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# SIX-FOLD-SYMMETRY INTERNAL ROTATION IN TOLUENES: THE LOW BARRIER CHALLENGE OF 2,6- AND 3,5-DIFLUOROTOLUENE

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## Abstract

Pure six-fold symmetry ($V_6$) internal rotation poses significant challenges to experimental and theoretical determinations, as the very low torsional barriers result in huge tunneling splittings difficult to identify and to model. Here we resolved the methyl group internal rotation dynamics of 2,6- and 3,5-difluorotoluene using a newly developed computer code especially adapted to $V_6$ problems. The jet-cooled rotational spectra of the title molecules in the $5-25$ GHz region revealed internal rotation tunneling doublings of up to 3.6 GHz, which translated in methyl group potential barriers of $V_6 = 0.14872(24)$ and $0.0856(10)$ kJ mol$^{-1}$, respectively, in the vibrational ground-state. Additional information on Stark effects and carbon isotopic species in natural abundance provided structural data and the electric dipole moments for both molecules. *Ab initio* calculations at the MP2 level do not reproduce the tiny torsional barriers, calling for experiments on other systems and additional theoretical models.

Keywords: Rotational spectroscopy, Jet Spectroscopy, Six-fold symmetry, Internal rotation, Difluorotoluenes

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## 1. Introduction

The study of conformational problems arising from hindered internal motions is a classic topic in structural Chemistry [1]. Even for small molecules the internal rotation around single bonds may result in a large number of rotamers, and a detailed description of the conformational distribution requires investigating both the spectral signature and the potential energy surface of the molecule. Among the experimental methods the investigation of the pure rotational spectrum in the microwave region provides the most accurate description of molecular structure [2,3], since the sensitivity of the moments of inertia to the mass distribution results in independent spectra for all species in the sample, either rotamers or tautomers. For terminal methyl groups the internal rotation effects produce tunneling splittings in the rotational transitions, from which the barrier potentials can be precisely determined [4,5]. This method has been applied extensively for many three-fold $V_3$ barriers, which are occurring when the methyl top is attached to a molecular frame of $C_1$ or $C_s$ symmetry. Higher terms in the ($\cos 3n\tau$) torsion potential expansion, in particular $V_6$, are usually small in comparison with the leading $V_3$ term. However, for molecular frames of higher symmetry, like $C_{2v}$ aromatic rings, the internal rotation of a $C_{3v}$-symmetric methyl group around the $C_{2v}$ axis will be hindered by a pure six-fold $V_6$ potential, giving an opportunity to examine the molecular properties governing this kind of barrier, much less studied in the literature. We recently started a systematic investigation of fluorinated toluenes and we report here our results for the internal rotation potentials determined from the microwave spectra of 2,6- and 3,5-difluorotoluene. While the toluenes are rigid backbone molecular systems for which the detection of the rotational spectrum could be relatively easy, the presence of low internal rotation barriers produces large (on the order of GHz) frequency splittings, making the spectral assignment and analysis a considerable challenge. In the case of

2,6-difluorotoluene, many lines have splittings for the transitions in the lowest torsional states, i.e., $m = 0$ and $m = 1$, as large as 3 GHz (e.g. 3.16 GHz, 3.20 GHz or 3.58 GHz in the $6_{1,5} \leftarrow 5_{2,4}$, $7_{3,5} \leftarrow 6_{2,4}$ or $8_{3,6} \leftarrow 7_{2,5}$ transitions, respectively).

The molecular prototype of six-fold internal rotation barriers is toluene. The initial measurements by Rudolph, Dreizler, Jaeschke and Wendling [6], restricted to cm-wave low-$J$ rigid-rotor transitions in the ground ($m = 0$) and $m = 3$ free-rotor vibrational quantum states, led to a barrier of 13.94(10) cal mol$^{-1}$ (4.88(3) cm$^{-1}$). Kisiel *et al.* extended the measurements first to the high $J$ $m = 0$ torsional ground state [7] and then to a simultaneous analysis of $m = 0$, 1, 2, 3 and -3 states [8], finally leading to a potential barrier of $V_6 = 13.832068(3)$ cal mol$^{-1}$ (4.8378362(9) cm$^{-1}$). The rotational spectra of the toluene $^{13}$C isotopologues are also known and were used for the structural determination [9,10]. Recently Gascooke et al. [11,12] reported an analysis of torsion-vibration coupling mechanism in toluene that leads to a significant revision of torsional barrier height in this molecule. This study raises an interesting question of interpretation of the results obtained for many molecules with large amplitude motions (LAM) in the framework of widely used models which assume a possibility to separate a large amplitude vibrational motion from small amplitude vibrational motions in a nonrigid molecule at least for some selection of low lying states associated with LAM. Whereas we believe that the barrier height revision of Gascooke et al. [11,12] should be confirmed by further analysis of torsion-vibration coupling in toluene with incorporation of high-precision microwave data it is clear that investigation of similar molecular systems will be of great interest in resolving this controversy between different barrier height results. 2,6-difluorotoluene and 3,5-difluorotoluene seem to be good testing cases since at least for 2,6-difluorotoluene analogous torsion-vibration coupling was reported for the S1 state by Walker et al. [13] and therefore it is likely that the same coupling will be present in the S0 state also. Since jet cooled rotational spectra provide information only on low lying torsion-rotation states an analysis of possible vibration-torsion couplings in 2,6-difluorotoluene and 3,5-difluorotoluene was beyond the scope of our current investigation. At the same time our study provides a necessary basis for further investigation of higher excited torsional-vibrational states of these molecules using high-precision microwave spectroscopic techniques.

How will the six-fold torsional barrier of toluene be affected by $C_{2v}$-preserving halogen substitution in different positions of the ring? We found in the bibliography several rotational studies of monohalogenated toluenes [14-18] but only a few of disubstituted ones [19], none with a six-fold barrier. For this reason we investigated several difluoro and dichloro derivatives. In this report we examine the results of symmetrically attaching two fluorine atoms ($C_7H_6F_2$) in *ortho*- and *meta*-positions. Since fluorine produces no hyperfine structure due to nuclear quadrupole coupling we could concentrate on resolving the fine structure due to the internal rotation. The experimental study has been carried out using Fourier-transform microwave (FT-MW) spectroscopy in a supersonic jet [2]. The adiabatic expansion not only reduces the collisional linewidth, but also produces a strong rovibrational cooling, populating only the lowest-lying states and thus simplifying the spectrum. The rotational analysis was supplemented by the determination of the molecular electric dipole moments using the Stark effect. Finally, we conducted *ab initio* calculations on the two molecules to test the predictive value of the theoretical data against the experiment. Atom labelling and principal axes orientation in these molecules are shown in Figure 1.

## 2. Experimental and computational methods

The spectra were taken on a pulsed supersonic jet Fourier transform microwave spectrometer in Hannover, using the coaxially oriented beam and resonator arrangement (COBRA) [20-22] described before. The principal advantage in the COBRA arrangement is the longer transit time of the molecular jet, which can be exploited for Stark effect experiments if, rather than using external electrode plates, the spherical reflectors forming the resonator are utilized as high-voltage electrodes (coaxially aligned electrodes for Stark effect applied in resonators, CAESAR [23]). In the experiment the direction of the electric Stark field is perpendicular to the polarized microwave field, leading exclusively to the $\Delta M_J = \pm 1$ transitions. For the Stark effect measurements the applied voltages were calibrated for the electric field strengths using the Stark effect in the $J = 1 \leftarrow 0$ rotational transition of the $OC^{36}S$ and $^{18}OCS$ isotopologues of OCS using a dipole moment value of $\mu = 0.71519(3)\,D$ [24], as described in Ref [25]. The substance, commercial samples of 2,6- and 3,5-difluorotoluene obtained from Alfa-Aesar GmbH, were used without further purification. The sample was kept in a small reservoir at the nozzle exit, using neon as carrier gas (stagnation pressures of 200 kPa). The spectra were measured in the frequency range 5-25 GHz. All frequency measurements were referenced to a GPS-disciplined rubidium frequency standard and have an estimated uncertainty of <1 kHz. Lines separated more than ~5 kHz are resolved.

*Ab initio* calculations were used to obtain predictions of the rotational parameters (centrifugal distortion and rotational constants), electric dipole moments and the torsional potential function. In the course of this work we used several computational models. We present in Table 1 the results of second-order perturbation theory (MP2, frozen core), combined with a standard Pople's 6-311++G(2df,2p) basis set. The centrifugal distortion constants resulted from the harmonic force field. The calculations were performed with the GAUSSIAN package [26]. The torsion potential for the two molecules are shown in Figure S1 (ESI).

## 3. Results

### 3.1 Rotational spectrum and internal rotation barrier

The first spectral predictions used rotational constants derived from the *ab initio* methods. A large number of lines were then initially observed in the frequency region 10-16 GHz (Figures 2 and S2, ESI). However, in order to rationalize the spectrum some considerations should be given on the torsional fine structure. The internal rotation governed by a pure $V_6$ barrier splits the six-fold degeneracy of the ground vibrational state (v = 0) in a quartet of torsional vibrational states which can be labeled using free-rotor quantum numbers $m = 0, 1, 2, 3$ ($m = 1$ and $m = 2$ states are doubly degenerate). The torsion-rotation levels belonging to these $m$-states may be labeled according to the permutation-inversion molecular symmetry (MS) group $G_{12}$ i.e. $A_1/A_2$, $B_1/B_2$, $E_1$, $E_2$, [27]. Spin statistics for 2,6- and 3,5-difluorotoluene, both having a $C_{3v}$-symmetric methyl group as well as pairs of equivalent protons and fluorine atoms if exchanged by $G_{12}$ symmetry operations, are 80, 48, 48 and 80, respectively. Symmetry species exhibiting the same spin statistical weights were expected to relax to the lowest energy species within the stack. Under the experimental conditions of a supersonic jet (estimated effective rotational temperature of several K) it was anticipated that only the $m = 0$ and $m = 1$ sub states of the ground vibrational state would be populated and each rotational transition due to internal rotation would appear as a doublet. Out of the two lines belonging to a particular rotational transition, the $m = 0$ lines usually (in absence of intertorsional interactions) effectively follows an asymmetric top pattern and hence the observed lines which were fitted by a rigid rotor asymmetric top model were identified as $m = 0$ lines.

As there were no earlier predictions or determinations of the potential barrier for 2,6- and 3,5-difluorotoluene from any other experimental method, we first estimated the splitting between the $m = 0$ and $m = 1$ lines with different assumed potential barriers obtained from chemical intuition and information from similar molecules. First we tried to map the $m = 0 - m = 1$ splittings on the *A*-*E* splittings of the usual three-fold problem using the XIAM program written by Hartwig, which employs the Combined Axis Method [28]. This idea worked rather well, giving us an opportunity after several trial calculations to make initial assignments of a number of $m = 1$ *R*-type transitions. Nevertheless rather high residuals for the fitted $m = 1$ transition frequencies with respect to estimated experimental uncertainty as well as unexpectedly high values of "effective" barriers spoke in favor of using a code written specifically for the $V_6$ case.

The final analysis was based on the theoretical framework developed by Sorensen and Pedersen in their application of the Longuet-Higgins permutation-inversion group ideas to the microwave spectrum of $CH_3NO_2$ [29]. We employed the program RAM36 (Rho-Axis-Method for 3- and 6- fold barriers), which uses the Rho Axis Method and was successfully applied previously to the analysis of the rotational spectra of both a light-top (toluene [8]) and a heavy-top molecule (benzotrifluoride [30]). A detailed description of the program can be found in those references. The computer code uses a least-squares optimizer that fits the values of selected Hamiltonian parameters to the set of observed transition frequencies. It has a "global" nature in the sense that the whole set of energy levels associated with torsional motion of a $C_{3v}$ top is treated simultaneously with one set of parameters [8].

Although the 2,6- and 3,5-difluorotoluenes are derivatives of the toluene molecule, they are near-oblate tops in contrast to toluene (a prolate top with $\kappa=-0.59$). In these two molecules it is the *b* axis which coincides with the methyl top internal rotation axis rather than the *a* axis as in toluene. Therefore in our calculations we used the representation II[1] ($x,y,z = a,c,b$). The Hamiltonian may be presented as follows:

$$H = H_r + H_{cd} + H_t + H_{tr},$$

with

$$H_t + H_r = F(p_\alpha - \rho J_z)^2 + (1/2)V_6(1+\cos 6\alpha) + BJ_z^2 + AJ_x^2 + CJ_y^2$$

where $p_\alpha$ is an angular momentum conjugated to the internal rotation angle $\alpha$.

$$H_{cd} = -\Delta_J P^4 - \Delta_{JK} P^2 P_z^2 - \Delta_K P_z^4 - 2\delta_J P^2 (P_x^2 - P_y^2) - \delta_K \{P_z^2, (P_x^2 - P_y^2)\}$$

The $H_{tr}$ contains higher order torsion-rotation interaction terms. In Table 1 only those terms which were actually used in the fits of the investigated spectra may be found.

The initial sets of *R*-type transitions assigned with the help of the XIAM program were refitted using the RAM36 program without much problem, giving rather good root-mean-square (rms) deviations of the fits for both $m=0$ and $m=1$ states of 2,6- and 3,5-difluorotoluene. Based on this analysis we additionally assigned a number of *Q*-type transitions that gave us an opportunity to confirm the consistency of our assignments with the help of combination differences. As a final step we fulfilled a search for the rather weak $m=2$ lines, which according to our new predictions were at the detection limit of the FTMW spectrometer in use. We were able to assign 9 $m=2$ lines for 2,6-difluorotoluene and only 3 $m=2$ for 3,5-difluorotoluene using reasonable integration times.

In total, for 2,6-difluorotoluene we have fit 173 line frequencies that due to blending correspond to 176 transitions with angular momentum quantum numbers from $J=2$ up to $J=12$, among which assignment of 81 transitions was confirmed by combination differences. The theoretical model included 17 parameters: 5 parameters of 2nd order (one fixed) and 12 parameters of 4th order. The rms deviation of the fit was 2.7 kHz with separate rms deviations for the $m=0$, 1, 2 states of 2.3 kHz, 2.8 kHz and 4.5 kHz. Although the obtained rms deviation is slightly higher than the estimated measurement uncertainty, it should be noted that a number of transitions (both in 2,6- and 3,5-difluorotoluene) were split presumably by spin-spin or spin-rotation interactions and therefore their frequency determination errors may be larger than the stated 1 kHz. To take this fact into account we weighted all measurements with uncertainties of 2 kHz and in several cases 10 kHz (the weight was proportional to the reciprocal of the squared uncertainty). The parameters resulting from the fit for 2,6-difluorotoluene are presented in Table 1.

For 3,5-difluorotoluene, in total, we have fit 98 line frequencies that due to blending correspond to 156 transitions with angular momentum quantum numbers $J=2$ up to $J=15$, among which the assignment of 46 transitions was confirmed by combination differences. The theoretical model included 14 parameters: 5 parameters of 2nd order (one fixed) and 9 parameters of 4th order. The rms deviation of the fit was 1.6 kHz with separate rms deviations for $m=0$, 1, 2 states being 1.1 kHz, 1.9 kHz and 1.2 kHz. The resulting parameters for 3,5-difluorotoluene are also in Table 1.

It should be noted that besides the fact that we were able to measure several $m=2$ lines the torsion parameters in both 2,6- and 3,5-difluorotoluene remain highly correlated. Therefore we fixed $F$ at a 5.327 cm$^{-1}$ value that corresponds to $I_\alpha \approx 3.2$ uÅ$^2$. The high correlation in both cases says that the confidence intervals obtained for the $V_6$ barrier heights should be taken with caution and to our opinion ±1 cm$^{-1}$ interval will be more reasonable estimate of the barrier height determination uncertainty. In this sense the room temperature experiment which will give an opportunity to access $m=3,-3$

states would be very valuable, since the splitting between these two states gives a direct measure of the $V_6$ [8]. Also it should be noted that it was not possible with the current dataset to determine the sign of the $V_6$ potential term (see [8] and [30] for a detailed discussion) and therefore we adopted the sign choice which was found appropriate for the parent toluene molecule (i.e. plus sign, see Table 1). Finally we would like to point out that the barrier heights obtained with the RAM36 program of $V_6 = 0.14872(24)$ and 0.0856(10) kJ mol$^{-1}$ for 2,6- and 3,5-difluorotoluene, respectively, are of the same order of magnitude as determined for the toluene. Conversely, the XIAM code, which was not written for V6-symmetry, gives more than one order of magnitude higher barrier.

Once the transitions due to the parent species were identified and analyzed, it was straightforward to locate the lines due to the monosubstituted $^{13}$C isotopologues for all independent ring positions and the methyl group. All isotopic lines were measured at their natural abundance (ca. 1 %), so the number of lines measured for the monosubstituted $^{13}$C isotopologues was rather sparse. Since we were mainly interested in the rotational constants the following approach to the data analysis was adopted. The torsional parameters $F$ and $V_6$ as well as quartic centrifugal distortion parameters were fixed at the parent species values and only $A$, $B$, $C$ and $\rho$ were varied together with some appropriate higher order terms. The derived rotational constants of the isotopic species are given in Tables S1 and S2 (ESI). The assigned transition frequencies together with the residuals of all the fits are given in the Supplementary material (Tables S5-S16).

There is one additional issue that should be discussed in connection with the monosubstituted $^{13}$C isotopologues of 2,6- and 3,5-difluorotoluene. The $^{13}$C atoms substituted at positions (4), (1), (7) along the $C_2$ axis do not affect the $G_{12}$ symmetry of the system. Therefore for these isotopologues the $V_6$ treatment described above is exact. At the same time $^{13}$C atoms substituted off-axis in the (3)=(5) or (2)=(6) positions destroy the $G_{12}$ symmetry of the problem and the $V_3$ treatment with a $G_6$ group should be applied. This is clearly seen from a comparison of relative intensities of ${}^{b}R_{\pm1,1}$ transitions with $K_a$ = 0,1 which form close pairs of lines in the spectrum of 2,6-difluorotoluene. The relative intensities of these transitions are governed by the nuclear spin statistic weights which assume 3 to 5 ratio in the case of $G_{12}$ symmetry and 1 to 1 ratio when $G_{12}$ symmetry is destroyed and $G_6$ group should be applied. This is what indeed was observed in our spectral records for 2,6-difluorotoluene. Therefore the $V_3$ mode of the RAM36 program [8] was used for nonsymmetrical substituted isotopologues of 2,6- and 3,5-difluorotoluene. It should be noted that in this case the axis system in use does not coincide with the principal axis system of the molecule. Since the isotopic perturbation is assumed to be rather small it is expected that the $V_6$ term in a Fourier expansion of the potential would be of the same order, but a small or comparable $V_3$ term will appear. Nevertheless our analysis shows that (3)=(5) and (2)=(6) $^{13}C$ isotopologues are fitted without any problem using the $V_6$ model and therefore there is no information available in the experimental data on the ratio between the $V_3/V_6$ terms (the attempts to introduce the $V_3$ term in the model lead to divergence of the fits). So the issue of $V_3/V_6$ ratio in the case of small deviation from the $G_{12}$ symmetry appeared to be beyond the scope of the current investigation though we note in passing that it is possible that the $V_3$ term in this case is much lower that the $V_6$ term. The results of the structure analysis based on these data are discussed in section 3.3.

### 3.2. Electric Dipole Moment

The electric dipole moment components of both molecules were evaluated using the Stark effect. For this analysis it is desirable to limit the measurements to low-$J$ transitions, which involve smaller number of spatial ($M_J$) components. Transitions involving low-$J$ values are also especially valuable when using coaxially aligned electrodes for Stark-effect applied resonators (CAESAR), since the selection rule $\Delta M_J=\pm 1$ gives rise to a higher (approximately twice) number of $M_J$ components compared to the common parallel plate arrangement where $\Delta M_J=0$ transitions are observed. In order to determine the dipole moment we selected the set of rotational transitions and electric fields given in the Supplementary Information (Tables S17 and S18). Figure 3 illustrates the Stark effect measurements, showing transitions of the two title compounds. A fit of several $A$ species transitions, each of them measured at different $E$-fields, was done with the program QSTARK developed by Kisiel [31], and yielded dipole moment components of $|\mu_b|=0.907(2)$ D for 2,6-difluorotoluene and $|\mu_b|=2.059(2)$ D for 3,5-difluorotoluene. These values are compared with the predictions in Table 1.

### 3.3. Molecular Structure

The molecular structures of the title compounds were derived from the multiple isotopic data. The position of each substituted carbon atom was first calculated using the substitution method ($r_s$) of Kraitchman, which provides the absolute atomic coordinates in the principal axis system [32]. This method computes the position of each atom without assumptions about the rest of the molecule, only from the changes on the moments of inertia upon isotopic substitution. This approach exploits the differences in the moments of inertia of different isotopic species rather than their absolute values in order to try a partial cancellation of the inherent vibrational effects contained in the ground-state moments of inertia. This procedure is somewhat affected by slightly different contributions to the moments of inertia of different isotopologues that become noticeable for atoms close to one of the inertial axis [33]. Three carbon atoms (C1, C4 and C7) are lying along the *b* (≡ $C_2$) inertial axis in 2,6- and 3,5-difluorotoluene. Additionally, the a coordinates of atoms C2 and C6 are very close to the a axis in 2,6-difluorotoluene. For this reason, this set of coordinates resulted in imaginary values of the atomic positions and had to be fixed to zero, hampering the accuracy of the structural determination, as in other high-symmetry molecules. The resulting atomic coordinates for the two molecules are compared with the *ab initio* data in the Supplementary Information (Tables S3 and S4). The derived bond lengths and valence angles are collected in Table 2). However, this procedure is unreliable for atoms close to one of the inertial axes [34] and the results were unrealistic. For this reason we tried an effective structure ($r_0$) calculation, in which the rotational constants were fitted to a selection of structural parameters. The derived bond lengths and valence angles assuming only a planar heavy atom skeleton and a symmetric C7 position are also collected in Table 2, together with the theoretical near-equilibrium ($r_e$) *ab initio* values.

## 4. Discussion and Conclusions

We have observed the rotational spectra of two symmetrically disubstituted fluorine derivatives of toluene in positions *ortho* and *meta*. The spectrum is dominated by the large torsional doublings arising from the pure six-fold potential barriers hindering internal rotation. In order to simplify the spectrum analysis the experiment was conducted in a supersonic jet expansion, allowing the detection of the lowest-lying torsional substates of the ground vibrational state. Stark effect measurements yielded the electric dipole moments, which confirm the larger polarity of 3,5-difluorotoluene (2.00 D vs. 0.88 D), and only differ by 3 % to the *ab initio* calculations. The sensitivity of our experiment allowed the additional observation of all $^{13}$C monosubstituted isotopologues in natural abundance. Structural calculations using the substitution and effective methods provided accurate information on the carbon skeleton of the molecule. The main objectives of this work, including the rotational assignment of the title compounds, the determination of molecular structures, the calculation of the electric dipole moments and the comparison of the internal rotation potential barriers with that of toluene, are thus fully accomplished, both experimentally and theoretically. In particular, the difficult internal rotation problem was solved thanks to a new computer program specially designed for six-fold $V_6$ problems [8]. Comparisons are now possible between the experimental and theoretical predictions for the most relevant molecular properties of 2,6- and 3,5-difluorotoluene in Table 1. The *ab initio* predictions show a reasonable description of the rotational parameters (relative deviations below ca. 0.8%). However, *ab initio* predictions of the internal rotation barrier are much more difficult, not unexpected considering the very small magnitude of the potential barriers. The theoretical predictions suggest that the barrier in 3,5-difluorotoluene is more than one order of magnitude larger than in 2,6-difluorotoluene (0.16 and 0.006 kJ mol$^{-1}$, respectively), failing to reproduce the magnitude and reversed trend of the experimental values in 2,6- (0.148 kJ mol$^{-1}$) vs. the more polar 3,5-difluorotoluene (0.0856 kJ mol$^{-1}$). In conclusion, the computationally effective MP2 method proves effective for the prediction of spectral properties, but a more accurate description of the small torsional barriers seems to require a more advanced calculation, which is out of the scope of the present work. Comparisons of the barrier to internal rotation in toluene and mono and disubstituted halotoluenes is also revealing. A comparison of available experimental data in Table 3 shows that para-monosubstituted fluoro or chlorotoluenes have barriers very similar to toluene (0.0578 and 0.0583 vs. 0.05787 kJ mol$^{-1}$, respectively), suggesting that there is a small effect of the substituents in para position on the bonding characteristics of the C-$CH_3$ of toluene.

