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# Neighborhood matters: Steric effects on methyl internal rotation and chlorine nuclear quadrupole coupling in 2-fluoro-4-chlorotoluene

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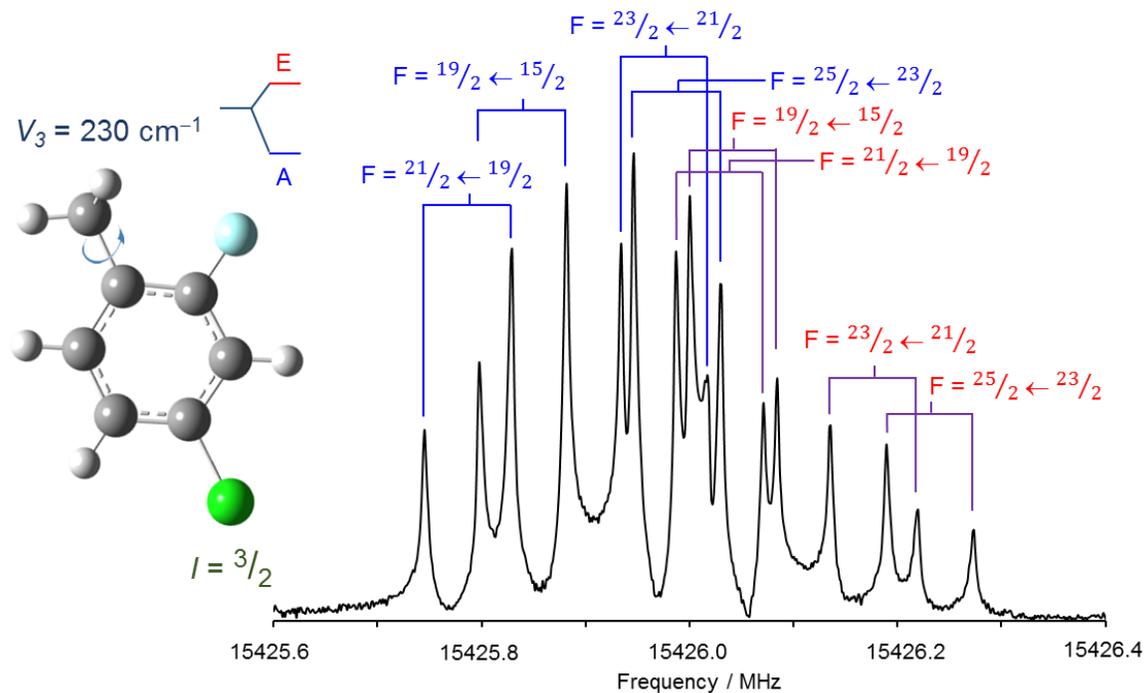
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## Abstract

The rotational spectrum of 2-fluoro-4-chlorotoluene was studied in the frequency range 4 to 24 GHz by Fourier transform microwave spectroscopy. Fine torsional splitting into doublets was observed for all rotational transitions due to methyl group internal rotation hindering with a barrier height of about  $230\text{ cm}^{-1}$ . In combination with the quadrupole coupling hyperfine splittings in the same order of magnitude originating from the chlorine nucleus, rich spectral features were observed for every rotational line. Rotational and quadrupole coupling constants for the two  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  isotopologues studied in natural abundance were precisely determined. Results from the experiment were supported by quantum chemical calculations at several levels of theory for the rotational parameters and by Bailey's semi-experimental method for the quadrupole coupling constants. The  $\chi_{cc}$  quadrupole coupling tensor element and the barrier to methyl internal rotation were compared with those of other halogen-substituted toluene derivatives.

