Microwave Spectrum, Nuclear Quadrupole Coupling Constants, Dipole Moment, and Structure of Chlorine Pentafluoride, ClF_5*

H. K. Bodenseh, W. Hüttner, and P. Nowicki

Abteilung Chemische Physik der Universität Ulm

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Several rotational transitions in the ground vibrational state of $^{35}ClF_5$ and $^{37}ClF_5$ have been measured. From the frequency data the following constants have been derived: $B_0(^{35}ClF_5) = 3550.272(4)$ MHz; $B_0(^{37}ClF_5) = 3545.885(4)$ MHz; $D_J = 0.76(9)$ kHz; $D_{JK} = -0.67(15)$ kHz; $e\,Q\,q(^{35}ClF_5) = 43.93(8)$ MHz; $e\,Q\,q(^{37}ClF_5) = 34.63(6)$ MHz; $\mu = 0.536(10)$ D.

The bond angle $F_{ax}-Cl-F_{eq}$ is estimated at $86.5(1.0)°$.

I. Introduction

The Halogen Pentafluorides show an increasing reactivity going from JF_5 to ClF_5, and the knowledge of as many molecular properties as possible of the binary halogen fluorides seems desirable[1]. The microwave spectra of JF_5 and BrF_5 have been measured by Bradley, Brier and Whittle[2,3], and the rotational spectrum of ClF_5 in the mm region was reported by Jurek et al.[4]. The latter publication appeared while our own measurements of some rotational transitions of ClF_5 in the microwave region were in progress. Since we do not agree with their quadrupole coupling constants we considered it worthwhile also to report our results in some detail.

II. Experimental

The sample was found by IR spectroscopy to be better than 98% pure. It decomposed quickly due to reaction with the cell materials, even when the absorption cell was cooled down to −65 °C. Among the reaction products ClO_2 could be identified by its absorption lines which interfered sometimes strongly with the investigated spectrum. The ClO_2 formed made it somewhat hazardous to handle the reaction products which were pumped out of the cell and trapped by liquid nitrogen. Hydrolysis at low pressure was found to be a suitable method to dispose of these compounds. Due to the rapid decay of the gas, there was no chance to find the unknown rotational transitions by conventional recording techniques. Since the absorption lines were rather weak they could also not be observed on the oscilloscope. Therefore, the output of the Stark spectrometer which was equipped with BWO sweepers as radiation sources was fed into a LAB-8/e system from Digital Equipment Corporation for time averaging.

On-line computer and spectrometer were controlled by a common time base. The sweep range was varied from 300 MHz for searching to 2 MHz for measuring the frequencies. The narrow frequency ranges could be swept by phase locking the sweeper to a secondary frequency standard, and wobbling the reference frequency of the phase-locking unit. The secondary frequency standard was monitored against the well defined frequency of the radio station Droitwich.

Once the approximate position of the absorption lines was known, they also could be recorded using high time constant and low sweep rate.

To measure the transition $J = 0 \rightarrow 1$ at 7.1 GHz, a solid state sweeper (Wiltron, mod. 610 B, plug in 6247, frequency range 10 MHz to 18 GHz) was used which contained a YIG oscillator ranging from 4 to 8 GHz. The "fast" modulation coil of this unit which was not used in the sweeper was driven by a power amplifier for wobbling or phase locking. There was no difference in performance compared to a BWO unit.

The complete transition $J = 4 \rightarrow 5$ of $^{35}ClF_5$ at medium resolution, and averaged over 1000 sweeps is shown in Figure 1. The first of the two frequency markers was used to trigger the computer. The frequency range within the insert is shown once more in Fig. 2 on an expanded scale for precise frequency measurement under higher resolution. The pressure was lower and the BWO was phase locked during these 1000 sweeps. The markers are 0.5 MHz apart. To measure the dipole moment the Stark electrode was biased with a high-precision dc-power supply whose output in turn was checked by means of a digital voltmeter.