Conversely, the introduction of two symmetric electronegative substituents in *ortho* or *meta* positions considerably increases the internal rotation barrier (0.085 and 0.148 kJ mol$^{-1}$, respectively, in *meta* and *ortho*) reflecting a much larger influence in the molecular orbital distribution of the halotoluenes.

In conclusion, the investigation of internal rotation barriers in toluenes with different halogenated substituents will progressively provide a general view of the subtle effects affecting intramolecular dynamics in these molecules. To this effect the combination of experimental data, new spectroscopic methods and *ab initio* calculations proves to be extremely efficient.

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## Supplementary material

Supplementary data associated with this article can be found in the online version.

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**Figure 1**. Atom labelling and principal inertial axes of 2,6- and 3,5-difluorotoluene

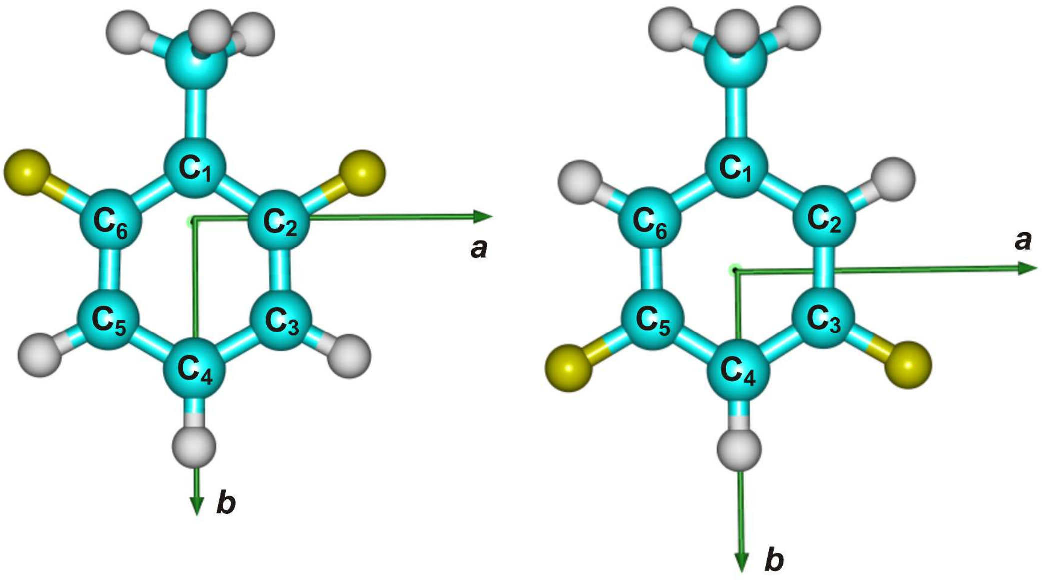

**Figure 2**. An illustration of rotational transitions of 3,5-difluorotoluene (top trace, *m*=0 torsional state) and $^{13}$C transitions of 2,6-difluorotoluene in natural abundance ($^{13}$C(3) and $^{13}$C(5), lower trace). All lines are split by the Doppler effect (the intensity has been normalized for clarity).

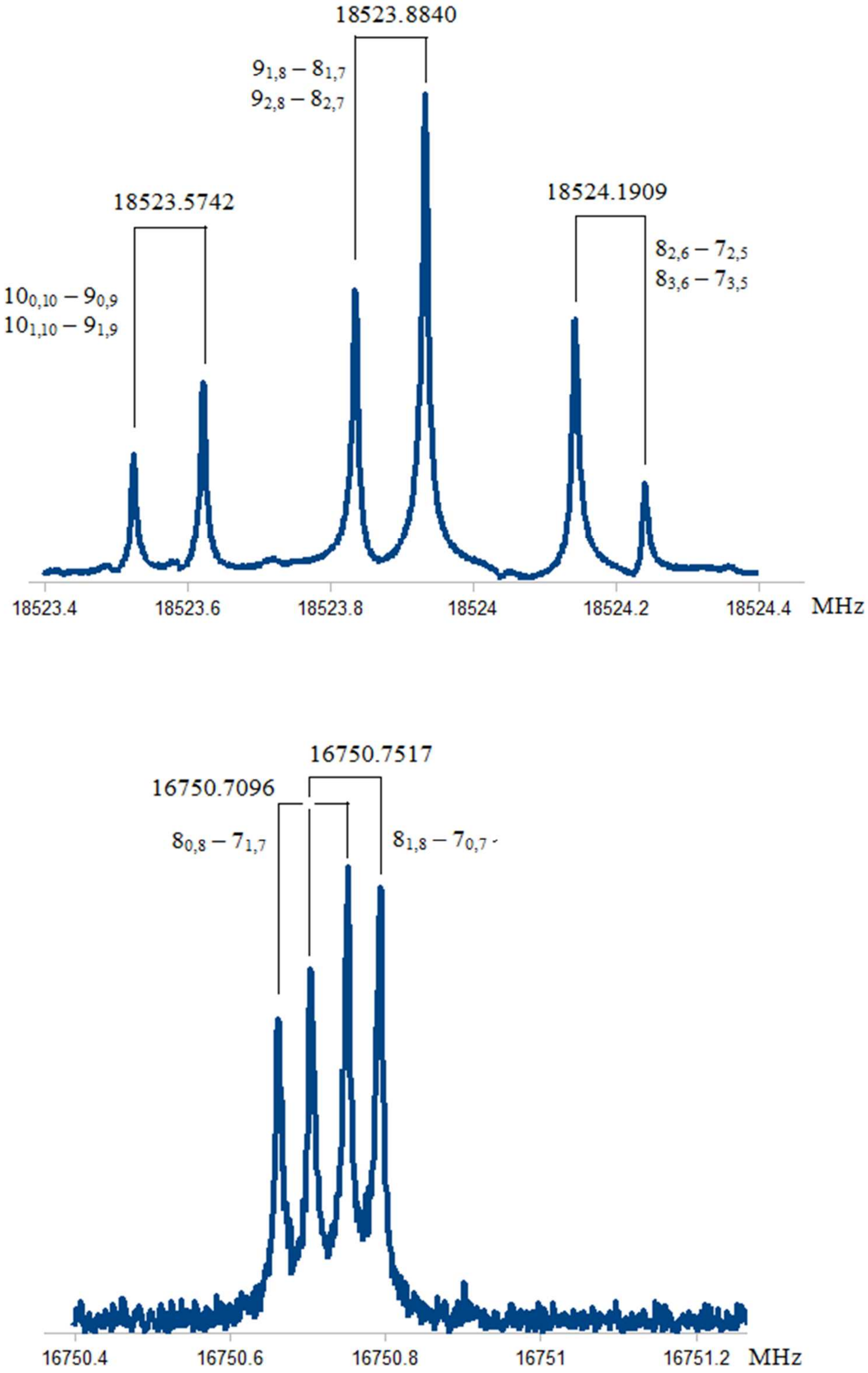

**Figure 3**. Illustration of Stark effect measurements on the $J_{K\text{-}1,K+1}=4_{1,4}\leftarrow3_{0,3}$ rotational transition of 3,5-difluorotoluene

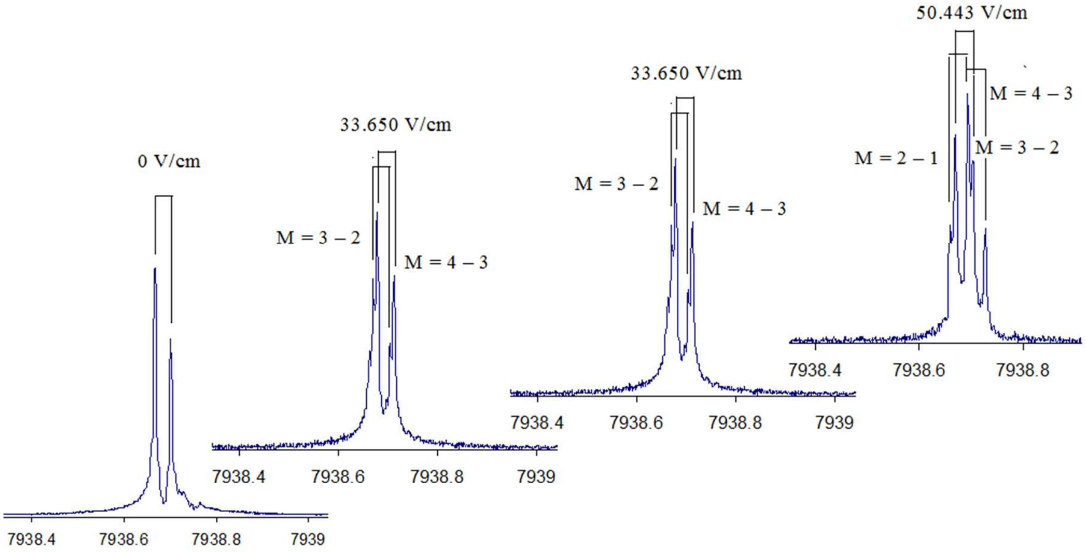

**Table 1**. Rotational parameters of 2,6- and 3,5-difluorotoluene.

| | | 2,6-difluorotoluene | | 3,5-difluorotoluene | |
|---|---|---|---|---|---|
| Parameter[a] | operator | Experiment | *Ab initio*[d] | Experiment | *Ab initio* |
| $V_6$ (kJ mol$^{-1}$)[c] | | 0.14872(24) | 0.006 | 0.0856(10) | 0.16 |
| $V_6$ (cm$^{-1}$) | $(½)(1+\cos 6\alpha)$ | 12.432(20)[c] | | 7.162(84) | |
| $F$ (cm$^{-1}$) | $p_\alpha^2$ | [5.327] | | [5.327] | |
| $\rho$ | $p_\alpha J_z$ | 0.010861576(55) | | 0.01096923(13) | |
| $A$ (MHz) | $J_x^2$ | 2270.38931(19) | 2283.0 | 1764.21314(19) | 1771.5 |
| $B$ (MHz) | $J_z^2$ | 1742.95949(14) | 1748.0 | 1745.18099(17) | 1748.9 |
| $C$ (MHz) | $J_y^2$ | 991.998415(52) | 996.0 | 882.069370(38) | 884.9 |
| $\Delta_J$ (kHz) | $-J^4$ | 0.0637(21) | 0.055 | 0.00873(18) | 0.055 |
| $\Delta_{JK}$ (kHz) | $-J^2J_z^2$ | 0.1120(66) | 0.68 | 0.1438(48) | 0.021 |
| $\Delta_K$ (kHz) | $-J_z^4$ | -0.0597(42) | -0.60 | 0.0579(70) | 0.028 |
| $\delta_J$ (kHz) | $-2J^2(J_x^2-J_y^2)$ | 0.0261(11) | 0.022 | | 0.023 |
| $\delta_K$ (kHz) | $-\{J_z^2,(J_x^2-J_y^2)\}$ | 0.0960(16) | 0.31 | 0.0538(20) | 0.049 |
| $F_J$ (MHz) | $p_\alpha^2J^2$ | -0.006575(59) | | -0.005006(51) | |
| $\rho_J$ (MHz) | $p_\alpha J_z J^2$ | | | 0.001681(27) | |
| $F_{xy}$ (MHz) | $(J_x^2-J_y^2)p_\alpha^2$ | -0.007472(86) | | | |
| $\rho_{xy}$ (MHz) | $(½)\{J_z,(J_x^2-J_y^2)\}p_\alpha$ | 0.001423(21) | | | |
| $F_K$ (MHz) | $p_\alpha^2J_z^2$ | -0.01522(19) | | -0.00584(30) | |
| $\rho_K$ (MHz) | $p_\alpha J_z^3$ | 0.000628(29) | | | |
| $\rho_m$ (MHz) | $p_\alpha^3J_z$ | 1.496(13) | | 0.465(33) | |
| $N^b$ | | 173 | | 98 | |
| σ (kHz)[c] | | 2.7 | | 1.6 | |
| $\|\mu_a$ (D)$\|$[d] | | | 0.00 | | 0.01 |
| $\|\mu_b$ (D)$\|$ | | | 0.88 | | 2.00 |
| $\|\mu_c$ (D)$\|$ | | | 0.01 | | 0.03 |
| $\|\mu_{total}$ (D)$\|$ | | 0.907(2) | 0.88 | 2.059(2) | 2.00 |

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[a] {A,B}=AB+BA. The product of the parameter and operator from a given row yields the term actually used in the rotation–torsion Hamiltonian, except for F and ρ which occur in the Hamiltonian in the form $F(p_\alpha-\rho J_z)^2$ . [b]Number of fitted transitions and MW rms deviation of the fit. [c]Standard errors in parentheses in units of the last digit, [d]MP2/6-311++G(2df,2p). [d]Electric dipole moment components in Debye (1D ≈ $10^{-30}$ C m): $\mu_\alpha$ ($\alpha$=a, b, c).

**Table 2**. Molecular structure of 2,6- and 3,5-difluorotoluene.

| | 2,6-Difluorotoluene | | | 3,5-Difluorotoluene | | |
|---|---|---|---|---|---|---|
| | $r_s$ | $r_0$ | $r_e$[c] | $r_s$ | $r_0$ | $r_e$[c] |
| r[a] (C1-C2) | 1,36899(8) | 1,387(3) | 1,391 | 1,40483(5) | 1,403(2) | 1,395 |
| r (C2-C3) | 1,41816(4) | 1,380(3) | 1,385 | 1,3677(1) | 1,359(15) | 1,384 |
| r (C3-C4) | 1,39371(5) | 1,400(5) | 1,391 | 1,38534(6) | 1,405(12) | 1,384 |
| r (C1-C7) | 1,50635(2) | 1,515(4) | 1,497 | 1,51174(4) | 1,509(18) | 1,502 |
| r (C-F) | | 1,358(5) | 1,346 | | 1,354(9) | 1,344 |
| ∠[b](C1-C2-C3) | 122,951(8) | 124,2(2) | 123,6 | 118,91(1) | 119,3(2) | 119,3 |
| ∠ (C2-C3-C4) | 118,270(6) | 118,0(2) | 118,6 | 123,80(1) | 123,5(1) | 122,8 |
| ∠ (C3-C4-C5) | 120,265(8) | 120,5(1) | 120,4 | 115,602(7) | 115,1(6) | 116,5 |
| ∠ (C2-C1-C6) | 117,29(1) | 115,1(3) | 115,1 | 118,993(6) | 119,3(2) | 120,4 |
| ∠ (C2-C1-C7) | 121,354(7) | [122,5][d] | 123,5 | 120,504(7) | [120,4][d] | 120,4 |
| ∠ (C-C-F) | | 117,5(3) | 117,8 | | 120,3(10) | 118,9 |

[a] Bond length. [b] Bond angles. [c] MP2/6-311++G(2df,p). [d] Derived value. [e] Fixed value.

**Table 3**. Internal rotation barriers in toluene derivatives.

| Molecule | $V_6$ (J/mol) | μ (D) |
|---|---|---|
| Toluene[a] | 57.87439532(13) | 0.37 |
| p-fluorotoluene[b,c,d] | 57.777(76) | 1.96 (2) |
| p-chlorotoluene[e] | 58.28(17) | 1.71(2) |
| 3,5-difluorotoluene[f] | 85.6(10) | 2.0603(21) |
| 2,6-difluorotoluene[f] | 148.72(24) | 0.897 (14) |

[a]Ref.8 [b]Ref.16a. [c]Ref.16d.[d]Ref.16b. [e]Ref.16c. [f]Present work.

# SIX-FOLD SYMMETRY INTERNAL ROTATION IN TOLUENES: THE LOW BARRIER CHALLENGE OF 2,6- AND 3,5-DIFLUOROTOLUENE

## ELECTRONIC SUPPLEMENTARY INFORMATION

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**Figure S1**. Torsional potential function for 2,6- and 3,5-difluorotoluene (torsion dihedral angle defined as H-C7-C1-C2; torsion origin for a methyl C-H bond coplanar with the benzyl ring).

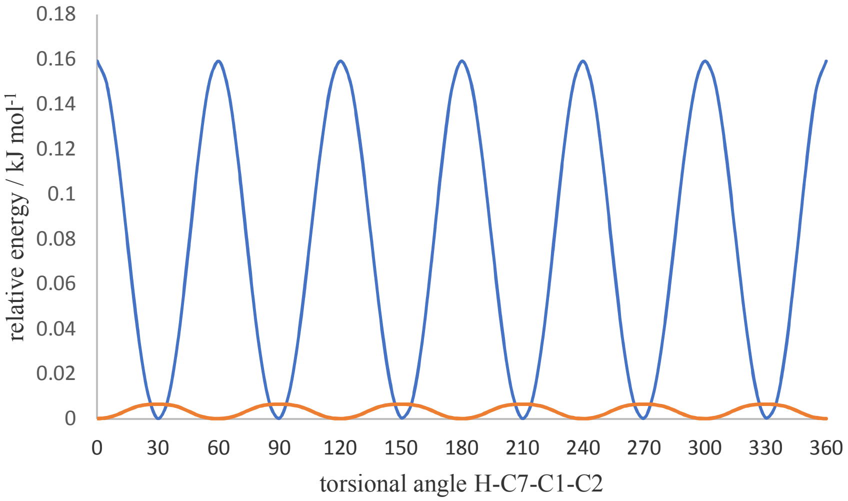

**Figure S2**. Illustration of rotational transitions in 2,6- and 3,5-diflurotoluene (top and down traces, respectively).

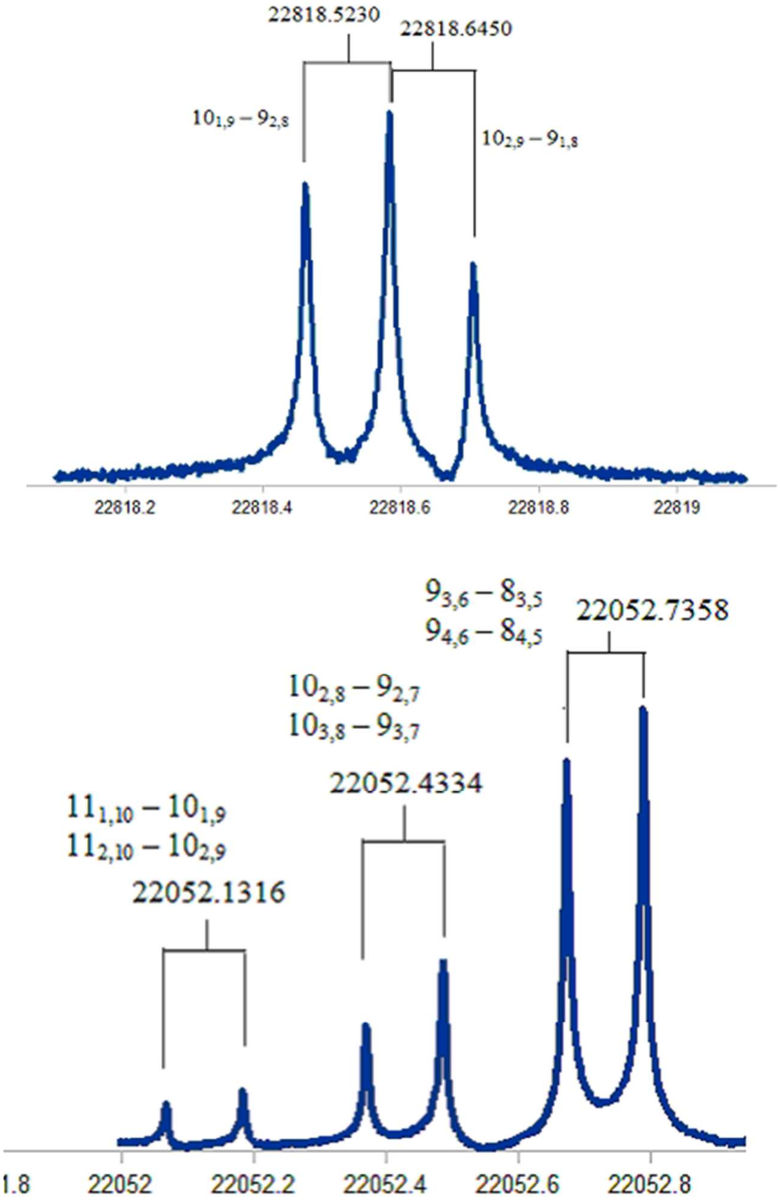

**Table S1**. Rotational parameters for the $^{13}$C isotopic species of 2,6-difluorotoluene.

| | $^{13}$C(1) | $^{13}$C(2),$^{13}$C(6) | $^{13}$C(3), $^{13}$C(5) | $^{13}$C(4) | $^{13}$C(7) |
|---|---|---|---|---|---|
| $A$ (MHz) | 2265.24743(25) | 2270.4559(15) | 2250.6222(11) | 2226.00964(20) | 2221.48138(22) |
| $B$ (MHz) | 1743.06740(12) | 1734.8370(15) | 1734.0077(11) | 1742.99541(21) | 1742.99796(19) |
| $C$ (MHz) | 991.045912(22) | 989.368957(29) | 985.316430(22) | 983.436666(38) | 982.547947(37) |
| $N$ | 53 | 61 | 68 | 57 | 47 |
| $\sigma$ (kHz) | 1.0 | 1.6 | 1.2 | 1.8 | 1.8 |

**Table S2**. Rotational parameters for the $^{13}$C isotopic species of 3,5-difluorotoluene.

| | $^{13}$C(1) | $^{13}$C(2),$^{13}$C(6) | $^{13}$C(3), $^{3}$C(5) | $^{13}$C(4) | $^{13}$C(7) |
|---|---|---|---|---|---|
| *A* (MHz) | 1751.37601(58) | 1762.02786(65) | 1762.57786(68) | 1752.76720(21) | 1745.19054(20) |
| *B* (MHz) | 1745.21262(55) | 1735.31944(66) | 1736.21712(68) | 1745.28119(29) | 1711.98540(19) |
| *C* (MHz) | 878.855314(37) | 878.999347(21) | 879.365172(17) | 879.224262(44) | 868.815129(27) |
| *N* | 36 | 42 | 43 | 42 | 27 |
| $\sigma$ (kHz) | 1.8 | 1.1 | 1.0 | 1.6 | 1.1 |

**Table S3**. Atomic coordinates for the substitution ($r_s$) and *ab initio* ($r_e$) structures of 2,6-difluorotoluene (Principal inertial axes labeled as *a*, *b*, *c*; all coordinates in ängstrom).

| | $r_s$ | | | *Ab initio* | | |
|---|---|---|---|---|---|---|
| | *a* | *b* | *c* | *a* | *b* | *c* |
| C1 | [0][a] | -0.71232(2) | [0] | 0.000 | -0.714 | 0.005 |
| C2 | -1.16907(9) | [0] | [0] | -1.174 | 0.032 | 0.000 |
| C3 | -1.20860(5) | 1.41761(4) | [0] | -1.207 | 1.416 | -0.001 |
| C4 | [0] | 2.11167(1) | [0] | 0.001 | 2.108 | 0.001 |
| C5 | 1.20860(5) | 1.41761(4) | [0] | 1.207 | 1.416 | 0.001 |
| C6 | 1.16907(9) | [0.000] | [0] | 1.174 | 0.032 | 0.000 |
| C7 | [0] | -2.21867(1) | [0] | -0.001 | -2.210 | 0.003 |
| F | | | | -2.343 | -0.636 | -0.003 |
| F | | | | 2.342 | -0.637 | -0.003 |
| H | | | | -2.162 | 1.927 | -0.001 |
| H | | | | 0.001 | 3.192 | 0.000 |
| H | | | | 2.163 | 1.926 | 0.000 |
| H | | | | 0.003 | -2.600 | -1.019 |
| H | | | | -0.892 | -2.593 | 0.501 |
| H | | | | 0.884 | -2.597 | 0.509 |

[a] Values in squared brackets were kept fixed to zero.

