrich Canada was used without further purification. It is liquid at room temperature (mp:  $-29\text{ }^\circ\text{C}$ ) and has a relatively high boiling temperature (182-183  $^\circ\text{C}$ ). The sample was added into a glass bubbler and neon (100 kPa) was used as a carrier gas to transfer the sample into the spectrometer. To create a supersonic jet expansion, the sample mixture was expanded into the high vacuum chamber of the spectrometer using a pulsed nozzle.

The rotational spectrum of 2-FAN was measured using both chirped pulse (cp) and a Balle-Flygare FTMW instruments which were previously described in detail [19,20]. Initially, the broadband spectrum was recorded in the frequency range from 8 to 18 GHz in segments of 2 GHz employing the cp-FTMW instrument. These survey spectra were sufficient for assigning the most intense rotational transitions of the parent species and the minor isotopologues ( $^{13}\text{C}$  and  $^{15}\text{N}$ ). Under the conditions used for the acquisition of the cp-FTMW spectrum, the FIDs were collected for only 16  $\mu\text{s}$  which resulted in line widths of  $\sim 200\text{ kHz}$  (FWHM) and allowed for rough assignment of lines to within  $\pm 20\text{ kHz}$ . Later, on the basis of these preliminary assignments, the Balle-Flygare FTMW spectrometer, which provides higher resolution and sensitivity, was used to measure the spectral lines for individual  $^{14}\text{N}$  hyperfine components from 6 to 19 GHz. The

transitions observed with this instrument generally have line widths of  $\sim 7$  kHz (FWHM) and the spectra show a doublet splitting due to the Doppler effect which arises from the collinear arrangement of the molecular beam and the resonator axis. The uncertainties in the measurement of the frequencies are usually within  $\pm 1$  kHz.

## COMPUTATIONAL DETAILS

Optimization of the equilibrium geometry of 2-FAN was done at the B3LYP/aug-cc-pVTZ level of theory in the Gaussian 16 software [21]. The resulting equilibrium structure is shown in Figure 1 in its principal inertial axis system and the rotational constants were found to be satisfactory in comparison to the literature data [8,9]. To verify the nature of stationary points, vibrational frequency calculations were done at the same level of theory.

Next, to estimate the energy barrier for the tunneling motion of the amine center that moves H and H' in Figure 1 from pointing into the ring plane to pointing out of the ring plane, we performed geometry optimizations for the three transition state geometries interconnecting the two equivalent forms (I and I', Figure 2) of 2-FAN: one due to the umbrella inversion motion and the others due to an internal rotation motion of the NH<sub>2</sub> group either toward or away from the fluorine atom. Vibrational frequency calculations were also carried out for the three transition state structures whose natures have been confirmed by the presence of a single imaginary frequency. For the optimization and vibrational frequency calculations of the transition state geometries, we employed the MP2/cc-pVTZ level which was the method used to estimate the energy barrier to inversion in aniline in a previous study [22]. The calculated energy barriers for the interconversion of 2-FAN and labels are shown in Figure 2. The lowest energy barrier is found for the umbrella inversion motion which happens through a planar transition state shown in Figure 2 and the barrier

height was found to be similar to that reported for aniline (6.998 kJ/mol). The results indicate that the presence of F in 2-FAN does not play major role in the inversion motion of the amine group.

NBO, QTAIM and NCI analyses were performed to identify possible intramolecular interactions between the amine and F substituents. These calculations were completed using the NBO 7.0,[23] AIMAll,[24] and NCIPLOT[25] programs, respectively.

## SPECTRAL ANALYSIS

The most intense features in the cp-FTMW survey spectrum were assigned to *b*-type transitions of 2-FAN as expected based on the calculated dipole moment components:  $|\mu_a| = 0.11$  D,  $|\mu_b| = 1.40$  D and  $|\mu_c| = 0.87$  D (B3LYP/aug-cc-pVTZ). Following closer inspection, analogous transitions due to the six  $^{13}\text{C}$  and one  $^{15}\text{N}$  isotopologues were identified as were several *a*-type transitions of the parent with the latter having only about 5-7% the intensity of the *b*-type lines. Following preliminary assignment of the broadband spectrum, individual  $^{14}\text{N}$  hyperfine components were re-investigated with the Balle-Flygare FTMW instrument to improve the quality of the fit. An example of the observed hyperfine pattern of a single rotational transition is shown in Figure 3. In total, 169 *a*-type and *b*-type hyperfine components were measured for the parent species. Although, the *c*-dipole component of the electric dipole is calculated to be greater than the *a*-component, the *c*-type spectrum is not experimentally observable due to the inversion tunneling of H and H' along the *c*-axis which is consistent with previous studies of 2-FAN [8,9] and other substituted anilines such as 3-aminophenol [22].