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Reprint requests to Dr. H. K. Bodenseh, Abteilung Chemische Physik, Universität Ulm, Mähringer Weg 165, *D-7900 Ulm.*

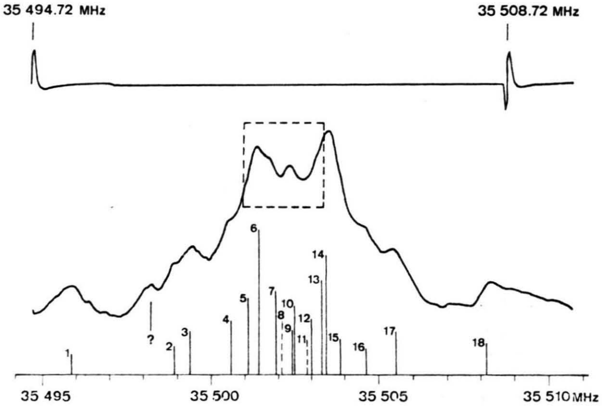

Fig. 1. Transition $J = 4 \rightarrow 5$ of $^{35}ClF_5$, and calculated positions of the hyperfine components. Numbers refer to Table 1. Lines 8 and 11 are not modulated. Insert is shown on Figure 2.

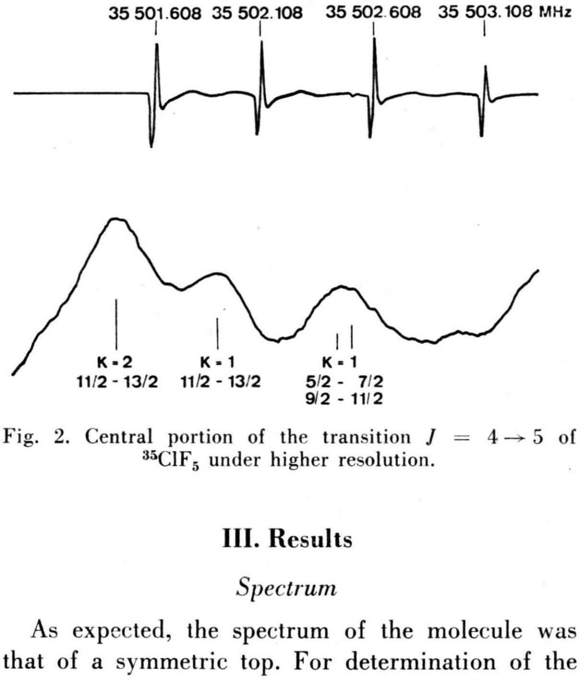

Fig. 2. Central portion of the transition $J = 4 \rightarrow 5$ of $^{35}ClF_5$ under higher resolution.

III. Results

Spectrum

As expected, the spectrum of the molecule was that of a symmetric top. For determination of the spectroscopic constants the transitions $J = 0 \rightarrow 1$, $J = 1 \rightarrow 2$, and $J = 4 \rightarrow 5$ for the $^{35}ClF_5$ species were accurately measured.

The frequencies were fitted to the expression

$$
\begin{aligned}
f_{K,J\rightarrow J+1,F\rightarrow F'} &= 2\,B_0(J+1) - 4\,D_J(J+1)^3 \\
&\quad - 2\,D_{JK}(J+1)\,K^2 + (1/h)\,(\langle H_{eQq}\rangle_{J+1,K,F'} \\
&\quad - \langle H_{eQq}\rangle_{J,K,F}) \qquad (1)
\end{aligned}
$$

where the parameters have their usual meaning, and $\langle H_{eQq}\rangle_{JKF}$ is the first-order quadrupole energy of the level $\langle J, K, F|$. The observed and calculated frequencies for the two isotopic species are given in Tables 1 and 2. Table 3 shows the derived spectroscopic constants compared to those obtained by Jurek et al [4].

The theoretical $\Delta F = +1$ quadrupole-hyperfine pattern of the $J = 4 \rightarrow 5$ rotational transition obtained with our parameters, and relative intensities including spin statistics of fourfold symmetry is shown below the experimental spectrum in Figure 1. The lines Nr. 8 and 11 ($K = 0$) are not modulated. The line at 35 498.22 MHz marked with an interrogation sign is due to an unknown impurity.

Nuclear Quadrupole Coupling Constant

Special care was taken for the numerical evaluation of the quadrupole-coupling constant. All measured lines were subject to a least-squares fit under the following conditions:

1) Only one coupling constant for both isotopes was introduced using the known ratio of the nuclear quadrupole moments of the two chlorine nuclei $Q_{35}/Q_{37} = 1.2688$.

2) Using these low-J transitions, it could not be expected to find an isotope effect in the centrifugal distortion constants beyond the limits of error. Therefore, for both molecules $^{35}ClF_5$ and $^{37}ClF_5$ only one set of parameters D_J and D_{JK} was fitted.