Keywords: microwave spectroscopy, internal rotation, chlorine nuclear quadrupole coupling, large amplitude motion

## Graphical Abstract



## 1. Introduction

There is a wealth of molecules studied by microwave spectroscopy featuring a methyl internal rotor [1]. Among them, toluene and its fluoro-substituted derivatives (Figure 1) form a large body with more than 20 molecules reported in the literature, e.g. fluorotoluenes (molecules **5** and **6** in Figure 1) [2-4], difluorotoluenes (**7**) [5-9], trifluorotoluenes (**8**)[10], and dimethylfluorobenzenes (**9**) [11,12]. In contrast, the number of investigations on chloro-substituted toluenes is rather small and limited to the three isomers *ortho*- [13], *meta*- [14], and *para*-chlorotoluene [15]. Recently, we studied the first mixed halogen-substituted toluene, 2-chloro-4-fluorotoluene (**2**), and revealed that the additional fluorine atom at the 4-position of the toluene ring does not affect the methyl torsion [16]. The barrier to methyl internal rotation is almost the same as that in *o*-chlorotoluene (**3**) [13,16]. It is interesting to see how its height depends on the positions of the two halogen atoms. Since, except fluorine, all other halogen nuclei have a non-zero electric quadrupole moment, it is also interesting to study how the electric nuclear quadrupole coupling tensor, which is a measure for the electric field gradient at the site of the nucleus, changes. In the present paper, we report the microwave spectrum of 2-fluoro-4-chlorotoluene (**1**), an isomer of 2-chloro-4-fluorotoluene (**2**) where the positions of the fluorine and the chlorine atoms have been exchanged.

Methyl internal rotation causes fine splitting doublets in rotational spectra comprising A-E torsional symmetry species pairs while chlorine nuclear quadrupole moment causes hyperfine splittings due to the nuclear spin  $I = 3/2$  of the chlorine nucleus coupling to the molecules end-to-end rotation, making the spectral features of 2-fluoro-4-chlorotoluene (**1**) quite rich. With this combination, additional terms accounting for the two effects need to be included in the semi-rigid rotor Hamiltonian. This can be done in a global fit using the program *XIAM* [17], which is set-up in a combined axis system to treat the methyl internal rotation and uses a first order perturbation treatment to address the chlorine nuclear quadrupole hyperfine structure (nq-hfs).

From our previous study on 2-chloro-4-fluorotoluene (**2**), we know that treatment of the chlorine nq-hfs using the program *XIAM* is at the useful limit of the first-order perturbation method [16]. The conclusion was confirmed by a fit using the *RAM36hf* program set-up in the rho axis system [18]. However, the number of studies on molecules with one methyl internal rotor in the presence of one chlorine nucleus is too limited to draw a conclusive statement on the performance of *XIAM* and *RAM36hf* for this combination. In comparison to 2-chloro-4-fluorotoluene (**2**), the

methyl torsional barrier should be lower for of 2-fluoro-4-chlorotoluene (**1**) because the fluorine atom is smaller than the chlorine atom and therefore, steric hindrance of the methyl torsion should be smaller in the latter molecule, leading to a lower torsional barrier. Also, in the case of 2-fluoro-4-chlorotoluene, we checked the assignment of the chlorine nq-hfs with the program *SPFIT* [19] by fitting the A torsional symmetry species separately with an effective semi-rigid rotor Hamiltonian. Using this code, the nq-hfs is treated exactly by diagonalizing the Hamiltonian matrix rather than applying perturbation theory. Our study on 2-fluoro-4-chlorotoluene adds a further important contribution to understand the methyl torsion and chlorine quadrupole coupling in mixed halogenated toluenes.

	(1)	(2)	(3)	(4)	(5)
$V_3 / \text{cm}^{-1}$	229.7	462.5	469.2	3.2	17.2
$^{35}\text{Cl } \chi_{cc} / \text{MHz}$	33.59	31.97	31.56	32.95	
$^{37}\text{Cl } \chi_{cc} / \text{MHz}$	26.55	25.15	24.87	25.92	
	(6)	(7)	(8)	(9)	
$V_3 / \text{cm}^{-1}$	227.3	210.5	216.3	236.8	

**Figure 1:** Halogen substituted derivatives of toluene: (**1**) 2-fluoro-4-chlorotoluene(this work), (**2**) 2-chloro-4-fluorotoluene [16], (**3**) 2-chlorotoluene ([13]), (**4**) 3-chlorotoluene [14], (**5**) 3-fluorotoluene [3], (**6**) 2-fluorotoluene [2], (**7**) 2,3-difluorotoluene [5], (**8**) 2,3,4-trifluorotoluene [10], and (**9**) 2,6-dimethylfluorobenzene [11].

