The Hyperfine Structure in the Rotational Spectrum of CuCl

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(Z. Naturforsch. **32 a**, 1477 – 1479 [1977] ; received October 3, 1977)

The hyperfine structure of the rotational transition $J=1 \leftarrow 0$ of $^{63}Cu^{35}Cl$ in the ground vibrational state was observed. The analysis resulted in the following nuclear quadrupole coupling constants: ^{63}Cu: $e\,q_0\,Q = +16.08(20)$ MHz; ^{35}Cl: $e\,q_0\,Q = -32.25(15)$ MHz. The influence of the small magnetic spin rotational coupling of both nuclei on the hyperfine spectrum is discussed.

This investigation is part of systematic studies on the quadrupole hyperfine structure of copper monohalides to get information about the bonding character. In this concern the comparision of hyperfine structure parameters of groups of isovalence molecules is of special interest. In former publications we reported the analysis of the hyperfine structure of rotational transitions of AgF and CuF [1], AgCl, AgBr and AgI [2], and CuI [3].

The existence of the monomeric molecule in the gaseous phase was evident by the analysis of band spectra in the optical region by Ritschl [4], Rao et al. [5, 6]. Recently several pure rotational transitions were measured by Manson et al. [7] in the mm-wave region. Hyperfine structure splittings due to the quadrupole interactions with the nuclei of copper or chlorine were not observed.

We restricted our hyperfine structure investigation of the rotational transition $J=1 \leftarrow 0$ in the 3 cm band to the most abundant isotopic species $^{63}Cu^{35}Cl$. The quadrupole coupling constants of the other isotopes ^{65}Cu and ^{37}Cl can be evaluated from the results on ^{63}Cu and ^{35}Cl by using the ratios of the nuclear quadrupole moments of the both corresponding isotopes which are known from the hyperfine structure analysis of other copper [1] and chlorine [8] compounds, respectively. In our measurements on CuF [1] and AgCl [2] the vibrational dependence of the quadrupole coupling constants $e\,q_v\,Q$ could not be observed because of the small frequency shifts expected compared to the typical resolution of microwave spectroscopy. The same is to be expected in the case of CuCl. Therefore we confined our investigation to the ground vibrational state of $^{63}Cu^{35}Cl$.

CuCl was produced by the reaction of chlorine gas with copper in the heated zone of a splitted wave guide made of stainless steel. This type of absorption cell is described in a former publication (type III) [9]. Before each run the inner walls of the absorption cell were covered by a thin paste made of fine copper powder and methyl alcohol. During the measurements a continous stream of chlorine gas passed through the hot region coming from a lecture bottle outside the absorption cell and the mean pressure in the cell is estimated to be 0.1 mbar. The spectrum was observed at temperatures between 750 and 800 °C. The excess of Cl_2 was collected in a trap cooled by liquid nitrogen. Thus the preparation method for CuCl was quite similar to the one used by Manson et al [7]. In our spectrometer we used the conventional 100 kHz Stark effect modulation.

A full half width of 400 kHz was observed for a completly resolved hyperfine component. Because of the small signal to noise ratio the lines were recorded with a signal averager. Weak lines required integration times up to 21 minutes from 64 sweeps, each of which has a sweep time of 20 s and a time constant of 100 ms at 6 dB/octave.

The theory for interpretation of the hyperfine structure of rotational transitions of diatomic molecules in the $^1\Sigma$ state with quadrupole coupling of both nuclei is compiled in [10]. For analysis we estimated a value of the coupling constant $e\,q\,Q$ of ^{63}Cu in CuCl from the known constant of CuF [1] and the systematic behaviour of the metal coupling constants in the alkali halides. In a similar manner we got the constant of ^{35}Cl in CuCl using the value of ^{35}Cl in AgCl [2] and the ratio of the constants of ^{127}I in AgI [2] and CuI [3]. From these estimations the coupling constants in CuCl differ only by a factor two in magnitude (+ 15 MHz and – 30 MHz re-

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spectively). Consequently the usual coupling scheme of successive addition of angular momenta $\boldsymbol{J}$, $\boldsymbol{I}_1$ to form $\boldsymbol{F}_1$ and $\boldsymbol{F}_1$, $\boldsymbol{I}_2$ to give $\boldsymbol{F}$ is not an adequate description of the molecule. Therefore the corresponding quantum number F_1 cannot be used for the assignment of the spectrum. The only exact quantum number F is given by the total angular momentum $\boldsymbol{F}$ which is the vector sum of $\boldsymbol{J}$, $\boldsymbol{I}_1$ and $\boldsymbol{I}_2$. Because of the large rotational energy ($Y_{01} = 5.3$ GHz) in comparision to the coupling energies of both nuclei the hyperfine structure levels can be definitely assigned to the 'good' quantum number J characterizing the rotational state of the molecule. The quantum number F_1 has to be replaced by the number X which counts the hyperfine sublevels of each system (J, F) in increasing order of energy.

Tab. 1. Measured frequencies ν_{meas} in comparison with calculated frequencies ν_{calc} and calculated relative intensities of hyperfine structure components of the rotational transition $J=1 \leftarrow 0$ of ^{63}Cu^{35}Cl in the ground vibrational state. In this presentation the magnetic spin rotational constants c_I are set to zero (results see fit A, Table 2).

