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## Fourier Transform Microwave Spectroscopic and *Ab Initio* Study of the Rotamers of 2-Fluorobenzaldehyde and 3-Fluorobenzaldehyde

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## Abstract

The rotational spectra of 2-fluorobenzaldehyde (2-FBD) and 3-fluorobenzaldehyde (3-FBD) were recorded using Fourier transform microwave (FTMW) spectroscopy from 4 to 26 GHz. Two planar rotamers were observed for each species which correspond to structures in which the carbonyl bond is directed toward (*O-cis*) or away from (*O-trans*) the C1-C2 bond. Observation of transitions due to heavy atom isotopes ( $^{13}\text{C}$ ,  $^{18}\text{O}$ ) in natural abundance allowed derivation of the ground state effective ( $r_0$ ) structures and mass dependence ( $r_m$ ) structures for the lowest energy rotamer of 2-FBD (*O-trans*) and both rotamers of 3-FBD which compare favourably with *ab initio* estimates of the equilibrium ( $r_e$ ) geometries at the MP2/aug-cc-pVTZ level. The resultant parameters are consistent with the introduction of bond length alternation in the benzene ring which is dependent on the orientation of the aldehyde group. Careful study of the experimental structure and results of natural bond orbital (NBO) analysis do not support the presence of intramolecular hydrogen bonding as the source of its stabilization of *O-trans* 2-FBD over its *cis* counterpart. Furthermore, calculations of the interconversion pathways between rotamers suggest that despite being 9.39 kJ/mol higher in energy, the *O-cis* 2-FBD moiety is metastable in the molecular beam which has allowed the observation of its microwave spectrum for the first time.

## Introduction

The effects of fluorine substitution on the physical and chemical properties of organic compounds are of considerable interest as such species find increasing use in the development of new materials,<sup>1</sup> pharmaceuticals<sup>2</sup> and agrochemicals such as pesticide, herbicides and fungicides.<sup>3</sup> While the van der Waals radius of fluorine is similar to that of hydrogen, its electron withdrawing prowess alters the electronic properties of the parent compounds including dipole moments and molecular geometry. High resolution microwave spectroscopy is a valuable tool for probing the effects of fluorine on the electronic structure of compounds as the spectral pattern is intrinsically dependent on the molecular geometry and the species under study, seeded in a supersonic jet, is free of intermolecular forces.

In recent years, fluorinated aromatic compounds of benzene,<sup>4,5,6</sup> pyridine,<sup>7,8</sup> and benzonitrile<sup>9</sup> have served as simple prototypes to probe the geometric changes that accompany fluorination of organic compounds as only a single conformer is observed for each. As expected, the largest geometric changes were reported near the site of fluorination and these changes typically involved an increase in the ring angle at that site by 3-4° and a shortening of the adjacent C-C bonds by 0.005-0.010 Å. While a number of studies of weakly bound dimers involving small fluorinated molecules<sup>10,11,12</sup> have provided important insights into the nature of non-covalent interactions involving fluorine, the observation of these effects may be masked in

intramolecular systems as the optimal  $180^\circ$  angle for X-H...F is often unfeasible.<sup>13</sup> Despite these geometric constraints, however, recent studies of *ortho* fluorinated phenols<sup>14</sup> and thiophenols<sup>15</sup> have successfully identified subtle structural changes that are indicative of weak intramolecular forces involving F. These non-covalent interactions resulted in the stabilization of one planar conformer over the other.

Like the fluorophenols, there are two possible planar rotational isomers of 2-fluorobenzaldehyde (2-FBD) and 3-fluorobenzaldehyde (3-FBD). These differ in the orientation of the carbonyl bond of the formyl group when it is pointed toward (*O-cis*) or away from (*O-trans*) the fluorine substituent of the ring. The two rotamers have been identified by NMR,<sup>16</sup> infrared<sup>17,18</sup> and phosphorescence measurements.<sup>19,20,21</sup> From the IR spectrum of 2-FBD recorded in a cold Ar matrix, Itoh *et al.*<sup>22</sup> reported an intramolecular C-H...F hydrogen bond in the more stable *O-trans* rotamer based on observation of a blue-shift in the C-H stretching frequency of the formyl group. While counterintuitive that the C-H bond should shorten, this assignment was based on the earlier work of Pinchas<sup>23,24</sup> who investigated a series of *ortho* substituted benzaldehydes and attributed similar blue-shifts to intramolecular hydrogen bonding. While the observation of improper hydrogen bonding<sup>25</sup> has been acknowledged in the IUPAC convention for hydrogen bonding,<sup>13</sup> the claims of Pinchas have been revisited more recently using *ab initio* methods.<sup>26</sup> The authors of that study attribute the shortened C-H bond in similar compounds to a sterically induced compression of the intramolecular X-H...Y contact rather than a hydrogen bond.

In the microwave region, transitions due to both rotamers of 3-FBD were recorded in the 26.5-40 GHz region in a waveguide and based on intensity measurements, the authors estimated that the *O-cis* form was more stable by  $300\pm 200$  cal/mol.<sup>27</sup> For 2-FBD, the observed spectrum

was consistent with the presence of only the lower energy *O-trans* rotamer in the gas phase. Spectra of minor isotopologues have not been reported for either compound. By comparison, more extensive rotational spectroscopic studies have been reported for the parent benzaldehyde (BD), including transitions in the cm and mmwave range and those of minor isotopologues ( $^{13}\text{C}$ ,  $^{18}\text{O}$  and deuteration of the formyl group).<sup>28,29</sup> The geometry of BD was of interest as a potential candidate for experimental confirmation of the so-called AGIBA (Angular Group Induced Bond Alternation) effect that has been identified by quantum chemical calculations.<sup>30,31</sup> This phenomenon is predicted to be observed in substituted benzenes in which the substituent is asymmetric (formyl, methoxy, vinyl, ethyl). In such compounds, the substituent induces a C-C bond length alternation in the phenyl ring through stabilization of one Kekulé structure over another. For anisole, for example, the experimental geometry showed an average alternation in the C-C bonds of  $\sim 0.010 \text{ \AA}$ , however, the effect was determined to be too small in BD and masked by the experimental uncertainties in the bond lengths themselves.<sup>28</sup> The addition of a fluorine substituent to BD, as in the present study, affords the opportunity to explore whether an electron withdrawing group enhances the proposed AGIBA effect.

In this paper, we report the first rotational spectroscopic study of the minor isotopologues of 2-FBD and 3-FBD with the goal of establishing whether a non-covalent interaction affects the geometry of the former and whether the AGIBA effect is measurable in either. Transitions due to the minor isotopologues of *O-trans* 2-FBD ( $^{13}\text{C}$ ,  $^{18}\text{O}$ ) and both rotamers of 3-FBD ( $^{13}\text{C}$ ) were assigned and analysed and the parent compounds were observed in the region below 26 GHz for the first time. In addition, we report the first gas phase spectroscopic observation of the higher energy *O-cis* rotamer of 2-FBD. The experimental rotational constants determined for the full set of isotopologues of 2-FBD (*O-trans*) and 3-FBD (both) were used to derive the  $r_0$  and  $r_m$

geometries of the heavy atom BD backbones for comparison with the equilibrium geometry ( $r_e$ ) calculated at the MP2/aug-cc-pVTZ level. Comparison of the C-C bond lengths in the phenyl ring of each shows a dependence on the orientation of the asymmetric formyl group which is consistent with the AGIBA effect. Finally, the experimental geometries are considered along with the results of a natural bond orbital (NBO) analysis to investigate whether intramolecular hydrogen bonding stabilizes the *O-trans* 2-FBD rotamer relative to the *O-cis* species.

### Experimental Section

2-FBD (97%) and 3-FBD (98%+) are commercially available from ACROS Organics and were used without further purification in this study. As both samples are liquid at room temperature, they were added to glass bubblers individually and neon was used to carry the chemicals to the spectrometers with a stagnation pressure of  $\sim 1$  bar. The sample mixtures were expanded into the high vacuum chamber of the microwave spectrometers through a pulsed nozzle to create a supersonic jet.

The experiments were carried out with both the chirped pulse FTMW spectrometer and the Balle-Flygare FTMW spectrometer which have been previously described.<sup>32,33</sup> The chirped pulse FTMW spectrometer was first used to record the broadband spectra in segments of 2 GHz from 8 to 18 GHz. Based on these survey spectra, transitions corresponding to two different rotamers were identified for both 2- and 3-FBD including those attributed to minor isotopologues. Next, spectral lines for individual rotational transitions were collected in the range of 4-26 GHz with higher resolution and sensitivity using the Balle-Flygare FTMW spectrometer. Spectra recorded with the cavity-based instrument have linewidths (FWHM) of  $\sim 7$  kHz and individual frequencies are typically measured to within  $\pm 1$  kHz.

## Computational Details

Although the rotational spectra of the parent species of *O-trans* 2-FBD and both 3-FBD rotamers were studied earlier,<sup>27</sup> *ab initio* calculations were carried out in this work to investigate the energy difference between the rotamers for 2-FBD and 3-FBD. Geometry optimizations were conducted at the MP2/aug-cc-pVTZ level using Gaussian 09 software along with the NBO (natural bond orbital) keyword.<sup>34</sup> The resulting equilibrium structures are shown in Figure 1 in their principal inertial axis systems; the internal coordinates along with those of the parent benzaldehyde (BD) are tabulated as Supplementary data to this article. To estimate the conversion barrier between the rotamers, energy scans for the C2-C1-C7-O dihedral angles were run at the MP2/6-311++G(2d,2p) level with a step size of 10° from the *O-cis* to *O-trans* geometry for both 2-FBD and 3-FBD as shown in Figure 2. At each dihedral angle of C2-C1-C7-O, all other geometric parameters were relaxed.