All assigned rotational transitions for the parent and minor isotopologues are listed in the supplementary material file. Pickett's SPFIT program [26], set to Watson's A-reduced Hamiltonian I' representation, was used to fit the recorded transition frequencies of each

isotopologue. The resulting rotational, centrifugal distortion and  $^{14}\text{N}$  hyperfine constants are tabulated in Table 1 with their quantum chemical values for comparison. The centrifugal distortion constants  $\Delta_J, \Delta_{JK}, \Delta_K, \delta_J,$  and  $\delta_K$  for all minor isotopologues were fixed to those of the parent species as too few transitions were measured to obtain accurate experimental values. The observed transitions correspond to those of the  $0^+$  state of 2-FAN reported by previous investigators [8,9] using a microwave waveguide cell. We were unable to observe their reported transitions involving the  $0^-$  excited inversion state using either the cp-FTMW or Balle-Flygare instrument despite having sufficient sensitivity to observe  $^{15}\text{N}$  features in natural abundance (0.4%). This is consistent with other FTMW investigations of related molecules in supersonic jets such as 3-aminophenol [22] and 4-toluidine [27]. In the former, no inversion tunnelling was observed and in the latter, the  $0^-$  components were considerably lower intensity (~4%) in comparison to those of the  $0^+$  state indicating that the population of the excited inversion state is low in the molecular beam.



**Table 1.** Ground State Spectroscopic Constants of 2-Fluoroaniline Including Its  $^{13}\text{C}$  and  $^{15}\text{N}$  Isotopologues

	Parent	$^{13}\text{C1}$	$^{13}\text{C2}$	$^{13}\text{C3}$	$^{13}\text{C4}$	$^{13}\text{C5}$	$^{13}\text{C6}$	$^{15}\text{N}$
A	3310.35787(17)	3298.51980(23)	3301.57682(25)	3269.79878(24)	3300.05859(18)	3300.82166(20)	3268.56956(22)	3268.71901(25)
B	2218.61306(11)	2216.35190(61)	2216.58902(83)	2213.77881(74)	2183.02666(59)	2182.57709(70)	2213.14748(70)	2190.35535(25)
C	1329.592332(69)	1326.868141(67)	1327.449511(93)	1321.280708(90)	1315.095989(68)	1315.053451(84)	1320.855610(85)	1312.73833(10)
$\Delta_J$	0.0816(18)	[0.0816]	[0.0816]	[0.0816]	[0.0816]	[0.0816]	[0.0816]	[0.0816]
$\Delta_{JK}$	0.0392(83)	[0.0392]	[0.0392]	[0.0392]	[0.0392]	[0.0392]	[0.0392]	[0.0392]
$\Delta_K$	0.576(17)	[0.576]	[0.576]	[0.576]	[0.576]	[0.576]	[0.576]	[0.576]
$\delta_J$	0.02872(83)	[0.02872]	[0.02872]	[0.02872]	[0.02872]	[0.02872]	[0.02872]	[0.02872]
$\delta_K$	0.1154(47)	[0.1154]	[0.1154]	[0.1154]	[0.1154]	[0.1154]	[0.1154]	[0.1154]
$3/2 \chi_{aa}$	3.4462(18)	3.415(19)	3.489(20)	3.432(24)	3.491(19)	3.389(23)	3.389(23)	-
$1/4 (\chi_{bb} - \chi_{cc})$	1.55027(47)	1.5556(35)	1.5526(25)	1.5455(46)	1.5494(35)	1.5489(41)	1.5490(44)	-
no. of lines	169	29	30	32	31	31	32	16
rms (kHz)	1.9	1.7	2.5	2.3	1.7	2.1	2.2	2.1

<sup>a</sup>Calculated rotational constants (B3LYP/aug-cc-pVTZ) for 2-FAN: A = 3319.0 MHz, B = 2224.6 MHz, C = 1333.2 MHz. Rotational constants from ref [9]: A = 3310.363(440) MHz, B = 2218.614(26) MHz, C = 1329.586(23) MHz. Values in [] were fixed to the parent value.