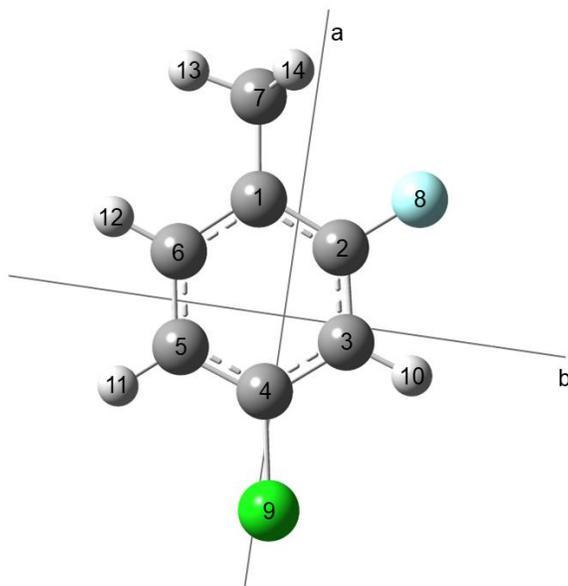
## 2. Quantum chemical calculations

To predict rotational constants guiding the spectral search and initial spectral assignment, in a first step, structure optimizations were conducted at the B3LYP-D3BJ/6-311++G(2d,2p) and MP2/6-311++G(2d,2p) levels of theory using the *Gaussian* 16 program package [20]. These two levels were chosen due to their reliability in many other toluene derivatives [3,5-10,13,14] including the isomer 2-chloro-4-fluorotoluene [16]. The optimized geometry of the only conformer of 2-fluoro-4-chlorotoluene is illustrated in Figure 2, with its nuclear coordinates in the inertial principal axis system given in Table S-1 of the Supplementary Material. The optimization was subsequently repeated at different levels of theory by applying several DFT methods such as B3LYP-D3(BJ) [21,22], M06-2X [23], wB97X-D [24], or Møller-Plesset (MP2) [25] and coupled cluster (CCSD) [26] *ab initio* methods to check the consistency of the calculations and to identify the method-basis set combination which yields predicted rotational constants matching the experimental values best. The calculated constants are listed in Table S-2 of the Supplementary Material. Ground state rotational constants and centrifugal distortion constants are obtained from anharmonic frequency calculations where molecular vibration is described beyond the harmonic approximation by treating the anharmonicity with vibrational perturbation theory and using rovibrational corrections calculated from the cubic force field.

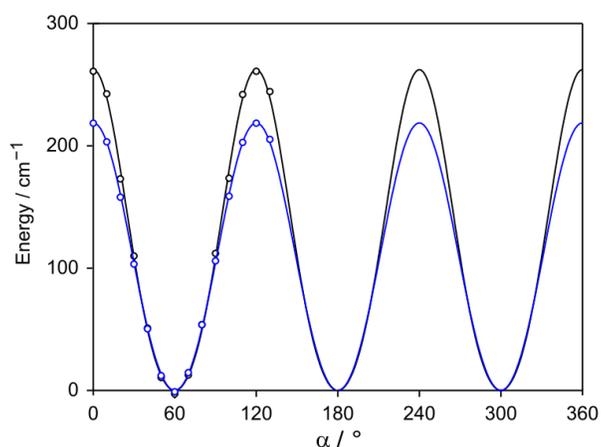
To predict the potential energy curve as function of the methyl internal rotation, we varied the dihedral angle  $\alpha = \angle(C_2, C_1, C_7, H_{13})$  in  $10^\circ$  steps and allowed for structure relaxations of all other geometry parameters. A three-fold potential was obtained as shown in Figure 3. The potential energy points were fitted successfully by a  $V_3$  term and a  $V_6$  term of  $262.4 \text{ cm}^{-1}$  and  $21.8 \text{ cm}^{-1}$ , respectively, for calculations at the MP2/6-311++G(2d,2p) level as well as  $218.8 \text{ cm}^{-1}$  and  $5.0 \text{ cm}^{-1}$  for the potential energy points obtained at the B3LYP/6-311++G(2d,2p) level.