**Table S4**. Atomic coordinates for the substitution ($r_s$) and *ab initio* ($r_e$) structures of 3,5-difluorotoluene (Principal inertial axes labeled as *a*, *b*, *c*; all coordinates in angstrom).

| | $r_s$ | | | *Ab initio* | | |
|---|---|---|---|---|---|---|
| | *a* | *b* | *c* | *A* | *B* | *C* |
| C1 | [0] | 1.45130(3) | [0] | -0.007 | -1.456 | -0.013 |
| C2 | -1.21040(3) | 0.73822(8) | [0] | 1.200 | -0.755 | -0.009 |
| C3 | -1.17228(4) | -0.6289(1) | [0] | 1.181 | 0.629 | 0.001 |
| C4 | [0] | -1.36711(2) | [0] | 0.006 | 1.362 | 0.007 |
| C5 | 1.17228(4) | -0.6289(1) | [0] | -1.175 | 0.639 | 0.001 |
| C6 | 1.21040(3) | 0.73822(8) | [0] | -1.207 | -0.744 | -0.010 |
| C7 | [0] | 2.96304(2) | [0] | -0.014 | -2.957 | 0.012 |
| F | | | | 2.348 | 1.295 | 0.001 |
| F | | | | -2.336 | 1.316 | 0.002 |
| H | | | | 2.153 | -1.273 | -0.016 |
| H | | | | 0.011 | 2.445 | 0.009 |
| H | | | | -2.165 | -1.253 | -0.018 |
| H | | | | -0.030 | -3.326 | 1.042 |
| H | | | | 0.874 | -3.365 | -0.473 |
| H | | | | -0.894 | -3.356 | -0.495 |

[a] Values in squared brackets were kept fixed to zero.

**Table S5**. Rotational transitions of the parent species of 2,6-difluorotoluene, sorted by branch, together with fit residuals (o.-c., frequencies in MHz). Rotational transitions labeled with symmetry species, free rotor quantum number (*m*), and asymmetric rotor quantum numbers (*J*, $K_a$, $K_c$).