## Results

### **I. 2-fluorobenzaldehyde (2-FBD)**

According to *ab initio* calculations, the energy difference between the *O-trans* and *O-cis* rotamer of 2-FBD is 9.39 kJ/mol and thus, the relative population of the higher energy *O-cis* geometry is predicted to be ~2.3% at room temperature. The barrier to rotate the formyl group out of the plane to convert between rotamers is 19.52 kJ/mol or ~1632 cm<sup>-1</sup> from the higher energy conformer. Previous microwave studies on a range of species seeded in a supersonic jet provide a useful rule of thumb that barriers greater than 4.8 kJ/mol (~400 cm<sup>-1</sup>) allow observation of the metastable species while those with smaller barriers allow relaxation to the

lowest energy conformer.<sup>35</sup> Based on the high conversion barrier in 2-FBD, the *O-cis* rotamer will survive in the supersonic jet.

In the rotational spectrum of 2-FBD, the *O-trans* species was observed to be the dominant isomer as expected. In addition to expanding the list of observed transitions for the parent species to a new region, spectra from seven <sup>13</sup>C singly substituted species and the <sup>18</sup>O substituted species were also assigned in natural abundance as seen in Figure 3. In total, 124 new *a*-type transitions were collected for the parent isotopologue of *O-trans* 2-FBD while *b*-type transitions were not observed due to the small dipole component along this axis:  $|\mu_a|=3.87$  D and  $|\mu_b|=0.17$  D (MP2/aug-cc-pVTZ). Following assignment of the lower energy isomer, the *O-cis* rotamer was identified for the first time by assignment of 22 *a*-type and three *b*-type transitions in accordance with its calculated dipole components:  $|\mu_a|=4.75$  D and  $|\mu_b|=2.14$  D and magnitude of the rotational constants. The intensity of observed *a*-type transitions of *O-cis* 2-FBD was ~1-2% that of the dominant *O-trans* 2-FBD rotamer.

The transition frequencies were fit using Pickett's SPFIT program (Watson's A-reduced Hamiltonian I<sup>r</sup> representation).<sup>36</sup> The resulting rotational and centrifugal distortion constants are shown in Table 1 along with the *ab initio* parameters for comparison. For all minor isotopologues of the *O-trans* conformer, the centrifugal distortion constant  $\Delta_K$  was fixed at the value obtained for the parent species. The  $\Delta_K$  was not well-determined for *O-cis* conformer and was subsequently excluded from the fit. In the end, the Watson Hamiltonian provided a good model for the energy levels of 2-FBD as the rms error of each fit was below 1 kHz.

## II. 3-fluorobenzaldehyde (3-FBD)



The parent transitions of both the *O-cis* and *O-trans* rotamers were readily observed as the energy difference predicted via *ab initio* calculations in Figure 2 is small (0.87 kJ/mol) and the conversion barrier is 31.91 kJ/mol or  $\sim 2667\text{ cm}^{-1}$ . For *O-cis* 3-FBD, 26 *a*-type and 55 *b*-type transitions were collected for the parent which is consistent with its dipole moment components from *ab initio* calculations:  $|\mu_a|=1.58\text{ D}$  and  $|\mu_b|=3.90\text{ D}$  and rotational constants. For the *O-trans* conformer, 39 new *a*-type transitions and 10 new *b*-type transitions were also assigned as expected based on the previous study in which the dipole components were estimated from benzaldehyde and fluorobenzene as  $|\mu_a|=1.81\text{ D}$ ,  $|\mu_b|=0.52\text{ D}$ .<sup>27</sup> These values are consistent with the observed intensities in this work but inconsistent with the initially estimated dipole moment ( $|\mu_a|=2.18\text{ D}$ ,  $|\mu_b|=0.08\text{ D}$ ) at the MP2/aug-cc-pVTZ level. Further investigation revealed that the dipole components of *O-trans* 3-FBD are surprisingly basis-set dependent due to a slight rotation in the inertial axes. The cc-pVTZ basis set, for example, providing an estimate ( $|\mu_a|=2.10\text{ D}$ ,  $|\mu_b|=0.33\text{ D}$ ) that is more consistent with experiment. In addition to the expanded line list for the parent 3-FBD rotamers, analogous transitions due to seven <sup>13</sup>C singly substituted species were identified for each as shown in Table 2 and Table 3. As fewer transitions were collected for minor isotopologues, only the rotational constants and the  $\Delta J$  centrifugal distortion constants were determined with the other centrifugal distortion constants held fixed at the value of the parent species. The rms error of each fit was below 1 kHz suggesting that the model Hamiltonian provides a good representation of various species.

### III. Structural Determination

Like the benzaldehyde (BD) parent, the fluorinated analogs studied in this work have planar equilibrium structures as evidenced by their small inertial defects ( $\Delta I = I_c - I_a - I_b$ ): -0.111

amu $\cdot\text{\AA}^2$  (*O-trans* 2-FBD), -0.226 amu $\cdot\text{\AA}^2$  (*O-cis* 2-FBD), -0.113 amu $\cdot\text{\AA}^2$  (*O-trans* 3-FBD) and -0.075 amu $\cdot\text{\AA}^2$  (*O-cis* 3-FBD). The small negative values are consistent with contributions from low frequency out-of-plane motions such as the torsion of the formyl substituent which is only about 111 cm<sup>-1</sup> in the parent BD.<sup>37</sup> The observation of rotational transitions for several minor isotopologues of *O-trans* 2-FBD, *O-trans* 3-FBD and *O-cis* 3-FBD provides a means by which the geometry of the heavy atom backbone of each can be derived from their respective experimental rotational constants. For the *O-cis* 2-FBD moiety, only the spectrum of the parent was observed and consequently, a structural estimate was not possible.

As a first approximation, the molecules were treated as planar and their substitution ( $r_s$ ) structures were estimated via Kraitchman analysis<sup>38</sup> using Kisiel's KRA program.<sup>39</sup> As the Kraitchman equations provide only absolute values of the coordinates, *ab initio* results were used in tandem to establish the relative sign of the coordinates. The coordinates and their respective Costain errors<sup>40</sup> were then used to calculate the geometry of the carbon backbone of each using the EVAL routine.<sup>39</sup> As transitions for the <sup>18</sup>O isotopologue were observed for *O-trans* 2-FBD, the C7-O bond length and  $\angle\text{O-C7-C1}$  angle were also estimated for this species. A summary of the resulting  $r_s$  coordinates is provided as supplemental data to this article. As reported for BD itself, the derivation of  $r_s$  structures is fraught with pitfalls as atoms lying close to inertial axes have imaginary or very small coordinates with correspondingly large Costain errors. This was indeed the case for one or two atoms in each of the three FBD species. This led to poorly determined geometric parameters which were not in close agreement with *ab initio* results and are themselves summarized in Tables 4 and 5 under the  $r_e$  headings.

Ground state effective ( $r_0$ ) structures are less prone to issues arising from small coordinates and as rotational constants from a large number of isotopologues were available

from this study, this least squares fitting method may, in principle, be used to derive the heavy atom skeletons of the FBD rings. For *O-trans* 2-FBD, 27 rotational constants were available to fit the 13 independent parameters that define the phenyl ring and carbonyl group using Kisiel's STRFIT program.<sup>39</sup> For the rotamers of 3-FBD, transitions due to the <sup>18</sup>O isotopologues were not observed resulting in three fewer rotational constants as input to the least squares fit. Internal coordinates involving hydrogen and fluorine were extracted from the *ab initio* calculations and held fixed. For all three FBD species, the fits did not converge or resulted in large uncertainties in parameters when all three rotational constants were included for each isotopologue as expected for planar molecules. If only two constants (A, B) were chosen for each species, the fits converged, however, and the resulting geometric parameters are given in Tables 4 and 5 for 2-FBD and 3-FBD, respectively, under the  $r_0$  headings. The  $1\sigma$  uncertainties were too large to draw meaningful comparisons of the bond lengths within the phenyl ring of the FBD compounds and this is presumably a consequence of their non-zero inertial defects. A similar result was reported for the  $r_0$  analysis of BD.<sup>28</sup>

To improve the structural estimates by addressing the out-of-plane vibrational contributions, the mass dependence structures ( $r_m$ ) were derived as described by Watson.<sup>41</sup> In this case, all three rotational constants of each isotopologue were included as input to the STRFIT program and the Laurie parameter  $\delta_H$  was fixed at 0.01 Å for each CH bond following reference 28. Although various combinations of the  $c_\alpha$  model parameter were tested, the condition  $c_a=c_b=c_c$  was ultimately used as reported for BD itself as this condition yielded the lowest uncertainty in this correction parameter. In order to allow direct comparison of the geometries of 2-FBD and 3-FBD with the unsubstituted parent, the same procedure was followed to obtain an updated  $r_m$  geometry for BD using input from the MP2/aug-cc-pVTZ calculation (this work)

rather than that from the basis set (6-31G(d,p) reported earlier.<sup>28</sup> The results are summarized in Tables 4 and 5 under the  $r_m$  headings.