To predict the chlorine nuclear quadrupole coupling constants, Bailey's method [27,28] was applied because it has yielded quite reliable results for 2-chloro-4-fluorotoluene [16]. The electric field gradient at the site of the chlorine nucleus was calculated at the B1LYP/TZV [29-32] (3df,2p) [33,34] level using the geometric parameters obtained at the MP2/6-311++G(2d,2p) level (given in Figure 2). We used the conversion factors  $eQ/h$  of  $-19.185 \text{ MHz/a.u.}$  and  $-15.120 \text{ MHz/a.u.}$  for the  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  nuclei, respectively, calculated directly from the respective values

of  $Q = -81.65(80)$  mb and  $-64.35(64)$  mb given by Pyykkö and Li [35]. The resulting nuclear quadrupole coupling constants (NQCCs) are compared with the experimental values in Table 1.



**Figure 2:** The molecular structure of 2-fluoro-4-chlorotoluene optimized at the MP2/6-311++G(2d,2p) level of theory, showing the projection onto the *ab*-plane of the principal axes system. Carbon atoms are grey; hydrogen atoms white; the fluorine atom is light blue and the chlorine atom green.



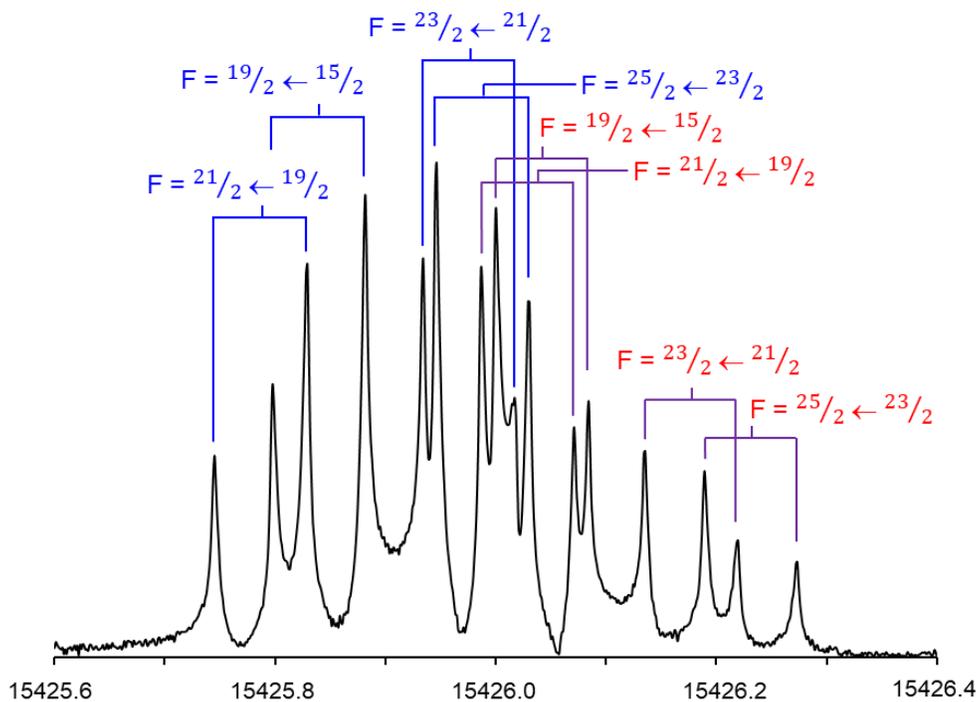
**Figure 3:** The potential energy curves of 2-fluoro-4-chlorotoluene calculated at MP2/6-311++G(2d,2p) level of theory (black curve) and the B3LYP/6-311++G(2d,2p) level

of theory, obtained by varying the dihedral angle  $\alpha = \angle(\text{C}_2, \text{C}_1, \text{C}_7, \text{H}_{13})$  in a grid of  $10^\circ$ . The predicted  $V_3$  terms are  $262.4 \text{ cm}^{-1}$  and  $218.8 \text{ cm}^{-1}$ , respectively.