## STRUCTURE DETERMINATION

With experimental rotational constants from eight isotopologues available, substitution ( $r_s$ ) structures were first estimated using Kraitchman's equations [28] as implemented in Kisiel's KRA program [29]. The signs of the derived Kraitchman coordinates were inferred by comparison with the equilibrium ( $r_e$ ) geometry (B3LYP/aug-cc-pVTZ). These parameters are reported in the supplementary material file. Using the atomic coordinates and their Costain errors [30], the geometry of the heavy atom backbone was calculated using the EVAL routine [29] after setting imaginary  $c$ -coordinates to zero. The results are summarized in Table 2 with the  $r_e$  parameters for comparison. Overall, the general structural trends are captured by the Kraitchman method with most values matching to within two standard deviations. Although the heavy atoms lie largely in the  $ab$ -plane, the molecule is not strictly planar and the large Costain errors in the  $c$ -coordinates, along with contributions from low lying vibrational states, are likely the main reason for the observed discrepancies from the  $r_e$  geometry.

Next, the effective ground state ( $r_0$ ) structures were estimated via direct least squares fitting of key geometric parameters to the 24 moments of inertia derived from the isotopologues using Kisiel's STRFIT program [29]. The internal coordinates involving hydrogen and fluorine were fixed at the  $r_e$  values (B3LYP/aug-cc-pVTZ) during this process. As in other fluorine substituted aromatic systems such as the mono-, di- and perfluorinated cyanobenzenes [31], fluorophenols [32] and fluorothiophenols [33], the orientations of the C-H, C-F and C-N bonds relative to the aromatic ring were preserved by fixing the differences in the external angles (for example,  $\angle F-C2-C1$  and  $\angle F-C2-C3$ ) at the value from the quantum chemical calculations. One external angle could then be varied in the least squares fitting procedure and the internal angle ( $\angle C1-C2-C3$ ) of interest

was subsequently calculated by trigonometry. The  $r_0$  parameters are summarized in Table 2 and show excellent agreement with their  $r_e$  counterparts.

Based on a recent FTMW study of 2-fluoroanisole and 3-fluoroanisole [34], we were also curious as to whether the amine group in the present system added significant out-of-plane vibrational effects that the  $r_0$  method does not taken into account. In such cases, the mass dependence ( $r_m^{(1)}$ ) structure has been shown to provide a better geometric estimate [35]. As reported for anisole [36], the Laurie parameter  $\delta_H$  was fixed at 0.01 Å for each C-H bond, and the condition that  $c_a = c_b = c_c$  was also used. The  $r_m^{(1)}$  results, shown in Table 2, are strikingly similar to the corresponding  $r_0$  values but with standard deviations of individual parameters and of the

**Table 2.** Equilibrium ( $r_e$ ) (B3LYP and MP2/aug-cc-pVTZ), Substitution ( $r_s$ ), Ground State Effective ( $r_0$ )<sup>a</sup> and Mass Dependence ( $r_m^{(1)}$ )<sup>a</sup> Structural Parameters (Bond Lengths in Å, Angles in deg) Determined for 2-Fluoroaniline and Equilibrium structural ( $r_e$ ) (B3LYP/aug-cc-pVTZ) parameters for Aniline.<sup>c</sup>

