

The Molecular Electric Dipole Moment for 1,2,4-Trifluorobenzene and a Comparison with Related Molecules

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The rotational Stark effect of 1,2,4-Trifluorobenzene has been studied for four low J rotational transitions in an oversized waveguide absorption cell with inner cross section of 1 by 5 cm. Improved vibronic ground state expectation values were obtained for the components of the molecular electric dipole moment as $|\mu_a| = 0.884(10)$ D and $|\mu_b| = 1.088(4)$ D. For the analysis numerical diagonalisation of the truncated effective Hamiltonian matrix was used rather than the standard second order perturbation treatment. The result is compared with experimental dipole moments of related molecules.

The molecular electric dipole moment components of 1,2,4-Trifluorobenzene have been reported first by Doraiswamy and Sharma [1]. When we started a rotational Zeeman-effect study of the compound we noticed discrepancies between the observed Stark effect multiplets and the patterns predicted from their values. So we decided to redetermine the dipole moment components with improved accuracy. To this end we used our standard Stark-effect modulated spectrometer [2, 3] (33 kHz square wave modulation) together with oversized wave guide cells with an inner cross section of 1 cm by 5 cm and central Stark electrode (thickness ca. 0.5 mm). Recording conditions were as follows: pressures around 5 mTorr; cell temperatures around -50°C . Linewidths of 150 to 200 kHz full width at half height were typical. The conversion factor of the Stark-cell (applied voltage $\rightarrow$ electric field strength) was calibrated using the second order Stark-effect of OCS as reference [4]. We studied the Stark-effect of the following vibronic ground state rotational transitions:

- $3_{03} \rightarrow 4_{04}$ (8255.601 MHz),
- $3_{03} \rightarrow 4_{14}$ (8980.573 MHz),
- $3_{21} \rightarrow 4_{22}$ (9159.521 MHz), and
- $4_{14} \rightarrow 5_{15}$ (9187.101 MHz).

To analyze the splittings we used the effective rotational Hamiltonian [4]

$$\tilde{\mathcal{H}} = h \cdot A \cdot \hat{J}_a^2 + h \cdot B \cdot \hat{J}_b^2 + h \cdot C \cdot \hat{J}_c^2 - \mu_a \cdot E_Z \cos(a, Z) - \mu_b \cdot E_Z \cos(b, Z). \quad (1)$$

$$\left. \begin{aligned} A &= 3083.994 \text{ MHz} \\ B &= 1278.362 \text{ MHz} \\ C &= 903.698 \text{ MHz} \end{aligned} \right\} \text{rotational constants,}$$

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$\hat{J}_a^2, \hat{J}_b^2, \hat{J}_c^2$ = squares of the rotational angular momentum operators in direction of the principal inertia axes measured in units of $\hbar^2$,

μ_a, μ_b = vibronic ground state expectation values for the molecular electric dipole moments (μ_c , the component perpendicular with respect to the plane of the molecule is zero by symmetry),

E_Z = applied electric field,

$\cos(a, Z), \cos(b, Z)$ = direction cosines between the space fixed Z -axis and the principal inertia axes a and b .

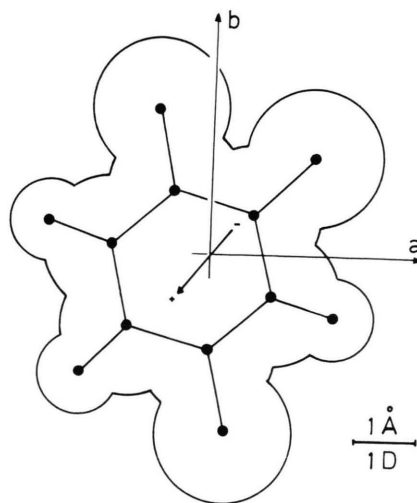


Fig. 1. To scale drawing of the structure of 1,2,4-Trifluorobenzene showing the orientation of the principal inertia axes system and the molecular electric dipole moment vector.