## Discussion

The spectroscopic constants obtained from fitting the rotational spectra of 2-FBD and 3-FBD are well-determined and in good agreement with *ab initio* estimates from MP2/aug-cc-pVTZ calculations for the parent species as summarized in Tables 1-3. Comparison with literature values for *O-trans* 2-FBD, *O-trans* 3-FBD and *O-cis* 3-FBD<sup>27</sup> reveals that the rotational and centrifugal distortion parameters are more precisely determined in this work due to the higher resolution of FTMW spectroscopy. In the earlier waveguide-based study, line positions were determined to within ~50 kHz and consequently, the distortion constants were not well-determined leading to less precision in the overall fit. Despite extensive searching, the authors did not observe transitions attributable to higher energy *O-cis* 2-FBD and concluded that it was not detectable due to low abundance of this rotamer in the gas phase.<sup>27</sup> In the present study, rotational transitions for this species are reported for the first time and the intensities are ~1-2% that of *O-trans* 2-FBD. Using the calculated  $\mu_a$  values, the relative intensity should be ~2.5% suggesting a small discrepancy in the calculated dipole components or in the predicted energy difference (9.39 kJ/mol) of the two rotamers. For 3-FBD, transitions of both isomers were readily observed as the *O-cis* moiety is calculated to be only 0.87 kJ/mol (0.21 kcal/mol) more stable. This prediction is in excellent agreement with the results from integrated intensities of the assigned transitions  $300 \pm 200$  cal/mol.<sup>27</sup>

The experimental geometries ( $r_0$  and  $r_m$ ) derived from the rotational constants of 2-FBD and 3-FBD are summarized in Tables 4 and 5 along with the *ab initio* derived structures ( $r_e$ ).

Comparison of the bond lengths and angles shows no significant difference in the values obtained from the  $r_0$  and  $r_m$  methods for a given rotamer, however, the  $1\sigma$  uncertainties in the  $r_m$  fit were smaller. The similarity of results obtained from the two fitting methods despite the exclusion of the C rotational constants from the  $r_0$  analysis suggests that contributions from out-of-plane vibrational motions (that give rise to the non-zero inertial defects) average out to some extent but may be serendipitous. In principle, the  $r_m$  parameters derived from all rotational constants should account for such vibrational effects and parameters derived from this method have been shown to closely match equilibrium geometries for small molecules and are thus expected to be more accurate.<sup>41</sup> Comparison of the  $r_m$  and  $r_e$  geometries in Tables 4 and 5 shows that many parameters match the theoretical estimate to within  $1\sigma$  uncertainties. For bond lengths, the greatest discrepancy is seen in the C1-C7 bonds which are 3-4 $\sigma$  longer (0.01-0.014 Å) than predicted by the *ab initio* results for all species including the parent BD. In the earlier study of BD, this was attributed to deficiencies in the calculated electron density at C7 as the calculated C1-C7 and C7-O bond lengths deviated from gas phase electron diffraction and microwave results.<sup>28</sup> With the larger basis set employed in this work however, the calculated C7-O bond length (1.219 Å) is now in good agreement with experiment for BD. Interestingly, the discrepancy with C1-C7 remains but closer inspection of Tables 4 and 5 shows that certain C-C bonds in the phenyl ring involving C1 are 2-3 $\sigma$  shorter than the  $r_e$  estimates. In particular, for all four species, it is the C-C bond lying *trans* to the C=O group that is overestimated in the *ab initio* calculation (C1-C2 for BD and the two O-*trans* species; C6-C1 for the O-*cis* species) suggesting that the delocalization of electron density from C=O into the phenyl ring to stabilize one Kekulé structure over the other is not fully captured at this level of theory.

The dominance of the resonance structure in which the C=O group is *trans* to the double bond of the phenyl ring should result in the introduction of a bond length alternation pattern in the ring (AGIBA effect). In the case of BD and anisole in reference 28, bond length alternation was assessed by looking at pairs of bonds across the ring (C2-C3 and C5-C6, C3-C4 and C4-C5). In the case of BD, those bonds are the same length to within  $1\sigma$  uncertainties (also in this work) but in anisole, they differed by as much as 0.015 Å (with typical  $1\sigma$  uncertainty in each bond of  $\sim 0.003$ -4 Å). For the monofluorinated versions in this study, the fluorine substituent itself induces structural changes which will further mask any AGIBA influence from the formyl group and in particular, in the bonds adjacent to the site of fluorination. In 2-FBD, that leaves one pair of bonds (C3-C4 and C4-C5) as shown in Figure 4 from which to assess whether the carbonyl group has an effect on the electronic structure of the phenyl moiety. Using the  $r_m$  parameters in Table 4 which are expected to be more accurate by accounting for vibrational effects to some extent, the C3-C4 bond is 0.011 Å shorter than the C4-C5 bond and this difference falls outside of the stated uncertainties. Although small (and not mirrored in the  $r_0$  results which have larger uncertainties), this change is similar in magnitude to that reported for anisole and thus supports the presence of AGIBA. If this observation is real, this would imply that the inclusion of the electron withdrawing F substituent on the ring enhances the AGIBA effect of the formyl group which is too small to be observed in BD itself.

The effect of fluorination on the ring geometry itself has been investigated in a number of related compounds and can be elucidated by comparing the geometry of the BD backbone with that of the fluorinated analogues in Tables 4 and 5. The C-C-C angle increases at the site of fluorination by  $\sim 3^\circ$  which is similar to the changes reported in fluorine-substituted benzenes,<sup>5,6</sup> pyridines,<sup>7,8</sup> benzonitriles,<sup>9</sup> phenols<sup>14</sup> and thiophenols<sup>15</sup> via FTMW spectroscopy. This angle

opening is consistent with a change in the hybridization of the substituted carbon atom as the orbital directed along the polar C-F bond has more p-character. This, in turn, increases the s-character of the C-C bonds within the aromatic ring leading to a larger C-C-C angle. Comparison of the hybridization at C2 or C3 in the NBO analysis shows that the increased p-character along the C-F bond is typically ~5-6% for the FBD moieties compared with the C-H bond in BD. A second effect of fluorination is the typical observation that the C-C bond lengths involving the substituted carbon are shortened by 0.005-0.010 Å relative to the parent species. In the singly-substituted fluorobenzonitriles and thiophenols, this was attributed to the strong electron-withdrawing character of fluorine which induces a positive natural charge on the substituted carbon and strengthens the bond with neighbouring carbon atoms which bear partial negative charges. The natural charges of the affected atoms in *O-trans* 2-FBD (*C1*: -0.281, *C2*: 0.504, *C3*: -0.289), *O-trans* 3-FBD (*C2*: -0.221, *C3*: 0.441, *C4*: -0.231) and *O-cis* 3-FBD (*C2*: -0.203, *C3*: 0.445, *C4*: -0.228) are consistent with the shortening of these bonds by 0.005-0.014 Å relative to the parent BD (*C1*: -0.207, *C2*: -0.135, *C3*: -0.209, *C4*: -0.147).

While it is difficult to partition the effects of the formyl and fluorine substituents on the ring geometry, the asymmetry of the bond shortening about C3 in 3-FBD may provide additional insight. Compared to the geometry of BD, the greatest effect of fluorination is seen is the shortening of C2-C3 for the *cis* rotamer (-0.022 Å) with a smaller change in C3-C4 (-0.005 Å) while the reverse is seen for the *trans* rotamer (C3-C4: -0.012 Å, C2-C3: -0.006 Å). For comparison, the bond shortenings reported for fluorination at the *meta* carbon in pyridine,<sup>7</sup> benzonitrile<sup>9</sup> and phenol<sup>14</sup> were fairly symmetric. The asymmetry observed in 3-FBD is consistent with a compounding of the effects of fluorination and the introduction of bond length

alternation (AGIBA) based on the orientation of the formyl group as seen from the resonance structures in Figure 5.

Finally, while an infrared study of 2-FBD has identified an intramolecular hydrogen bond involving fluorine as a source of stabilization of the *trans* rotamer,<sup>22</sup> the experimental geometry extracted from the microwave spectrum of O-*trans* 2-FBD does not provide support for this. If a non-covalent interaction is present, one would expect subtle geometry changes involving the formyl and fluorine substituents. For example, in *cis*-2-fluorophenol,<sup>14</sup> the CF and CO bonds were each tilted by  $\sim 2^\circ$  closer to each other relative to the analogous bonds in phenol and a stabilizing interaction (3.05 kJ/mol) was seen in the second order perturbation theory energy corrections in the NBO analysis. This arises from donation of electron density from fluorine into the  $\sigma^*(\text{OH})$  orbital and is similar in magnitude and character to that reported for intramolecular interactions in other rings such as 2-cyanophenol (3.01 kJ/mol).<sup>42</sup> The NBO analyses of BD and its fluorinated analogues in this work does not yield such an interaction for O-*trans* 2-FBD. From the experimentally-derived structural parameters, comparison of the angles of the C1-C7 bond to the phenyl ring shows that the formyl group actually tilts  $0.6^\circ$  further from the C-F bond in O-*trans* 2-FBD than the C-H bond in BD. This is likely to accommodate the larger van der Waals radius of F. Furthermore, the F-H separation derived from the experimental geometry of O-*trans* 2-FBD is 2.45 Å which is close to the sum of the van der Waals radii (2.47 Å) and significantly larger than reported for *cis*-2-fluorophenol (2.219 Å) which involves a non-covalent intramolecular interaction. Without geometry changes to support an interaction, we thus conclude that the energy difference between the two rotamers is better explained by the destabilization of the O-*cis* structure that arises from the natural charges on O (-0.588) and F (-0.378) in closer proximity.



