NOTIZEN

On the Hyperfine Structure in the Rotational Spectrum of CuI

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The observation of the $J=2 \leftarrow 1$ rotational transition of $^{63}Cu^{127}I$ at 9 GHz resulted in the determination of the quadrupole coupling constants for $^{63}Cu : e\,q_0\,Q = 8.14(20)$ MHz and $^{127}I : e\,q_0\,Q = -938.07(20)$ MHz.

Measurements of the hyperfine structure in the rotational spectrum of CuI are part of systematic studies in the group of Ib halides (Ib/VII) in comparison to the well known alkali halides (Ia/VII) [1] and other groups of molecules. The main goal of these investigations is getting information about variation of the bonding character of isovalence molecules or about bonding characters of different groups according to the periodic table of elements.

Our first observation of a hyperfine splitting in the rotational spectra of Ib halides resulted in the determination of quadrupole coupling and spin rotational coupling constants of $^{63}Cu^{19}F$ and $^{65}Cu^{19}F$ [2]. First evidence of the free monomeric molecule CuI was given by the observations of band spectra in the optical region by Mullikan [3] and Ritschl [4]. Later on high resolution experiments gave information about the rotational structure [5–7]. Measurements of the pure rotational spectrum were done by Manson et al. [8] in the mm-wave region from which precise rotational and potential constants were derived. The analysis of the small hyperfine splittings of some rotational transitions of $^{63}Cu^{127}I$ in the 60 to 100 GHz region yields a good estimation of the predominant coupling constant $e\,q_0\,Q$ of ^{127}I. The small splitting due to the quadrupole interaction of ^{63}Cu was unresolvable by Manson et al. [8].

For further information about hyperfine structure and a more precise value of the coupling constant $e\,q_0\,Q(^{127}I)$ we made measurements on the rotational transition $J=2 \leftarrow 1$ in the X-band. In such a low rotational transition the quadrupole interaction of both nuclei should be observable with the typical resolving power of microwave spectroscopy. We restricted our measurements to the most abundant isotopic species $^{63}Cu^{127}I$ and to the mentioned rotational transition in the ground vibrational state. The quadrupole coupling constant of ^{65}Cu can be evaluated from the result of ^{63}Cu by using the ratio of the nuclear quadrupole moments of both isotopes which is known from hyperfine analysis of other Cu-compounds [2]. The characteristics of the vibrational dependence of $e\,q\,Q$ of Ib halides is well known by our results on AgCl, AgBr and AgI [9] for the halide nucleus and was not observable for the Cu-interaction in CuF [2] which is larger than the coupling in CuI.

CuI was produced by a reaction of I_2 vapour with copper in the heated zone of a splitted wave guide (rectangular cross section), which is described in a former publication [10] (absorption cell III). 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 measurement a continuous stream of I_2 vapour passed the hot cell coming from a container outside the hot region. The excess of I_2 was collected in a liquid nitrogen trap to avoid corosion of the pumping system. This kind of preparation is quite similar to the production method which Manson et al. [8] used in their experiment. A conventional 100 kHz Stark effect spectrometer was used. The transitions were observed at a reaction temperature of about 750 °C. The gas flow rate of I_2 could not be measured but the mean pressure in the hot region was estimated to be 10^{-1} Torr.

In the case of fully resolved lines the full half width of a single hfs component was 400 kHz. Because of the low signal to noise ratio the lines were recorded with a signal averager. Weak lines required integration times of 43 minutes in maximum (sweep time 20 s, time constant 100 ms at 6 dB/octave).

The theory for interpretation of rotational transitions of diatomic molecules with quadrupole coupling of two nuclei is compiled in [11]. From the known coupling constant of ^{63}Cu in CuF [2] and the value for ^{127}I in CuI [8] one expects a ratio of the interaction energies of about 100. Therefore the coupling of the angular momenta in CuI may be described by the following scheme. The rotational angular momentum $\boldsymbol{J}$ couples with the nuclear spin $\boldsymbol{I}_1$ of iodine giving the angular momentum $\boldsymbol{F}_1$ with

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Tab. 1. Measured frequencies (corrected) $\nu_{\text{meas, corr}}$ in comparison with calculated frequencies ν_{calc} and relative intensities of hyperfine components of the rotational transition $J=2 \leftarrow 1$ of ^{63}Cu^{127}I in the ground vibrational state.