### 3. Microwave spectroscopy

#### 3.1. Experimental details

A sample of 2-fluoro-4-chlorotoluene was purchased from Alfa-Aesar with no significant impurity. Rotational transitions were recorded between 4 and 25 GHz, although the complete spectral range was not surveyed, using a molecular jet FTMW spectrometer in the coaxially oriented beam-resonator arrangement (COBRA) at Hannover [36]. Figure 4 illustrates a typical spectrum. 2-fluoro-4-chlorotoluene, placed in a small reservoir at the nozzle orifice, was seeded in neon or helium as carrier gas at stagnation pressures of 1-2 bar, and the mixture was fed to the resonator chamber. Though the experimental accuracy is better than 2 kHz, the measured rotational frequencies of 2-fluoro-4-chlorotoluene are less accurate due to line broadening arising probably from unresolved proton spin-spin or spin-rotation coupling.



**Figure 4:** A typical spectral line with nq-hfs of the  $^{35}\text{Cl}$  isotopologue of 2-fluoro-4-chlorotoluene, showing the  $J''_{K'_a K'_c} - J'_{K'_a K'_c} = 11_{1,11} - 10_{1,10}$  rotational transition. The frequencies are in MHz. The

Doppler doublets are marked by brackets. The A (blue) and E (red) torsional symmetry species are color-coded; chlorine quadrupole hyperfine components  $F = J + I$  are given.

### 3.2. Spectral assignment and fits

The equilibrium rotational constants  $A_e = 3040.5$  MHz,  $B_e = 854.6$  MHz, and  $C_e = 669.8$  MHz predicted at the MP2/6-311++G(2d,2p) level were used to obtain estimated line frequencies of the  $^{35}\text{Cl}$  isotopologue of 2-fluoro-4-chlorotoluene. The predicted dipole moment components are  $\mu_a = 1.21$  D,  $\mu_b = 1.47$  D, and  $\mu_c = 0.00$  D, i.e. both  $a$ - and  $b$ -type transitions are expected in the experimental spectrum. A number of lines were observed near the estimated frequencies and a fit was performed by Pickett's *SPFIT* program [19], confirming the assignment of A species lines with a standard deviation of 2.7 kHz. The hyperfine pattern appears twice in the high resolution spectrum (e.g., see Figure 4), which is the A-E symmetry species pair arising from the methyl internal rotation, and also the E species could be assigned straightforwardly. The program *XIAM* [17] was later used for simultaneous least-squares fit of the nq-hfs with the A and E torsional fine structure. In total, 157 and 155 hyperfine components belonging to the A and E species, respectively, were included. Adjusting the three rotational constants, three quartic centrifugal distortion constants  $D_J$ ,  $D_{JK}$ ,  $D_K$ , the  $V_3$  potential term, the angle  $\angle(i,a)$  between the internal rotor axis and the  $a$ -principal axis, and the higher order parameter  $D_{p_i^2 J}$  yielded a root-mean-square (rms) deviation of 7.7 kHz. The fit is given in Table 1 along with the *SPFIT* A species fit. The frequency list along with the residuals obtained with *XIAM* is given in Table S-3 in the Supplementary Material. Fitting further high order parameters available in *XIAM* did not decrease this value significantly.