## Conclusions

The rotational spectra of 2-FBD and 3-FBD are reported and confirm the presence of two planar rotamers for each which differ by the orientation of the formyl group. The *O-cis* rotamer of 2-FBD has been experimentally observed for the first time via microwave spectroscopy. Despite being 9.39 kJ/mol higher in energy than its *trans* counterpart (MP2/aug-cc-pVTZ), it is metastable in the cold supersonic jet as the barrier to interconversion is too high. The effective mass dependence structures ( $r_m$ ) were derived using the rotational constants of observed isotopologues for *O-trans* 2-FBD and for both rotamers of 3-FBD. The results are generally consistent with the *ab initio*  $r_e$  geometry except for the C1-C7 bond lengths and the C-C bond lengths in the phenyl ring that fall *trans* to the carbonyl group of the formyl substituent. This suggests that the  $r_e$  geometry has not fully captured the stabilization of one resonance contributor over the other to enhance conjugation with the C=O moiety. This preference for one Kekulé structure should manifest as a bond length alternation pattern in the C-C bonds of the phenyl ring but is interrupted by the presence of the fluorine substituent in the *ortho* or *meta* positions which provide additional structural perturbations. While previous spectroscopic studies suggest that an intramolecular interaction between the C=O and C-F moieties is responsible for stabilization of *O-trans* 2-FBD over its *cis* analogue, there is no evidence of this in the NBO calculations or in the  $r_m$  geometry of *O-trans* 2-FBD. The higher energy of the *O-cis* rotamer is instead explained using an electrostatic argument created by repulsion between the O and F atoms on neighbouring substituents.

## Supporting Information

Equilibrium structures of BD, 2-FBD and 3-FBD (Tables S1-S5)

Assigned transitions for 2-FBD and 3-FBD and their minor isotopologues (Tables S6-S31)

$R_s$  coordinates for *O-trans* 2-FBD and 3-FBD (Tables S32-S34)

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**Table 1.** Ground State Spectroscopic Constants of *O-trans* 2-Fluorobenzaldehyde Including its  $^{13}\text{C}$  and  $^{18}\text{O}$  Isotopologues and Parent Species of *O-cis* 2-Fluorobenzaldehyde

	<i>O-trans</i> 2-FBD	$^{13}\text{C1}$	$^{13}\text{C2}$	$^{13}\text{C3}$	$^{13}\text{C4}$	$^{13}\text{C5}$	$^{13}\text{C6}$	$^{13}\text{C7}$	$^{18}\text{O}$	<i>O-cis</i> 2-FBD
Rotational Constants <sup>a</sup> /MHz										
A	2567.59948(4)	2567.4848(6)	2557.2337(7)	2561.9733(4)	2562.3735(7)	2530.6969(6)	2540.6856(5)	2567.3102(5)	2555.4732(6)	3066.639(1)
B	1560.86522(1)	1559.7432(1)	1559.9980(1)	1545.3562(1)	1536.8745(1)	1552.1750(1)	1560.9019(1)	1542.7070(1)	1489.4772(1)	1474.6519(1)
C	970.95026(1)	970.50186(6)	969.12930(7)	964.13220(5)	960.87888(8)	962.29076(7)	967.09177(6)	963.85433(6)	941.19839(5)	996.24609(7)
Centrifugal Distortion Constants <sup>b</sup> /kHz										
$\Delta_J$	0.05923(9)	0.060(1)	0.059(2)	0.060(1)	0.060(1)	0.061(1)	0.058(1)	0.056(1)	0.0525(8)	0.042(1)
$\Delta_{JK}$	0.1329(3)	0.132(8)	0.13(1)	0.127(6)	0.08(1)	0.12(1)	0.140(7)	0.129(7)	0.168(6)	0.257(4)
$\Delta_K$	0.130(1)	[0.130]	[0.130]	[0.130]	[0.130]	[0.130]	[0.130]	[0.130]	[0.130]	\
$\delta_J$	0.02189(4)	0.0226(6)	0.022(1)	0.0230(7)	0.0229(8)	0.0231(6)	0.0215(6)	0.0206(6)	0.0187(3)	0.0112(5)
$\delta_K$	0.1585(3)	0.16(1)	0.16(1)	0.161(6)	0.12(1)	0.15(1)	0.15(1)	0.13(1)	0.163(9)	0.14(1)
# lines	124	25	25	28	28	25	29	28	21	25
rms /kHz	0.48	0.52	0.55	0.41	0.69	0.57	0.54	0.54	0.47	0.62

<sup>a</sup>Calculated rotational constants (MP2/aug-cc-pVTZ) for *O-trans* 2-FBD: A = 2566.2 MHz, B = 1564.3 MHz, C = 971.9 MHz; for *O-cis* 2-FBD: A = 3068.5 MHz, B = 1476.8 MHz, C = 997.0 MHz; Rotational constants from ref. 27 for *O-trans* 2-FBD: A = 2567.609(3) MHz, B = 1560.8694(9) MHz, C = 970.954(1) MHz

<sup>b</sup> $\Delta_K$  centrifugal distortion constant for the minor isotopologues of *O-trans* 2-FBD was held fixed to that of the parent;  $\Delta_K$  for *O-cis* 2-FBD was not included in the fit

**Table 2.** Ground State Spectroscopic Constants of O-*cis* 3-Fluorobenzaldehyde and its <sup>13</sup>C Isotopologues

	parent	13C-1	13C-2	13C-3	13C-4	13C-5	13C-6	13C-7
Rotational Constants <sup>a</sup> /MHz								
<i>A</i>	2919.25087(6)	2917.6533(1)	2909.0616(1)	2914.8384(1)	2909.58802(6)	2863.32738(5)	2875.9044(1)	2919.14712(9)
<i>B</i>	1269.70085(4)	1267.1681(3)	1269.76281(1)	1264.1835(2)	1258.93513(7)	1266.7247(1)	1269.1589(1)	1252.1191(1)
<i>C</i>	884.96162(2)	883.5857(4)	884.0559(1)	881.8747(2)	878.83993(8)	878.3215(1)	880.67368(9)	876.3768(1)
Centrifugal Distortion Constants <sup>b</sup> /kHz								
$\Delta_J$	0.0649(3)	0.074(6)	0.069(1)	0.069(2)	0.0633(7)	0.068(1)	0.0651(9)	0.065(1)
$\Delta_{JK}$	-0.179(1)	[-0.179]	[-0.179]	[-0.179]	[-0.179]	[-0.179]	[-0.179]	[-0.179]
$\Delta_K$	0.640(3)	[0.640]	[0.640]	[0.640]	[0.640]	[0.640]	[0.640]	[0.640]
$\delta_J$	0.0236(1)	[0.0236]	[0.0236]	[0.0236]	[0.0236]	[0.0236]	[0.0236]	[0.0236]
$\delta_K$	0.104(1)	[0.104]	[0.104]	[0.104]	[0.104]	[0.104]	[0.104]	[0.104]
# lines	81	7	9	7	13	9	17	18
RMS/kHz	0.81	0.55	0.70	0.51	0.51	0.36	0.90	0.95

<sup>a</sup>Calculated rotational constants (MP2/aug-cc-pVTZ) for O-*cis* 3-FBD: *A* = 2921.7 MHz, *B* = 1271.7 MHz, *C* = 886.0 MHz;

Rotational constants from ref. 27: *A* = 2919.255(2) MHz, *B* = 1269.697(2) MHz, *C* = 884.964(2) MHz

<sup>b</sup>Centrifugal distortion constants (except  $\Delta_J$ ) for the minor isotopologues were held fixed to the parent values

**Table 3.** Ground State Spectroscopic Constants of *O-trans* 3-Fluorobenzaldehyde and its <sup>13</sup>C Isotopologues

	parent	13C-1	13C-2	13C-3	13C-4	13C-5	13C-6	13C-7
Rotational Constants <sup>a</sup> /MHz								
<i>A</i>	3657.2024(4)	3656.567(6)	3633.151(3)	3654.609(4)	3628.331(3)	3570.749(5)	3618.057(5)	3639.224(4)
<i>B</i>	1114.78543(6)	1113.04418(9)	1114.61702(6)	1109.1313(1)	1108.1248(1)	1114.2068(1)	1113.3613(1)	1103.2535(1)
<i>C</i>	854.52291(4)	853.4669(2)	853.1059(1)	851.0561(1)	849.0324(1)	849.3776(1)	851.5353(2)	846.7620(1)
Centrifugal Distortion Constants <sup>b</sup> /kHz								
$\Delta_J$	0.0237(3)	0.024(1)	0.023(1)	0.025(1)	0.025(1)	0.022(1)	0.021(1)	0.021(1)
$\Delta_{JK}$	0.124(1)	[0.124]	[0.124]	[0.124]	[0.124]	[0.124]	[0.124]	[0.124]
$\delta_J$	0.0061(2)	[0.0061]	[0.0061]	[0.0061]	[0.0061]	[0.0061]	[0.0061]	[0.0061]
$\delta_K$	0.092(8)	[0.092]	[0.092]	[0.092]	[0.092]	[0.092]	[0.092]	[0.092]
# lines	49	6	9	8	9	8	10	9
RMS/kHz	0.50	0.36	0.40	0.63	0.56	0.67	0.83	0.77

<sup>a</sup>Calculated rotational constants (MP2/aug-cc-pVTZ) for *O-trans* 3-FBD: *A* = 3668.1 MHz, *B* = 1115.7 MHz, *C* = 855.5 MHz;

Rotational constants from ref. 27: *A* = 3657.169(5) MHz, *B* = 1114.781(2) MHz, *C* = 854.530(2) MHz

<sup>b</sup>Centrifugal distortion constants (except  $\Delta_J$ ) for the minor isotopologues were held fixed to the parent values;  $\Delta_K$  was not included in the fit

**Table 4.** Equilibrium ( $r_e$ ) (MP2/aug-cc-pVTZ) Ground State Effective ( $r_0$ )<sup>a</sup> and Mass Dependence ( $r_m$ ) Structural Parameters (Bond Lengths in Å, Angles in Degrees) Determined for Benzaldehyde<sup>b</sup> and 2-Fluorobenzaldehyde.

