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Measurements on the Microwave spectra of meta-fluoro-chloro-benzene

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Sommaire.

On a mesuré le spectre en microondes de la molécule 1-3 C₆H₄ClF avec un spectromètre à modulation Stark d'absorption en gaz. On a utilisé divers klystrons, en couvrant la région dès 11,5 GHz. jusqu'au 26,3 GHz. En comparant le spectre mesuré et le spectre calculé d'après un modèle de la molécule, on donne les premières interprétations et on discute ses fondements.

It has been measured the microwave absorption spectra of the molecule 1-3 C₆H₄ClF on the way to continue a systematic study of the substituted benzene ring [1, 2, 3, 4]. The measurements have been made in a conventional 100 KHz Stark effect modulated gas absorption spectrometer with square wave modulation, described in [2]. Several klystrons have been used and the spectra was measured from 11,5 GHz up to 26,3 GHz.

A commercial sample was used, measuring at room temperature. The absorption lines frequencies were measured with markers produced by a frequency standard, driven by a 10 MHz quartz crystal oscillator, which was kept in a thermostatic oven. The frequency standard was calibrated with very well measured lines. In order to determine in unambiguous form the harmonic of the fundamental standard frequency, that fits a line, the arrangement described in [5] for coarse measurements was used. But for stability reasons some improvements have been made. A variable frequency oscillator inserted in the frequency standard was substituted by a signal generator, which feeds with 150 MHz an amplifying-tripler stage of 450 MHz that finally drives a 1N26 crystal multiplier. Tuning slightly both signal generator and tripler stage it is possible to have in general two settings of markers over the line or if one is lacking, a coarse measurement with a wavemeter is possible without any loss of accuracy in the deter-

* This work is being performed at the Institute of physics of the university of Stockholm in use of a fellowship of the university of Buenos Aires.

mination of the harmonic. With this molecule it is possible to repeat frequency measurements of medium and strong lines within the range of $\pm 0,2$ MHz, due to the rather large half-width of the lines, that reaches in this case several MHz.

INTERPRETATION AND DISCUSSION

The observed spectra is rather complicated (almost 300 lines measured) due to:

- 1) the molecule is heavy, then high rotational J value lines and transitions in low vibrational states are observable,
- 2) the quadrupole electric moment of the chlorine nucleus causes an hyperfine splitting,
- 3) the presence of two isotopes: Cl^{35} and Cl^{37} , increases the number of observable lines.

Yet it has not been possible to resolve Stark patterns, of low J value lines, then another kind of analysis was chosen. With the internuclear lengths and bond angles given in [2, 3], a planar model of the molecule was built. Following Bragg and Golden's theory [6], a careful study, on the model, of the relative quadrupole splitting was made, which is defined by

$$\frac{E_Q}{eqQ} = f(J, \kappa) \cdot Y(I, J, F)$$

where E_Q is the quadrupole perturbation energy and eqQ is the quadrupole coupling constant. It was assumed that the field around the Cl-nucleus has rotational symmetry around the C-Cl bond. J is the rotational quantum number, κ the asymmetry parameter and $Y(I, J, F)$ the Casimir's function. Using the Cl^{35} isotope, it showed that it is possible "to pick up" two series of μ_b type, R -branch rotational lines with high relative intensities [7], somehow equidistants and of low relative quadrupole splitting. These two series are characterized by J, K_{-1} and K_{+1} numbers connected in a form that

$$J_{0,J} \rightarrow J + 1_{1, J+1}$$

$$J_{1,J} \rightarrow J + 1_{0, J+1}.$$

They were found and a first interpretation is given in Table I.

TABLE I.
1—3 C₆H₄Cl³⁵F.

| Observed lines MHz | Interpretation | Observed lines MHz | Interpretation |
|-----------------------|----------------|-----------------------|----------------|
| 12.106,9 | 50.5 — 61.6 | | |
| 13.621.0 | 60.6 — 71.7 | 12.662.6 | 61.6 — 70.7 |
| 15.173.5 | 70.7 — 81.8 | 14.596.7 | 71.7 — 80.8 |
| 16.826.8 | 80.8 — 91.9 | 16.465.9 | 81.8 — 90.9 |
| 18.502.4 | 90.9 — 101.10 | 18.289.8 | 91.9 — 100.10 |
| 20.210.9 | 100.10—111.11 | 20.084.6 | 101.10—110.11 |
| 21.939.0 | 110.11—121.12 | 21.867.5 | 111.11—120.12 |
| 23.675.2 | 120.12—131.13 | 23.627.5 | 121.12—130.13 |
| 25.410.4 | 130.13—141.14 | 25.389.5 | 131.13—140.14 |

The observed low J -value lines from Table I were found to be unresolvable from the point of view of the quadrupole splitting, like it was predicted by the theory. The calculations were carried out using electronic computing machine methods for rigid asymmetric rotor levels and the assignments were made assuming planarity of the molecule. But it must be noticed that they should be considered as an attempt and not definitive.

The comparison between observed and calculated Stark effect components gives evidence of the correctness of the assignments; the calculations were carried following Golden and Wilson's theory for Stark effect of a rigid asymmetric rotor [8], assuming that the dipole electric moment component on the b -axis is much greater than on the a -axis, using the well known convention for principal inertia moments that $I_a < I_b < I_c$. With the energy levels calculated from the supposed molecular model for the four first transitions in both series, it is possible to explain satisfactorily the inversion of the Stark effect on the lines 80.8 — 91.9 and 91.9 — 100.10, like is showed in table II.

The measurements shall be continued down to 8.5 GHz in the X-band to try to find lower J value transitions of both series. Calculations are carried on the way to give accurate values of the rotational constants and the "inertia defect".

I wish to express my thanks to Laborator Gunnar Erlandsson of the university of Stockholm for valuable advice and help in performing this work.

TABLE II.

| Transition | Observed Stark ef. | Calculated Stark ef. |
|-------------|--------------------|----------------------|
| 50.5— 61.6 | Regular | Regular |
| 60.6— 71.7 | Regular | Regular |
| 70.7— 81.8 | Regular | Regular |
| 80.8— 91.9 | Inverted | Inverted |
| 61.6— 70.7 | Inverted | Inverted |
| 71.7— 80.8 | Inverted | Inverted |
| 81.8— 90.9 | Inverted | Inverted |
| 91.9—100.10 | Regular | Regular |

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