	Aniline		2-Fluoroaniline			
	$r_e$	$r_e$	$r_e$	$r_s$	$r_0$	$r_m^{(1)d}$
	B3LYP	B3LYP	MP2			
C1 – C2	1.399	1.396	1.396	1.402(3)	1.392(6)	1.3910 (15)
C2 – C3	1.388	1.377	1.381	1.374(4)	1.379(5)	1.3779(13)
C3 – C4	1.391	1.392	1.394	1.384(4)	1.398(6)	1.3988(15)
C4 – C5		1.390	1.392	1.392(4)	1.399(7)	1.3974(19)
C5 – C6		1.389	1.393	1.399(3)	1.396(5)	1.3963(14)
C6 – C1		1.398	1.397	1.392(3)	<i>1.399(10)</i>	<i>1.398(3)</i>
N – C1	1.395	1.389	1.395	1.400(8)	1.396(9)	1.397(2)
$\angle$ C6-C1-C2	118.6	116.7	116.9	117.4(3)	117.1(6)	117.18(16)
$\angle$ C1-C2-C3	120.5	123.2	123.1	123.9(4)	123.6(5)	123.61(11)
$\angle$ C2-C3-C4	120.8	119.1	119.0	118.4(4)	118.7(3)	118.66(8)
$\angle$ C3-C4-C5	118.9	119.3	119.5	119.3(1)	119.3(3)	119.33(8)
$\angle$ C4-C5-C6		120.7	120.4	120.6(2)	120.6(3)	120.63(7)
$\angle$ C5-C6-C1		121.0	121.1	120.4(3)	<i>120.7(4)</i>	<i>120.6(10)</i>
$\angle$ N-C1-C2	120.7	120.5	120.2	120.4(4)	120.4(6)	120.41(16)
$\angle$ N-C1-C6		122.8	122.8	122.2(7)	122.4(4)	122.35(11)

<sup>c</sup>Italicized parameters were not varied in the least squares fit. The reported uncertainties are from EVAL based on the uncertainties in the other ring parameters that were fit.

<sup>d</sup> Additional parameters:  $c_a=c_b=c_c=-0.00392(22) \text{ u}^{1/2}\text{Å}$

overall fit improved by about a factor of four. This may simply be the result of including an additional parameter ( $c_a=c_b=c_c=-0.0039(2) \text{ u}^{1/2} \text{ \AA}$ ) in the fit but the agreement in the  $I_c$  moments of inertia (calculated versus experimental) show the largest improvement as one would expect if the model corrects for the effects of the low frequency out-of-plane modes of 2-FAN.

## DISCUSSION

The ground state spectroscopic constants derived from fitting the observed transitions of 2-FAN are well-determined and in good agreement with those calculated at the B3LYP/aug-cc-pVTZ level of theory as summarized in Table 1. In comparison to previous studies of this molecule [8,9], the rotational constants are more precisely determined here using modern FTMW techniques and the full set of centrifugal distortion constants and the  $^{14}\text{N}$  quadrupole coupling parameters have been derived for the first time. It is somewhat surprising that we were unable to observe transitions from the  $0^-$  state (despite having published line lists) as the far infrared spectrum indicates that the excited inversion state is only 0.60 kJ/mol [7] higher in energy than the ground state in 2-FAN. Nonetheless, these results are consistent with other supersonic jet-based studies on substituted anilines in which transitions attributable to the higher energy tunnelling component were difficult to detect [27] or similarly absent [22].

The parameters corresponding to the equilibrium  $r_e$  geometry (B3LYP/aug-cc-pVTZ) of the aniline heavy atom backbone are summarized in Table 2 in order to deduce the effect of the addition of the electron withdrawing fluorine atom in 2-FAN. As seen in the related fluorine substituted rings such as pyridines [37,38], benzenes [39–41], cyanobenzenes [31], phenols [32], thiophenols [33], benzaldehydes [42] and anisoles [34], the largest changes occur at the site of fluorination. In 2-FAN, the value of  $\angle\text{C1-C2-C3}$  increases by  $\sim 3^\circ$  compared to the corresponding

parameter of the parent aniline due to the increased p-character in the orbital directed along the C2-F bond (and resulting increased s-character in the remaining hybrid orbitals of that carbon centre). One also observes contraction of the C2-C3 bond by  $\sim 0.011 \text{ \AA}$  ( $r_e$ ) and a smaller contraction of the C1-C2 bond  $\sim 0.003 \text{ \AA}$ . The smaller effect on C1-C2 was observed in other cases in which there are two *ortho* substituents such as the difluoropyridines [38] and difluorocyanobenzenes [31]. The bond shortening is explained in terms of natural charges on the atoms involved as the electron withdrawing fluorine induces a positive natural charge on the substituted atom resulting in stronger bonds with the adjacent carbons that bear partial negative charges. This is consistent with the calculated values of positive natural charge on C1 (0.0812) and C2 (0.355) from the NBO results as a result of the attached electronegative atoms at these sites bearing negative natural charges: N (-0.785) and F (-0.355).