| Upper level | | | | | Lower level | | | | | Measured(Unc. ) | o.-c.(MHz) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sym' | m' | J' | Ka' | Kc' | Sym | m | J | Ka | Kc | | |
| B1 | 0 | 2 | 1 | 2 | B2 | 0 | 1 | 0 | 1 | 5246.3820(0.002) | -0.0011 |
| A2 | 0 | 3 | 1 | 3 | A1 | 0 | 2 | 0 | 2 | 7058.6730(0.002) | -0.0022 |
| B1 | 0 | 4 | 1 | 4 | B2 | 0 | 3 | 0 | 3 | 8956.8990(0.002) | 0.0016 |
| A2 | 0 | 5 | 1 | 5 | A1 | 0 | 4 | 0 | 4 | 10918.4910(0.002) | 0.0007 |
| B1 | 0 | 6 | 1 | 6 | B2 | 0 | 5 | 0 | 5 | 12897.7080(0.002) | 0.0008 |
| A2 | 0 | 7 | 1 | 7 | A1 | 0 | 6 | 0 | 6 | 14880.6620(0.002) | -0.0001 |
| B1 | 0 | 8 | 1 | 8 | B2 | 0 | 7 | 0 | 7 | 16864.3640(0.002) | 0.0007 |
| A2 | 0 | 9 | 1 | 9 | A1 | 0 | 8 | 0 | 8 | 18848.2310(0.002) | 0.0023 |
| B1 | 0 | 5 | 1 | 4 | B2 | 0 | 5 | 0 | 5 | 8780.3766(0.002) | 0.0043 |
| A2 | 0 | 6 | 1 | 5 | A1 | 0 | 6 | 0 | 6 | 10805.0584(0.002) | -0.0007 |
| B1 | 0 | 7 | 1 | 6 | B2 | 0 | 7 | 0 | 7 | 12802.7847(0.002) | -0.0046 |
| A2 | 0 | 8 | 1 | 7 | A1 | 0 | 8 | 0 | 8 | 14792.8227(0.002) | -0.0012 |
| B1 | 0 | 9 | 1 | 8 | B2 | 0 | 9 | 0 | 9 | 16780.3770(0.002) | -0.0021 |
| B1 | 0 | 10 | 0 | 10 | B2 | 0 | 9 | 0 | 9 | 20832.1420(0.002) | -0.0002 |
| B2 | 0 | 11 | 0 | 11 | B1 | 0 | 10 | 0 | 10 | 22816.0760(0.002) | 0.0005 |
| B1 | 0 | 12 | 0 | 12 | B2 | 0 | 11 | 0 | 11 | 24800.0180(0.002) | -0.0010 |
| B2 | 0 | 2 | 2 | 1 | B1 | 0 | 1 | 1 | 0 | 7803.1620(0.002) | 0.0002 |
| B2 | 0 | 4 | 2 | 3 | B1 | 0 | 3 | 1 | 2 | 11434.7910(0.002) | -0.0070 |
| A1 | 0 | 5 | 2 | 4 | A2 | 0 | 4 | 1 | 3 | 13095.0120(0.002) | 0.0010 |
| B2 | 0 | 6 | 2 | 5 | B1 | 0 | 5 | 1 | 4 | 14938.3040(0.002) | 0.0017 |
| A1 | 0 | 7 | 2 | 6 | A2 | 0 | 6 | 1 | 5 | 16881.5600(0.002) | 0.0007 |
| B2 | 0 | 8 | 2 | 7 | B1 | 0 | 7 | 1 | 6 | 18854.9850(0.002) | 0.0003 |
| A1 | 0 | 9 | 2 | 8 | A2 | 0 | 8 | 1 | 7 | 20835.8880(0.002) | 0.0008 |
| B2 | 0 | 10 | 2 | 9 | B1 | 0 | 9 | 1 | 8 | 22818.6450(0.002) | 0.0007 |
| A1 | 0 | 11 | 2 | 10 | A2 | 0 | 10 | 1 | 9 | 24801.9540(0.002) | -0.0011 |
| A1 | 0 | 6 | 2 | 4 | A2 | 0 | 6 | 1 | 5 | 8472.9084(0.002) | -0.0001 |
| B2 | 0 | 7 | 2 | 5 | B1 | 0 | 7 | 1 | 6 | 10616.8335(0.002) | -0.0024 |
| A1 | 0 | 8 | 2 | 6 | A2 | 0 | 8 | 1 | 7 | 12662.0328(0.002) | -0.0002 |
| A1 | 0 | 10 | 2 | 8 | A2 | 0 | 10 | 1 | 9 | 16669.4469(0.002) | 0.0039 |
| A1 | 0 | 5 | 2 | 4 | A2 | 0 | 5 | 1 | 5 | 8852.1951(0.002) | -0.0001 |
| B2 | 0 | 6 | 2 | 5 | B1 | 0 | 6 | 1 | 6 | 10820.9657(0.002) | -0.0016 |
| A1 | 0 | 7 | 2 | 6 | A2 | 0 | 7 | 1 | 7 | 12805.9550(0.002) | -0.0013 |
| B2 | 0 | 8 | 2 | 7 | B1 | 0 | 8 | 1 | 8 | 14793.4083(0.002) | -0.0024 |
| A1 | 0 | 9 | 2 | 8 | A2 | 0 | 9 | 1 | 9 | 16780.4813(0.002) | -0.0010 |
| A1 | 0 | 2 | 0 | 2 | A2 | 0 | 1 | 1 | 1 | 4556.3270(0.002) | 0.0003 |
| B2 | 0 | 3 | 0 | 3 | B1 | 0 | 2 | 1 | 2 | 6833.5910(0.002) | -0.0010 |
| A1 | 0 | 4 | 0 | 4 | A2 | 0 | 3 | 1 | 3 | 8904.6180(0.002) | -0.0001 |
| B2 | 0 | 5 | 0 | 5 | B1 | 0 | 4 | 1 | 4 | 10908.3320(0.002) | 0.0010 |
| A1 | 0 | 6 | 0 | 6 | A2 | 0 | 5 | 1 | 5 | 12895.9170(0.002) | 0.0003 |
| B2 | 0 | 7 | 0 | 7 | B1 | 0 | 6 | 1 | 6 | 14880.3660(0.002) | 0.0007 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| A1 | 0 | 8 | 0 | 8 | A2 | 0 | 7 | 1 | 7 | 16864.3170(0.002) | 0.0009 |
| B2 | 0 | 9 | 0 | 9 | B1 | 0 | 8 | 1 | 8 | 18848.2190(0.002) | -0.0025 |
| A1 | 0 | 10 | 1 | 10 | A2 | 0 | 9 | 1 | 9 | 20832.1420(0.002) | 0.0009 |
| A2 | 0 | 11 | 1 | 11 | A1 | 0 | 10 | 1 | 10 | 22816.0760(0.002) | 0.0004 |
| A1 | 0 | 12 | 1 | 12 | A2 | 0 | 11 | 1 | 11 | 24800.0180(0.002) | -0.0010 |
| A2 | 0 | 4 | 1 | 3 | A1 | 0 | 3 | 2 | 2 | 10361.0980(0.002) | -0.0029 |
| B1 | 0 | 5 | 1 | 4 | B2 | 0 | 4 | 2 | 3 | 12741.5330(0.002) | -0.0039 |
| A2 | 0 | 6 | 1 | 5 | A1 | 0 | 5 | 2 | 4 | 14848.7810(0.002) | 0.0004 |
| B1 | 0 | 7 | 1 | 6 | B2 | 0 | 6 | 2 | 5 | 16862.1880(0.002) | 0.0007 |
| A2 | 0 | 8 | 1 | 7 | A1 | 0 | 7 | 2 | 6 | 18851.1840(0.002) | 0.0003 |
| B1 | 0 | 9 | 1 | 8 | B2 | 0 | 8 | 2 | 7 | 20835.1910(0.002) | 0.0012 |
| A2 | 0 | 10 | 1 | 9 | A1 | 0 | 9 | 2 | 8 | 22818.5230(0.002) | 0.0005 |
| B1 | 0 | 11 | 1 | 10 | B2 | 0 | 10 | 2 | 9 | 24801.9380(0.002) | 0.0034 |
| A2 | 0 | 5 | 3 | 3 | A1 | 0 | 4 | 2 | 2 | 16169.8604(0.002) | -0.0034 |
| A2 | 0 | 7 | 3 | 5 | A1 | 0 | 6 | 2 | 4 | 19112.5030(0.002) | 0.0041 |
| B1 | 0 | 8 | 3 | 6 | B2 | 0 | 7 | 2 | 5 | 20920.8190(0.002) | 0.0020 |
| A2 | 0 | 9 | 3 | 7 | A1 | 0 | 8 | 2 | 6 | 22849.9580(0.002) | 0.0016 |
| B1 | 0 | 3 | 3 | 0 | B2 | 0 | 2 | 2 | 1 | 13151.1520(0.002) | 0.0000 |
| B1 | 0 | 5 | 3 | 2 | B2 | 0 | 4 | 2 | 3 | 22601.1060(0.002) | 0.0012 |
| A2 | 0 | 5 | 3 | 3 | A1 | 0 | 5 | 2 | 4 | 7041.0404(0.002) | 0.0031 |
| B1 | 0 | 6 | 3 | 4 | B2 | 0 | 6 | 2 | 5 | 8786.5790(0.002) | -0.0017 |
| A2 | 0 | 7 | 3 | 5 | A1 | 0 | 7 | 2 | 6 | 10703.8475(0.002) | -0.0006 |
| B1 | 0 | 8 | 3 | 6 | B2 | 0 | 8 | 2 | 7 | 12682.6678(0.002) | -0.0004 |
| A2 | 0 | 9 | 3 | 7 | A1 | 0 | 9 | 2 | 8 | 14676.1063(0.002) | 0.0040 |
| A2 | 0 | 8 | 3 | 5 | A1 | 0 | 8 | 2 | 6 | 10255.0970(0.002) | 0.0044 |
| B2 | 0 | 4 | 4 | 1 | B1 | 0 | 3 | 3 | 0 | 17221.0370(0.002) | 0.0030 |
| A1 | 0 | 5 | 4 | 2 | A2 | 0 | 4 | 3 | 1 | 19528.7730(0.002) | -0.0047 |
| B2 | 0 | 6 | 4 | 3 | B1 | 0 | 5 | 3 | 2 | 21198.5720(0.002) | -0.0018 |
| A1 | 0 | 7 | 4 | 4 | A2 | 0 | 6 | 3 | 3 | 22431.1230(0.002) | -0.0010 |
| B2 | 0 | 8 | 4 | 5 | B1 | 0 | 7 | 3 | 4 | 23620.4100(0.002) | 0.0012 |
| A1 | 0 | 10 | 2 | 8 | A2 | 0 | 9 | 3 | 7 | 24811.8650(0.002) | 0.0017 |
| A1 | 0 | 7 | 4 | 4 | A2 | 0 | 7 | 3 | 5 | 8797.5426(0.002) | 0.0020 |
| A1 | 0 | 9 | 4 | 6 | A2 | 0 | 9 | 3 | 7 | 12522.2201(0.002) | 0.0027 |
| B2 | 0 | 5 | 4 | 1 | B1 | 0 | 4 | 3 | 2 | 21069.6850(0.002) | 0.0000 |
| B1 | 0 | 5 | 5 | 0 | B2 | 0 | 4 | 4 | 1 | 21939.2140(0.002) | -0.0012 |
| A2 | 0 | 6 | 3 | 3 | A1 | 0 | 5 | 4 | 2 | 15423.1802(0.002) | -0.0033 |
| A2 | 0 | 8 | 3 | 5 | A1 | 0 | 7 | 4 | 4 | 22266.9196(0.002) | -0.0011 |
| A2 | 0 | 7 | 5 | 3 | A1 | 0 | 7 | 4 | 4 | 7902.3806(0.002) | 0.0041 |
| A2 | 0 | 5 | 5 | 1 | A1 | 0 | 4 | 4 | 0 | 21847.3400(0.002) | -0.0001 |
| B1 | 0 | 6 | 5 | 2 | B2 | 0 | 5 | 4 | 1 | 24435.4050(0.002) | 0.0018 |
| A1 | 0 | 6 | 6 | 0 | A2 | 0 | 6 | 5 | 1 | 8487.5639(0.002) | -0.0059 |
| B2 | 0 | 7 | 4 | 3 | B1 | 0 | 6 | 5 | 2 | 16845.8636(0.002) | 0.0018 |
| A1 | 0 | 8 | 4 | 4 | A2 | 0 | 7 | 5 | 3 | 21406.7351(0.002) | -0.0035 |
| B2 | 0 | 8 | 6 | 3 | B1 | 0 | 8 | 5 | 4 | 8780.1893(0.002) | 0.0031 |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| E2 | 1 | 2 | 1 | 2 | E2 | 1 | 1 | 0 | 1 | 6087.2890(0.002) | -0.0037 |
| E2 | 1 | 4 | 1 | 4 | E2 | 1 | 3 | 0 | 3 | 10389.3220(0.002) | -0.0006 |
| E1 | 1 | 5 | 1 | 5 | E1 | 1 | 4 | 0 | 4 | 11892.4451(0.002) | 0.0011 |
| E2 | 1 | 6 | 1 | 6 | E2 | 1 | 5 | 0 | 5 | 13340.4850(0.002) | 0.0003 |
| E1 | 1 | 7 | 1 | 7 | E1 | 1 | 6 | 0 | 6 | 15051.2920(0.002) | 0.0000 |
| E2 | 1 | 8 | 1 | 8 | E2 | 1 | 7 | 0 | 7 | 16944.4190(0.002) | -0.0003 |
| E1 | 1 | 9 | 1 | 9 | E1 | 1 | 8 | 0 | 8 | 18897.8165(0.002) | 0.0000 |
| E2 | 1 | 10 | 1 | 10 | E2 | 1 | 9 | 0 | 9 | 20868.2258(0.002) | -0.0009 |
| E1 | 1 | 11 | 1 | 11 | E1 | 1 | 10 | 0 | 10 | 22844.2687(0.002) | -0.0010 |
| E2 | 1 | 12 | 1 | 12 | E2 | 1 | 11 | 0 | 11 | 24822.8419(0.002) | -0.0001 |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| E2 | 1 | 7 | 1 | 6 | E2 | 1 | 7 | 0 | 7 | 10859.7707(0.002) | 0.0012 |
| E2 | 1 | 9 | 1 | 8 | E2 | 1 | 9 | 0 | 9 | 15842.5178(0.002) | 0.0014 |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| E1 | 1 | 4 | 0 | 4 | E1 | 1 | 3 | 1 | 3 | 6987.3722(0.002) | 0.0026 |
| E2 | 1 | 5 | 0 | 5 | E2 | 1 | 4 | 1 | 4 | 10198.5916(0.002) | 0.0003 |
| E1 | 1 | 6 | 0 | 6 | E1 | 1 | 5 | 1 | 5 | 12752.1919(0.002) | 0.0001 |
| E2 | 1 | 7 | 0 | 7 | E2 | 1 | 6 | 1 | 6 | 14902.3230(0.002) | -0.0001 |
| E1 | 1 | 8 | 0 | 8 | E1 | 1 | 7 | 1 | 7 | 16913.1750(0.002) | 0.0000 |
| E2 | 1 | 9 | 0 | 9 | E2 | 1 | 8 | 1 | 8 | 18891.9408(0.002) | -0.0002 |
| E1 | 1 | 10 | 0 | 10 | E1 | 1 | 9 | 1 | 9 | 20867.1995(0.002) | 0.0015 |
| E2 | 1 | 11 | 0 | 11 | E2 | 1 | 10 | 1 | 10 | 22844.0972(0.002) | -0.0012 |
| E1 | 1 | 12 | 0 | 12 | E1 | 1 | 11 | 1 | 11 | 24822.8125(0.002) | -0.0021 |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| E2 | 1 | 2 | 2 | 1 | E2 | 1 | 1 | 1 | 0 | 6962.2023(0.002) | 0.0028 |
| E2 | 1 | 4 | 2 | 3 | E2 | 1 | 3 | 1 | 2 | 12784.9210(0.002) | 0.0040 |
| E1 | 1 | 5 | 2 | 4 | E1 | 1 | 4 | 1 | 3 | 15456.4180(0.002) | 0.0005 |
| E2 | 1 | 6 | 2 | 5 | E2 | 1 | 5 | 1 | 4 | 17562.2300(0.002) | -0.0006 |
| E1 | 1 | 7 | 2 | 6 | E1 | 1 | 6 | 1 | 5 | 18881.1076(0.002) | -0.0010 |
| E2 | 1 | 8 | 2 | 7 | E2 | 1 | 7 | 1 | 6 | 19905.6965(0.002) | -0.0015 |
| E1 | 1 | 9 | 2 | 8 | E1 | 1 | 8 | 1 | 7 | 21286.8131(0.002) | -0.0009 |
| E2 | 1 | 10 | 2 | 9 | E2 | 1 | 9 | 1 | 8 | 23040.1202(0.002) | -0.0005 |
| E1 | 1 | 11 | 2 | 10 | E1 | 1 | 10 | 1 | 9 | 24940.9032(0.002) | -0.0013 |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| E2 | 1 | 4 | 2 | 3 | E2 | 1 | 4 | 1 | 4 | 8518.5291(0.002) | -0.0050 |
| E2 | 1 | 6 | 2 | 5 | E2 | 1 | 6 | 1 | 6 | 10200.2775(0.002) | 0.0028 |
| E1 | 1 | 7 | 2 | 6 | E1 | 1 | 7 | 1 | 7 | 11847.1561(0.002) | 0.0035 |
| E2 | 1 | 8 | 2 | 7 | E2 | 1 | 8 | 1 | 8 | 13821.0498(0.002) | 0.0016 |
| E2 | 1 | 10 | 2 | 9 | E2 | 1 | 10 | 1 | 10 | 18014.4116(0.002) | 0.0012 |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| E2 | 1 | 3 | 2 | 1 | E2 | 1 | 3 | 1 | 2 | 8779.6542(0.002) | 0.0095 |
| E2 | 1 | 9 | 2 | 7 | E2 | 1 | 9 | 1 | 8 | 12161.1180(0.002) | -0.0027 |
| E2 | 1 | 11 | 2 | 9 | E2 | 1 | 11 | 1 | 10 | 17531.4598(0.002) | -0.0042 |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| E2 | 1 | 5 | 1 | 4 | E2 | 1 | 4 | 1 | 4 | 16177.1212(0.002) | 0.0011 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| E2 | 1 | 4 | 3 | 2 | E2 | 1 | 4 | 2 | 3 | 9742.6611(0.002) | 0.0003 |
| E1 | 1 | 5 | 3 | 3 | E1 | 1 | 5 | 2 | 4 | 10239.5750(0.002) | 0.0027 |
| E1 | 1 | 7 | 3 | 5 | E1 | 1 | 7 | 2 | 6 | 11066.0051(0.002) | 0.0001 |
| E2 | 1 | 8 | 3 | 6 | E2 | 1 | 8 | 2 | 7 | 12048.2467(0.002) | -0.0025 |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| E1 | 1 | 7 | 3 | 5 | E1 | 1 | 6 | 2 | 4 | 22311.8156(0.002) | -0.0021 |
| E2 | 1 | 8 | 3 | 6 | E2 | 1 | 7 | 2 | 5 | 24499.3116(0.002) | -0.0043 |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| E1 | 1 | 6 | 1 | 5 | E1 | 1 | 5 | 2 | 4 | 11682.5470(0.002) | -0.0014 |
| E2 | 1 | 7 | 1 | 6 | E2 | 1 | 6 | 2 | 5 | 15561.8180(0.002) | 0.0001 |
| E1 | 1 | 8 | 1 | 7 | E1 | 1 | 7 | 2 | 6 | 18589.6372(0.002) | 0.0010 |
| E2 | 1 | 9 | 1 | 8 | E2 | 1 | 8 | 2 | 7 | 20913.4104(0.002) | 0.0012 |
| E1 | 1 | 10 | 1 | 9 | E1 | 1 | 9 | 2 | 8 | 22954.5080(0.002) | -0.0008 |
| E2 | 1 | 11 | 1 | 10 | E2 | 1 | 10 | 2 | 9 | 24923.4842(0.002) | -0.0019 |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| E2 | 1 | 5 | 3 | 2 | E2 | 1 | 5 | 2 | 3 | 10651.2463(0.002) | 0.0022 |
| E1 | 1 | 6 | 3 | 3 | E1 | 1 | 6 | 2 | 4 | 10984.7166(0.002) | 0.0027 |
| E2 | 1 | 7 | 3 | 4 | E2 | 1 | 7 | 2 | 5 | 10585.9296(0.002) | 0.0023 |
| E2 | 1 | 3 | 3 | 0 | E2 | 1 | 2 | 2 | 1 | 18038.7706(0.010) | -0.0012 |
| E2 | 1 | 7 | 2 | 5 | E2 | 1 | 6 | 2 | 5 | 23016.4464(0.002) | -0.0029 |
| E2 | 1 | 5 | 4 | 1 | E2 | 1 | 5 | 3 | 2 | 10227.8840(0.002) | -0.0020 |
| E1 | 1 | 6 | 4 | 2 | E1 | 1 | 6 | 3 | 3 | 11676.2812(0.002) | 0.0005 |
| E2 | 1 | 7 | 4 | 3 | E2 | 1 | 7 | 3 | 4 | 12501.1035(0.002) | 0.0006 |
| E2 | 1 | 9 | 4 | 5 | E2 | 1 | 9 | 3 | 6 | 12377.0149(0.002) | 0.0001 |
| E2 | 1 | 4 | 4 | 1 | E2 | 1 | 3 | 3 | 0 | 15275.7366(0.002) | 0.0038 |
| E1 | 1 | 5 | 4 | 2 | E1 | 1 | 4 | 3 | 1 | 17658.5800(0.002) | 0.0041 |
| E2 | 1 | 6 | 4 | 3 | E2 | 1 | 5 | 3 | 2 | 20526.8258(0.002) | 0.0010 |
| E1 | 1 | 7 | 4 | 4 | E1 | 1 | 6 | 3 | 3 | 23452.8368(0.002) | -0.0034 |
| E1 | 1 | 8 | 2 | 6 | E1 | 1 | 7 | 3 | 5 | 16697.9088(0.002) | -0.0001 |
| E2 | 1 | 9 | 2 | 7 | E2 | 1 | 8 | 3 | 6 | 21026.2843(0.002) | 0.0036 |
| E1 | 1 | 10 | 2 | 8 | E1 | 1 | 9 | 3 | 7 | 24428.2364(0.002) | 0.0040 |
| E1 | 1 | 5 | 4 | 2 | E1 | 1 | 5 | 3 | 3 | 10722.8960(0.002) | -0.0039 |
| E2 | 1 | 6 | 4 | 3 | E2 | 1 | 6 | 3 | 4 | 11615.4529(0.002) | 0.0014 |
| E1 | 1 | 7 | 4 | 4 | E1 | 1 | 7 | 3 | 5 | 12125.7369(0.002) | 0.0004 |
| E2 | 1 | 8 | 4 | 5 | E2 | 1 | 8 | 3 | 6 | 12457.7841(0.002) | -0.0041 |
| E2 | 1 | 7 | 5 | 2 | E2 | 1 | 7 | 4 | 3 | 12353.8773(0.002) | -0.0011 |
| E1 | 1 | 5 | 5 | 1 | E1 | 1 | 4 | 4 | 0 | 19887.0356(0.002) | -0.0055 |
| E2 | 1 | 6 | 5 | 2 | E2 | 1 | 5 | 4 | 1 | 21669.6732(0.002) | -0.0015 |
| E1 | 1 | 7 | 5 | 3 | E1 | 1 | 6 | 4 | 2 | 24413.9916(0.002) | -0.0037 |
| E2 | 1 | 6 | 5 | 2 | E2 | 1 | 6 | 4 | 3 | 11370.7300(0.002) | -0.0059 |
| E2 | 1 | 8 | 5 | 4 | E2 | 1 | 8 | 4 | 5 | 13447.5100(0.002) | 0.0019 |
| E2 | 1 | 5 | 4 | 1 | E2 | 1 | 4 | 4 | 1 | 18149.8765(0.002) | 0.0112 |
| E1 | 1 | 6 | 4 | 2 | E1 | 1 | 5 | 4 | 2 | 21016.3692(0.002) | 0.0025 |
| E2 | 1 | 7 | 4 | 3 | E2 | 1 | 6 | 4 | 3 | 23920.2723(0.002) | -0.0032 |
| E2 | 1 | 9 | 3 | 6 | E2 | 1 | 8 | 4 | 5 | 17494.5451(0.002) | -0.0018 |
| E2 | 1 | 5 | 5 | 0 | E2 | 1 | 4 | 4 | 1 | 24858.5476(0.002) | -0.0013 |
| E2 | 1 | 7 | 5 | 2 | E2 | 1 | 6 | 5 | 2 | 24903.4203(0.002) | 0.0024 |
| E2 | 2 | 9 | 1 | 9 | E2 | 2 | 8 | 0 | 8 | 19463.1213(0.002) | 0.0025 |
| E2 | 2 | 5 | 2 | 4 | E2 | 2 | 4 | 1 | 3 | 15600.9320(0.002) | -0.0083 |
| E2 | 2 | 6 | 1 | 5 | E2 | 2 | 5 | 1 | 5 | 17778.5195(0.002) | 0.0029 |
| E2 | 2 | 5 | 3 | 3 | E2 | 2 | 4 | 2 | 2 | 16485.5760(0.002) | 0.0055 |
| E2 | 2 | 7 | 3 | 5 | E2 | 2 | 6 | 2 | 4 | 22266.4936(0.010) | -0.0026 |
| E2 | 2 | 6 | 2 | 4 | E2 | 2 | 5 | 2 | 4 | 18922.8913(0.002) | -0.0072 |
| E2 | 2 | 8 | 2 | 6 | E2 | 2 | 7 | 2 | 6 | 24575.8030(0.002) | 0.0032 |
| E2 | 2 | 6 | 3 | 3 | E2 | 2 | 5 | 3 | 3 | 19835.7953(0.002) | 0.0017 |

```
E2  2   7   4   4    E2  2   6   3   3    23197.7720(0.002)  0.0001
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**Table S6**. Rotational transitions of the parent species of 3,5-difluorotoluene sorted by branch, together with fit residuals (o.-c., frequencies in MHz). Rotational transitions labeled with symmetry species, free rotor quantum number (*m*), and asymmetric rotor quantum numbers ($J$, $K_a$, $K_c$).

| Upper level | | | | | Lower level | | | | | Measured(Unc. ) | o.-c.(MHz) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sym' | m' | J' | Ka' | Kc' | Sym | m | J | Ka | Kc | | |
| B2 | 0 | 3 | 0 | 3 | B1 | 0 | 2 | 0 | 2 | 6174.6440(0.002) | 0.0008 |
| B1 | 0 | 4 | 0 | 4 | B2 | 0 | 3 | 0 | 3 | 7938.7798(0.002) | -0.0003 |
| B2 | 0 | 5 | 0 | 5 | B1 | 0 | 4 | 0 | 4 | 9702.9157(0.002) | -0.0003 |
| B1 | 0 | 6 | 0 | 6 | B2 | 0 | 5 | 0 | 5 | 11467.0502(0.002) | -0.0006 |
| B2 | 0 | 7 | 0 | 7 | B1 | 0 | 6 | 0 | 6 | 13231.1836(0.002) | -0.0006 |
| B1 | 0 | 8 | 0 | 8 | B2 | 0 | 7 | 0 | 7 | 14995.3156(0.002) | -0.0004 |
| B2 | 0 | 9 | 0 | 9 | B1 | 0 | 8 | 0 | 8 | 16759.4461(0.002) | 0.0000 |
| B1 | 0 | 10 | 0 | 10 | B2 | 0 | 9 | 0 | 9 | 18523.5742(0.002) | 0.0000 |
| B2 | 0 | 11 | 0 | 11 | B1 | 0 | 10 | 0 | 10 | 20287.7001(0.002) | 0.0001 |
| B1 | 0 | 12 | 0 | 12 | B2 | 0 | 11 | 0 | 11 | 22051.8236(0.002) | 0.0001 |
| B2 | 0 | 13 | 0 | 13 | B1 | 0 | 12 | 0 | 12 | 23815.9443(0.002) | 0.0000 |
| B1 | 0 | 7 | 1 | 6 | B2 | 0 | 7 | 0 | 7 | 11468.9288(0.002) | -0.0017 |
| B2 | 0 | 8 | 1 | 7 | B1 | 0 | 8 | 0 | 8 | 13233.3680(0.002) | -0.0036 |
| B1 | 0 | 9 | 1 | 8 | B2 | 0 | 9 | 0 | 9 | 14997.8102(0.002) | 0.0006 |
| A2 | 0 | 3 | 1 | 3 | A1 | 0 | 2 | 1 | 2 | 6174.6440(0.002) | 0.0009 |
| A1 | 0 | 4 | 1 | 4 | A2 | 0 | 3 | 1 | 3 | 7938.7798(0.002) | -0.0003 |
| A2 | 0 | 5 | 1 | 5 | A1 | 0 | 4 | 1 | 4 | 9702.9157(0.002) | -0.0003 |
| A1 | 0 | 6 | 1 | 6 | A2 | 0 | 5 | 1 | 5 | 11467.0502(0.002) | -0.0006 |
| A2 | 0 | 7 | 1 | 7 | A1 | 0 | 6 | 1 | 6 | 13231.1836(0.002) | -0.0006 |
| A1 | 0 | 8 | 1 | 8 | A2 | 0 | 7 | 1 | 7 | 14995.3156(0.002) | -0.0004 |
| A2 | 0 | 9 | 1 | 9 | A1 | 0 | 8 | 1 | 8 | 16759.4461(0.002) | 0.0000 |
| A1 | 0 | 10 | 1 | 10 | A2 | 0 | 9 | 1 | 9 | 18523.5742(0.002) | 0.0000 |
| A2 | 0 | 11 | 1 | 11 | A1 | 0 | 10 | 1 | 10 | 20287.7001(0.002) | 0.0001 |
| A1 | 0 | 12 | 1 | 12 | A2 | 0 | 11 | 1 | 11 | 22051.8236(0.002) | 0.0001 |
| A2 | 0 | 13 | 1 | 13 | A1 | 0 | 12 | 1 | 12 | 23815.9443(0.002) | 0.0000 |
| B1 | 0 | 5 | 1 | 4 | B2 | 0 | 4 | 1 | 3 | 11467.3651(0.002) | -0.0003 |
| B2 | 0 | 6 | 1 | 5 | B1 | 0 | 5 | 1 | 4 | 13231.4976(0.002) | -0.0001 |
| B1 | 0 | 7 | 1 | 6 | B2 | 0 | 6 | 1 | 5 | 14995.6283(0.002) | 0.0000 |
| B2 | 0 | 8 | 1 | 7 | B1 | 0 | 7 | 1 | 6 | 16759.7571(0.002) | -0.0001 |
| B1 | 0 | 9 | 1 | 8 | B2 | 0 | 8 | 1 | 7 | 18523.8840(0.002) | -0.0001 |
| B2 | 0 | 10 | 1 | 9 | B1 | 0 | 9 | 1 | 8 | 20288.0096(0.002) | 0.0009 |
| B1 | 0 | 11 | 1 | 10 | B2 | 0 | 10 | 1 | 9 | 22052.1316(0.002) | 0.0007 |
| B1 | 0 | 3 | 3 | 0 | B2 | 0 | 2 | 1 | 1 | 11468.2560(0.002) | -0.0023 |
| B1 | 0 | 8 | 2 | 6 | B2 | 0 | 8 | 1 | 7 | 11468.8906(0.002) | 0.0010 |
| B2 | 0 | 9 | 2 | 7 | B1 | 0 | 9 | 1 | 8 | 13233.3186(0.002) | 0.0000 |
| B1 | 0 | 10 | 2 | 8 | B2 | 0 | 10 | 1 | 9 | 14997.7447(0.002) | 0.0019 |
| A1 | 0 | 7 | 2 | 6 | A2 | 0 | 7 | 1 | 7 | 11468.9288(0.002) | -0.0017 |
| A2 | 0 | 8 | 2 | 7 | A1 | 0 | 8 | 1 | 8 | 13233.3680(0.002) | -0.0036 |
| A1 | 0 | 9 | 2 | 8 | A2 | 0 | 9 | 1 | 9 | 14997.8102(0.002) | 0.0006 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| B1 | 0 | 9 | 3 | 6 | B2 | 0 | 9 | 2 | 7 | 11468.8455(0.002) | 0.0018 |
| B2 | 0 | 10 | 3 | 7 | B1 | 0 | 10 | 2 | 8 | 13233.2581(0.002) | -0.0016 |
| B1 | 0 | 11 | 3 | 8 | B2 | 0 | 11 | 2 | 9 | 14997.6697(0.002) | 0.0003 |
| | | | | | | | | | | | |
| B2 | 0 | 5 | 2 | 3 | B1 | 0 | 4 | 2 | 2 | 13231.8111(0.002) | -0.0012 |
| B1 | 0 | 6 | 2 | 4 | B2 | 0 | 5 | 2 | 3 | 14995.9396(0.002) | -0.0001 |
| B2 | 0 | 7 | 2 | 5 | B1 | 0 | 6 | 2 | 4 | 16760.0662(0.002) | 0.0000 |
| B1 | 0 | 8 | 2 | 6 | B2 | 0 | 7 | 2 | 5 | 18524.1909(0.002) | 0.0002 |
| B2 | 0 | 9 | 2 | 7 | B1 | 0 | 8 | 2 | 6 | 20288.3136(0.002) | 0.0005 |
| B1 | 0 | 10 | 2 | 8 | B2 | 0 | 9 | 2 | 7 | 22052.4334(0.002) | 0.0005 |
| | | | | | | | | | | | |
| A1 | 0 | 8 | 3 | 6 | A2 | 0 | 8 | 2 | 7 | 11468.8906(0.002) | 0.0010 |
| A2 | 0 | 9 | 3 | 7 | A1 | 0 | 9 | 2 | 8 | 13233.3186(0.002) | 0.0000 |
| A1 | 0 | 10 | 3 | 8 | A2 | 0 | 10 | 2 | 9 | 14997.7447(0.002) | 0.0019 |
| | | | | | | | | | | | |
| A1 | 0 | 5 | 2 | 4 | A2 | 0 | 4 | 2 | 3 | 11467.3651(0.002) | -0.0003 |
| A2 | 0 | 6 | 2 | 5 | A1 | 0 | 5 | 2 | 4 | 13231.4976(0.002) | -0.0001 |
| A1 | 0 | 7 | 2 | 6 | A2 | 0 | 6 | 2 | 5 | 14995.6283(0.002) | 0.0000 |
| A2 | 0 | 8 | 2 | 7 | A1 | 0 | 7 | 2 | 6 | 16759.7571(0.002) | -0.0001 |
| A1 | 0 | 9 | 2 | 8 | A2 | 0 | 8 | 2 | 7 | 18523.8840(0.002) | -0.0001 |
| A2 | 0 | 10 | 2 | 9 | A1 | 0 | 9 | 2 | 8 | 20288.0096(0.002) | 0.0009 |
| A1 | 0 | 11 | 2 | 10 | A2 | 0 | 10 | 2 | 9 | 22052.1316(0.002) | 0.0007 |
| | | | | | | | | | | | |
| A1 | 0 | 4 | 4 | 0 | A2 | 0 | 3 | 2 | 1 | 14997.0908(0.002) | 0.0041 |
| | | | | | | | | | | | |
| A1 | 0 | 4 | 3 | 2 | A2 | 0 | 3 | 2 | 1 | 11468.1892(0.002) | 0.0032 |
| | | | | | | | | | | | |
| B1 | 0 | 10 | 4 | 6 | B2 | 0 | 10 | 3 | 7 | 11468.7896(0.002) | -0.0030 |
| B2 | 0 | 11 | 4 | 7 | B1 | 0 | 11 | 3 | 8 | 13233.1946(0.002) | -0.0004 |
| B1 | 0 | 12 | 4 | 8 | B2 | 0 | 12 | 3 | 9 | 14997.5889(0.002) | -0.0005 |
| | | | | | | | | | | | |
| B1 | 0 | 7 | 3 | 4 | B2 | 0 | 6 | 3 | 3 | 18524.5003(0.002) | 0.0003 |
| B2 | 0 | 8 | 3 | 5 | B1 | 0 | 7 | 3 | 4 | 20288.6189(0.002) | 0.0001 |
| B1 | 0 | 9 | 3 | 6 | B2 | 0 | 8 | 3 | 5 | 22052.7358(0.002) | 0.0006 |
| | | | | | | | | | | | |
| A2 | 0 | 5 | 3 | 3 | A1 | 0 | 4 | 3 | 2 | 13231.8111(0.002) | 0.0007 |
| A1 | 0 | 6 | 3 | 4 | A2 | 0 | 5 | 3 | 3 | 14995.9396(0.002) | -0.0001 |
| A2 | 0 | 7 | 3 | 5 | A1 | 0 | 6 | 3 | 4 | 16760.0662(0.002) | 0.0000 |
| A1 | 0 | 8 | 3 | 6 | A2 | 0 | 7 | 3 | 5 | 18524.1909(0.002) | 0.0002 |
| A2 | 0 | 9 | 3 | 7 | A1 | 0 | 8 | 3 | 6 | 20288.3136(0.002) | 0.0005 |
| A1 | 0 | 10 | 3 | 8 | A2 | 0 | 9 | 3 | 7 | 22052.4334(0.002) | 0.0005 |
| | | | | | | | | | | | |
| B1 | 0 | 5 | 4 | 2 | B2 | 0 | 4 | 3 | 1 | 14997.0908(0.002) | 0.0015 |
| A2 | 0 | 6 | 4 | 3 | A1 | 0 | 5 | 3 | 2 | 16760.3832(0.002) | 0.0020 |
| | | | | | | | | | | | |
| A1 | 0 | 9 | 4 | 6 | A2 | 0 | 9 | 3 | 7 | 11468.8455(0.002) | 0.0018 |
| A2 | 0 | 10 | 4 | 7 | A1 | 0 | 10 | 3 | 8 | 13233.2581(0.002) | -0.0016 |
| A1 | 0 | 11 | 4 | 8 | A2 | 0 | 11 | 3 | 9 | 14997.6697(0.002) | 0.0003 |
| | | | | | | | | | | | |
| A1 | 0 | 7 | 4 | 4 | A2 | 0 | 6 | 4 | 3 | 18524.5003(0.002) | 0.0003 |
| A2 | 0 | 8 | 4 | 5 | A1 | 0 | 7 | 4 | 4 | 20288.6189(0.002) | 0.0001 |
| A1 | 0 | 9 | 4 | 6 | A2 | 0 | 8 | 4 | 5 | 22052.7358(0.002) | 0.0006 |
| | | | | | | | | | | | |
| A1 | 0 | 10 | 5 | 6 | A2 | 0 | 10 | 4 | 7 | 11468.7896(0.002) | -0.0030 |