	Benzaldehyde <sup>a</sup>		O- <i>trans</i> -2FBD			O- <i>cis</i> -2FBD
	$r_e$	$r_m^{(1)}$	$r_e$	$r_0$	$r_m^{(1)}$	$r_e$
C1-C2	1.396	1.389(4)	1.393	1.387(11)	1.375(8)	1.398
C2-C3	1.393	1.400(3)	1.385	1.387(4)	1.389(3)	1.386
C3-C4	1.394	1.395(3)	1.392	1.395(6)	1.390(4)	1.393
C4-C5	1.397	1.399(2)	1.397	1.400(4)	1.401(3)	1.394
C5-C6	1.390	1.399(4)	1.388	1.402(10)	1.398(8)	1.389
C6-C1	1.398	1.390(5)	1.400	1.400(14)	1.404(10)	1.400
C1-C7	1.477	1.492(3)	1.480	1.492(7)	1.494(4)	1.479
C7-O	1.219	1.212(2)	1.220	1.219(10)	1.214(8)	1.216
C7-H	1.106	1.100(3)	1.099			1.107
$\angle(\text{C1-C2-C3})$	120.0	119.5(2)	122.5	122.7(5)	122.6(3)	121.7
$\angle(\text{C2-C3-C4})$	119.7	119.6(1)	118.5	118.2(3)	118.3(2)	119.3
$\angle(\text{C3-C4-C5})$	120.3	120.3(1)	120.5	120.6(1)	120.6(1)	120.4
$\angle(\text{C4-C5-C6})$	120.1	120.1(1)	119.9	120.0(2)	119.9(1)	119.4
$\angle(\text{C5-C6-C1})$	119.6	118.9(2)	120.6	119.8(2)	119.6(4)	121.4
$\angle(\text{C6-C1-C2})$	120.3	121.5(3)	118.1	118.8(6)	119.0(4)	117.8
$\angle(\text{C2-C1-C7})$	119.1	118.6(3)	121.5	121.4(11)	121.9(8)	124.5
$\angle(\text{C1-C7-O})$	124.6	124.3(2)	123.0	122.4(11)	123.2(8)	126.3
$\angle(\text{C1-C7-H})$	114.8	115.4(2)	116.1			112.9
$c_\alpha$ ( $\text{u}^{1/2} \text{Å}$ )		0.0155(3)			0.0121(3)	
$\sigma_{\text{fit}}$ ( $\text{u} \text{Å}^2$ )		0.0034		0.0056	0.0046	

<sup>a</sup>For the  $r_0$  fit, only A, B constants were used for each isotopologue.

<sup>b</sup>Rotational constants (A, B, C) from ref. 28 and 29. Note that the numbering around the ring is reversed from ref. 28 for direct comparison with the O-*trans* species here. For example, C1-C6 (this work) = C1-C2 (ref. 28), etc.

**Table 5.** Equilibrium ( $r_e$ ) (MP2/aug-cc-pVTZ) Ground State Effective ( $r_0$ )<sup>a</sup> and Mass Dependence ( $r_m$ ) Structural Parameters (Bond Lengths in Å, Angles in Degrees) Determined for 3-Fluorobenzaldehyde.

	O- <i>trans</i> -3FBD			O- <i>cis</i> -3FBD		
	$r_e$	$r_0$	$r_m^{(1)}$	$r_e$	$r_0$	$r_m^{(1)}$
C1-C2	1.397	1.382(11)	1.378(6)	1.398	1.403(10)	1.394(7)
C2-C3	1.385	1.395(8)	1.394(5)	1.382	1.381(11)	1.378(8)
C3-C4	1.387	1.385(4)	1.383(2)	1.391	1.394(4)	1.390(3)
C4-C5	1.396	1.395(5)	1.395(4)	1.393	1.395(5)	1.395(3)
C5-C6	1.390	1.400(7)	1.398(4)	1.392	1.404(11)	1.400(7)
C6-C1	1.398	1.407(10)	1.405(7)	1.396	1.383(8)	1.385(6)
C1-C7	1.479	1.489(7)	1.490(4)	1.479	1.491(5)	1.493(3)
C7-O	1.218			1.218		
C7-H	1.106			1.105		
$\angle(\text{C1-C2-C3})$	118.4	117.9(5)	118.1(3)	117.9	117.2(5)	117.6(3)
$\angle(\text{C2-C3-C4})$	121.2	122.6(3)	122.5(2)	122.5	123.0(3)	122.9(2)
$\angle(\text{C3-C4-C5})$	118.7	118.6(2)	118.6(1)	118.8	118.5(2)	118.5(2)
$\angle(\text{C4-C5-C6})$	120.5	120.5(2)	120.5(1)	120.1	120.0(2)	119.9(2)
$\angle(\text{C5-C6-C1})$	119.5	119.0(4)	119.0(2)	119.8	119.5(5)	119.5(4)
$\angle(\text{C6-C1-C2})$	120.7	121.4(6)	121.4(3)	120.8	121.8(6)	121.6(4)
$\angle(\text{C2-C1-C7})$	118.7	118.9(10)	119.0(5)	119.9	119.2(6)	119.4(4)
$\angle(\text{C1-C7-O})$	124.4			124.4		
$\angle(\text{C1-C7-H})$	114.9			114.8		
$c_\alpha$ ( $\text{u}^{1/2} \text{Å}$ )			0.0129(4)			0.0082(4)
$\sigma_{\text{fit}}$ ( $\text{u} \text{Å}^2$ )		0.0064	0.0052		0.0077	0.0066

<sup>a</sup>For the  $r_0$  fit, only A, B constants were used for each isotopologue.

Figure 1. Principal axis systems of *O-cis* and *O-trans* 2-FBD (top); *O-cis* and *O-trans* 3-FBD (bottom).

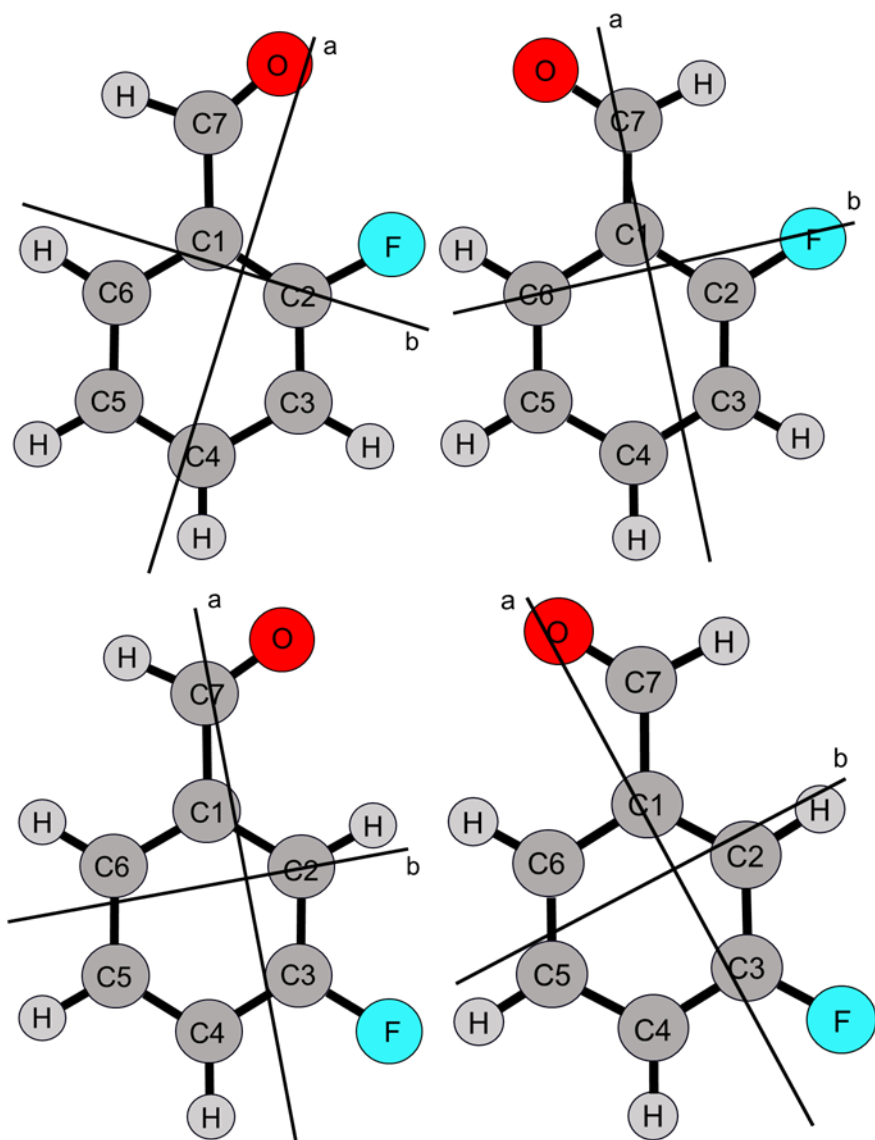




Figure 2. Calculated barrier (MP2/6-311++G(2d,2p)) for C2-C1-C7-O torsion between O-*cis* and O-*trans* rotamers of 2-FBD (top) and 3-FBD (bottom).