Previous far infrared and microwave spectroscopic studies of haloanilines have suggested that the inversion barriers in the *ortho*-substituted species and the distortion of the  $\text{NH}_2$  geometry are caused by formation of an intramolecular hydrogen bond [7,9]. In 2-FAN, for example, this was used to explain why the amine H atom closest to F had a smaller *c*-coordinate (0.245-0.287  $\text{\AA}$  depending on the isotopologue used in the derivation) in the substitution structure than the H' atom (0.325-0.357  $\text{\AA}$ ) on the far side. The  $r_e$  geometry of 2-FAN in this work confirms that the C-N bond is twisted to move the former closer to the molecular *ab*-plane as the dihedral angles  $\angle \text{C1-C2-N-H}$  ( $20.5^\circ$ ) and  $\angle \text{C3-C2-N-H}'$  ( $-26.2^\circ$ ) show a slight asymmetry (B3LYP/aug-cc-pVTZ). The N-H $\cdots$ F interaction must be minor as no charge transfer interactions between the amine and F groups were observed in the standard NBO analysis which uses a threshold of  $0.5 \text{ kcal mol}^{-1}$  for the interaction second order perturbation energies. From the QTAIM results, graphically depicted in Figure 4, no bond critical point was identified between the N-H and F moieties although this

method is more suitable for medium to strong interactions and is known to fail in cases involving weaker interactions such as the O-H $\cdots$ O hydrogen bond in 1,2-ethanediol [43,44] and 3-hydroxytetrahydropyran [45]. The NCI analysis, on the other hand, detects a small attractive interaction which appears as a blue region on the isosurface between NH and F in Figure 4. The red part, in contrast, is a consequence of repulsive interactions from the formation of a 5-membered ring through this weak NH $\cdots$ F contact. This interaction does not meet the typical criteria to be unambiguously classified as a hydrogen bond using international conventions [46] as for example, the angle  $\angle$ N-H-F is only 100° which is below the lower limit of the IUPAC definition of a hydrogen bond (110°) [46]. In 2-fluorophenol [32], the alcohol analog of 2-FAN, the interaction angle  $\angle$ O-H-F is 112.3° and in this case, the NBO results showed charge transfer from the fluorine lone pair to the antibonding  $\sigma^*(\text{OH})$  orbital (3.1 kJ/mol) which is consistent with the hydrogen bond descriptor. Nonetheless, the experimental determination that the amine group is twisted in 2-FAN supports the presence of a weak non-covalent interaction and we welcome further experimental studies that may shed light on this matter.

## CONCLUSIONS

The rotational spectra of 2-FAN and its heavy atom  $^{13}\text{C}$  and  $^{15}\text{N}$  analogues have been recorded and analysed to derive accurate experimental geometries using the  $r_s$ ,  $r_0$  and  $r_m^{(1)}$  methods. The results compare favourably with the B3LYP/aug-cc-pVTZ equilibrium  $r_e$  geometry and show evidence of the electron withdrawing fluorine substituent on the benzene backbone. As noted in earlier studies of 2-FAN in the far infrared [7] and microwave [9] regions, the amine group is twisted along the C-N bond to bring one of the nearest H atom closer to the ab-plane of 2-FAN to facilitate a weak interaction between the neighbouring functional groups. While too minor to be

detected by NBO or QTAIM calculations, a weak N-H...F interaction is revealed in the NCI analysis which is consistent with the experimental and quantum chemical structures of 2-FAN.

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## SUPPLEMENTARY MATERIAL

**Appendix 1:** Cartesian coordinates for the 2- Fluoroaniline (2-FAN) structures obtained at the B3LYP/aug-cc-pVTZ and MP2/cc-pVTZ level of theory.

**Appendix 2:** Kraitchman Coordinates for 2-FAN

**Appendix 3:** Assigned Transitions for the Parent and Isotopologues of 2-FAN

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## TOC Graphic