3) The lines were weighed according to their experimental accuracy.

The resulting parameters can be found in Table 3. Tables 1 and 2 show that the theoretical spectrum is in good agreement with the measurements.

There exists a close analogy in the nuclear quadrupole coupling constants in the two series of compounds XF and XF_5 where X = Cl, Br and I. Table 4 shows the coupling constants of these compounds and their ratio in each corresponding pair, where the latter is identical with the ratio of the field gradients in the directions of the respective figure axes. It is seen that all values are approximately equal ($-3.5 \pm 11\%$). Unfortunately, reliable values for the nuclear quadrupole moments are not available for Cl, Br and I so that absolute field-gradient values cannot be discussed.

Dipole Moment

The rather weak absorption spectrum as well as the high Stark voltage necessary for the detection of $K = 0$ transitions gave some hint that a dipole mo-

Table 1. Observed and calculated frequencies of $^{35}ClF_5$. Estimated errors of measured frequencies are given in parentheses in units of the last digit.

J	K	$F \rightarrow F'$	f_{obs} (MHz)	f_{calc} (MHz)	Δf (MHz)	Nr. in Fig. 1
0 → 1	0	3/2 → 5/2	7 098.38 (10)	7 098.35	+0.03	
	0	3/2 → 3/2	7 109.28 (5)	7 109.33	−0.05	
1 → 2	1	1/2 → 1/2	14 190.01 (10)	14 190.08	+0.07	
	1	5/2 → 7/2	14 198.39 (3)	14 198.40	+0.01	
	0	5/2 → 7/2	14 200.09 (3)	14 200.12	−0.03	
	1	3/2 → 5/2	14 209.44 (3)	14 209.38	+0.06	
4 → 5	4	5/2 → 7/2	35 495.85 (3)	35 495.86	+0.01	1
	3	5/2 → 7/2	35 498.94 (3)	35 498.93	+0.01	2
	4	11/2 → 13/2	35 499.41 (5)	35 499.39	+0.02	3
	3	11/2 → 13/2	35 500.60 (2)	35 500.58	+0.02	4
	2	5/2 → 7/2	35 501.16 (10)	35 501.11	+0.05	5
	2	11/2 → 13/2	35 501.43 (5)	35 501.43	0.00	6
	1	11/2 → 13/2	35 501.93 (6)	35 501.94	−0.01	7
	0	9/2 → 11/2	not modulated	35 502.11	—	8
	0	11/2 → 13/2				
	1	5/2 → 7/2		35 502.43		9
	1	9/2 → 11/2	35 502.47 (10)	35 502.49	−0.02	10
	0	5/2 → 7/2	not modulated	35 502.87	—	11
	0	7/2 → 9/2				
	1	7/2 → 9/2		35 502.98		12
	2	7/2 → 9/2		35 503.31		13
	2	9/2 → 11/2	35 503.63 (10)	35 503.63	0.00	14
	3	7/2 → 9/2		35 503.87		15
	4	7/2 → 9/2	35 504.64 (10)	35 504.65	−0.01	16
	3	9/2 → 11/2	35 505.52 (5)	35 505.53	−0.01	17
	4	9/2 → 11/2	35 508.16 (5)	35 508.18	−0.02	18

Table 2. Observed and calculated frequencies of $^{37}ClF_5$. Estimated errors of measured frequencies are given in parentheses in units of the last digit.

J	K	$F \rightarrow F'$	f_{obs} (MHz)	f_{calc} (MHz)	Δf (MHz)
1 → 2	1	5/2 → 7/2	14 181.46 (5)	14 181.42	+0.04
	0	5/2 → 7/2	14 182.81 (3)	14 182.78	+0.03
	1	3/2 → 5/2	14 190.01 (10)	14 190.07	−0.06
4 → 5	4	5/2 → 7/2	35 453.37 (8)	35 453.39	−0.02
	3	5/2 → 7/2	35 455.82 (7)	35 455.79	+0.03
	4	11/2 → 13/2	35 456.20 (7)	35 456.17	+0.03
	3	11/2 → 13/2	35 457.18 (10)	35 457.10	+0.08
	2	11/2 → 13/2	35 457.77 (4)	35 457.76	+0.01
	1	11/2 → 13/2	35 458.09 (15)	35 458.16	−0.07
	1	9/2 → 11/2	35 458.58 (3)	35 458.59	−0.01
	2	9/2 → 11/2	35 459.47 (10)	35 459.49	−0.02
	4	7/2 → 9/2	35 460.30 (10)	35 460.31	−0.01
	3	9/2 → 11/2	35 461.00 (8)	35 461.00	0.00
	4	9/2 → 11/2	35 463.08 (25	35 463.10	−0.02

Table 3. Spectroscopic constants of ClF_5. Errors are given in units of the last digit.