In the study on 2-chloro-4-fluorotoluene, a better standard deviation of 4.8 kHz has been achieved with *XIAM*, close to that of the *SPFIT* fit (4.0 kHz) and to the measurement accuracy. However, the  $V_3$  potential of  $462.5 \text{ cm}^{-1}$  found for 2-chloro-4-fluorotoluene is almost two times that of 2-fluoro-4-chlorotoluene. It is known that *XIAM* can encounter difficulties in fitting spectra with torsional splittings arising from low-barrier methyl torsion [37-40]. To evaluate the fitting performance of *XIAM* set-up using the combined axis method, we applied the *RAM36hf* code, working exclusively in the rho axis system [18]. *RAM36hf* can treat molecules with one methyl

rotor and one weakly coupled quadrupole nucleus employing first order perturbation theory, which is borderline in case of a chlorine nucleus. The advantage of *RAM36hf* over *XIAM* is its ability to add effective high-order Hamiltonian terms directly from the input file and the rms deviation can be decreased. Applying *RAM36hf* on the data set, we obtained essentially the same rms deviation as *XIAM* (7.5 kHz for the  $^{35}\text{Cl}$  data set). The complete set of fitted parameters using the *RAM36hf* code is presented in Table S-4 of the Supplementary Material. Therefore, we conclude that the quadrupole coupling of the chlorine nucleus treated by perturbation theory is dominating the rms deviation obtained with *XIAM* and *RAM36hf*, being twice the expected measurement accuracy.

For the  $^{37}\text{Cl}$  isotopologue, a total of 226 hyperfine components could be measured, and it was possible to determine some of the centrifugal distortion constants as well as the higher order parameter  $D_{p_i^2 J}$  by fitting the data set with *XIAM*. However, to decrease the correlation, we decided to keep those constants at their values of the  $^{35}\text{Cl}$  isotopologue and only adjust the  $V_3$  potential term and the angle  $\angle(i,a)$  together with the rotational constants and the NQCCs  $\chi_{aa}$  and  $\chi_{bb}-\chi_{cc}$ . The rms deviation of 6.9 kHz of the  $^{37}\text{Cl}$  fit, also given in Table 1, is essentially the same as that of the  $^{35}\text{Cl}$  fit. The frequency list is given in Table S-5 in the Supplementary Material.

**Table 2:** Molecular parameters of 2-fluoro-4-chlorotoluene in the principal axis system obtained from fits with the programs *SPFIT* and *XIAM*.

Par. <sup>a</sup>	Unit	<sup>35</sup> Cl <i>SPFIT</i> <sup>b</sup>	<sup>35</sup> Cl <i>XIAM</i>	<sup>35</sup> Cl <i>RAM36hf</i>	<sup>35</sup> Cl <sub>calc.</sub> <sup>c</sup>	<sup>37</sup> Cl <i>XIAM</i>	<sup>37</sup> Cl <sub>calc.</sub> <sup>d</sup>
$A_0$	MHz	3038.05565(58)	3036.2860(35)	3036.35(23)	3021.5 <sup>c</sup>	3035.0792(28)	3020.5 <sup>c</sup>
$B_0$	MHz	859.022295(29)	859.01991(16)	859.11(23)	851.1 <sup>c</sup>	836.23190 (15)	828.5 <sup>c</sup>
$C_0$	MHz	672.369544(17)	672.365965(86)	672.4555(45)	666.8 <sup>c</sup>	658.266546(40)	652.8 <sup>c</sup>
$D_J$	kHz	0.007291(50)	0.00691(26)	0.00809(22)	0.01184 <sup>c</sup>	0.006914 <sup>d</sup>	0.01140 <sup>c</sup>
$D_{JK}$	kHz	0.0761(47)	0.138(25)		0.06572 <sup>c</sup>	0.137824 <sup>d</sup>	0.06356 <sup>c</sup>
$D_K$	kHz	2.67(12)	2.21(58)		0.43161 <sup>c</sup>	2.209727 <sup>d</sup>	0.43297 <sup>c</sup>
$d_1$	kHz				-0.00310 <sup>c</sup>		-0.00293 <sup>c</sup>
$d_2$	kHz				-0.00059 <sup>c</sup>		-0.00055 <sup>c</sup>
$F_0$	GHz		161.8148 <sup>e</sup>	161.6637 <sup>g</sup>	161.8148 <sup>f</sup>	161.8148 <sup>e</sup>	161.8148 <sup>f</sup>
$V_3$	cm <sup>-1</sup>		229.712(35)	227.22(12)	218.8 <sup>h</sup>	229.731(57)	218.8 <sup>h</sup>
$D_{p_i^2 J}$	kHz		7.21(21)			7.207314 <sup>d</sup>	
$\angle(i,a)^i$	°		11.628(93)	11.59(13)	8.07 <sup>f</sup>	11.48(13)	7.93 <sup>f</sup>
$\angle(i,b)$	°		78.372(93)	78.41(13)	81.93 <sup>f</sup>	78.52(13)	82.07 <sup>f</sup>
$\chi_{aa}$	MHz	-68.900(11)	-69.144(66)	-69.443(72)	-69.93 <sup>j</sup>	-54.76(15)	-55.11 <sup>j</sup>
$\chi_{bb}$	MHz	35.4830(96)	35.550(53)	35.881(35)	36.20 <sup>j</sup>	28.207(99)	28.53 <sup>j</sup>
$\chi_{cc}$	MHz	33.417(18)	33.594(92)	33.552(37)	33.73 <sup>j</sup>	26.55(16)	26.58 <sup>j</sup>
rms <sup>k</sup>	kHz	3.6	7.0	7.5		6.9	
$N_A/N_E^l$		157/0	157/155	157/155		99/127	