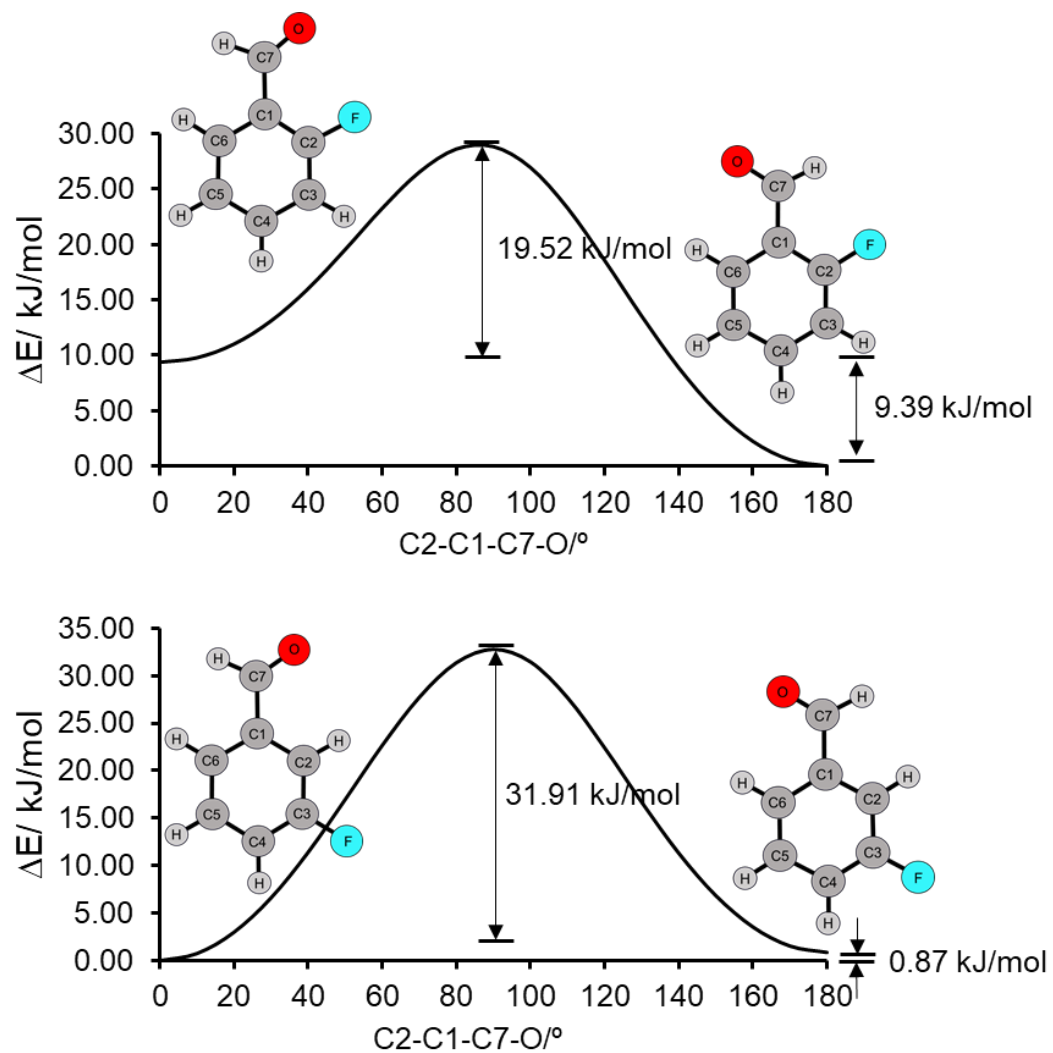


Figure 3. Portion of the cp-FTMW spectrum (1.5 million FIDs averaged) of *O-trans* 2-FBD showing the relative intensity of the  $J K_a$   $K_c$ :  $4_{14}-3_{13}$  transition for the parent, seven  $^{13}\text{C}$  isotopologues and one  $^{18}\text{O}$  isotopologue. The inset is a magnification of the bottom trace

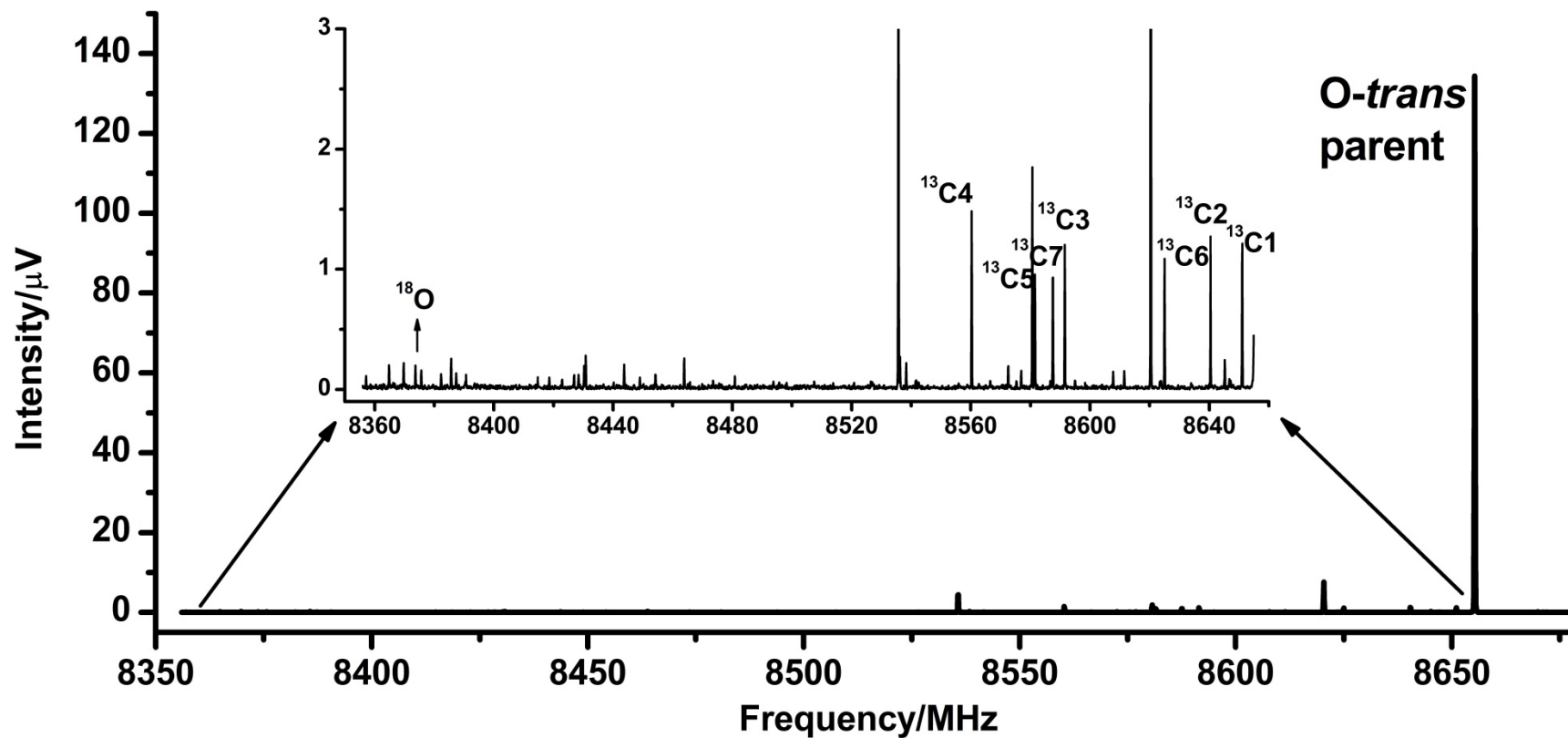


Figure 4. Comparison between the experimental  $r_m^{(1)}$  geometries of benzaldehyde (left) and *O-trans* 2-fluorobenzaldehyde (right) showing possible bond length alternation of the latter. Due to the fluorine atom on C2, only one pair of bonds in the ring (C3-C4 and C4-C5) can be compared. *Ab initio*  $r_e$  values (MP2/aug-cc-pVTZ) are also given.