Molecule	B_0 (MHz)		D_J (kHz)		D_{JK} (kHz)		$e\,Q\,q$ (MHz)		μ (D)
	a	b	a	b	a	b	a	b	a
$^{35}ClF_5$	3 550.272 (4)	3 550.275 (2)	0.76 (9)	0.766 (2)	−0.67 (15)	−0.365 (4)	43.93 (8)	35.5 (20)	0.536 (10)
$^{37}ClF_5$	3 545.885 (4)	3 545.887 (4)		0.758 (10)		−0.360 (20)	34.63 (6)	30 (4)	

a) This work; quoted errors are standard deviations. b) Jurek et al.; Ref. [4].

Table 4. Comparison of nuclear quadrupole coupling constants in the bonding systems XF and XF_5.

Molecule	$e\,Q\,q$ (MHz)	Ref.	$q\,(XF)/q\,(X_5)$
IF	−3 438.15	a	−3.25
IF_5	1 056.6	b	
^{79}BrF	1 089.0	c	−3.88
$^{79}BrF_5$	−280.9	d	
^{35}ClF	145.871	e	−3.32
$^{35}ClF_5$	43.93	f	

a) E. Tieman, J. Hoeft, and T. Törring, Z. Naturforsch. **28 a**, 1405 [1973].
b) Ref. [2].
c) D. F. Smith, M. Tidwell, and D. V. P. Williams, Phys. Rev. 77, 420 L [1950].
d) Ref. [1].
e) R. E. Davis and J. S. Muenter, J. Chem. Phys. **57,** 2836 [1972].
f) This work.

ment of less than one Debye should be anticipated. Field strength against voltage was calibrated with the Stark effect of OCS, and a precise molecular-beam value of the dipole moment of this molecule $\mu = 0.71521$ D [5]. The $J = 0 \rightarrow 1$ transition was considered convenient for detection and analysis of the Stark spectrum since its three hyperfine components are well enough seperated to avoid interference of their Stark components at moderately low field-strength values. However, overlap of the spectra of the two isotopic species takes place. Since the equally strong transitions $\Delta F = +1$ of $^{37}ClF_5$, and $\Delta F = -1$ of $^{35}ClF_5$ fall almost together only the $F = 3/2 \rightarrow 5/2$ and $F = 3/2 \rightarrow 3/2$ transitions of $^{35}ClF_5$ were considered for the determination of the dipole moment. Also the $^{37}ClF_5$, $3/2 \rightarrow 3/2$ hyperfine line is predicted to coincide with the $3/2 \rightarrow 5/2$ line of the more abundant isotope. However, its intensity is weak, and in addition it can be shown that its $M_F = 3/2$ Stark component which carries 90% of the total intensity has approximately the same field sensitivity as the $M_F = 1/2$ component of the $\Delta F = +1$ transition of $^{35}ClF_5$, at moderately low field-strength values. Thus, is was chosen to concentrate on the Stark effect of the strongest line of the $J = 0 \rightarrow 1$ quadrupole multiplet. Under the influence of low field strengths, the line shifted to higher frequencies. At $\mathfrak{E} = 900$ V/cm, splitting into its $M_F = 3/2$ and $M_F = 1/2$ components was observed. The frequency-versus-field data have been compiled in Figure 3. The frequency displacements from the zero-field position would depend linearly on $\mathfrak{E}^2$ if F remained a good quantum number. It is clearly seen that decoupling occurs at higher field strengths. Fortunately, the mean values of the frequencies of both Stark components still show linear behaviour over the whole range of field strengths applied in this experiment.

