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 \( \mu_a = 0.884 \pm 0.010 \) D and \( \mu_b = 1.088 \pm 0.004 \) 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:

\[
\begin{align*}
\Delta \nu_3 & \rightarrow 4\nu_2 \ (8255.601 \text{ MHz}), \\
\Delta \nu_3 & \rightarrow 4\nu_4 \ (8380.573 \text{ MHz}), \\
\Delta \nu_3 & \rightarrow 4\nu_1 \ (9159.521 \text{ MHz}), \\
\Delta \nu_4 & \rightarrow 5\nu_1 \ (9187.101 \text{ MHz}),
\end{align*}
\]

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

\[
\hat{H} = h \cdot A \cdot J_a^2 + h \cdot B \cdot J_b^2 + h \cdot C \cdot J_z^2 - \mu_a \cdot E_z \cos (a, Z) - \mu_b \cdot E_z \cos (b, Z).
\]

\( A = 3083.994 \text{ MHz} \)

\( B = 1278.362 \text{ MHz} \)

\( C = 903.698 \text{ MHz} \)

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

Table I. Experimental and calculated 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: \( \mu_a = 0.884 \pm 0.010 \) D and \( \mu_b = 1.088 \pm 0.004 \) 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.

<table>
<thead>
<tr>
<th>Transition ( \nu(0)/\text{MHz} )</th>
<th>Stark field ( v_{\text{EF}} - v(0) )/MHz</th>
<th>( \text{calc. Stark shift} ) ( v_{\text{EF}} - v(0) )/MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta \nu_3 \rightarrow 4\nu_1 ) ( (8980.573) )</td>
<td>( 234.8 )</td>
<td>1.583</td>
</tr>
<tr>
<td></td>
<td>( 273.5 )</td>
<td>2.114</td>
</tr>
<tr>
<td></td>
<td>( 315.6 )</td>
<td>2.846</td>
</tr>
<tr>
<td></td>
<td>( 315.6 )</td>
<td>1.569</td>
</tr>
<tr>
<td>( \Delta \nu_3 \rightarrow 4\nu_4 ) ( (8255.601) )</td>
<td>( 189.8 )</td>
<td>0.750</td>
</tr>
<tr>
<td></td>
<td>( 315.6 )</td>
<td>0.784</td>
</tr>
<tr>
<td></td>
<td>( 368.2 )</td>
<td>1.071</td>
</tr>
</tbody>
</table>

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Since $J_z$ commutes with the effective Hamiltonian, the matrix corresponding to (1) is diagonal in the quantum number $M (M \cdot \hbar = Z \text{ component of the angular momentum})$. The matrix was set up in the limiting prolate symmetric top basis ($\alpha$-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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