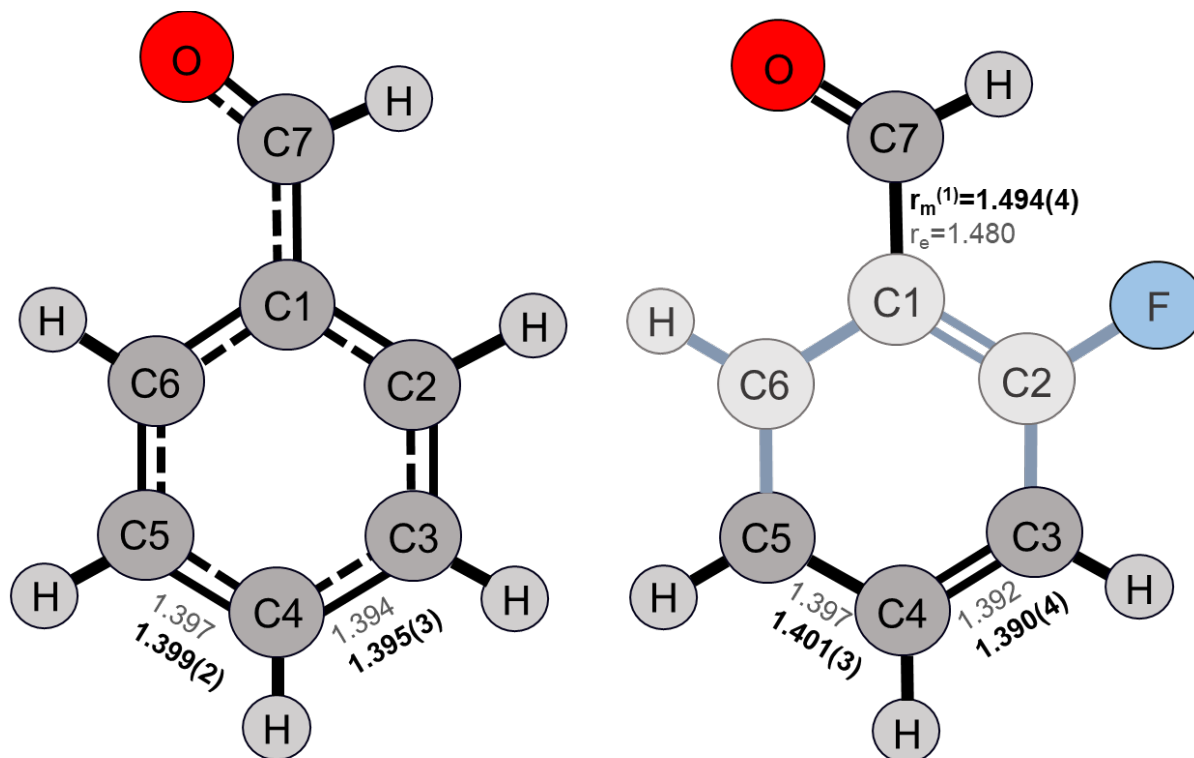
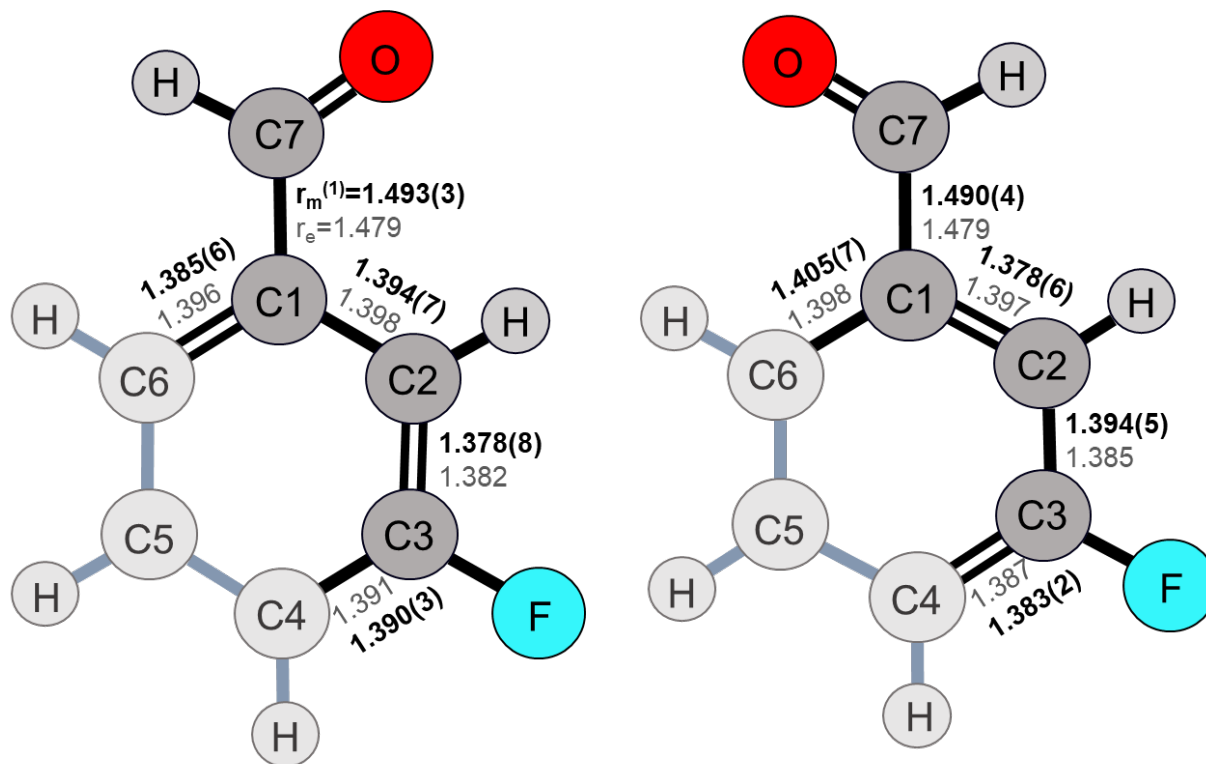
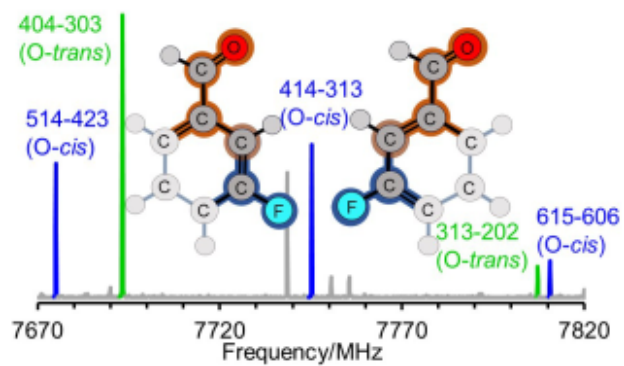


Figure 5. Comparison between the experimental  $r_m^{(1)}$  geometries of O-*cis* (left) and O-*trans* (right) 3-FBD showing asymmetric shortening of the C-C bonds adjacent to the fluorination site that is consistent with bond length alternation induced by the formyl substituent. *Ab initio*  $r_e$  values (MP2/aug-cc-pVTZ) are also given.



# TOC Graphic



## References

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- <sup>1</sup> Berger, R.; Resnati, G.; Metrangolo, P.; Weber, E.; Hulliger, J. Organic Fluorine Compounds: A Great Opportunity for Enhanced Materials Properties. *Chem. Soc. Rev.* **2011**, *40*, 3496-3508.
- <sup>2</sup> Müller, K.; Faeh, C.; Diederich, F. Fluorine in Pharmaceuticals: Looking Beyond Intuition. *Science* **2007**, *317*, 1881-1886.
- <sup>3</sup> Jeschke, P. The Unique Role of Fluorine in the Design of Active Ingredients for Modern Crop Protection. *Chem. Bio. Chem.* **2004**, *5*, 570-589.
- <sup>4</sup> Kisiel, Z.; Białkowska-Jaworska, E.; Pszczołkowski, L. The Millimeter-Wave Rotational Spectrum of Fluorobenzene. *J. Mol. Spectrosc.* **2005**, *232*, 47-54.
- <sup>5</sup> Nygaard, L.; Bojesen, I.; Pedersen, T.; Rastrup-Andersen, J. Structure of Fluorobenzene. *J. Mol. Struct.* **1968**, *2*, 209-215.
- <sup>6</sup> Doraiswamy, S.; Sharma, S. D. R<sub>0</sub> Geometries of Fluorobenzenes and Distortions in Benzene Ring Structure on Substitution. *J. Mol. Struct.* **1983**, *102*, 81-92.
- <sup>7</sup> van Dijk, C.W.; Sun, M.; van Wijngaarden, J. Microwave Rotational Spectra and Structures of 2-Fluoropyridine and 3-Fluoropyridine. *J. Phys. Chem. A* **2012**, *116*, 4082-4088.
- <sup>8</sup> van Dijk, C.W.; Sun, M.; van Wijngaarden, J. Investigation of Structural Trends in Difluoropyridine Rings Using Chirped-Pulse Fourier Transform Microwave Spectroscopy and *Ab Initio* Calculations. *J. Mol. Spectrosc.* **2012**, *280*, 34-41.
- <sup>9</sup> Kamaee, M.; Sun, M.; Luong, H.; van Wijngaarden, J. Investigation of Structural Trends in Mono-, Di-, and Pentafluorobenzonitriles Using Fourier Transform Microwave Spectroscopy. *J. Phys. Chem. A* **2015**, *119*, 10279-10292.
- <sup>10</sup> Caminati, W.; Lopez, J. C.; Alonso, J. L.; Grabow, J. -U. Weak CH...F Bridges and Internal Dynamics in the CH<sub>3</sub>F-CHF<sub>2</sub> Molecular Complex. *Angew. Chem. Int. Ed.* **2005**, *44*, 3840-3844.