Table 1. Experimental and calculates Stark shifts observed under $\Delta M = 0$ selection rule. The calculated shifts are based on the rotational constants and on the least squares result obtained for the dipole moments: $\mu_a = 0.884(10)$ D and $\mu_b = 1.088(4)$ D. They were calculated by numerical diagonalization of the Hamiltonian matrix as described in the text. Given uncertainties are single standard deviations. They include a 0.25% calibration uncertainty.

Transition $v(0)/\text{MHz}$		Stark field [V/cm]	exp. Stark shift [$v_M(E) - v(0)$]/ MHz	calc. Stark shift [$v_M(E) - v(0)$]/ MHz
$3_{03} \rightarrow 4_{14}$ (8980.573)	3	189.3	0.998	1.021
	3	234.8	1.583	1.570
	3	273.5	2.114	2.131
	3	315.6	2.846	2.838
	2	315.6	1.569	1.559
$3_{03} \rightarrow 4_{04}$ (8255.601)	3	189.8	0.750	0.729
	2	315.6	0.784	0.778
	2	368.2	1.071	1.066

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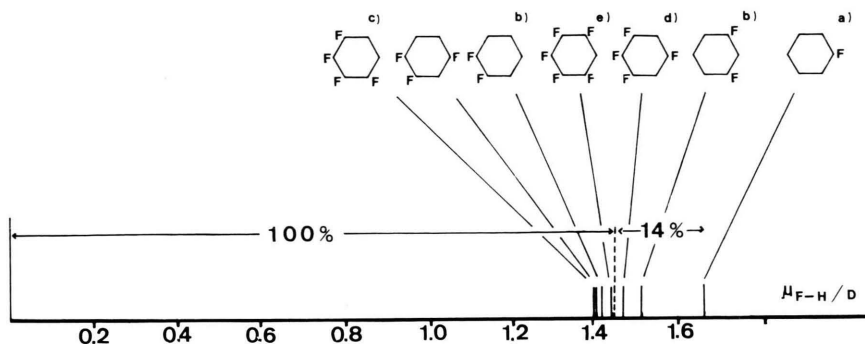


Fig. 2. Within the most simple additivity scheme of bond moments, one should be able to derive the dipole moments of all Fluorine substituted Benzenes from a single dipole moment corresponding to a Fluorine atom and a Hydrogen atom substituted in para position. Reversing the process, this "standard dipole" should be derivable from any one of the experimentally determined dipole moments. The corresponding values derived from the individual Fluorobenzenes are plotted here. They are indeed closely grouped around a value of 1.46 D with the only exception of Monofluorobenzene.

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Since $\hat{J}_Z$ commutes with the effective Hamiltonian, the matrix corresponding to (1) is diagonal in the quantum number M ($M \cdot \hbar = Z$ component of the angular momentum). The matrix was set up in the limiting prolate symmetric top basis (a -axis as internal quantization axis).

To calculate the Stark-effect shifts of the different M sublevels of a given rotational state the corresponding infinite matrix was truncated to include only all neighbouring J -states ($J' = J - 1, J, J + 1$) and was diagonalized numerically. In heavy molecules with closely spaced rotational levels this method is numerically superior to the standard second order perturbation treatment.

In Table 1 we present our results and a comparison between calculated and observed splittings for some M -satellites of the $3_{03} \rightarrow 4_{04}$ and $3_{03} \rightarrow 4_{14}$ rotational transitions.

In Fig. 1 we show the orientation of the electric dipole moment within the molecule and in Fig. 2 we present a perhaps unusual comparison of the electric dipole moments of all fluorobenzenes measured so far. The idea

behind Fig. 2 is that within a simple model of bond-moments all dipole moments should be obtainable by vector addition from a "standard dipole moment" corresponding to a Hydrogen-Fluorine pair in para position. What is plotted on the ordinate is the value of this hypothetical "standard dipole" as it would be calculated from the experimental values of the different individual fluorobenzenes. The figure shows that, with the only exception of fluorobenzene itself, the dipole moments of the polyfluorobenzenes can indeed be predicted to better than 4% within such a simple additivity scheme. Therefore we assume that with the appropriate modification Fig. 2 can also be used to predict the dipole moments of yet unmeasured other halobenzenes and benzonitriles.

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