$F_1 \rightarrow F_1'$	$F \rightarrow F'$	Int. (%)	ν_{calc} (MHz)	$\nu_{\text{meas, corr}}$ (MHz)	$\Delta\nu$ (kHz) *
$3/2 \rightarrow 5/2$	$1 \rightarrow 2$	0.8	8575.275		
	$3 \rightarrow 4$	2.3	8575.519	8575.551	32
	$1 \rightarrow 1$	0.4	8575.885		
$3/2 \rightarrow 3/2$	$2 \rightarrow 1$	0.9	8707.243		
	$2 \rightarrow 3$	0.8	8707.251		
	$3 \rightarrow 3$	3.3	8707.553	8707.566	13
	$1 \rightarrow 1$	0.2	8707.570		
	$0 \rightarrow 1$	0.6	8707.887		
$7/2 \rightarrow 9/2$	$3 \rightarrow 3$	0.6	8790.602	8790.576	−26
	$4 \rightarrow 4$	0.8	8791.654		
	$2 \rightarrow 3$	5.2	8791.731		
	$5 \rightarrow 6$	10.8	8791.743	8791.746	3
	$4 \rightarrow 5$	8.5	8792.138	8792,130	−8
	$3 \rightarrow 4$	6.7	8792.144		
$5/2 \rightarrow 7/2$	$1 \rightarrow 2$	2.0	8806.134	8806.157	23
	$4 \rightarrow 5$	5.9	8807.108	8807.126	18
	$4 \rightarrow 4$	0.4	8807.370		
	$2 \rightarrow 2$	0.6	8807.648		
	$2 \rightarrow 3$	3.0	8807.922	8807.901	−21
	$3 \rightarrow 3$	0.7	8808.762		
	$3 \rightarrow 4$	4.4	8808.873	8808.855	−18
$3/2 \rightarrow 1/2$	$3 \rightarrow 2$	2.9	8827.953	8827.954	1
	$1 \rightarrow 1$	1.0	8827.977		
	$1 \rightarrow 2$	0.2	8827.978		
$5/2 \rightarrow 5/2$	$4 \rightarrow 3$	0.5	8856.412		
	$1 \rightarrow 1$	1.1	8856.534	8856.520	−14
	$4 \rightarrow 4$	4.2	8857.043	8857.050	7
	$2 \rightarrow 3$	0.7	8857.075		
	$3 \rightarrow 3$	2.4	8857.915	8857.895	−20
	$2 \rightarrow 1$	0.5	8858.047		
$5/2 \rightarrow 3/2$	$4 \rightarrow 3$	1.5	8989.077	8989.043	−34
	$1 \rightarrow 0$	0.2	8989.388		
	$3 \rightarrow 2$	0.9	8989.409	8989.454	45

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

the quantum number F_1 which can still be interpreted as a 'good' quantum number. $\boldsymbol{F}_1$ couples with the spin $\boldsymbol{I}_2$ of the copper nucleus yielding the total angular momentum $\boldsymbol{F}$ with the quantum number F.

Table 1 contains the measured transition frequencies. For the assignement of the observed lines the spectrum of CuI was predicted using the estimated coupling constants and the rotational constants measured by Manson et al.[8]. According to the mentioned coupling scheme each energy level is characterized by the three quantum numbers J, F_1 and F. The relative intensities which are shown in Table 1 are normalized to the sum of all hyperfine structure components of $J=2 \leftarrow 1$ of ^{63}Cu^{127}I in the ground vibrational state (= 100%). The calculated frequencies ν_{calc} are only given where lines are measured. In most cases the observed line contains two or more overlapping hyperfine components. Therefore the measured center frequencies were corrected in order to get the frequencies of single hfs components $\nu_{\text{meas, corr}}$ as it is given in Table 1 for the strongest lines in each overlapping group. This frequency shift (normally only few kHz) was calculated by a line profile simulation with a line width of 400 kHz for a single component using hfs coupling constants of a fit without such corrections. To check the convergence of the fit this

Tab. 2. Molecular constants of $^{63}Cu^{127}I$ in the ground vibrational state given in MHz.

	This work	Manson et al. [8]
$^{63}Cu : e\,q_0\,Q$	$+8.14$ (20)	—
$^{127}I : e\,q_0\,Q$	-938.07 (20)	-935 (15)
$B_0+8\,Y_{02}$	2192.846 (3)	2192.843 (1)

procedure was repeated with the new hfs parameters. Fits of the total lineprofile will probably give no better results because of small signal to noise ratio and some background variations. The difference between the corrected frequencies $\nu_{\text{meas, corr}}$ and single lines of the calculated spectrum is given in the last column of Table 1. The standard deviation of the least squares fit is 22 kHz which is to be compared with the estimated accuracy of ± 40 kHz for the primarily measured frequencies.

Table 2 shows the results of the fit to the three parameters $e\,q_0\,Q\,(^{63}\text{Cu})$, $e\,q_0\,Q\,(^{127}\text{I})$ and $B_0 + 2\,Y_{02}(J+1)^2 = B_0 + 8\,Y_{02}$. The latter fit parameter, the effective rotational constant

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

has to be compared with the results of Manson et el.[8] (Y_{lk}: Dunham coefficients[12]). The errors given have a 90% confidence level, thus the agreement of both results is good.

A test fit with an additional magnetic spin rotation parameter of the ^{127}I nucleus gave no evidence for this parameter, which was to be expected from the small standard deviation of the fit for the quadrupole coupling alone.

The coupling constant of ^{63}Cu changes from 21.95 (10) MHz in CuF[2] to 8.14 (20) MHz in CuI. This variation ratio is comparable in magnitude to the potassium halides[1].

The change of the iodine coupling from AgI[9] to CuI is only about 10% and the constant itself is ten times larger than in KI[13] which indicates the difference of the chemical bonding in CuI and KI.

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