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- <sup>11</sup> Leung, H. O.; Marshall, M. D.; Drake, T. L.; Pudlik, T.; Saviji, N.; McCune, D. W. Fourier Transform Microwave Spectroscopy and Molecular Structure of the 1,1-Difluoroethylene-Hydrogen Fluoride Complex. *J. Chem. Phys.* **2009**, *131*, 204301.
- <sup>12</sup> Ernst, A.; Christenholz, C. L.; Dhahir, Y. J.; Peebles, S. A.; Peebles, R. A. Alkynes as CH/ $\pi$  Acceptors: Microwave Spectra and Structures of the CH<sub>2</sub>F<sub>2</sub>•••Propyne and CH<sub>2</sub>ClF•••Propyne Dimers. *J. Phys. Chem. A* **2015**, *119*, 12999-13008.
- <sup>13</sup> Arunan, E.; Desiraju, G. R.; Klein, R. A.; Sadlej, J.; Scheiner, S.; Alkorta, I.; Clary, D. C.; Crabtree, R. H.; Dannenberg, J. J.; Hobza, P., et al. Definition of the Hydrogen Bond (IUPAC Recommendations 2011). *Pure Appl. Chem.* **2011**, *83*, 1637-1641.
- <sup>14</sup> Bell, A.; Singer, J.; Desmond, D.; Mahassneh, O.; van Wijngaarden, J. Rotational Spectra and Conformer Geometries of 2-Fluorophenol and 3-Fluorophenol. *J. Mol. Spectrosc.* **2017**, *331*, 53-59.
- <sup>15</sup> Sun, W.; van Wijngaarden, J. Structural Elucidation of 2-Fluorothiophenol From Fourier Transform Microwave Spectra and *Ab Initio* Calculations. *J. Mol. Struct.* **2017**, *1144*, 496-501.
- <sup>16</sup> Wasylishen, R.; Schaefer, T. Nuclear Magnetic Resonance Spectra, Conformations, Spin Coupling Mechanisms, and INDO Molecular Orbital Calculations for the Monofluorobenzaldehydes and Some Derivatives. *Can. J. Chem.* **1971**, *49*, 3216-3228.
- <sup>17</sup> Miller, F. A.; Fateley, W. G.; Witkowski, R. E. Torsional Frequencies in the Far Infrared—V. Torsions Around the C-C Single Bond in Some Benzaldehydes, Furfural, and Related Compounds. *Spectrochim. Acta* **1967**, *23A*, 891-908
- <sup>18</sup> Green, J. H. S.; Harrison, D. J. Vibrational Spectra of Benzene Derivatives—XVI. Benzaldehyde and Mono-Substituted Benzaldehydes. *Spectrochim. Acta* **1976**, *32A*, 1265-1277.

- 
- <sup>19</sup> Haque, M. K.; Takur, S. N. Rotational Isomerism in Fluoro- and Chloro-Benzaldehydes. *Chem. Phys. Lett.* **1979**, *66*, 561-564.
- <sup>20</sup> Yamamoto, S.; Ebata, T.; Itoh, M. Discrimination and Selective Reaction of Rotational Isomers of Jet-Cooled Substituted Benzaldehydes as Studied by Sensitized Phosphorescence Excitation Spectroscopy. *J. Phys. Chem.* **1990**, *94*, 5786-5791.
- <sup>21</sup> Itoh, T. Temperature Dependence of the Emission Spectra of O-, P- and M-Fluorobenzaldehyde in the Vapor Phase: Rotational Isomers of O- and M-Derivatives. *J. Mol. Struct.* **2004**, *705*, 113-120.
- <sup>22</sup> Itoh, T.; Akai, N.; Ohno, K. Infrared Spectra of P-, M- and O-Fluorobenzaldehyde in Low Temperature Argon Matrices. *J. Mol. Struct.* **2006**, *786*, 39-45.
- <sup>23</sup> Pinchas, S. Infrared Absorption of the Aldehydic C-H Group. *Anal. Chem.* **1955**, *27*, 2-6.
- <sup>24</sup> Pinchas, S. Infrared Absorption of the Aldehydic C-H Group Ortho-Substituted Benzaldehydes. *Anal. Chem.* **1957**, *29*, 334-339.
- <sup>25</sup> Delanoye, S. N.; Herrebout, W. A.; van der Veken, B. J. Improper or Classical Hydrogen Bonding: A Comparative Cryosolutions Infrared Study of the Complexes of HCClF<sub>2</sub>, HCCl<sub>2</sub>F, and HCCl<sub>3</sub> with Dimethyl Ether. *J. Am. Chem. Soc.* **2002**, *124*, 7490-7498.
- <sup>26</sup> Jabłoński, M.; Sadlej, A. Blue-Shifting Intramolecular C-H...O Interactions. *J. Phys. Chem. A* **2007**, *111*, 3423-3431.
- <sup>27</sup> Alonso, J. L.; Villamañán, R. M. Rotational Isomerism in Monofluorobenzaldehydes. *J. Chem. Soc., Faraday Trans.* **1989**, *85*, 137-149.
- <sup>28</sup> Desyatnyk, O.; Pszczółkowski, L.; Thorwirth, S.; Krygowski, T. M.; Kisiel, Z. The Rotational Spectra, Electric Dipole Moments and Molecular Structures of Anisole and Benzaldehyde. *Phys. Chem. Chem. Phys.* **2005**, *7*, 1708-1715.



- 
- <sup>29</sup> Kakar, R. K.; Rinehart, E. A.; Quade, C. R.; Kojima, T. Microwave Spectrum of Benzaldehyde. *J. Chem. Phys.* **1970**, *52*, 3803-3813.
- <sup>30</sup> Krygowski, T. M.; Wisiorowski, M.; Howard, S. T.; Stolarczyk, L. Z. Angular-Group-Induced Bond Alternation. I. Origin of the Effect from *Ab Initio* Calculations. *Tetrahedron* **1997**, *53*, 13027-13036.
- <sup>31</sup> Krygowski, T. M.; Cyrański, M. K. Angular Group Induced Bond Alternation (AGIBA). A New Face of Substituent Effect Detected in Molecular Geometry. *Synlett.* **2003**, *7*, 922-936.
- <sup>32</sup> Sedo, G.; van Wijngaarden, J. Fourier Transform Microwave Spectra of a “New” Isomer of OCS-CO<sub>2</sub>. *J. Chem. Phys.* **2009**, *131*, 044303.
- <sup>33</sup> Evangelisti, L.; Sedo, G.; van Wijngaarden, J. Rotational Spectrum of 1,1,1-Trifluoro-2-butanone Using Chirped-Pulse Fourier Transform Microwave Spectroscopy. *J. Phys. Chem. A* **2011**, *115*, 685-690.
- <sup>34</sup> Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A., et al. *Gaussian 09*, Revision B.01; Gaussian, Inc.; Wallingford, CT, 2010.
- <sup>35</sup> Ruoff, R. S.; Klots, T. D.; Emilsson, T.; Gutowsky, H. S. Relaxation of Conformers and Isomers in Seeded Supersonic Jets of Inert Gases. *J. Chem. Phys.* **1990**, *93*, 3142-3150.
- <sup>36</sup> Pickett, H. M. The Fitting and Prediction of Vibration-Rotation Spectra with Spin Interactions. *J. Mol. Spectrosc.* **1991**, *148*, 371-377.
- <sup>37</sup> Durig, J. R.; Bist, H. D.; Furic, K.; Qiu, J.; Little, T. S. Rotation of Benzaldehyde, Benzoyl Fluoride, Benzoyl Chloride and Acetophenone. *J. Mol. Struct.* **1985**, *129*, 45-56.
- <sup>38</sup> Kraitchman, J. Determination of Molecular Structure from Microwave Spectroscopic Data. *Am. J. Phys.* **1953**, *21*, 17-24.

---

<sup>39</sup> Kisiel, Z. PROSPE-Programs for ROTational SPectroscopy. Available from

<http://info.ifpan.edu.pl/~kisiel/prospe.htm>.

<sup>40</sup> Costain, C. C. Further Comments on the Accuracy of R<sub>s</sub> Substitution Structures. *Trans. Am. Crystallogr. Assoc.* **1966**, **2**, 157.

<sup>41</sup> Watson, J. K. G.; Roytburg, A.; Ulrich, W. Least-Squares Mass-Dependence Molecular Structures. *J. Mol. Spectrosc.* **1999**, *196*, 102-119.

<sup>42</sup> Conrad, A. R.; Barefoot, N. Z.; Tubergen, M. J. Rotational Spectra of O-, M- and P-Cyanophenol and Internal Rotation of P-Cyanophenol. *Phys. Chem. Chem. Phys.* **2010**, *12*, 8350-8356.