In order to obtain the dipole moment from these mean values, and conveniently employ the low-field approximation we set up the matrix of the perturbation operator

$$H' = H_{eQq} + H_{\text{Stark}} = H_{eQq} - \mu_a\, \mathfrak{E}_z \cos(a, z) \quad (2)$$

in the coupled basis, $\langle J\,K\,I\,F\,M_F|$. The advantage

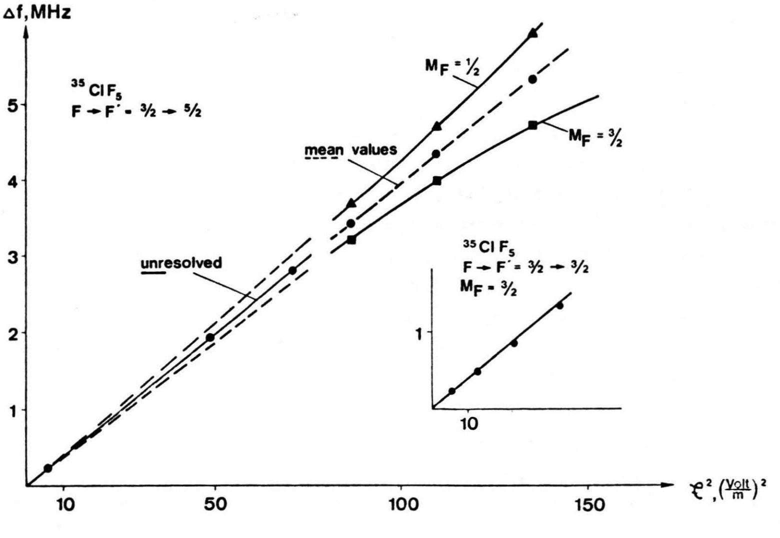

Fig. 3. Frequency shifts of some measured Stark components of the $J = 0 \rightarrow 1$ rotational transition versus their corresponding field-strength values squared. A linear dependence is seen to exist for the mean values of the frequency shifts of the two Stark components of the $\Delta F = +1$ transition which could only be resolved above 900 V/cm. A linear relation is also seen to hold for the $M_F = 3/2$ component of the $\Delta F = 0$ transition at low field strengths (the lower right. same scaling).

of this approach is that H_{eQq} stays diagonal up to second order in J. Using irreducible tensor techniques [6] the relevant result is

$$
\begin{aligned}
&(n = F' - M_F + J' + I + F + 1) \\
&\langle J' K I F' M_F | H_{\text{Stark}} | J K I F M_F \rangle \\
&= -(-1)^n [(2F+1)(2F'+1)]^{1/2} \\
&\times \begin{pmatrix} F' & 1 & F \\ -M_F & 0 & M_F \end{pmatrix} \begin{Bmatrix} J' & F' & I \\ F & J & 1 \end{Bmatrix} \mu_a \mathfrak{E}_z \\
&\times \begin{cases} \left[\dfrac{(J+1)^2 - K^2}{J+1} \right]^{1/2} & J' = J+1 \,, \\ \left[\dfrac{(2J+1) \cdot K^2}{J(J+1)} \right]^{1/2} & J' = J \,, \\ \left[\dfrac{J^2 - K^2}{J} \right]^{1/2} & J' = J-1 \,. \end{cases}
\end{aligned}
\tag{3}
$$

For the $J = 0 \rightarrow 1$ transition $K = 0$, and all diagonal elements vanish. The 3-j and 6-j symbols were obtained from Rotenberg et al [7]. Second-order perturbation theory yields the following expressions for the two M_F components which were observed experimentally (Δf in MHz, $\mathfrak{E}$ in V/cm, $F = 3/2 \rightarrow 5/2$): $\Delta f = 1.4746 \times 10^{-5} \mu_a^2 \mathfrak{E}^2$ for $M_F = 1/2$, and $\Delta f = 1.2605 \times 10^{-5} \mu_a^2 \mathfrak{E}^2$ for $M_F = 3/2$.

Thus, μ_a was fitted to the mean values with the expression $\Delta f = 1.3676 \times 10^{-5} \mu_a^2 \mathfrak{E}^2$. The result is $\mu_a = (0.536 \pm 0.010)$ D for the dipole moment of ClF_5. In order to have an independent check we also measured the Stark shift of the $F = 3/2 \rightarrow 3/2$, $M_F = 1/2$ component up to 600 V/cm where decoupling effects should be negligible. The result is also shown in Figure 3, and fitting to the corresponding second-order expression, $\Delta f = 1.4746 \times 10^{-5} \mu_a^2 \mathfrak{E}^2$, yields the value $\mu_a = (0.526 \pm 0.015)$ D.