<sup>a</sup> All parameters refer to the principal axis system. Watson's S reduction in the  $I'$  representation was used. The  $d_1$  and  $d_2$  quartic centrifugal distortion constants could not be determined and therefore were not fitted. Standard errors are in units of the last digit given.

<sup>b</sup> Including only the hyperfine components of the A symmetry species.

<sup>c</sup> Ground state rotational constants and centrifugal distortion constants obtained from anharmonic frequency calculations at the B3LYP-D3BJ/6-311++G(2d,2p) level of theory.

<sup>d</sup> Fixed at the value of the <sup>35</sup>Cl *XIAM* fit.

<sup>e</sup> Kept fixed at the calculated value.

<sup>f</sup> Calculated at the MP2/6-311++G(2d,2p) level.

<sup>g</sup> Derived from  $F$  which was kept fixed to 163.3569 GHz.

<sup>h</sup> Calculated at the B3LYP-D3BJ/6-311++G(2d,2p) level.

<sup>i</sup>  $\angle(i,c) = 90^\circ$  by symmetry.

<sup>j</sup> Predicted at the B1LYP/TZV(3df,2p)//MP2/6-311++G(2d,2p) level and corrected using the calibration factor  $-19.185$  MHz/a.u. (see text).  $\chi_{ab} = 18.99$  MHz,  $\chi_{ac} = \chi_{bc} = 0$  by symmetry.

<sup>k</sup> Root-mean-square deviation of the fit.

<sup>l</sup> Number of A and E torsional symmetry species lines including nuclear quadrupole coupling components.

## 4. Discussion

For both chlorine isotopologues, the program *XIAM* achieved an rms deviation of about 7 kHz for the global fits, two times the value obtained by fitting the A torsional symmetry species lines separately with the *SPFIT* code, and similar to the value yielded by the program *RAM36hf*. Since *SPFIT* treats the chlorine nuclear quadrupole coupling exactly by matrix diagonalization and a semi-rigid rotor Hamiltonian is sufficient to model the A torsional lines, the higher deviations of the *XIAM* and *RAM36hf* fits is attributed to the treatment using perturbation theory which, with respect to the measurement accuracy, is no longer suitable in the case of 2-fluoro-4-chlorotoluene.

The rotational constants could be determined with high accuracy for both, the  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  isotopologues of 2-fluoro-4-chlorotoluene. Comparing the experimental rotational constants deduced from the *XIAM* fit with those calculated at different levels of theory (see Section 2 and Tables S-2 of the Supplementary Material), we observed deviations of about 1%. Though the predicted rotational constants are sufficiently reliable to guide the assignment of the microwave spectrum, the results are generally worse than in the case of the isomer 2-chloro-4-fluorotoluene where many levels of theory perform well [16]. For 2-fluoro-4-chlorotoluene, MP2/6-31G(d,p) has again proven itself to serve as a cost-efficient level yielding  $B_e$  rotational constants calculated accidentally close to the experimental  $B_0$  constants due to error compensations, as it did for a number of aromatic ring containing molecules like coumarin [41], quinoline and isoquinoline [42], dimethylfluorobenzenes [11,12], phenetole [43], and 2-ethylfuran [44].