| A2 | 0 | 11 | 5 | 7 | A1 | 0 | 11 | 4 | 8 | 13233.1946(0.002) | -0.0004 |
| A1 | 0 | 12 | 5 | 8 | A2 | 0 | 12 | 4 | 9 | 14997.5889(0.002) | -0.0005 |
| | | | | | | | | | | | |
| B2 | 0 | 6 | 3 | 3 | B1 | 0 | 5 | 4 | 2 | 16760.3739(0.002) | -0.0029 |
| | | | | | | | | | | | |
| B1 | 0 | 11 | 5 | 6 | B2 | 0 | 11 | 4 | 7 | 11468.7355(0.002) | -0.0010 |
| B2 | 0 | 12 | 5 | 7 | B1 | 0 | 12 | 4 | 8 | 13233.1250(0.002) | 0.0007 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| B1 | 0 | 13 | 5 | 8 | B2 | 0 | 13 | 4 | 9 | 14997.5024(0.002) | -0.0002 |
| A1 | 0 | 11 | 6 | 6 | A2 | 0 | 11 | 5 | 7 | 11468.7355(0.002) | -0.0010 |
| A2 | 0 | 12 | 6 | 7 | A1 | 0 | 12 | 5 | 8 | 13233.1250(0.002) | 0.0007 |
| A1 | 0 | 13 | 6 | 8 | A2 | 0 | 13 | 5 | 9 | 14997.5024(0.002) | -0.0002 |
| B1 | 0 | 12 | 6 | 6 | B2 | 0 | 12 | 5 | 7 | 11468.6757(0.002) | 0.0005 |
| B2 | 0 | 13 | 6 | 7 | B1 | 0 | 13 | 5 | 8 | 13233.0476(0.002) | -0.0001 |
| B1 | 0 | 14 | 6 | 8 | B2 | 0 | 14 | 5 | 9 | 14997.4095(0.002) | 0.0003 |
| A1 | 0 | 12 | 7 | 6 | A2 | 0 | 12 | 6 | 7 | 11468.6757(0.002) | 0.0005 |
| A2 | 0 | 13 | 7 | 7 | A1 | 0 | 13 | 6 | 8 | 13233.0476(0.002) | -0.0001 |
| A1 | 0 | 14 | 7 | 8 | A2 | 0 | 14 | 6 | 9 | 14997.4095(0.002) | 0.0003 |
| B1 | 0 | 13 | 7 | 6 | B2 | 0 | 13 | 6 | 7 | 11468.6080(0.002) | -0.0009 |
| B1 | 0 | 15 | 7 | 8 | B2 | 0 | 15 | 6 | 9 | 14997.3089(0.002) | -0.0002 |
| A1 | 0 | 13 | 8 | 6 | A2 | 0 | 13 | 7 | 7 | 11468.6080(0.002) | -0.0009 |
| A1 | 0 | 15 | 8 | 8 | A2 | 0 | 15 | 7 | 9 | 14997.3089(0.002) | -0.0002 |
| B1 | 0 | 14 | 8 | 6 | B2 | 0 | 14 | 7 | 7 | 11468.5383(0.002) | 0.0009 |
| B2 | 0 | 15 | 8 | 7 | B1 | 0 | 15 | 7 | 8 | 13232.8769(0.002) | -0.0001 |
| A1 | 0 | 14 | 9 | 6 | A2 | 0 | 14 | 8 | 7 | 11468.5383(0.002) | 0.0009 |
| A2 | 0 | 15 | 9 | 7 | A1 | 0 | 15 | 8 | 8 | 13232.8769(0.002) | -0.0001 |
| B1 | 0 | 15 | 9 | 6 | B2 | 0 | 15 | 8 | 7 | 11468.4613(0.002) | 0.0005 |
| A1 | 0 | 15 | 10 | 6 | A2 | 0 | 15 | 9 | 7 | 11468.4613(0.002) | 0.0005 |
| E2 | 1 | 10 | 0 | 10 | E2 | 1 | 9 | 0 | 9 | 18545.9842(0.002) | -0.0006 |
| E2 | 1 | 11 | 0 | 11 | E2 | 1 | 10 | 0 | 10 | 20305.6635(0.002) | 0.0001 |
| E2 | 1 | 12 | 0 | 12 | E2 | 1 | 11 | 0 | 11 | 22066.5509(0.002) | -0.0024 |
| E2 | 1 | 13 | 0 | 13 | E2 | 1 | 12 | 0 | 12 | 23828.2453(0.002) | 0.0002 |
| E1 | 1 | 3 | 1 | 3 | E1 | 1 | 2 | 0 | 2 | 7157.5945(0.002) | 0.0008 |
| E2 | 1 | 4 | 1 | 4 | E2 | 1 | 3 | 0 | 3 | 8719.2607(0.002) | 0.0004 |
| E1 | 1 | 5 | 1 | 5 | E1 | 1 | 4 | 0 | 4 | 9997.5114(0.002) | 0.0027 |
| E2 | 1 | 6 | 1 | 6 | E2 | 1 | 5 | 0 | 5 | 11564.5157(0.002) | 0.0009 |
| E1 | 1 | 7 | 1 | 7 | E1 | 1 | 6 | 0 | 6 | 13286.2219(0.002) | -0.0006 |
| E2 | 1 | 8 | 1 | 8 | E2 | 1 | 7 | 0 | 7 | 15033.8052(0.002) | 0.0031 |
| E1 | 1 | 9 | 1 | 9 | E1 | 1 | 8 | 0 | 8 | 16788.2340(0.002) | -0.0012 |
| E2 | 1 | 7 | 1 | 6 | E2 | 1 | 7 | 0 | 7 | 10682.6720(0.002) | 0.0060 |
| E2 | 1 | 9 | 1 | 8 | E2 | 1 | 9 | 0 | 9 | 14464.7536(0.002) | -0.0018 |
| E2 | 1 | 10 | 1 | 9 | E2 | 1 | 10 | 0 | 10 | 16300.7707(0.002) | 0.0019 |
| E1 | 1 | 10 | 1 | 10 | E1 | 1 | 9 | 1 | 9 | 18545.9842(0.002) | -0.0006 |
| E1 | 1 | 11 | 1 | 11 | E1 | 1 | 10 | 1 | 10 | 20305.6635(0.002) | 0.0001 |
| E1 | 1 | 12 | 1 | 12 | E1 | 1 | 11 | 1 | 11 | 22066.5509(0.002) | -0.0024 |
| E1 | 1 | 13 | 1 | 13 | E1 | 1 | 12 | 1 | 12 | 23828.2453(0.002) | 0.0002 |
| E2 | 1 | 6 | 2 | 5 | E2 | 1 | 6 | 1 | 6 | 8769.3315(0.002) | 0.0019 |
| E2 | 1 | 8 | 2 | 7 | E2 | 1 | 8 | 1 | 8 | 12601.6664(0.002) | 0.0021 |
| E1 | 1 | 9 | 2 | 8 | E1 | 1 | 9 | 1 | 9 | 14464.7654(0.002) | -0.0039 |
| E1 | 1 | 10 | 2 | 9 | E1 | 1 | 10 | 1 | 10 | 16300.7707(0.002) | 0.0022 |
| E2 | 1 | 10 | 1 | 9 | E2 | 1 | 9 | 1 | 8 | 20381.9976(0.002) | -0.0006 |
| E2 | 1 | 11 | 1 | 10 | E2 | 1 | 10 | 1 | 9 | 22124.4842(0.002) | 0.0001 |
| E1 | 1 | 4 | 0 | 4 | E1 | 1 | 3 | 1 | 3 | 7359.0809(0.002) | -0.0030 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| E2 | 1 | 5 | 0 | 5 | E2 | 1 | 4 | 1 | 4 | 9709.1838(0.002) | -0.0025 |
| E1 | 1 | 6 | 0 | 6 | E1 | 1 | 5 | 1 | 5 | 11538.7194(0.002) | -0.0019 |
| E2 | 1 | 7 | 0 | 7 | E2 | 1 | 6 | 1 | 6 | 13284.9587(0.002) | -0.0008 |
| E1 | 1 | 8 | 0 | 8 | E1 | 1 | 7 | 1 | 7 | 15033.7583(0.002) | -0.0036 |
| E2 | 1 | 9 | 0 | 9 | E2 | 1 | 8 | 1 | 8 | 16788.2340(0.002) | -0.0003 |
| E1 | 1 | 7 | 2 | 6 | E1 | 1 | 6 | 1 | 5 | 15408.4296(0.002) | 0.0032 |
| E2 | 1 | 8 | 2 | 7 | E2 | 1 | 7 | 1 | 6 | 16952.8008(0.002) | 0.0004 |
| E1 | 1 | 9 | 2 | 8 | E1 | 1 | 8 | 1 | 7 | 18651.8641(0.002) | -0.0005 |
| E2 | 1 | 9 | 2 | 7 | E2 | 1 | 9 | 1 | 8 | 12420.9640(0.002) | -0.0006 |
| E2 | 1 | 10 | 3 | 8 | E2 | 1 | 10 | 1 | 9 | 14335.9283(0.002) | -0.0013 |
| E1 | 1 | 10 | 2 | 9 | E1 | 1 | 9 | 2 | 8 | 20381.9866(0.002) | 0.0027 |
| E1 | 1 | 11 | 2 | 10 | E1 | 1 | 10 | 2 | 9 | 22124.4842(0.002) | -0.0002 |
| E2 | 1 | 7 | 1 | 6 | E2 | 1 | 6 | 2 | 5 | 15198.2922(0.002) | -0.0038 |
| E1 | 1 | 8 | 1 | 7 | E1 | 1 | 7 | 2 | 6 | 16938.9423(0.002) | -0.0008 |
| E2 | 1 | 9 | 1 | 8 | E2 | 1 | 8 | 2 | 7 | 18651.3250(0.002) | -0.0004 |
| E1 | 1 | 10 | 2 | 8 | E1 | 1 | 10 | 2 | 9 | 14335.8159(0.002) | 0.0003 |
| E2 | 1 | 8 | 3 | 6 | E2 | 1 | 8 | 2 | 7 | 10453.9947(0.002) | -0.0002 |
| E1 | 1 | 9 | 3 | 7 | E1 | 1 | 9 | 2 | 8 | 12424.6128(0.002) | -0.0012 |
| E2 | 1 | 8 | 4 | 5 | E2 | 1 | 8 | 3 | 6 | 8542.5154(0.002) | 0.0013 |
| E1 | 1 | 10 | 2 | 8 | E1 | 1 | 9 | 3 | 7 | 22293.1862(0.002) | 0.0007 |
| E2 | 1 | 6 | 5 | 2 | E2 | 1 | 6 | 4 | 3 | 10678.2273(0.002) | -0.0007 |
| E1 | 1 | 8 | 3 | 5 | E1 | 1 | 7 | 4 | 4 | 17636.3211(0.002) | 0.0006 |
| E2 | 2 | 9 | 1 | 9 | E2 | 2 | 8 | 0 | 8 | 16912.6245(0.002) | 0.0008 |
| E2 | 2 | 6 | 2 | 4 | E2 | 2 | 5 | 2 | 4 | 16011.6707(0.002) | -0.0009 |
| E2 | 2 | 6 | 3 | 3 | E2 | 2 | 5 | 3 | 3 | 16425.3845(0.002) | 0.0016 |

**Table S7**. Rotational transitions of the $^{13}$C(2) and $^{13}$C(6) isotopologues of 2,6-difluorotoluene.

| Upper level | | | | | Lower level | | | | | Measured(Unc. ) | o.-c.(MHz) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sym' | m' | J' | Ka' | Kc' | Sym | m | J | Ka | Kc | | |
| A1 | 0 | 10 | 0 | 10 | A2 | 0 | 9 | 0 | 9 | 20776.9300(0.002) | -0.0007 |
| A2 | 0 | 11 | 0 | 11 | A1 | 0 | 10 | 0 | 10 | 22755.6030(0.002) | -0.0005 |
| A1 | 0 | 12 | 0 | 12 | A2 | 0 | 11 | 0 | 11 | 24734.2880(0.002) | 0.0013 |
| A1 | 0 | 4 | 1 | 4 | A2 | 0 | 3 | 0 | 3 | 8934.7930(0.002) | 0.0008 |
| A2 | 0 | 5 | 1 | 5 | A1 | 0 | 4 | 0 | 4 | 10890.0030(0.002) | -0.0016 |
| A1 | 0 | 6 | 1 | 6 | A2 | 0 | 5 | 0 | 5 | 12863.6408(0.002) | 0.0002 |
| A2 | 0 | 7 | 1 | 7 | A1 | 0 | 6 | 0 | 6 | 14841.2580(0.002) | 0.0010 |
| A1 | 0 | 8 | 1 | 8 | A2 | 0 | 7 | 0 | 7 | 16819.6780(0.002) | -0.0011 |
| A2 | 0 | 9 | 1 | 9 | A1 | 0 | 8 | 0 | 8 | 18798.2808(0.002) | 0.0016 |
| A2 | 0 | 3 | 0 | 3 | A1 | 0 | 2 | 1 | 2 | 6810.8930(0.002) | -0.0008 |
| A1 | 0 | 4 | 0 | 4 | A2 | 0 | 3 | 1 | 3 | 8879.5760(0.002) | -0.0002 |
| A2 | 0 | 5 | 0 | 5 | A1 | 0 | 4 | 1 | 4 | 10879.0750(0.002) | -0.0005 |
| A1 | 0 | 6 | 0 | 6 | A2 | 0 | 5 | 1 | 5 | 12861.6780(0.002) | -0.0007 |
| A2 | 0 | 7 | 0 | 7 | A1 | 0 | 6 | 1 | 6 | 14840.9260(0.002) | 0.0002 |
| A1 | 0 | 8 | 0 | 8 | A2 | 0 | 7 | 1 | 7 | 16819.6250(0.002) | -0.0005 |
| A2 | 0 | 9 | 0 | 9 | A1 | 0 | 8 | 1 | 8 | 18798.2697(0.002) | -0.0011 |
| A1 | 0 | 10 | 1 | 10 | A2 | 0 | 9 | 1 | 9 | 20776.9300(0.002) | 0.0003 |
| A2 | 0 | 11 | 1 | 11 | A1 | 0 | 10 | 1 | 10 | 22755.6030(0.002) | -0.0004 |
| A1 | 0 | 12 | 1 | 12 | A2 | 0 | 11 | 1 | 11 | 24734.2880(0.002) | 0.0013 |
| A1 | 0 | 5 | 2 | 4 | A2 | 0 | 4 | 1 | 3 | 13070.7745(0.002) | -0.0004 |
| A2 | 0 | 6 | 2 | 5 | A1 | 0 | 5 | 1 | 4 | 14902.6939(0.002) | 0.0001 |
| A1 | 0 | 7 | 2 | 6 | A2 | 0 | 6 | 1 | 5 | 16838.0810(0.002) | -0.0001 |
| A2 | 0 | 8 | 2 | 7 | A1 | 0 | 7 | 1 | 6 | 18805.4380(0.002) | -0.0003 |
| A1 | 0 | 9 | 2 | 8 | A2 | 0 | 8 | 1 | 7 | 20780.8510(0.002) | 0.0009 |
| A2 | 0 | 3 | 3 | 1 | A1 | 0 | 2 | 2 | 0 | 12514.6220(0.002) | 0.0003 |
| A2 | 0 | 5 | 3 | 3 | A1 | 0 | 4 | 2 | 2 | 16164.2806(0.002) | -0.0016 |
| A1 | 0 | 6 | 3 | 4 | A2 | 0 | 5 | 2 | 3 | 17539.6200(0.002) | -0.0009 |
| A2 | 0 | 7 | 3 | 5 | A1 | 0 | 6 | 2 | 4 | 19079.0945(0.002) | 0.0047 |
| A1 | 0 | 8 | 3 | 6 | A2 | 0 | 7 | 2 | 5 | 20872.0644(0.002) | -0.0002 |
| A1 | 0 | 3 | 3 | 0 | A2 | 0 | 2 | 2 | 1 | 13135.7850(0.002) | -0.0038 |
| A2 | 0 | 4 | 3 | 1 | A1 | 0 | 3 | 2 | 2 | 17249.9736(0.002) | 0.0032 |
| A1 | 0 | 5 | 1 | 4 | A2 | 0 | 4 | 2 | 3 | 12698.3172(0.002) | -0.0022 |
| A2 | 0 | 6 | 1 | 5 | A1 | 0 | 5 | 2 | 4 | 14806.5420(0.002) | -0.0010 |
| A1 | 0 | 7 | 1 | 6 | A2 | 0 | 6 | 2 | 5 | 16816.8817(0.002) | 0.0009 |
| A2 | 0 | 8 | 1 | 7 | A1 | 0 | 7 | 2 | 6 | 18801.2000(0.002) | -0.0007 |
| A1 | 0 | 9 | 1 | 8 | A2 | 0 | 8 | 2 | 7 | 20780.0600(0.002) | 0.0018 |
| A1 | 0 | 6 | 2 | 4 | A2 | 0 | 5 | 3 | 3 | 16203.3522(0.002) | -0.0014 |
| A2 | 0 | 7 | 2 | 5 | A1 | 0 | 6 | 3 | 4 | 18629.5000(0.002) | -0.0007 |
| A1 | 0 | 8 | 2 | 6 | A2 | 0 | 7 | 3 | 5 | 20750.3864(0.002) | -0.0005 |
| E | 1 | 5 | 1 | 5 | E | 1 | 4 | 0 | 4 | 11875.7050(0.002) | 0.0017 |
| E | 1 | 6 | 1 | 6 | E | 1 | 5 | 0 | 5 | 13316.5432(0.002) | 0.0017 |
| E | 1 | 7 | 1 | 7 | E | 1 | 6 | 0 | 6 | 15016.3250(0.002) | 0.0018 |
| E | 1 | 8 | 1 | 8 | E | 1 | 7 | 0 | 7 | 16901.2020(0.002) | 0.0003 |
| E | 1 | 6 | 0 | 6 | E | 1 | 5 | 1 | 5 | 12708.6909(0.002) | -0.0018 |

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E   1   7   0   7    E   1   6   1   6    14859.8670(0.002)  0.0002
E   1   8   0   8    E   1   7   1   7    16867.8428(0.002) -0.0009
E   1   9   0   9    E   1   8   1   8    18841.9953(0.002)  0.0002

E   1   4   2   3    E   1   3   1   2    12761.5351(0.002) -0.0025
E   1   5   2   4    E   1   4   1   3    15426.7443(0.002) -0.0015
E   1   6   2   5    E   1   5   1   4    17537.7435(0.002)  0.0013
E   1   7   2   6    E   1   6   1   5    18866.6509(0.002)  0.0006
E   1   8   2   7    E   1   7   1   6    19885.4907(0.002)  0.0004
E   1   9   2   8    E   1   8   1   7    21246.5109(0.002)  0.0002

E   1   3   1   2    E   1   2   1   2     9467.0763(0.002)  0.0009
E   1   4   1   3    E   1   3   1   3    12479.2290(0.002)  0.0008
E   1   5   1   4    E   1   4   1   4    16117.3107(0.002)  0.0027

E   1   3   2   1    E   1   2   2   1    10343.6873(0.002)  0.0000
E   1   4   2   2    E   1   3   2   2    13265.8853(0.002) -0.0043
E   1   5   2   3    E   1   4   2   3    16192.2560(0.002) -0.0017
E   1   6   2   4    E   1   5   2   4    19265.3411(0.002)  0.0023

E   1   7   1   6    E   1   6   2   5    15465.9853(0.002)  0.0016
E   1   8   1   7    E   1   7   2   6    18513.4255(0.002) -0.0020
E   1   9   1   8    E   1   8   2   7    20849.5412(0.002) -0.0032

E   1   4   3   2    E   1   3   2   1    13729.7239(0.002)  0.0018
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**Table S8**. Rotational transitions of the $^{13}C$ (1) isotopologue of 2,6-difluorotoluene.

| Upper level | | | | | Lower level | | | | | Measured(Unc. ) | o.-c.(MHz) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sym' | m' | J' | Ka' | Kc' | Sym | m | J | Ka | Kc | | |
| B1 | 0 | 4 | 1 | 4 | B2 | 0 | 3 | 0 | 3 | 8947.5178(0.002) | 0.0007 |
| A2 | 0 | 5 | 1 | 5 | A1 | 0 | 4 | 0 | 4 | 10907.7892(0.002) | -0.0003 |
| B1 | 0 | 6 | 1 | 6 | B2 | 0 | 5 | 0 | 5 | 12885.2636(0.002) | 0.0004 |
| A2 | 0 | 7 | 1 | 7 | A1 | 0 | 6 | 0 | 6 | 14866.3536(0.002) | 0.0012 |
| B1 | 0 | 8 | 1 | 8 | B2 | 0 | 7 | 0 | 7 | 16848.1568(0.002) | -0.0017 |
| A2 | 0 | 9 | 1 | 9 | A1 | 0 | 8 | 0 | 8 | 18830.1239(0.002) | 0.0018 |
| B1 | 0 | 10 | 0 | 10 | B2 | 0 | 9 | 0 | 9 | 20812.1316(0.002) | -0.0006 |
| B2 | 0 | 11 | 0 | 11 | B1 | 0 | 10 | 0 | 10 | 22794.1617(0.002) | 0.0003 |
| B2 | 0 | 6 | 2 | 5 | B1 | 0 | 5 | 1 | 4 | 14922.0739(0.002) | -0.0005 |
| A1 | 0 | 7 | 2 | 6 | A2 | 0 | 6 | 1 | 5 | 16864.7469(0.002) | -0.0016 |
| B2 | 0 | 8 | 2 | 7 | B1 | 0 | 7 | 1 | 6 | 18836.6690(0.002) | 0.0003 |
| A1 | 0 | 9 | 2 | 8 | A2 | 0 | 8 | 1 | 7 | 20815.7814(0.002) | 0.0013 |
| A1 | 0 | 10 | 1 | 10 | A2 | 0 | 9 | 1 | 9 | 20812.1316(0.002) | 0.0004 |
| A2 | 0 | 11 | 1 | 11 | A1 | 0 | 10 | 1 | 10 | 22794.1617(0.002) | 0.0002 |
| B2 | 0 | 3 | 0 | 3 | B1 | 0 | 2 | 1 | 2 | 6829.2246(0.002) | -0.0006 |
| A1 | 0 | 4 | 0 | 4 | A2 | 0 | 3 | 1 | 3 | 8896.7455(0.002) | 0.0002 |
| B2 | 0 | 5 | 0 | 5 | B1 | 0 | 4 | 1 | 4 | 10898.0122(0.002) | -0.0001 |
| A1 | 0 | 6 | 0 | 6 | A2 | 0 | 5 | 1 | 5 | 12883.5573(0.002) | 0.0017 |
| B2 | 0 | 7 | 0 | 7 | B1 | 0 | 6 | 1 | 6 | 14866.0721(0.002) | 0.0002 |
| A1 | 0 | 8 | 0 | 8 | A2 | 0 | 7 | 1 | 7 | 16848.1139(0.002) | -0.0004 |
| B2 | 0 | 9 | 0 | 9 | B1 | 0 | 8 | 1 | 8 | 18830.1129(0.002) | -0.0025 |
| B1 | 0 | 5 | 1 | 4 | B2 | 0 | 4 | 2 | 3 | 12733.7656(0.002) | -0.0005 |
| A2 | 0 | 6 | 1 | 5 | A1 | 0 | 5 | 2 | 4 | 14835.8523(0.002) | -0.0018 |
| B1 | 0 | 7 | 1 | 6 | B2 | 0 | 6 | 2 | 5 | 16846.2624(0.002) | -0.0002 |
| A2 | 0 | 8 | 1 | 7 | A1 | 0 | 7 | 2 | 6 | 18833.0750(0.002) | 0.0003 |
| A2 | 0 | 5 | 3 | 3 | A1 | 0 | 4 | 2 | 2 | 16136.2159(0.010) | -0.0001 |
| B1 | 0 | 6 | 3 | 4 | B2 | 0 | 5 | 2 | 3 | 17522.4218(0.010) | 0.0027 |
| A2 | 0 | 7 | 3 | 5 | A1 | 0 | 6 | 2 | 4 | 19085.9826(0.010) | 0.0023 |
| B1 | 0 | 8 | 3 | 6 | B2 | 0 | 7 | 2 | 5 | 20897.5882(0.002) | 0.0000 |
| A1 | 0 | 6 | 2 | 4 | A2 | 0 | 5 | 3 | 3 | 16281.2322(0.002) | 0.0002 |
| B2 | 0 | 7 | 2 | 5 | B1 | 0 | 6 | 3 | 4 | 18680.7407(0.002) | 0.0005 |
| A1 | 0 | 8 | 2 | 6 | A2 | 0 | 7 | 3 | 5 | 20791.1189(0.002) | 0.0006 |
| E1 | 1 | 5 | 1 | 5 | E1 | 1 | 4 | 0 | 4 | 11873.7329(0.002) | 0.0008 |
| E2 | 1 | 6 | 1 | 6 | E2 | 1 | 5 | 0 | 5 | 13322.1086(0.002) | 0.0008 |
| E1 | 1 | 7 | 1 | 7 | E1 | 1 | 6 | 0 | 6 | 15034.4638(0.002) | -0.0008 |
| E2 | 1 | 8 | 1 | 8 | E2 | 1 | 7 | 0 | 7 | 16927.3320(0.002) | 0.0000 |
| E1 | 1 | 9 | 1 | 9 | E1 | 1 | 8 | 0 | 8 | 18879.3532(0.002) | -0.0001 |
| E2 | 1 | 4 | 2 | 3 | E2 | 1 | 3 | 1 | 2 | 12767.5067(0.002) | -0.0002 |
| E1 | 1 | 5 | 2 | 4 | E1 | 1 | 4 | 1 | 3 | 15436.0087(0.002) | -0.0013 |
| E2 | 1 | 6 | 2 | 5 | E2 | 1 | 5 | 1 | 4 | 17534.4046(0.002) | 0.0000 |
| E1 | 1 | 7 | 2 | 6 | E1 | 1 | 6 | 1 | 5 | 18845.4116(0.002) | -0.0001 |
| E2 | 1 | 8 | 2 | 7 | E2 | 1 | 7 | 1 | 6 | 19870.7551(0.002) | 0.0005 |
| E2 | 1 | 3 | 1 | 2 | E2 | 1 | 2 | 1 | 2 | 9470.0591(0.002) | 0.0007 |
| E1 | 1 | 4 | 1 | 3 | E1 | 1 | 3 | 1 | 3 | 12497.4798(0.002) | 0.0000 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| E2 | 1 | 5 | 0 | 5 | E2 | 1 | 4 | 1 | 4 | 10199.1274(0.002) | 0.0011 |
| E1 | 1 | 6 | 0 | 6 | E1 | 1 | 5 | 1 | 5 | 12744.6144(0.002) | -0.0012 |
| E2 | 1 | 7 | 0 | 7 | E2 | 1 | 6 | 1 | 6 | 14889.4069(0.002) | 0.0000 |
| E1 | 1 | 8 | 0 | 8 | E1 | 1 | 7 | 1 | 7 | 16897.1535(0.002) | -0.0004 |
| E2 | 1 | 9 | 0 | 9 | E2 | 1 | 8 | 1 | 8 | 18873.7246(0.002) | -0.0001 |
| | | | | | | | | | | | |
| E2 | 1 | 7 | 1 | 6 | E2 | 1 | 6 | 2 | 5 | 15573.4168(0.002) | -0.0001 |
| E1 | 1 | 8 | 1 | 7 | E1 | 1 | 7 | 2 | 6 | 18584.6388(0.002) | 0.0005 |
| | | | | | | | | | | | |
| E1 | 1 | 4 | 2 | 2 | E1 | 1 | 3 | 2 | 2 | 13268.1832(0.002) | -0.0002 |
| E2 | 1 | 5 | 2 | 3 | E2 | 1 | 4 | 2 | 3 | 16205.8536(0.002) | 0.0008 |
| | | | | | | | | | | | |
| E2 | 1 | 4 | 3 | 2 | E2 | 1 | 3 | 2 | 1 | 13725.8127(0.002) | -0.0010 |
| | | | | | | | | | | | |
| E1 | 1 | 4 | 3 | 1 | E1 | 1 | 3 | 3 | 1 | 14225.7354(0.002) | 0.0007 |

**Table S9**. Rotational transitions of the $^{13}$C(3) and $^{13}$C(5) isotopologues of 2,6-difluorotoluene.

| Upper level | | | | | Lower level | | | | | Measured(Unc. ) | o.-c.(MHz) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sym' | m' | J' | Ka' | Kc' | Sym | m | J | Ka | Kc | | |
| A1 | 0 | 4 | 1 | 4 | A2 | 0 | 3 | 0 | 3 | 8895.3999(0.002) | 0.0003 |
| A2 | 0 | 5 | 1 | 5 | A1 | 0 | 4 | 0 | 4 | 10844.6241(0.002) | 0.0005 |
| A1 | 0 | 6 | 1 | 6 | A2 | 0 | 5 | 0 | 5 | 12810.7441(0.002) | 0.0001 |
| A2 | 0 | 7 | 1 | 7 | A1 | 0 | 6 | 0 | 6 | 14780.3983(0.002) | -0.0007 |
| A1 | 0 | 8 | 1 | 8 | A2 | 0 | 7 | 0 | 7 | 16750.7517(0.002) | -0.0008 |
| A2 | 0 | 9 | 1 | 9 | A1 | 0 | 8 | 0 | 8 | 18721.2602(0.002) | 0.0008 |
| A1 | 0 | 10 | 0 | 10 | A2 | 0 | 9 | 0 | 9 | 20691.8105(0.002) | -0.0009 |
| A2 | 0 | 11 | 0 | 11 | A1 | 0 | 10 | 0 | 10 | 22662.3826(0.002) | 0.0000 |
| A1 | 0 | 12 | 0 | 12 | A2 | 0 | 11 | 0 | 11 | 24632.9633(0.002) | 0.0001 |
| A2 | 0 | 3 | 0 | 3 | A1 | 0 | 2 | 1 | 2 | 6790.8584(0.002) | -0.0012 |
| A1 | 0 | 4 | 0 | 4 | A2 | 0 | 3 | 1 | 3 | 8845.6556(0.002) | 0.0000 |
| A2 | 0 | 5 | 0 | 5 | A1 | 0 | 4 | 1 | 4 | 10835.0878(0.002) | -0.0015 |
| A1 | 0 | 6 | 0 | 6 | A2 | 0 | 5 | 1 | 5 | 12809.0860(0.002) | -0.0005 |
| A2 | 0 | 7 | 0 | 7 | A1 | 0 | 6 | 1 | 6 | 14780.1274(0.002) | -0.0006 |
| A1 | 0 | 8 | 0 | 8 | A2 | 0 | 7 | 1 | 7 | 16750.7096(0.002) | -0.0004 |
| A2 | 0 | 9 | 0 | 9 | A1 | 0 | 8 | 1 | 8 | 18721.2514(0.002) | -0.0015 |
| A1 | 0 | 10 | 1 | 10 | A2 | 0 | 9 | 1 | 9 | 20691.8105(0.002) | -0.0002 |
| A2 | 0 | 11 | 1 | 11 | A1 | 0 | 10 | 1 | 10 | 22662.3826(0.002) | 0.0001 |
| A1 | 0 | 12 | 1 | 12 | A2 | 0 | 11 | 1 | 11 | 24632.9633(0.002) | 0.0002 |
| A2 | 0 | 4 | 2 | 3 | A1 | 0 | 3 | 1 | 2 | 11345.0875(0.002) | -0.0011 |
| A1 | 0 | 5 | 2 | 4 | A2 | 0 | 4 | 1 | 3 | 12999.3101(0.002) | 0.0001 |
| A2 | 0 | 6 | 2 | 5 | A1 | 0 | 5 | 1 | 4 | 14834.8717(0.002) | 0.0002 |
| A1 | 0 | 7 | 2 | 6 | A2 | 0 | 6 | 1 | 5 | 16766.9593(0.002) | 0.0000 |
| A2 | 0 | 8 | 2 | 7 | A1 | 0 | 7 | 1 | 6 | 18727.6750(0.002) | 0.0009 |
| A1 | 0 | 9 | 2 | 8 | A2 | 0 | 8 | 1 | 7 | 20695.3989(0.002) | 0.0001 |
| A2 | 0 | 10 | 2 | 9 | A1 | 0 | 9 | 1 | 8 | 22664.8554(0.002) | 0.0017 |
| A1 | 0 | 5 | 1 | 4 | A2 | 0 | 4 | 2 | 3 | 12662.4075(0.002) | -0.0008 |
| A2 | 0 | 6 | 1 | 5 | A1 | 0 | 5 | 2 | 4 | 14750.7597(0.002) | -0.0005 |
| A1 | 0 | 7 | 1 | 6 | A2 | 0 | 6 | 2 | 5 | 16749.0127(0.002) | 0.0008 |
| A2 | 0 | 8 | 1 | 7 | A1 | 0 | 7 | 2 | 6 | 18724.2014(0.002) | 0.0002 |
| A1 | 0 | 9 | 1 | 8 | A2 | 0 | 8 | 2 | 7 | 20694.7697(0.002) | -0.0007 |
| A2 | 0 | 10 | 1 | 9 | A1 | 0 | 9 | 2 | 8 | 22664.7481(0.002) | 0.0026 |
| A2 | 0 | 3 | 3 | 1 | A1 | 0 | 2 | 2 | 0 | 12407.7668(0.002) | 0.0004 |
| A2 | 0 | 5 | 3 | 3 | A1 | 0 | 4 | 2 | 2 | 16033.7073(0.002) | 0.0008 |
| A1 | 0 | 6 | 3 | 4 | A2 | 0 | 5 | 2 | 3 | 17413.4098(0.002) | 0.0004 |
| A2 | 0 | 7 | 3 | 5 | A1 | 0 | 6 | 2 | 4 | 18971.5497(0.002) | 0.0005 |
| A1 | 0 | 8 | 3 | 6 | A2 | 0 | 7 | 2 | 5 | 20775.2226(0.002) | 0.0004 |
| A1 | 0 | 3 | 3 | 0 | A2 | 0 | 2 | 2 | 1 | 13048.4905(0.002) | -0.0022 |
| A1 | 0 | 6 | 2 | 4 | A2 | 0 | 5 | 3 | 3 | 16195.3042(0.002) | -0.0004 |
| A2 | 0 | 7 | 2 | 5 | A1 | 0 | 6 | 3 | 4 | 18575.8856(0.002) | -0.0003 |
| A1 | 0 | 8 | 2 | 6 | A2 | 0 | 7 | 3 | 5 | 20671.7948(0.002) | 0.0013 |
| E | 1 | 4 | 1 | 4 | E | 1 | 3 | 0 | 3 | 10310.2779(0.002) | -0.0014 |
| E | 1 | 5 | 1 | 5 | E | 1 | 4 | 0 | 4 | 11800.9316(0.002) | -0.0020 |
| E | 1 | 6 | 1 | 6 | E | 1 | 5 | 0 | 5 | 13241.9621(0.002) | -0.0022 |
| E | 1 | 7 | 1 | 7 | E | 1 | 6 | 0 | 6 | 14946.2324(0.002) | -0.0011 |
| E | 1 | 8 | 1 | 8 | E | 1 | 7 | 0 | 7 | 16829.0236(0.002) | 0.0003 |

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E   1   9   1   9    E   1   8   0   8    18770.0331(0.002) -0.0010
E   1  10   1  10    E   1   9   0   9    20727.4036(0.002) -0.0011

E   1   5   0   5    E   1   4   1   4    10146.0171(0.002)  0.0021
E   1   6   0   6    E   1   5   1   5    12673.5276(0.002)  0.0016
E   1   7   0   7    E   1   6   1   6    14804.0827(0.002)  0.0002
E   1   8   0   8    E   1   7   1   7    16799.5786(0.002) -0.0009
E   1   9   0   9    E   1   8   1   8    18764.5659(0.002) -0.0007
E   1  10   0  10    E   1   9   1   9    20726.4576(0.002) -0.0020

E   1   4   2   3    E   1   3   1   2    12690.8254(0.002) -0.0006
E   1   5   2   4    E   1   4   1   3    15343.6783(0.002) -0.0003
E   1   6   2   5    E   1   5   1   4    17426.8345(0.002)  0.0026
E   1   7   2   6    E   1   6   1   5    18726.5735(0.002)  0.0004
E   1   8   2   7    E   1   7   1   6    19747.0967(0.002)  0.0033
E   1   9   2   8    E   1   8   1   7    21131.5390(0.002)  0.0006

E   1   3   1   2    E   1   2   1   2     9412.8464(0.002) -0.0011
E   1   4   1   3    E   1   3   1   3    12424.8396(0.002) -0.0021
E   1   5   1   4    E   1   4   1   4    16081.6829(0.002) -0.0005

E   1   7   1   6    E   1   6   2   5    15498.1552(0.002)  0.0016
E   1   8   1   7    E   1   7   2   6    18484.2001(0.002)  0.0008
E   1   9   1   8    E   1   8   2   7    20778.5214(0.002)  0.0000
E   1  10   1   9    E   1   9   2   8    22800.7052(0.002)  0.0007

E   1   3   2   1    E   1   2   2   1    10270.7840(0.002)  0.0015
E   1   4   2   2    E   1   3   2   2    13187.7304(0.002)  0.0006
E   1   5   2   3    E   1   4   2   3    16109.7445(0.002) -0.0006
E   1   6   2   4    E   1   5   2   4    19189.1987(0.002) -0.0022
```