$F' \leftarrow F$	$X' \leftarrow X$	Int. (%)	ν_{calc} (MHz)	ν_{meas} (MHz)	$\Delta\nu$ * (kHz)
2−3	1−1	3.7	10648.347	10648.342	− 5
2−1	1−1	1.7	10648.347		
2−2	1−1	5.1	10648.348		
1−1	1−1	2.4	10650.075	10650.074	− 2
1−2	1−1	3.4	10650.077		
3−3	1−1	9.1	10650.897	10650.893	− 5
3−2	1−1	5.5	10650.899		
0−1	1−1	2.1	10653.860		
1−0	2−1	5.5	10657.269		
1−1	2−1	0.7	10657.270		
4−3	1−1	18.8	10657.900	10657.995 **	+15 **
2−3	2−1	1.1	10658.267		
2−1	2−1	8.7	10658.267		
2−2	2−1	0.6	10658.268		
3−3	2−1	5.5	10660.862	10660.879	+17
3−2	2−1	9.1	10660.863		
1−1	3−1	3.2	10665.549	10665.561	+12
1−2	3−1	2.8	10665.550		
2−3	3−1	5.6	10666.279	10666.251	−29
2−2	3−1	4.7	10666.281		

* $\Delta\nu = \nu_{\text{meas}} - \nu_{\text{calc}}$.

** Because of the not completely resolved triplett around 10658 MHz the measured center frequency was corrected to 10657.915 MHz for the fit as the $F=4 \leftarrow 3$, $X=1 \leftarrow 1$ transition.

Tab. 2. Molecular constants of ^{63}Cu^{35}Cl in the ground vibrational state given in MHz. In fit A c_I(^{63}Cu) and c_I(^{35}Cl) are set to zero. In fit B c_I(^{63}Cu) is set to zero. In fit C c_I (^{35}Cl) is set to zero.

	A	B	C
^{63}Cu: $e\,q_0\,Q$	+16.08 (20)	+15.94 (20)	+16.12 (20)
^{63}Cu: c_I	—	—	+0.010 (7)
^{35}Cl: $e\,q_0\,Q$	−32.25 (15)	−32.29 (20)	−32.28 (15)
^{35}Cl: c_I	—	+0.008 (10)	—
$B_0 + 2\,Y_{02}$ *	5328.545 (10)	5328.547 (10)	5328.546 (10)
Standard deviation of the fit	0.015	0.016	0.009

* The result of Manson et al. [7] for comparison from mm-work: $B_0 + 2\,Y_{02} = 5328.544(2)$ MHz.

In Table 1 the measured frequencies are given. For the assignment of the observed lines the spectrum of CuCl was calculated using estimated coupling constants and the rotational parameters measured by Manson et al [7]. As mentioned above each hyperfine level is characterized by the three quantum numbers J, X and F. The calculated relative intensities shown in Table 1 are normalized to the sum ($=100\%$) of all hyperfine components of the rotational transition $J = 1 \leftarrow 0$ of ^{63}Cu^{35}Cl in the ground vibrational state. In most cases the observed lines contain two or more oberlapping components. But the splitting is in all cases less than 3 kHz. Thus a line profile simulation in order to correct measured center frequencies was unnecessary. The difference $\Delta\nu$ between the measured frequencies ν_{meas} and single lines of the calculated spectrum ν_{calc} is given in the last column of Table 1 for the calculation A as explained in Table 2. The standard deviation of the least squares fit of 15 kHz is in a satisfying agreement with the estimated accuracy of ± 40 kHz for the measured frequencies.

Table 2 shows in column A the results of the fit to the three parameters $e\,q_0\,Q$ (^{63}Cu), $e\,q_0\,Q$ (^{35}Cl) and $B_0 + 2\,Y_{02}\,(J+1)^2 = B_0 + 2\,Y_{02}$. The results for the 'effective' rotational constant [11]

$$B_0 + 2\,Y_{02} + \ldots = Y_{01} + \tfrac{1}{2}\,Y_{11} + \tfrac{1}{4}\,Y_{21} + \tfrac{1}{8} \cdot Y_{31} + \ldots + 2\,Y_{02} + \ldots$$

(Y_{lk}: Dunham coefficients [12])
has to be compared with the results of Manson et al.[7]: $B_0 + 2\,Y_{02} = 5328.544(2)$ MHz. The agreement is satisfying. The errors of our results are believed to have a 90% confidence level.

Although the standard deviation of the fit is smaller than the estimated accuracy of the measurements, fits with one additional magnetic spin rotation parameter for the Cl-nucleus or the Cu-nucleus were performed. The results are shown in column *B* and *C* of the Table 2. In the case B the standard deviation increases slightly, but in *C* we get a remarkable reduction. The obtained coupling constant for ^{63}Cu has the right magnitude compared to the value in CuF [1] [$c_I = +36(10)$ kHz]. The calculated value for the Cl-nucleus is smaller and can be set to zero within its error limit. This is in accordance with the coupling constants in other chlorine compounds. Thus we conclude, that the calculation *C* including the magnetic spin rotation interaction of copper should be prefered against the other results shown.

Summarizing we state, that the coupling $e q_0 Q$ of ^{63}Cu varies in the Ib halides in the following manner:

CuF: 21.95(10) MHz [1]; CuCl: 16.08(20) MHz;
CuI: 8.14(20) MHz [3].

This systematic trend should be confirmed by measurements on the hyperfine structure of CuBr. The decrease of the halogen coupling constants of AgI [2] to CuI [3] of about 10% is confirmed for the chlorine coupling constants of AgCl [2] and CuCl. In comparision to corresponding alkali halides the halogen coupling constants are larger by about one order of magnitude. This fact indicates the remarkable difference of chemical bonding between Ia and Ib halides. For discussion of the bonding character additional measurements of electric dipole moments are of special interest.

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