Determination of a High Potential Barrier Hindering Internal Rotation from the Ground State Spectrum

The Methylbarrier of Ethylchloride

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We present an analysis of the rotational spectrum of ethylchloride-\(^{35}\)Cl in the ground state. The \(^{35}\)Cl-hfs analysis was extended and the barrier to internal rotation determined from narrow splittings of high \(J\)-transitions.

Introduction

With the higher resolution of microwave Fourier transform (MWFT) spectroscopy it is possible to resolve fine structures, which could not be measured before [1–3].

We noticed that the barrier to internal rotation \(V_3\) of ethylchloride, \(\text{CH}_3\text{CH}_2\text{Cl}\), was determined [4, 5] from two splittings in the first torsional excited state. As there is in some molecules an interaction of the internal rotation and other vibrations [6] we thought it interesting to determine the barrier from ground state measurements.

Experimental

The sample was purchased from FLUKA with a 98% purity. The spectra were recorded by a conventional Stark spectrometer [7, 8] in the region of 8–40 GHz with temperatures from -30 to -45 °C and pressures between 4 and 15 mTorr and for high resolution with a MWFT-Spectrometer from 8 to 18 GHz [1] with temperatures from -60 to -75 °C and pressures between 0.3 and 1.5 mTorr. The measuring errors are 50 kHz and 10 kHz respectively.

Measurements and Analysis

As the barrier \(V_3\) is rather high, splittings could only be observed for high \(J\) lines within the range of our MWFT spectrometer. For correct assignment a centrifugal distortion and extended chlorine hfs analysis was necessary.

In Table 1 we give the lines measured by us and by other authors [5]. They are marked by *. With FT we indicate MWFT measurements. In Fig. 1 we give a multiplet pattern.

Reprint requests to Prof. Dr. H. Dreizler, Institut für Physikalische Chemie der Christian-Albrechts-Universität Kiel, Olshausenstr. 40, D-2300 Kiel.
Table 1. Measured lines \( (v_{\text{exp}}) \) of ethylchloride-\(^{35}\)Cl [MHz], \( v_{\text{ave}} \): averaged by hfs-shifts, \( \Delta v_{\text{exp}} \): calculated hfs-shifts. FT: measured by MWFT-spectroscopy, *: measured by other authors [5].

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<th>( J - K - ) ( J' - K' )</th>
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<th>( 2F' )</th>
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| \( J \& K^- \) | \( J'_\& K'^- \) | \(
\begin{array}{r}
2F & 2F' & \text{Oexp} & -pave & \Delta V_{\text{exp}} & \mu & \text{pcalc} & j & K^- & K^+ & J'_\& K'^-\\
18 & 5 & 14 & 19 & 4 & 15 & 32 & 35 & 34567.094 & 34567.569 & -0.475 & -0.475 & 2F & 2F' & \text{Oexp} & -pave & \Delta V_{\text{exp}} & \mu & \text{pcalc} & j & K^- & K^+ & J'_\& K'^- \\
39 & 61 & 35 & 37 & 34568.044 & 0.475 & 0.480 & 2F & 2F' & \text{Oexp} & -pave & \Delta V_{\text{exp}} & \mu & \text{pcalc} & j & K^- & K^+ & J'_\& K'^-
\end{array}
|
The centrifugal distortion and hfs analysis were made independently. For the centrifugal distortion analysis unsplit lines \( v_{ave} \) corrected for hfs were used. For the hfs analysis it was assumed that the components of one transition are equally shifted by centrifugal distortion. In Table 2 we give the rotational and centrifugal distortion constants according to the fourth order Hamiltonian of Watson's S-reduction [9]. The standard deviation of the fit is 142 kHz, the highest correlation is \( |(D_j, D_{JK})| = 0.999 \).

Table 3. Chlorine hfs coupling constants [MHz] of \( \text{CH}_3\text{CH}_2^{35}\text{Cl} \) calculated with different selections of lines (column 1 \( J \) to 23 and column 2 \( J \) to 3) and first order approximation. Column 3 gives values from lines up to \( J = 3 \) calculated with diagonalisation [10]. Standard errors are given.

We also tried sixth order centrifugal distortion analysis, which improves the fit. But the constants are poorly determined, and many correlation coefficients are high.

The hfs analysis was based on lines with \( J \) up to 23. We omitted lines split by internal rotation. In Table 3 we give the quadrupole coupling constants \( \chi_{gg} \), \( g = a, b, c \), calculated with first order theory. A mean shift of 3.14 MHz was fitted with a standard deviation of 0.027 MHz. To check the influence of centrifugal distortion we give also the \( \chi_{gg} \) determined from lines with \( J \) up to 3. The approximation

Table 4. Internal Rotation splittings [kHz] of \( \text{CH}_3\text{CH}_2^{35}\text{Cl} \) averaged over hfs components.

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Table 5. Internal rotation parameters of \( \text{CH}_3\text{CH}_2^{35}\text{Cl} \). Standard errors in brackets. Assumptions in square brackets.

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of first order was controlled by a program [10] using 
diagonalisation of Hamiltonian matrices for lines up 
to $J = 3$. The values are given also in Table 3. The measured splittings are not sensitive to $\chi_{ab}$.

A comparison of the values of Table 3 shows 
agreement within the error limits. So the first order 
analysis is sufficient up to higher $J$ values.

The torsional analysis was based on the mean 
values of the splittings of the hfs components as 
given in Table 4. Thus we neglected interaction. We 
used a program by Woods [11–14] based on the 
internal axis method.

We tried to fit $w_j(s)$, with $s$ the reduced barrier, 
$I_2$ the moment of inertia of the methyl group and 
$\xi(a, i)$ the angle between the $a$ axis and the internal 
rotation axis. The fit converged, but the correlation 
is high. In a next step we assumed the angle $\xi(a, i)$ 
from the structure [5], taking the $\mathrm{C-CH}_2\mathrm{F}$ bond col-

linear to the internal rotation axis. A rather high 
value for $I_2$ resulted (Tab. 5, column 1). For com-
parison with literature we finally present in Table 5 
two fits with $I_2$ fixed to 3.1613 $\text{amuA}^2$ [5] and 
3.155 $\text{amuA}^2$ and $\xi(a, i) = \theta_m = 42.97^\circ$ [5]. The value 
$I_2 = 3.155$ $\text{amuA}^2$ was determined by a torsion 
analysis of ethylfluoride [15]. In Table 5 column 4 we 
repeat the values of [5] for convenience. We 
favour the values of column 3, as a comparison with 
$\mathrm{CH}_3\mathrm{CH}_2\mathrm{F}$ is possible. The last column of Table 4 is 
calculated with the first set of Table 5. The numbers 
vary slightly with the other sets.

It may be noticed that the $s$ and $V_3$ values are 
lower than in [5]. To our knowledge the barrier is 
the highest determined from an analysis of splittings 
of torsion ground state transitions. The errors 
indicate that we are near the limit of the MWFT-
technique.

Acknowledgements

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were made at the Kiel University computer center.

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