**Table S10**. Rotational transitions of the $^{13}$C(4) isotopologue of 2,6-difluorotoluene.

| Upper level | | | | | Lower level | | | | | Measured(Unc. ) | o.-c.(MHz) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sym' | m' | J' | Ka' | Kc' | Sym | m | J | Ka | Kc | | |
| B1 | 0 | 10 | 0 | 10 | B2 | 0 | 9 | 0 | 9 | 20652.3100(0.002) | 0.0002 |
| B2 | 0 | 11 | 0 | 11 | B1 | 0 | 10 | 0 | 10 | 22619.1275(0.002) | 0.0003 |
| B1 | 0 | 4 | 1 | 4 | B2 | 0 | 3 | 0 | 3 | 8873.4636(0.002) | -0.0001 |
| A2 | 0 | 5 | 1 | 5 | A1 | 0 | 4 | 0 | 4 | 10822.6136(0.002) | -0.0013 |
| B1 | 0 | 6 | 1 | 6 | B2 | 0 | 5 | 0 | 5 | 12785.9606(0.002) | -0.0001 |
| A2 | 0 | 7 | 1 | 7 | A1 | 0 | 6 | 0 | 6 | 14752.0878(0.002) | -0.0006 |
| B1 | 0 | 8 | 1 | 8 | B2 | 0 | 7 | 0 | 7 | 16718.7398(0.002) | -0.0008 |
| A2 | 0 | 9 | 1 | 9 | A1 | 0 | 8 | 0 | 8 | 18685.5072(0.002) | -0.0003 |
| B2 | 0 | 3 | 0 | 3 | B1 | 0 | 2 | 1 | 2 | 6792.3986(0.002) | -0.0004 |
| B2 | 0 | 5 | 0 | 5 | B1 | 0 | 4 | 1 | 4 | 10815.3739(0.002) | -0.0004 |
| B2 | 0 | 7 | 0 | 7 | B1 | 0 | 6 | 1 | 6 | 14751.9075(0.002) | -0.0006 |
| A1 | 0 | 8 | 0 | 8 | A2 | 0 | 7 | 1 | 7 | 16718.7141(0.002) | -0.0001 |
| B2 | 0 | 9 | 0 | 9 | B1 | 0 | 8 | 1 | 8 | 18685.5035(0.002) | -0.0003 |
| A1 | 0 | 5 | 2 | 4 | A2 | 0 | 4 | 1 | 3 | 12942.1351(0.002) | -0.0005 |
| B2 | 0 | 6 | 2 | 5 | B1 | 0 | 5 | 1 | 4 | 14794.9248(0.002) | -0.0008 |
| A1 | 0 | 7 | 2 | 6 | A2 | 0 | 6 | 1 | 5 | 16731.3808(0.002) | -0.0011 |
| B2 | 0 | 8 | 2 | 7 | B1 | 0 | 7 | 1 | 6 | 18690.7127(0.002) | 0.0002 |
| A1 | 0 | 9 | 2 | 8 | A2 | 0 | 8 | 1 | 7 | 20655.3449(0.002) | 0.0024 |
| B2 | 0 | 10 | 2 | 9 | B1 | 0 | 9 | 1 | 8 | 22621.2534(0.002) | -0.0031 |
| A1 | 0 | 10 | 1 | 10 | A2 | 0 | 9 | 1 | 9 | 20652.3100(0.002) | 0.0008 |
| A2 | 0 | 11 | 1 | 11 | A1 | 0 | 10 | 1 | 10 | 22619.1275(0.002) | 0.0002 |
| B1 | 0 | 5 | 1 | 4 | B2 | 0 | 4 | 2 | 3 | 12666.6844(0.002) | -0.0006 |
| A2 | 0 | 6 | 1 | 5 | A1 | 0 | 5 | 2 | 4 | 14730.7300(0.002) | 0.0008 |
| B1 | 0 | 7 | 1 | 6 | B2 | 0 | 6 | 2 | 5 | 16718.5778(0.002) | -0.0002 |
| A2 | 0 | 8 | 1 | 7 | A1 | 0 | 7 | 2 | 6 | 18688.3962(0.002) | 0.0009 |
| B1 | 0 | 9 | 1 | 8 | B2 | 0 | 8 | 2 | 7 | 20654.9498(0.002) | -0.0005 |
| A2 | 0 | 10 | 1 | 9 | A1 | 0 | 9 | 2 | 8 | 22621.1940(0.002) | 0.0007 |
| B1 | 0 | 4 | 3 | 2 | B2 | 0 | 3 | 2 | 1 | 14316.9244(0.002) | -0.0006 |
| A2 | 0 | 5 | 3 | 3 | A1 | 0 | 4 | 2 | 2 | 15879.0585(0.002) | 0.0038 |
| A2 | 0 | 7 | 3 | 5 | A1 | 0 | 6 | 2 | 4 | 18884.0148(0.002) | 0.0007 |
| B1 | 0 | 8 | 3 | 6 | B2 | 0 | 7 | 2 | 5 | 20716.6311(0.002) | -0.0008 |
| B1 | 0 | 3 | 3 | 0 | B2 | 0 | 2 | 2 | 1 | 12961.4930(0.002) | -0.0042 |
| A1 | 0 | 6 | 2 | 4 | A2 | 0 | 5 | 3 | 3 | 16268.5440(0.002) | 0.0015 |
| B2 | 0 | 7 | 2 | 5 | B1 | 0 | 6 | 3 | 4 | 18578.6965(0.002) | 0.0005 |
| A1 | 0 | 8 | 2 | 6 | A2 | 0 | 7 | 3 | 5 | 20642.2954(0.002) | -0.0013 |
| B2 | 0 | 9 | 2 | 7 | B1 | 0 | 8 | 3 | 6 | 22628.6021(0.002) | 0.0036 |
| E2 | 1 | 6 | 1 | 6 | E2 | 1 | 5 | 0 | 5 | 13180.1624(0.002) | 0.0058 |
| E2 | 1 | 8 | 1 | 8 | E2 | 1 | 7 | 0 | 7 | 16791.8338(0.002) | 0.0003 |
| E1 | 1 | 9 | 1 | 9 | E1 | 1 | 8 | 0 | 8 | 18732.2495(0.002) | 0.0008 |
| E2 | 1 | 10 | 1 | 10 | E2 | 1 | 9 | 0 | 9 | 20686.8141(0.002) | 0.0018 |
| E2 | 1 | 3 | 1 | 2 | E2 | 1 | 2 | 1 | 2 | 9365.7105(0.002) | 0.0025 |
| E2 | 1 | 5 | 0 | 5 | E2 | 1 | 4 | 1 | 4 | 10195.2446(0.002) | -0.0029 |
| E1 | 1 | 6 | 0 | 6 | E1 | 1 | 5 | 1 | 5 | 12679.4353(0.002) | -0.0019 |
| E2 | 1 | 7 | 0 | 7 | E2 | 1 | 6 | 1 | 6 | 14784.4713(0.002) | -0.0010 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| E1 | 1 | 8 | 0 | 8 | E1 | 1 | 7 | 1 | 7 | 16768.7438(0.002) | 0.0005 |
| E2 | 1 | 9 | 0 | 9 | E2 | 1 | 8 | 1 | 8 | 18728.2076(0.002) | -0.0007 |
| E1 | 1 | 10 | 0 | 10 | E1 | 1 | 9 | 1 | 9 | 20686.1544(0.002) | -0.0005 |
| | | | | | | | | | | | |
| E2 | 1 | 4 | 2 | 3 | E2 | 1 | 3 | 1 | 2 | 12631.4652(0.002) | 0.0005 |
| E1 | 1 | 5 | 2 | 4 | E1 | 1 | 4 | 1 | 3 | 15276.1589(0.002) | -0.0024 |
| E1 | 1 | 9 | 2 | 8 | E1 | 1 | 8 | 1 | 7 | 21042.9387(0.002) | -0.0033 |
| | | | | | | | | | | | |
| E2 | 1 | 3 | 2 | 1 | E2 | 1 | 2 | 2 | 1 | 10193.0762(0.002) | 0.0029 |
| E1 | 1 | 4 | 2 | 2 | E1 | 1 | 3 | 2 | 2 | 13116.8323(0.002) | -0.0006 |
| E2 | 1 | 5 | 2 | 3 | E2 | 1 | 4 | 2 | 3 | 16048.4324(0.002) | -0.0014 |
| E1 | 1 | 6 | 2 | 4 | E1 | 1 | 5 | 2 | 4 | 19161.2358(0.002) | 0.0025 |
| | | | | | | | | | | | |
| E2 | 1 | 7 | 1 | 6 | E2 | 1 | 6 | 2 | 5 | 15644.2909(0.002) | 0.0015 |
| E1 | 1 | 8 | 1 | 7 | E1 | 1 | 7 | 2 | 6 | 18530.1675(0.002) | -0.0001 |
| E2 | 1 | 9 | 1 | 8 | E2 | 1 | 8 | 2 | 7 | 20762.3243(0.002) | -0.0006 |
| | | | | | | | | | | | |
| E2 | 1 | 4 | 3 | 2 | E2 | 1 | 3 | 2 | 1 | 13553.5092(0.002) | -0.0021 |
| | | | | | | | | | | | |
| E1 | 1 | 4 | 3 | 1 | E1 | 1 | 3 | 3 | 1 | 14035.1509(0.002) | -0.0002 |

**Table S11**. Rotational transitions of the $^{13}$C(7) isotopologue of 2,6-difluorotoluene.

| Upper level | | | | | Lower level | | | | | Measured(Unc. ) | o.-c.(MHz) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sym' | m' | J' | Ka' | Kc' | Sym | m | J | Ka | Kc | | |
| B1 | 0 | 4 | 1 | 4 | B2 | 0 | 3 | 0 | 3 | 8864.8711(0.002) | 0.0015 |
| A2 | 0 | 5 | 1 | 5 | A1 | 0 | 4 | 0 | 4 | 10812.6858(0.002) | 0.0002 |
| B1 | 0 | 6 | 1 | 6 | B2 | 0 | 5 | 0 | 5 | 12774.3670(0.002) | 0.0001 |
| B1 | 0 | 8 | 1 | 8 | B2 | 0 | 7 | 0 | 7 | 16703.6238(0.002) | -0.0003 |
| A2 | 0 | 9 | 1 | 9 | A1 | 0 | 8 | 0 | 8 | 18668.6170(0.002) | 0.0013 |
| B1 | 0 | 10 | 0 | 10 | B2 | 0 | 9 | 0 | 9 | 20633.6422(0.002) | 0.0007 |
| B2 | 0 | 11 | 0 | 11 | B1 | 0 | 10 | 0 | 10 | 22598.6834(0.002) | 0.0012 |
| B2 | 0 | 3 | 0 | 3 | B1 | 0 | 2 | 1 | 2 | 6787.9855(0.002) | 0.0008 |
| A1 | 0 | 6 | 0 | 6 | A2 | 0 | 5 | 1 | 5 | 12773.2400(0.002) | -0.0009 |
| B2 | 0 | 7 | 0 | 7 | B1 | 0 | 6 | 1 | 6 | 14738.5710(0.002) | -0.0011 |
| A1 | 0 | 8 | 0 | 8 | A2 | 0 | 7 | 1 | 7 | 16703.5993(0.002) | 0.0001 |
| B2 | 0 | 9 | 0 | 9 | B1 | 0 | 8 | 1 | 8 | 18668.6111(0.002) | -0.0011 |
| A1 | 0 | 5 | 2 | 4 | A2 | 0 | 4 | 1 | 3 | 12926.6478(0.002) | -0.0016 |
| B2 | 0 | 6 | 2 | 5 | B1 | 0 | 5 | 1 | 4 | 14780.2427(0.002) | 0.0003 |
| A1 | 0 | 7 | 2 | 6 | A2 | 0 | 6 | 1 | 5 | 16715.8623(0.002) | -0.0009 |
| B2 | 0 | 8 | 2 | 7 | B1 | 0 | 7 | 1 | 6 | 18673.6816(0.002) | 0.0001 |
| A1 | 0 | 9 | 2 | 8 | A2 | 0 | 8 | 1 | 7 | 20636.6068(0.002) | -0.0004 |
| A1 | 0 | 10 | 1 | 10 | A2 | 0 | 9 | 1 | 9 | 20633.6422(0.002) | 0.0012 |
| A2 | 0 | 11 | 1 | 11 | A1 | 0 | 10 | 1 | 10 | 22598.6834(0.002) | 0.0011 |
| B1 | 0 | 3 | 3 | 0 | B2 | 0 | 2 | 2 | 1 | 12942.3609(0.002) | -0.0021 |
| B1 | 0 | 4 | 3 | 2 | B2 | 0 | 3 | 2 | 1 | 14289.4578(0.010) | -0.0052 |
| A2 | 0 | 5 | 3 | 3 | A1 | 0 | 4 | 2 | 2 | 15849.4187(0.002) | 0.0040 |
| B1 | 0 | 6 | 3 | 4 | B2 | 0 | 5 | 2 | 3 | 17251.6115(0.010) | -0.0026 |
| A2 | 0 | 7 | 3 | 5 | A1 | 0 | 6 | 2 | 4 | 18861.0975(0.002) | -0.0008 |
| B1 | 0 | 8 | 3 | 6 | B2 | 0 | 7 | 2 | 5 | 20695.8175(0.002) | -0.0014 |
| A2 | 0 | 4 | 1 | 3 | A1 | 0 | 3 | 2 | 2 | 10359.4458(0.002) | 0.0010 |
| B1 | 0 | 5 | 1 | 4 | B2 | 0 | 4 | 2 | 3 | 12658.5041(0.002) | 0.0002 |
| A2 | 0 | 6 | 1 | 5 | A1 | 0 | 5 | 2 | 4 | 14718.3035(0.002) | 0.0007 |
| B1 | 0 | 7 | 1 | 6 | B2 | 0 | 6 | 2 | 5 | 16703.6115(0.002) | -0.0055 |
| A2 | 0 | 8 | 1 | 7 | A1 | 0 | 7 | 2 | 6 | 18671.4835(0.002) | -0.0008 |
| B1 | 0 | 9 | 1 | 8 | B2 | 0 | 8 | 2 | 7 | 20636.2404(0.002) | 0.0018 |
| A1 | 0 | 6 | 2 | 4 | A2 | 0 | 5 | 3 | 3 | 16265.9046(0.002) | 0.0015 |
| B2 | 0 | 7 | 2 | 5 | B1 | 0 | 6 | 3 | 4 | 18566.1329(0.002) | 0.0015 |
| A1 | 0 | 8 | 2 | 6 | A2 | 0 | 7 | 3 | 5 | 20624.6596(0.002) | 0.0000 |
| E2 | 1 | 6 | 1 | 6 | E2 | 1 | 5 | 0 | 5 | 13163.2474(0.002) | 0.0027 |
| E2 | 1 | 8 | 1 | 8 | E2 | 1 | 7 | 0 | 7 | 16775.9843(0.002) | -0.0007 |
| E1 | 1 | 9 | 1 | 9 | E1 | 1 | 8 | 0 | 8 | 18715.0439(0.002) | 0.0001 |
| E1 | 1 | 6 | 0 | 6 | E1 | 1 | 5 | 1 | 5 | 12671.8644(0.002) | -0.0025 |
| E2 | 1 | 7 | 0 | 7 | E2 | 1 | 6 | 1 | 6 | 14772.1260(0.002) | -0.0009 |
| E1 | 1 | 8 | 0 | 8 | E1 | 1 | 7 | 1 | 7 | 16753.6781(0.002) | 0.0018 |
| E2 | 1 | 9 | 0 | 9 | E2 | 1 | 8 | 1 | 8 | 18711.1702(0.002) | -0.0006 |
| E1 | 1 | 5 | 2 | 4 | E1 | 1 | 4 | 1 | 3 | 15257.2248(0.002) | -0.0019 |
| E1 | 1 | 7 | 2 | 6 | E1 | 1 | 6 | 1 | 5 | 18536.9928(0.002) | -0.0002 |
| E2 | 1 | 8 | 2 | 7 | E2 | 1 | 7 | 1 | 6 | 19573.9891(0.002) | 0.0014 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| E2 | 1 | 5 | 1 | 4 | E2 | 1 | 4 | 1 | 4 | 16107.4937(0.002) | 0.0009 |
| | | | | | | | | | | | |
| E2 | 1 | 5 | 2 | 3 | E2 | 1 | 4 | 2 | 3 | 16030.3808(0.002) | -0.0030 |
| E1 | 1 | 6 | 2 | 4 | E1 | 1 | 5 | 2 | 4 | 19146.0954(0.002) | 0.0032 |
| | | | | | | | | | | | |
| E2 | 1 | 7 | 1 | 6 | E2 | 1 | 6 | 2 | 5 | 15653.4238(0.002) | 0.0005 |
| E1 | 1 | 8 | 1 | 7 | E1 | 1 | 7 | 2 | 6 | 18523.4712(0.002) | -0.0015 |