Structure

Assuming C_{4v} symmetry which is in agreement with the observed relative K-level population the molecule has three independent parameters: $r_1 = r_{\text{Cl-F}_{\text{ax}}}$, $r_2 = r_{\text{Cl-F}_{\text{eq}}}$, and $\varphi = \sphericalangle(F_{\text{eq}} - Cl - F_{\text{ax}})$ whereas only two moments of inertia are available. Thus, a complete structure determination is not possible but some conclusions may be drawn using the fact that all three parameters must stay within reasonable limits. For example, assuming the chlorine atom being in the same plane as the four equatorial F-atoms would lead to the unrealistic distances of 2.05 Å for r_1 and 1.40 Å for r_2 in a rigid-rotor calculation. There exists only a very limited range of angles which reproduce the measured moments of inertia, and lead to acceptable bond distances: The distance of the Chlorine atom to the center of mass, z_{Cl}, is determined by

$$
|z_{\text{Cl}}|^2 = \frac{1}{m} \Delta I \tag{4}
$$

where ΔI is the difference of the measured moments of inertia, and m is a mass dependent factor. z_{Cl} is not very sensitive to r_1, almost not sensitive at all to r_2 but depends highly on φ. The partial derivatives in the interesting region ($\varphi \approx 90°$, $r_1 \approx r_2 \approx 1.65$ Å) are

$$
\begin{aligned}
\partial \Delta I / \partial \varphi &= -0.018 \text{ amu} \cdot \text{Å}^2/\text{deg} \,, \\
\partial \Delta I / \partial r_1 &= 0.0018 \text{ amu} \cdot \text{Å}^2/0.01 \text{ Å} \,, \\
\partial \Delta I / \partial r_2 &= 0.0005 \text{ amu} \cdot \text{Å}^2/0.01 \text{ Å}
\end{aligned}
$$

which means that in order to cancel a change in angle of 1 degree r_1 ought to be changed by 0.1 Å or r_2 by 0.36 Å. There are only two regions of solutions for the system: the one implies an angle of about 145°, with corresponding distances $r_1 \approx 1.8$ Å and $r_2 \approx 1.2$ Å, and clearly needs not to be considered as a reasonable structure. The other solution results in an angle of 86.5° with distances about 1.65 Å. As soon as this angle is altered by more than 1 degree, the distances separate by more than 0.15 Å which does not seem reasonable. We therefore conclude $\varphi = (86.5 \pm 1)°$. The very same procedure based on the rotational constants of BrF_5 [2] leads us to a bond angle of $(85 \pm 1)°$ for this molecule which compares well with the electron diffraction result [8] of $(84.8 \pm 0.1)°$. The error introduced by the rigid-rotor approximation can presumably be neglected in these considerations.

IV. Discussion

The results of Ref. [4] and ours (see Table 3) agree in the values for B_0 and D_J but disagree in D_{JK} and eQq. It would seem reasonable that the high-J millimeter spectrum of Ref. [4] should lead to more accurate rotational and distortion constants but nevertheless the discrepancy is surprising: the difference in D_{JK} of 0.305 kHz would shift all of the 8 components $K = 4$ in the transition $J = 4 \rightarrow 5$ of both isotopic species by 50 kHz towards lower frequencies which is clearly beyond experimental error. eQq can be expected to be determinable to a high degree of accuracy from low-J transitions because of their wide hyperfine splittings. So we feel very confident in our value of the quadrupole coupling constant. We were not successfull in finding a term

R_6, postulated by Kupecek[9] which should split the $K = 2$ transitions by $\pm 4J(J+1)(J+2)R_6$. With the value $R_6 = 51.5$ Hz given in Ref.[4] we would expect a splitting of 49 kHz in the transition $J = 4 \rightarrow 5$. We achieved a full half width of 120 kHz for the hyperfine component $K = 2$, $11/2 \rightarrow 13/2$, the same as for the neighboured component $K = 1$, $11/2 \rightarrow 13/2$. So we can at least confirm that a value of about 50 Hz must be the upper limit for R_6.

Acknowledgements

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[10] Present address: M.A.N. Maschinenfabrik Augsburg-Nürnberg, Dachauer Str. 667, *D-8000 München.*