A comparison of the  $V_3$  potential term of  $229.7\text{ cm}^{-1}$  for 2-fluoro-4-chlorotoluene to those of 2-fluorotoluene (**6**), 2,3-difluorotoluene (**7**), 2,3,4-trifluorotoluene (**8**), and 2,6-dimethylfluorobenzene (**9**), shown in Figure 1, illustrates that just a single fluorine atom in the immediate neighborhood of the methyl group leaves the barrier hindering the methyl torsion largely invariant at a value around  $230\text{ cm}^{-1}$ . Further substitutions on the ring, either exhibiting a +I effect like the methyl group in (**9**) or exercising a -I effect like the fluorine or chlorine atom(s) in (**1**), (**7**), (**8**), do not affect the barrier height significantly. However, if the *ortho* fluorine atom is exchanged by a bulkier chlorine atom, as in the cases of 2-chloro-4-fluorotoluene (**2**) and 2-chlorotoluene (**3**), the barrier to internal rotation of the methyl group almost doubles due to steric effects (see Figure 1). If the steric hindrance is omitted, like in 3-chlorotoluene (**4**) or 3-

fluorotoluene (**5**), a very low torsional barrier is observed, and the methyl torsion is essentially an internal rotation free of frustration.

The B1LYP/TZV(3df,2p)//MP2/6-311++G(2d,2p) level predicted values for  $\chi_{aa}$ ,  $\chi_{bb}$ , and  $\chi_{cc}$  which match well the experimental values of 2-chloro-4-fluorotoluene [16]. Its performance for 2-fluoro-4-chlorotoluene is also very satisfactory for both isotopologues, as shown in Table 1. Therefore, we recommend this combination for calculations of chlorine NQCCs for halogen-substituted aromatic rings. Due to the planarity of all heavy atoms of 2-fluoro-4-chlorotoluene, the  $\chi_{cc}$  constant can be directly compared with that found for other molecules possessing all heavy atoms on a symmetry plane because the principal  $c$ -axis of inertia and a principal axis of the field gradient are collinear. As summarized in Figure 1, neither the position of the chlorine nucleus nor the presence of a fluorine substitution on the toluene ring significantly affects the value of  $\chi_{cc}$ , which remains around 32-33 MHz for the  $^{35}\text{Cl}$  and 25-26 MHz for the  $^{37}\text{Cl}$  isotopologues.

## 5. Conclusion

The molecular jet Fourier transform microwave spectrum of 2-fluoro-4-chlorotoluene shows rich spectral patterns containing hyperfine structure from the chlorine nucleus and fine splittings due to the methyl torsion. Modeling these splittings globally using the *XIAM* and the *RAM36hf* codes where the chlorine quadrupole coupling is treated employing perturbation theory results in accurately determined structural and internal rotation parameters, as well as nuclear quadrupole coupling constants, even though the rms deviation is twice the measurement accuracy. Fitting the hyperfine components of the A torsional symmetry species lines separately with the program *SPFIT* achieves measurement accuracy, pointing to the perturbation theory no longer being sufficient in treating the hyperfine splittings observed for 2-fluoro-4-chlorotoluene. By comparing the barrier to internal rotation of  $229.7\text{ cm}^{-1}$  of 2-fluoro-4-chlorotoluene to that of other fluorine and chlorine substituted toluene derivatives, we find the steric effect clearly dominating electrostatic effects and playing the decisive role in controlling the methyl torsion. Reasonably accurate predictions of the chlorine NQCCs can be obtained from calculations at the B1LYP/TZV(3df,2p)//MP2/6-311++G(2d,2p) level of theory.

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