**Table S12**. Rotational transitions of the $^{13}$C(1) isotopologue of 3,5-difluorotoluene.

| Upper level | | | | | Lower level | | | | | Measured(Unc. ) | o.-c.(MHz) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sym' | m' | J' | Ka' | Kc' | Sym | m | J | Ka | Kc | | |
| A2 | 0 | 3 | 0 | 3 | A1 | 0 | 2 | 0 | 2 | 6152.2218(0.002) | 0.0018 |
| B2 | 0 | 5 | 0 | 5 | B1 | 0 | 4 | 0 | 4 | 9667.5582(0.002) | -0.0016 |
| B1 | 0 | 6 | 0 | 6 | B2 | 0 | 5 | 0 | 5 | 11425.2657(0.002) | -0.0004 |
| B2 | 0 | 7 | 0 | 7 | B1 | 0 | 6 | 0 | 6 | 13182.9704(0.002) | -0.0009 |
| B1 | 0 | 8 | 0 | 8 | B2 | 0 | 7 | 0 | 7 | 14940.6743(0.002) | -0.0007 |
| B2 | 0 | 9 | 0 | 9 | B1 | 0 | 8 | 0 | 8 | 16698.3762(0.002) | -0.0007 |
| B1 | 0 | 10 | 0 | 10 | B2 | 0 | 9 | 0 | 9 | 18456.0750(0.002) | -0.0019 |
| B2 | 0 | 11 | 0 | 11 | B1 | 0 | 10 | 0 | 10 | 20213.7740(0.002) | -0.0006 |
| B1 | 0 | 12 | 0 | 12 | B2 | 0 | 11 | 0 | 11 | 21971.4691(0.002) | -0.0009 |
| A1 | 0 | 4 | 1 | 4 | A2 | 0 | 3 | 0 | 3 | 7909.8542(0.002) | 0.0007 |
| A2 | 0 | 5 | 1 | 5 | A1 | 0 | 4 | 1 | 4 | 9667.5582(0.002) | -0.0016 |
| A1 | 0 | 6 | 1 | 6 | A2 | 0 | 5 | 1 | 5 | 11425.2657(0.002) | -0.0004 |
| A2 | 0 | 7 | 1 | 7 | A1 | 0 | 6 | 1 | 6 | 13182.9704(0.002) | -0.0009 |
| A1 | 0 | 8 | 1 | 8 | A2 | 0 | 7 | 1 | 7 | 14940.6743(0.002) | -0.0007 |
| A2 | 0 | 9 | 1 | 9 | A1 | 0 | 8 | 1 | 8 | 16698.3762(0.002) | -0.0007 |
| A1 | 0 | 10 | 1 | 10 | A2 | 0 | 9 | 1 | 9 | 18456.0750(0.002) | -0.0019 |
| A2 | 0 | 11 | 1 | 11 | A1 | 0 | 10 | 1 | 10 | 20213.7740(0.002) | -0.0006 |
| A1 | 0 | 12 | 1 | 12 | A2 | 0 | 11 | 1 | 11 | 21971.4691(0.002) | -0.0009 |
| B1 | 0 | 4 | 0 | 4 | B2 | 0 | 3 | 1 | 3 | 7909.8542(0.002) | 0.0017 |
| B2 | 0 | 6 | 1 | 5 | B1 | 0 | 5 | 1 | 4 | 13183.2880(0.002) | 0.0001 |
| B1 | 0 | 7 | 1 | 6 | B2 | 0 | 6 | 1 | 5 | 14940.9871(0.002) | 0.0002 |
| B2 | 0 | 8 | 1 | 7 | B1 | 0 | 7 | 1 | 6 | 16698.6873(0.002) | 0.0014 |
| B1 | 0 | 9 | 1 | 8 | B2 | 0 | 8 | 1 | 7 | 18456.3853(0.002) | 0.0016 |
| B2 | 0 | 10 | 1 | 9 | B1 | 0 | 9 | 1 | 8 | 20214.0790(0.002) | -0.0007 |
| B1 | 0 | 11 | 1 | 10 | B2 | 0 | 10 | 1 | 9 | 21971.7748(0.002) | 0.0013 |
| A1 | 0 | 6 | 3 | 4 | A2 | 0 | 5 | 2 | 3 | 14941.3739(0.002) | 0.0008 |
| B2 | 0 | 7 | 2 | 5 | B1 | 0 | 6 | 2 | 4 | 16699.0217(0.002) | 0.0001 |
| B1 | 0 | 8 | 2 | 6 | B2 | 0 | 7 | 2 | 5 | 18456.7048(0.002) | 0.0009 |
| A2 | 0 | 6 | 2 | 5 | A1 | 0 | 5 | 2 | 4 | 13183.2880(0.002) | 0.0001 |
| A1 | 0 | 7 | 2 | 6 | A2 | 0 | 6 | 2 | 5 | 14940.9871(0.002) | 0.0002 |
| A2 | 0 | 8 | 2 | 7 | A1 | 0 | 7 | 2 | 6 | 16698.6873(0.002) | 0.0014 |
| A1 | 0 | 9 | 2 | 8 | A2 | 0 | 8 | 2 | 7 | 18456.3853(0.002) | 0.0016 |
| A2 | 0 | 10 | 2 | 9 | A1 | 0 | 9 | 2 | 8 | 20214.0790(0.002) | -0.0007 |
| A1 | 0 | 11 | 2 | 10 | A2 | 0 | 10 | 2 | 9 | 21971.7748(0.002) | 0.0013 |
| A2 | 0 | 7 | 3 | 5 | A1 | 0 | 6 | 3 | 4 | 16699.0217(0.002) | -0.0001 |
| A1 | 0 | 8 | 3 | 6 | A2 | 0 | 7 | 3 | 5 | 18456.7048(0.002) | 0.0009 |
| B2 | 0 | 6 | 3 | 3 | B1 | 0 | 5 | 3 | 2 | 16702.3679(0.002) | -0.0009 |
| B1 | 0 | 7 | 3 | 4 | B2 | 0 | 6 | 3 | 3 | 18457.2307(0.002) | 0.0071 |
| B1 | 0 | 6 | 2 | 4 | B2 | 0 | 5 | 3 | 3 | 14941.3446(0.002) | -0.0007 |
| A1 | 0 | 7 | 4 | 4 | A2 | 0 | 6 | 4 | 3 | 18457.1361(0.002) | -0.0044 |
| E2 | 1 | 8 | 0 | 8 | E2 | 1 | 7 | 0 | 7 | 14978.5998(0.002) | 0.0013 |
| E2 | 1 | 9 | 0 | 9 | E2 | 1 | 8 | 0 | 8 | 16726.7689(0.002) | 0.0016 |
| E2 | 1 | 10 | 0 | 10 | E2 | 1 | 9 | 0 | 9 | 18478.1874(0.002) | 0.0012 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| E2 | 1 | 6 | 1 | 6 | E2 | 1 | 5 | 0 | 5 | 11519.2833(0.002) | 0.0004 |
| E1 | 1 | 7 | 1 | 7 | E1 | 1 | 6 | 0 | 6 | 13237.0093(0.002) | -0.0002 |
| E1 | 1 | 8 | 1 | 8 | E1 | 1 | 7 | 1 | 7 | 14978.5747(0.002) | 0.0017 |
| E1 | 1 | 9 | 1 | 9 | E1 | 1 | 8 | 1 | 8 | 16726.7689(0.002) | 0.0011 |
| E1 | 1 | 10 | 1 | 10 | E1 | 1 | 9 | 1 | 9 | 18478.1874(0.002) | 0.0012 |
| E2 | 1 | 8 | 2 | 7 | E2 | 1 | 7 | 1 | 6 | 16886.0915(0.002) | -0.0012 |
| E1 | 1 | 6 | 0 | 6 | E1 | 1 | 5 | 1 | 5 | 11497.3759(0.002) | -0.0003 |
| E2 | 1 | 7 | 0 | 7 | E2 | 1 | 6 | 1 | 6 | 13236.0594(0.002) | 0.0005 |
| E1 | 1 | 6 | 1 | 5 | E1 | 1 | 5 | 2 | 4 | 13007.5134(0.002) | 0.0000 |
| E2 | 1 | 7 | 1 | 6 | E2 | 1 | 6 | 2 | 5 | 15151.0855(0.002) | -0.0027 |
| E1 | 1 | 8 | 1 | 7 | E1 | 1 | 7 | 2 | 6 | 16875.6367(0.002) | -0.0015 |
| E2 | 1 | 6 | 3 | 4 | E2 | 1 | 5 | 2 | 3 | 16886.6626(0.002) | -0.0018 |

**Table S13**. Rotational transitions of the $^{13}C(2)$ and $^{13}C(6)$ isotopologue of 3,5-difluorotoluene.

| Upper level | | | | | Lower level | | | | | Measured(Unc. ) | o.-c.(MHz) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sym' | m' | J' | Ka' | Kc' | Sym | m | J | Ka | Kc | | |
| A2 | 0 | 8 | 1 | 7 | A1 | 0 | 8 | 0 | 8 | 13187.1966(0.002) | 0.0000 |
| A2 | 0 | 3 | 0 | 3 | A1 | 0 | 2 | 0 | 2 | 6153.2213(0.002) | 0.0025 |
| A2 | 0 | 5 | 0 | 5 | A1 | 0 | 4 | 0 | 4 | 9669.1423(0.002) | -0.0001 |
| A1 | 0 | 6 | 0 | 6 | A2 | 0 | 5 | 0 | 5 | 11427.1360(0.002) | -0.0008 |
| A2 | 0 | 7 | 0 | 7 | A1 | 0 | 6 | 0 | 6 | 13185.1294(0.002) | -0.0007 |
| A1 | 0 | 8 | 0 | 8 | A2 | 0 | 7 | 0 | 7 | 14943.1210(0.002) | -0.0008 |
| A2 | 0 | 9 | 0 | 9 | A1 | 0 | 8 | 0 | 8 | 16701.1114(0.002) | -0.0004 |
| A1 | 0 | 10 | 0 | 10 | A2 | 0 | 9 | 0 | 9 | 18459.0996(0.002) | -0.0002 |
| A2 | 0 | 11 | 0 | 11 | A1 | 0 | 10 | 0 | 10 | 20217.0855(0.002) | -0.0001 |
| A1 | 0 | 12 | 0 | 12 | A2 | 0 | 11 | 0 | 11 | 21975.0689(0.002) | -0.0001 |
| A2 | 0 | 3 | 1 | 3 | A1 | 0 | 2 | 0 | 2 | 6153.2213(0.002) | 0.0016 |
| A2 | 0 | 6 | 1 | 5 | A1 | 0 | 5 | 1 | 4 | 13185.4415(0.002) | -0.0009 |
| A1 | 0 | 7 | 1 | 6 | A2 | 0 | 6 | 1 | 5 | 14943.4301(0.002) | 0.0003 |
| A2 | 0 | 8 | 1 | 7 | A1 | 0 | 7 | 1 | 6 | 16701.4169(0.002) | -0.0001 |
| A1 | 0 | 9 | 1 | 8 | A2 | 0 | 8 | 1 | 7 | 18459.4020(0.002) | -0.0009 |
| A1 | 0 | 5 | 2 | 4 | A2 | 0 | 4 | 1 | 3 | 11427.4644(0.002) | 0.0031 |
| A2 | 0 | 3 | 1 | 3 | A1 | 0 | 2 | 1 | 2 | 6153.0885(0.002) | -0.0009 |
| A2 | 0 | 5 | 1 | 5 | A1 | 0 | 4 | 1 | 4 | 9669.1423(0.002) | -0.0001 |
| A1 | 0 | 6 | 1 | 6 | A2 | 0 | 5 | 1 | 5 | 11427.1360(0.002) | -0.0008 |
| A2 | 0 | 7 | 1 | 7 | A1 | 0 | 6 | 1 | 6 | 13185.1294(0.002) | -0.0007 |
| A1 | 0 | 8 | 1 | 8 | A2 | 0 | 7 | 1 | 7 | 14943.1210(0.002) | -0.0008 |
| A2 | 0 | 9 | 1 | 9 | A1 | 0 | 8 | 1 | 8 | 16701.1114(0.002) | -0.0004 |
| A1 | 0 | 10 | 1 | 10 | A2 | 0 | 9 | 1 | 9 | 18459.0996(0.002) | -0.0002 |
| A2 | 0 | 11 | 1 | 11 | A1 | 0 | 10 | 1 | 10 | 20217.0855(0.002) | -0.0001 |
| A1 | 0 | 12 | 1 | 12 | A2 | 0 | 11 | 1 | 11 | 21975.0689(0.002) | -0.0001 |
| A2 | 0 | 3 | 0 | 3 | A1 | 0 | 2 | 1 | 2 | 6153.0885(0.002) | -0.0001 |
| A2 | 0 | 8 | 2 | 7 | A1 | 0 | 8 | 1 | 8 | 13187.1966(0.002) | 0.0000 |
| A2 | 0 | 5 | 3 | 3 | A1 | 0 | 4 | 2 | 2 | 13186.9203(0.002) | -0.0007 |
| A2 | 0 | 6 | 2 | 5 | A1 | 0 | 5 | 2 | 4 | 13185.4415(0.002) | -0.0009 |
| A1 | 0 | 7 | 2 | 6 | A2 | 0 | 6 | 2 | 5 | 14943.4301(0.002) | 0.0003 |
| A2 | 0 | 8 | 2 | 7 | A1 | 0 | 7 | 2 | 6 | 16701.4169(0.002) | -0.0001 |
| A1 | 0 | 9 | 2 | 8 | A2 | 0 | 8 | 2 | 7 | 18459.4020(0.002) | -0.0009 |
| A1 | 0 | 5 | 1 | 4 | A2 | 0 | 4 | 2 | 3 | 11427.4545(0.002) | -0.0008 |
| A1 | 0 | 6 | 2 | 4 | A2 | 0 | 5 | 2 | 3 | 14943.8045(0.002) | 0.0008 |
| A2 | 0 | 7 | 2 | 5 | A1 | 0 | 6 | 2 | 4 | 16701.7461(0.002) | 0.0000 |
| A1 | 0 | 8 | 2 | 6 | A2 | 0 | 7 | 2 | 5 | 18459.7177(0.002) | 0.0002 |
| A2 | 0 | 6 | 4 | 3 | A1 | 0 | 5 | 3 | 2 | 16704.8618(0.002) | 0.0002 |
| A1 | 0 | 7 | 4 | 4 | A2 | 0 | 6 | 3 | 3 | 18460.2113(0.002) | 0.0003 |
| A2 | 0 | 5 | 3 | 3 | A1 | 0 | 4 | 3 | 2 | 13184.9686(0.002) | 0.0002 |
| A1 | 0 | 6 | 3 | 4 | A2 | 0 | 5 | 3 | 3 | 14943.7805(0.002) | 0.0006 |
| A2 | 0 | 7 | 3 | 5 | A1 | 0 | 6 | 3 | 4 | 16701.7461(0.002) | 0.0003 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| A1 | 0 | 8 | 3 | 6 | A2 | 0 | 7 | 3 | 5 | 18459.7177(0.002) | 0.0002 |
| A2 | 0 | 5 | 2 | 3 | A1 | 0 | 4 | 3 | 2 | 13184.9446(0.002) | 0.0002 |
| A1 | 0 | 7 | 3 | 4 | A2 | 0 | 6 | 4 | 3 | 18460.1390(0.002) | 0.0010 |
| E | 1 | 10 | 0 | 10 | E | 1 | 9 | 0 | 9 | 18481.5238(0.002) | 0.0022 |
| E | 1 | 11 | 0 | 11 | E | 1 | 10 | 0 | 10 | 20235.0570(0.002) | 0.0022 |
| E | 1 | 6 | 1 | 6 | E | 1 | 5 | 0 | 5 | 11525.6794(0.002) | 0.0005 |
| E | 1 | 7 | 1 | 7 | E | 1 | 6 | 0 | 6 | 13240.3303(0.002) | 0.0004 |
| E | 1 | 8 | 1 | 8 | E | 1 | 7 | 0 | 7 | 14981.6522(0.002) | 0.0006 |
| E | 1 | 9 | 1 | 9 | E | 1 | 8 | 0 | 8 | 16729.9222(0.002) | 0.0005 |
| E | 1 | 4 | 2 | 3 | E | 1 | 3 | 1 | 2 | 10862.4063(0.002) | 0.0004 |
| E | 1 | 8 | 2 | 7 | E | 1 | 7 | 1 | 6 | 16896.0825(0.002) | -0.0027 |
| E | 1 | 5 | 0 | 5 | E | 1 | 4 | 1 | 4 | 9671.2324(0.002) | -0.0026 |
| E | 1 | 6 | 0 | 6 | E | 1 | 5 | 1 | 5 | 11498.1621(0.002) | -0.0011 |
| E | 1 | 7 | 0 | 7 | E | 1 | 6 | 1 | 6 | 13238.9102(0.002) | -0.0007 |
| E | 1 | 8 | 0 | 8 | E | 1 | 7 | 1 | 7 | 14981.6033(0.002) | 0.0004 |
| E | 1 | 9 | 0 | 9 | E | 1 | 8 | 1 | 8 | 16729.9222(0.002) | 0.0017 |
| E | 1 | 10 | 1 | 10 | E | 1 | 9 | 1 | 9 | 18481.5238(0.002) | 0.0022 |
| E | 1 | 11 | 1 | 11 | E | 1 | 10 | 1 | 10 | 20235.0570(0.002) | 0.0022 |
| E | 1 | 6 | 3 | 4 | E | 1 | 5 | 2 | 3 | 16905.7556(0.002) | -0.0007 |
| E | 1 | 4 | 2 | 2 | E | 1 | 3 | 2 | 2 | 11110.5527(0.002) | -0.0004 |
| E | 1 | 8 | 1 | 7 | E | 1 | 7 | 2 | 6 | 16880.5285(0.002) | -0.0024 |

**Table S14**. Rotational transitions of the $^{13}$C(3) and $^{13}$C(5) isotopologues of 3,5-difluorotoluene.

| Upper level | | | | | Lower level | | | | | Measured(Unc. ) | o.-c.(MHz) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sym' | m' | J' | Ka' | Kc' | Sym | m | J | Ka | Kc | | |
| A1 | 0 | 4 | 0 | 4 | A2 | 0 | 3 | 0 | 3 | 7914.4425(0.002) | -0.0006 |
| A1 | 0 | 6 | 0 | 6 | A2 | 0 | 5 | 0 | 5 | 11431.8950(0.002) | -0.0009 |
| A2 | 0 | 7 | 0 | 7 | A1 | 0 | 6 | 0 | 6 | 13190.6206(0.002) | -0.0002 |
| A1 | 0 | 8 | 0 | 8 | A2 | 0 | 7 | 0 | 7 | 14949.3442(0.002) | 0.0000 |
| A2 | 0 | 9 | 0 | 9 | A1 | 0 | 8 | 0 | 8 | 16708.0665(0.002) | 0.0007 |
| A1 | 0 | 10 | 0 | 10 | A2 | 0 | 9 | 0 | 9 | 18466.7859(0.002) | 0.0004 |
| A2 | 0 | 11 | 0 | 11 | A1 | 0 | 10 | 0 | 10 | 20225.5039(0.002) | 0.0009 |
| A1 | 0 | 12 | 0 | 12 | A2 | 0 | 11 | 0 | 11 | 21984.2180(0.002) | -0.0001 |
| A2 | 0 | 3 | 1 | 3 | A1 | 0 | 2 | 0 | 2 | 6155.7679(0.010) | 0.0014 |
| A2 | 0 | 8 | 1 | 7 | A1 | 0 | 8 | 0 | 8 | 13192.7490(0.002) | -0.0006 |
| A1 | 0 | 9 | 1 | 8 | A2 | 0 | 9 | 0 | 9 | 14951.7794(0.002) | 0.0007 |
| A1 | 0 | 4 | 1 | 4 | A2 | 0 | 3 | 1 | 3 | 7914.4425(0.002) | 0.0000 |
| A1 | 0 | 6 | 1 | 6 | A2 | 0 | 5 | 1 | 5 | 11431.8950(0.002) | -0.0009 |
| A2 | 0 | 7 | 1 | 7 | A1 | 0 | 6 | 1 | 6 | 13190.6206(0.002) | -0.0002 |
| A1 | 0 | 8 | 1 | 8 | A2 | 0 | 7 | 1 | 7 | 14949.3442(0.002) | 0.0000 |
| A2 | 0 | 9 | 1 | 9 | A1 | 0 | 8 | 1 | 8 | 16708.0665(0.002) | 0.0007 |
| A1 | 0 | 10 | 1 | 10 | A2 | 0 | 9 | 1 | 9 | 18466.7859(0.002) | 0.0004 |
| A2 | 0 | 11 | 1 | 11 | A1 | 0 | 10 | 1 | 10 | 20225.5039(0.002) | 0.0009 |
| A1 | 0 | 12 | 1 | 12 | A2 | 0 | 11 | 1 | 11 | 21984.2180(0.002) | -0.0001 |
| A2 | 0 | 6 | 1 | 5 | A1 | 0 | 5 | 1 | 4 | 13190.9384(0.002) | 0.0003 |
| A1 | 0 | 7 | 1 | 6 | A2 | 0 | 6 | 1 | 5 | 14949.6576(0.002) | -0.0003 |
| A2 | 0 | 8 | 1 | 7 | A1 | 0 | 7 | 1 | 6 | 16708.3774(0.002) | 0.0002 |
| A1 | 0 | 9 | 1 | 8 | A2 | 0 | 8 | 1 | 7 | 18467.0947(0.002) | -0.0002 |
| A1 | 0 | 5 | 2 | 4 | A2 | 0 | 4 | 1 | 3 | 11432.2202(0.002) | -0.0021 |
| A2 | 0 | 8 | 2 | 7 | A1 | 0 | 8 | 1 | 8 | 13192.7490(0.002) | -0.0006 |
| A1 | 0 | 9 | 2 | 8 | A2 | 0 | 9 | 1 | 9 | 14951.7794(0.002) | 0.0007 |
| A1 | 0 | 10 | 3 | 8 | A2 | 0 | 10 | 1 | 9 | 14951.6555(0.002) | -0.0007 |
| A2 | 0 | 3 | 0 | 3 | A1 | 0 | 2 | 1 | 2 | 6155.6668(0.010) | -0.0007 |
| A2 | 0 | 9 | 2 | 7 | A1 | 0 | 9 | 1 | 8 | 13192.6355(0.002) | -0.0014 |
| A1 | 0 | 5 | 1 | 4 | A2 | 0 | 4 | 2 | 3 | 11432.2202(0.002) | 0.0018 |
| A2 | 0 | 6 | 2 | 5 | A1 | 0 | 5 | 2 | 4 | 13190.9384(0.002) | 0.0003 |
| A1 | 0 | 7 | 2 | 6 | A2 | 0 | 6 | 2 | 5 | 14949.6576(0.002) | -0.0003 |
| A2 | 0 | 8 | 2 | 7 | A1 | 0 | 7 | 2 | 6 | 16708.3774(0.002) | 0.0002 |
| A1 | 0 | 9 | 2 | 8 | A2 | 0 | 8 | 2 | 7 | 18467.0947(0.002) | -0.0002 |
| A1 | 0 | 6 | 2 | 4 | A2 | 0 | 5 | 2 | 3 | 14950.0192(0.002) | -0.0009 |
| A2 | 0 | 7 | 2 | 5 | A1 | 0 | 6 | 2 | 4 | 16708.7059(0.002) | -0.0001 |
| A2 | 0 | 5 | 3 | 3 | A1 | 0 | 4 | 2 | 2 | 13192.1363(0.002) | -0.0004 |
| A1 | 0 | 6 | 3 | 4 | A2 | 0 | 5 | 2 | 3 | 14950.0192(0.002) | -0.0011 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| A2 | 0 | 10 | 3 | 7 | A1 | 0 | 10 | 2 | 8 | 13192.4975(0.002) | 0.0013 |
| A1 | 0 | 11 | 3 | 8 | A2 | 0 | 11 | 2 | 9 | 14951.5101(0.002) | 0.0014 |
| A1 | 0 | 10 | 2 | 8 | A2 | 0 | 10 | 2 | 9 | 14951.6555(0.002) | -0.0007 |
| A2 | 0 | 9 | 3 | 7 | A1 | 0 | 9 | 2 | 8 | 13192.6355(0.002) | -0.0014 |
| A2 | 0 | 10 | 4 | 7 | A1 | 0 | 10 | 3 | 8 | 13192.4975(0.002) | 0.0013 |
| A1 | 0 | 11 | 4 | 8 | A2 | 0 | 11 | 3 | 9 | 14951.5101(0.002) | 0.0014 |
| A2 | 0 | 11 | 4 | 7 | A1 | 0 | 11 | 3 | 8 | 13192.3233(0.002) | 0.0007 |
| A1 | 0 | 6 | 3 | 4 | A2 | 0 | 5 | 3 | 3 | 14950.0047(0.002) | 0.0003 |
| A2 | 0 | 7 | 3 | 5 | A1 | 0 | 6 | 3 | 4 | 16708.7059(0.002) | 0.0000 |
| A1 | 0 | 6 | 2 | 4 | A2 | 0 | 5 | 3 | 3 | 14950.0047(0.002) | 0.0004 |
| A2 | 0 | 6 | 4 | 3 | A1 | 0 | 5 | 4 | 2 | 16707.6946(0.002) | -0.0009 |
| A2 | 0 | 6 | 3 | 3 | A1 | 0 | 5 | 4 | 2 | 16707.6481(0.002) | 0.0001 |
| A2 | 0 | 11 | 5 | 7 | A1 | 0 | 11 | 4 | 8 | 13192.3233(0.002) | 0.0007 |
| E | 1 | 6 | 1 | 6 | E | 1 | 5 | 0 | 5 | 11530.5876(0.002) | 0.0018 |
| E | 1 | 7 | 1 | 7 | E | 1 | 6 | 0 | 6 | 13245.8748(0.002) | 0.0006 |
| E | 1 | 8 | 1 | 8 | E | 1 | 7 | 0 | 7 | 14987.9075(0.002) | 0.0000 |
| E | 1 | 9 | 1 | 9 | E | 1 | 8 | 0 | 8 | 16736.9005(0.002) | 0.0000 |
| E | 1 | 10 | 0 | 10 | E | 1 | 9 | 0 | 9 | 18489.2285(0.002) | 0.0017 |
| E | 1 | 6 | 0 | 6 | E | 1 | 5 | 1 | 5 | 11502.9366(0.002) | -0.0003 |
| E | 1 | 6 | 0 | 6 | E | 1 | 5 | 1 | 5 | 11502.9352(0.002) | -0.0017 |
| E | 1 | 7 | 0 | 7 | E | 1 | 6 | 1 | 6 | 13244.4449(0.002) | -0.0001 |
| E | 1 | 8 | 0 | 8 | E | 1 | 7 | 1 | 7 | 14987.8587(0.002) | 0.0003 |
| E | 1 | 9 | 0 | 9 | E | 1 | 8 | 1 | 8 | 16736.9005(0.002) | 0.0012 |
| E | 1 | 7 | 2 | 6 | E | 1 | 6 | 1 | 5 | 15371.8603(0.002) | 0.0014 |
| E | 1 | 8 | 2 | 7 | E | 1 | 7 | 1 | 6 | 16903.2970(0.002) | -0.0008 |
| E | 1 | 10 | 1 | 10 | E | 1 | 9 | 1 | 9 | 18489.2285(0.002) | 0.0018 |
| E | 1 | 5 | 2 | 3 | E | 1 | 4 | 2 | 3 | 14112.4503(0.002) | 0.0016 |
| E | 1 | 8 | 1 | 7 | E | 1 | 7 | 2 | 6 | 16887.6304(0.002) | -0.0028 |
| E | 1 | 6 | 3 | 4 | E | 1 | 5 | 2 | 3 | 16913.0595(0.002) | -0.0021 |
| E | 1 | 6 | 3 | 3 | E | 1 | 5 | 3 | 3 | 17217.2153(0.002) | -0.0006 |

**Table S15**. Rotational transitions of the $^{13}$C(4) isotopologue of 3,5-difluorotoluene.

| **Upper level** | | | | | **Lower level** | | | | | **Measured(Unc. )** | **o.-c.(MHz)** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Sym'** | **m'** | **J'** | **Ka'** | **Kc'** | **Sym** | **m** | **J** | **Ka** | **Kc** | | |
| A2 | 0 | 3 | 0 | 3 | A1 | 0 | 2 | 0 | 2 | 6154.7863(0.002) | 0.0000 |
| B2 | 0 | 5 | 0 | 5 | B1 | 0 | 4 | 0 | 4 | 9671.6170(0.002) | 0.0003 |
| B1 | 0 | 6 | 0 | 6 | B2 | 0 | 5 | 0 | 5 | 11430.0609(0.002) | -0.0001 |
| B2 | 0 | 7 | 0 | 7 | B1 | 0 | 6 | 0 | 6 | 13188.5037(0.002) | -0.0004 |
| B1 | 0 | 8 | 0 | 8 | B2 | 0 | 7 | 0 | 7 | 14946.9457(0.002) | 0.0001 |
| B2 | 0 | 9 | 0 | 9 | B1 | 0 | 8 | 0 | 8 | 16705.3854(0.002) | -0.0001 |
| B1 | 0 | 10 | 0 | 10 | B2 | 0 | 9 | 0 | 9 | 18463.8242(0.002) | 0.0009 |
| A1 | 0 | 4 | 1 | 4 | A2 | 0 | 3 | 0 | 3 | 7913.1716(0.002) | -0.0005 |
| B2 | 0 | 3 | 1 | 3 | B1 | 0 | 2 | 1 | 2 | 6154.6709(0.002) | 0.0007 |
| A2 | 0 | 5 | 1 | 5 | A1 | 0 | 4 | 1 | 4 | 9671.6170(0.002) | 0.0003 |
| A1 | 0 | 6 | 1 | 6 | A2 | 0 | 5 | 1 | 5 | 11430.0609(0.002) | -0.0001 |
| A2 | 0 | 7 | 1 | 7 | A1 | 0 | 6 | 1 | 6 | 13188.5037(0.002) | -0.0004 |
| A1 | 0 | 8 | 1 | 8 | A2 | 0 | 7 | 1 | 7 | 14946.9457(0.002) | 0.0001 |
| A2 | 0 | 9 | 1 | 9 | A1 | 0 | 8 | 1 | 8 | 16705.3854(0.002) | -0.0001 |
| A1 | 0 | 10 | 1 | 10 | A2 | 0 | 9 | 1 | 9 | 18463.8242(0.002) | 0.0009 |
| B1 | 0 | 5 | 1 | 4 | B2 | 0 | 4 | 1 | 3 | 11430.3852(0.002) | 0.0012 |
| B2 | 0 | 6 | 1 | 5 | B1 | 0 | 5 | 1 | 4 | 13188.8160(0.002) | -0.0003 |
| B1 | 0 | 7 | 1 | 6 | B2 | 0 | 6 | 1 | 5 | 14947.2538(0.002) | 0.0000 |
| B2 | 0 | 8 | 1 | 7 | B1 | 0 | 7 | 1 | 6 | 16705.6905(0.002) | -0.0006 |
| B1 | 0 | 9 | 1 | 8 | B2 | 0 | 8 | 1 | 7 | 18464.1279(0.002) | 0.0009 |
| B1 | 0 | 4 | 0 | 4 | B2 | 0 | 3 | 1 | 3 | 7913.1716(0.002) | 0.0002 |
| A2 | 0 | 5 | 2 | 3 | A1 | 0 | 4 | 2 | 2 | 13190.1502(0.002) | -0.0034 |
| B2 | 0 | 7 | 2 | 5 | B1 | 0 | 6 | 2 | 4 | 16706.0183(0.002) | 0.0005 |
| B1 | 0 | 8 | 2 | 6 | B2 | 0 | 7 | 2 | 5 | 18464.4408(0.002) | 0.0001 |
| A2 | 0 | 4 | 2 | 3 | A1 | 0 | 3 | 2 | 2 | 9671.6797(0.002) | 0.0019 |
| A1 | 0 | 5 | 2 | 4 | A2 | 0 | 4 | 2 | 3 | 11430.3781(0.002) | -0.0008 |
| A2 | 0 | 6 | 2 | 5 | A1 | 0 | 5 | 2 | 4 | 13188.8160(0.002) | -0.0002 |
| A1 | 0 | 7 | 2 | 6 | A2 | 0 | 6 | 2 | 5 | 14947.2538(0.002) | 0.0000 |
| A2 | 0 | 8 | 2 | 7 | A1 | 0 | 7 | 2 | 6 | 16705.6905(0.002) | -0.0006 |
| A1 | 0 | 9 | 2 | 8 | A2 | 0 | 8 | 2 | 7 | 18464.1279(0.002) | 0.0009 |
| A1 | 0 | 6 | 3 | 4 | A2 | 0 | 5 | 2 | 3 | 14947.6200(0.002) | -0.0006 |
| A2 | 0 | 7 | 3 | 5 | A1 | 0 | 6 | 3 | 4 | 16706.0183(0.002) | 0.0004 |
| A1 | 0 | 8 | 3 | 6 | A2 | 0 | 7 | 3 | 5 | 18464.4408(0.002) | 0.0001 |
| B1 | 0 | 6 | 2 | 4 | B2 | 0 | 5 | 3 | 3 | 14947.5997(0.002) | -0.0007 |
| B1 | 0 | 7 | 3 | 4 | B2 | 0 | 6 | 3 | 3 | 18464.9123(0.002) | -0.0003 |
| A2 | 0 | 6 | 4 | 3 | A1 | 0 | 5 | 4 | 2 | 16704.7622(0.002) | 0.0015 |
| A1 | 0 | 7 | 4 | 4 | A2 | 0 | 6 | 4 | 3 | 18464.8516(0.002) | -0.0007 |
| E2 | 1 | 6 | 1 | 6 | E2 | 1 | 5 | 0 | 5 | 11524.4453(0.002) | 0.0018 |
| E1 | 1 | 7 | 1 | 7 | E1 | 1 | 6 | 0 | 6 | 13242.6559(0.002) | 0.0015 |
| E2 | 1 | 8 | 0 | 8 | E2 | 1 | 7 | 0 | 7 | 14984.9347(0.002) | -0.0005 |
| E2 | 1 | 9 | 0 | 9 | E2 | 1 | 8 | 0 | 8 | 16733.8241(0.002) | 0.0002 |
| E2 | 1 | 10 | 0 | 10 | E2 | 1 | 9 | 0 | 9 | 18485.9705(0.002) | 0.0003 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| E1 | 1 | 8 | 1 | 8 | E1 | 1 | 7 | 1 | 7 | 14984.9068(0.002) | -0.0016 |
| E1 | 1 | 9 | 1 | 9 | E1 | 1 | 8 | 1 | 8 | 16733.8241(0.002) | -0.0003 |
| E1 | 1 | 10 | 1 | 10 | E1 | 1 | 9 | 1 | 9 | 18485.9705(0.002) | 0.0003 |
| | | | | | | | | | | | |
| E2 | 1 | 4 | 2 | 3 | E2 | 1 | 3 | 1 | 2 | 10848.1099(0.002) | 0.0041 |
| E2 | 1 | 8 | 2 | 7 | E2 | 1 | 7 | 1 | 6 | 16893.6937(0.002) | -0.0003 |
| | | | | | | | | | | | |
| E1 | 1 | 6 | 0 | 6 | E1 | 1 | 5 | 1 | 5 | 11502.1428(0.002) | -0.0013 |
| E2 | 1 | 7 | 0 | 7 | E2 | 1 | 6 | 1 | 6 | 13241.6734(0.002) | -0.0004 |
| | | | | | | | | | | | |
| E1 | 1 | 8 | 1 | 7 | E1 | 1 | 7 | 2 | 6 | 16882.9112(0.002) | -0.0016 |
| | | | | | | | | | | | |
| E1 | 1 | 4 | 2 | 2 | E1 | 1 | 3 | 2 | 2 | 11086.8810(0.002) | 0.0052 |
| E2 | 1 | 5 | 2 | 3 | E2 | 1 | 4 | 2 | 3 | 14112.6284(0.002) | -0.0008 |
| | | | | | | | | | | | |
| E2 | 1 | 4 | 3 | 2 | E2 | 1 | 3 | 2 | 1 | 11204.2460(0.002) | 0.0017 |
| E2 | 1 | 6 | 3 | 4 | E2 | 1 | 5 | 2 | 3 | 16894.8808(0.002) | 0.0019 |
| | | | | | | | | | | | |
| E2 | 1 | 5 | 3 | 2 | E2 | 1 | 4 | 3 | 2 | 14183.4562(0.002) | 0.0007 |
| | | | | | | | | | | | |
| E1 | 1 | 5 | 4 | 2 | E1 | 1 | 4 | 3 | 1 | 14267.1507(0.002) | -0.0043 |
| E2 | 1 | 6 | 4 | 3 | E2 | 1 | 5 | 3 | 2 | 17229.7887(0.002) | -0.0026 |

**Table S16**. Rotational transitions of the $^{13}C(7)$ isotopologue of 3,5-difluorotoluene.

| Upper level | | | | | Lower level | | | | | Measured(Unc. ) | o.-c.(MHz) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sym' | m' | J' | Ka' | Kc' | Sym | m | J | Ka | Kc | | |
| A1 | 0 | 4 | 0 | 4 | A2 | 0 | 3 | 0 | 3 | 7819.5593(0.002) | 0.0012 |
| B1 | 0 | 6 | 0 | 6 | B2 | 0 | 5 | 0 | 5 | 11294.7554(0.002) | -0.0008 |
| B2 | 0 | 7 | 0 | 7 | B1 | 0 | 6 | 0 | 6 | 13032.3756(0.002) | -0.0023 |
| B1 | 0 | 8 | 0 | 8 | B2 | 0 | 7 | 0 | 7 | 14769.9988(0.002) | -0.0007 |
| B1 | 0 | 10 | 0 | 10 | B2 | 0 | 9 | 0 | 9 | 18245.2385(0.002) | -0.0004 |
| B2 | 0 | 11 | 0 | 11 | B1 | 0 | 10 | 0 | 10 | 19982.8561(0.002) | 0.0003 |
| B1 | 0 | 12 | 0 | 12 | B2 | 0 | 11 | 0 | 11 | 21720.4709(0.002) | 0.0005 |
| B1 | 0 | 4 | 1 | 4 | B2 | 0 | 3 | 1 | 3 | 7819.4935(0.002) | 0.0008 |
| A1 | 0 | 6 | 1 | 6 | A2 | 0 | 5 | 1 | 5 | 11294.7554(0.002) | -0.0008 |
| A2 | 0 | 7 | 1 | 7 | A1 | 0 | 6 | 1 | 6 | 13032.3756(0.002) | -0.0023 |
| A1 | 0 | 8 | 1 | 8 | A2 | 0 | 7 | 1 | 7 | 14769.9988(0.002) | -0.0007 |
| A1 | 0 | 10 | 1 | 10 | A2 | 0 | 9 | 1 | 9 | 18245.2385(0.002) | -0.0004 |
| A2 | 0 | 11 | 1 | 11 | A1 | 0 | 10 | 1 | 10 | 19982.8561(0.002) | 0.0003 |
| A1 | 0 | 12 | 1 | 12 | A2 | 0 | 11 | 1 | 11 | 21720.4709(0.002) | 0.0005 |
| B1 | 0 | 5 | 1 | 4 | B2 | 0 | 4 | 1 | 3 | 11295.5862(0.002) | 0.0002 |
| B2 | 0 | 6 | 1 | 5 | B1 | 0 | 5 | 1 | 4 | 13032.8384(0.002) | -0.0026 |
| B1 | 0 | 7 | 1 | 6 | B2 | 0 | 6 | 1 | 5 | 14770.3970(0.002) | -0.0002 |
| A1 | 0 | 5 | 2 | 4 | A2 | 0 | 4 | 2 | 3 | 11295.1334(0.002) | 0.0010 |
| A2 | 0 | 6 | 2 | 5 | A1 | 0 | 5 | 2 | 4 | 13032.8294(0.002) | 0.0022 |
| A1 | 0 | 7 | 2 | 6 | A2 | 0 | 6 | 2 | 5 | 14770.3970(0.002) | 0.0001 |
| A1 | 0 | 4 | 2 | 2 | A2 | 0 | 3 | 2 | 1 | 11419.6888(0.002) | -0.0010 |
| A1 | 0 | 6 | 2 | 4 | A2 | 0 | 5 | 2 | 3 | 14772.7029(0.002) | 0.0008 |
| B1 | 0 | 6 | 3 | 4 | B2 | 0 | 5 | 3 | 3 | 14770.9076(0.002) | 0.0014 |
| E2 | 1 | 8 | 0 | 8 | E2 | 1 | 7 | 0 | 7 | 14806.2779(0.002) | -0.0012 |
| E2 | 1 | 9 | 0 | 9 | E2 | 1 | 8 | 0 | 8 | 16534.8410(0.002) | 0.0001 |
| E2 | 1 | 10 | 0 | 10 | E2 | 1 | 9 | 0 | 9 | 18266.4664(0.002) | 0.0012 |
| E2 | 1 | 6 | 1 | 6 | E2 | 1 | 5 | 0 | 5 | 11379.6033(0.002) | 0.0008 |
| E1 | 1 | 7 | 1 | 7 | E1 | 1 | 6 | 0 | 6 | 13083.6264(0.002) | -0.0001 |
| E1 | 1 | 8 | 1 | 8 | E1 | 1 | 7 | 1 | 7 | 14806.2779(0.002) | 0.0024 |
| E1 | 1 | 9 | 1 | 9 | E1 | 1 | 8 | 1 | 8 | 16534.8410(0.002) | 0.0001 |
| E1 | 1 | 10 | 1 | 10 | E1 | 1 | 9 | 1 | 9 | 18266.4664(0.002) | 0.0012 |
| E1 | 1 | 7 | 2 | 6 | E1 | 1 | 6 | 1 | 5 | 15098.9608(0.002) | -0.0011 |
| E2 | 1 | 8 | 2 | 7 | E2 | 1 | 7 | 1 | 6 | 16680.6163(0.002) | -0.0003 |
| E1 | 1 | 6 | 0 | 6 | E1 | 1 | 5 | 1 | 5 | 11367.2708(0.002) | 0.0006 |
| E2 | 1 | 7 | 0 | 7 | E2 | 1 | 6 | 1 | 6 | 13083.3024(0.002) | -0.0011 |
| E1 | 1 | 6 | 1 | 5 | E1 | 1 | 5 | 2 | 4 | 12995.5886(0.002) | 0.0000 |
| E1 | 1 | 6 | 3 | 3 | E1 | 1 | 5 | 3 | 3 | 16959.0156(0.002) | -0.0006 |

**Table S17**. Stark effect measurements on several rotational transitions of 2,6-difluorotoluene. For each electric field (V cm$^{-1}$) the Table presents the observed (Obs.), calculated (Calc.) and observed minus calculated (Obs.-Calc.) frequencies (MHz).

| $J' - J''$ | Electric field | Obs. | Calc. | Obs.-Calc. |
|---|---|---|---|---|
| $2_{0,2} - 1_{1,1}$ | 0.0 | 4556.32700 | 4556.3261 | 0.0009 |
| $M_{F'} - M_{F''}$=2 - 1 | 33.6504 | 4556.30987 | 4556.3118 | -0.0019 |
| | 37.0090 | 4556.30744 | 4556.3088 | -0.0014 |
| | 42.0469 | 4556.30297 | 4556.3038 | -0.0008 |
| | 50.4433 | 4556.29244 | 4556.2940 | -0.0016 |
| $2_{2,1} - 1_{1,0}$ | 0.0 | 7803.16250 | 7803.1616 | 0.00090 |
| $M_{F'} - M_{F''}$=2 - 1 | 16.8575 | 7803.15403 | 7803.1522 | 0.00185 |
| | 33.6504 | 7803.12560 | 7803.1241 | 0.00151 |
| | 42.0469 | 7803.10199 | 7803.1030 | -0.00105 |
| | 50.4433 | 7803.07728 | 7803.0773 | -0.00004 |
| | 58.8396 | 7803.04852 | 7803.0469 | 0.00159 |
| | 67.2361 | 7803.01066 | 7803.0119 | -0.00122 |
| $3_{0,3} - 2_{1,2}$ | 0.0 | 6833.59115 | 6833.5914 | -0.0003 |
| $M_{F'} - M_{F''}$=3 - 2 | 16.8575 | 6833.59133 | 6833.5917 | -0.0004 |
| | 33.6504 | 6833.59258 | 6833.5927 | -0.0001 |
| | 50.4433 | 6833.59376 | 6833.5943 | -0.0005 |
| | 67.2361 | 6833.59574 | 6833.5965 | -0.0007 |
| | 75.6325 | 6833.59707 | 6833.5978 | -0.0007 |
| | 84.0290 | 6833.59855 | 6833.5993 | -0.0007 |
| | 92.4253 | 6833.60022 | 6833.6010 | -0.0007 |
| | 100.8219 | 6833.60211 | 6833.6028 | -0.0007 |
| | 109.2182 | 6833.60401 | 6833.6048 | -0.0007 |
| | 117.6147 | 6833.60632 | 6833.6069 | -0.0006 |
| | 126.0111 | 6833.60820 | 6833.6092 | -0.0010 |
| | 134.4076 | 6833.61098 | 6833.6116 | -0.0007 |
| $3_{3,0} - 2_{2,1}$ | 0.0000 | 13151.15224 | 13151.1513 | 0.00094 |
| $M_{F'} - M_{F''}$=3 - 2 | 16.8575 | 13151.15292 | 13151.1534 | -0.00049 |
| | 50.4433 | 13151.17130 | 13151.1702 | 0.00105 |
| | 67.2361 | 13151.18333 | 13151.1850 | -0.00164 |
| | 84.0290 | 13151.20291 | 13151.2039 | -0.00098 |
| | 92.4253 | 13151.21580 | 13151.2149 | 0.00088 |
| $4_{0,4} - 3_{1,3}$ | 0.0 | 8904.61834 | 8904.6175 | 0.0008 |
| $M_{F'} - M_{F''}$=4 - 3 | 50.4433 | 8904.62216 | 8904.6228 | -0.0006 |
| | 84.0290 | 8904.63111 | 8904.6321 | -0.0009 |
| | 92.4353 | 8904.63531 | 8904.6351 | 0.0002 |
| | 100.8219 | 8904.63882 | 8904.6384 | 0.0004 |
| | 109.2182 | 8904.64245 | 8904.6421 | 0.0004 |
| | 117.6147 | 8904.64600 | 8904.6460 | 0.0001 |
| | 126.0111 | 8904.65015 | 8904.6502 | -0.0000 |
| $4_{0,4} - 3_{1,3}$ | 0.0 | 8904.61834 | 8904.6175 | 0.0008 |
| $M_{F'} - M_{F''}$=3 - 2 | 50.4433 | 8904.61720 | 8904.6176 | -0.00044 |
| | 84.0290 | 8904.61882 | 8904.6178 | -0.001 |
| | 92.4353 | 8904.61779 | 8904.6179 | -0.0001 |
| | 100.8219 | 8904.61699 | 8904.6180 | -0.001 |
| | 109.2182 | 8904.61681 | 8904.6181 | -0.001 |
| | 117.6147 | 8904.61845 | 8904.6181 | 0.0003 |
| | 126.0111 | 8904.61869 | 8904.6182 | 0.0004 |

**Table S18**. Stark effect measurements on several rotational transitions of 3,5-difluorotoluene. For each electric field (V cm$^{-1}$) the Table presents the observed (Obs.), calculated (Calc.) and observed minus calculated (Obs.-Calc.) frequencies (MHz).

| *J'* – *J''* | Electric field | Obs. | Calc. | Obs.-Calc. |
|---|---|---|---|---|
| $3_{0,3} - 2_{1,2}$ | 0.0 | 6174.64400 | 6174.6419 | 0.0021 |
| $M_{F'} - M_{F''}$=3 - 2 | 16.8575 | 6174.65011 | 6174.6505 | -0.0003 |
| | 33.6504 | 6174.67665 | 6174.6761 | 0.0005 |
| | 42.0468 | 6174.69567 | 6174.6953 | 0.0004 |
| | 50.4433 | 6174.71940 | 6174.7188 | 0.0006 |
| | 58.8396 | 6174.74740 | 6174.7465 | 0.0009 |
| | 67.2361 | 6174.77970 | 6174.7784 | 0.0013 |
| | 75.6325 | 6174.81581 | 6174.8147 | 0.0011 |
| | 84.0290 | 6174.85491 | 6174.8552 | -0.0002 |
| | 92.4253 | 6174.90086 | 6174.8999 | 0.0009 |
| | 100.8219 | 6174.94958 | 6174.9489 | 0.0007 |
| | | | | |
| $3_{0,3} - 2_{1,2}$ | 33.6504 | 6174.63820 | 6174.6380 | 0.0002 |
| $M_{F'} - M_{F''}$=2 - 1 | 42.0468 | 6174.63548 | 6174.6358 | -0.0003 |
| | 50.4433 | 6174.63351 | 6174.6331 | 0.0004 |
| | 58.8396 | 6174.63078 | 6174.6300 | 0.0008 |
| | 67.2361 | 6174.62793 | 6174.6263 | 0.0016 |
| | 75.6325 | 6174.62291 | 6174.6222 | 0.00074 |
| | 84.0290 | 6174.61847 | 6174.6176 | 0.00092 |
| | 100.8219 | 6174.60837 | 6174.6069 | 0.00015 |
| $3_{0,3} - 2_{1,2}$ | 58.8396 | 6174.61513 | 6174.6132 | 0.0020 |
| $M_{F'} - M_{F''}$=1 - 0 | 67.2361 | 6174.60510 | 6174.6044 | 0.00072 |
| | 75.6325 | 6174.59830 | 6174.5944 | 0.0039 |
| | 84.0290 | 6174.58567 | 6174.5833 | 0.00236 |
| | 100.8219 | 6174.55995 | 6174.5576 | 0.00238 |
| $4_{1,4} - 3_{0,3}$ | 0.0 | 7938.78039 | 7938.7790 | 0.0014 |
| $M_{F'} - M_{F''}$=4 - 3 | 16.8575 | 7938.78096 | 7938.7827 | -0.0018 |
| | 33.6504 | 7938.79291 | 7938.7939 | -0.0010 |
| | 42.0468 | 7938.80211 | 7938.8022 | -0.00013 |
| | 50.4433 | 7938.81164 | 7938.8124 | -0.00081 |
| | 58.8396 | 7938.82512 | 7938.8245 | 0.00061 |
| | 67.2361 | 7938.83746 | 7938.8384 | -0.0010 |
| | 75.6325 | 7938.85237 | 7938.8542 | -0.0018 |
| | 84.0290 | 7938.87196 | 7938.8718 | 0.000120 |
| $4_{1,4} - 3_{0,3}$ | 0.0000 | 7938.78039 | 7938.7790 | 0.0014 |
| $M_{F'} - M_{F''}$=3 – 2 | 33.6504 | 7938.78274 | 7938.7806 | 0.0021 |
| | 42.0468 | 7938.78194 | 7938.7815 | 0.0004 |
| | 50.4433 | 7938.78257 | 7938.7826 | -0.0000 |
| | 58.8396 | 7938.78371 | 7938.7839 | -0.0002 |
| | 67.2361 | 7938.78643 | 7938.7854 | 0.0010 |
| | 75.6325 | 7938.78796 | 7938.7871 | 0.0009 |
| | 84.0290 | 7938.78941 | 7938.7890 | 0.00041 |
| $4_{1,4} - 3_{0,3}$ | 50.4433 | 7938.77058 | 7938.7682 | 0.0023 |
| $M_{F'} - M_{F''}$=2 – 1 | 58.8396 | 7938.76526 | 7938.7643 | 0.00093 |