An investigation on possibility of observing *ortho-para* transition, based on new measurements of microwave spectrum of Disulfur Dichloride; S_2Cl_2

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1. Inroduction

One of the special properties of S_2Cl_2 is being a candidate for observing *"ortho-para"* transition [2]. In general, this transition is strictly forbidden by Pauli principle. But an interaction H_{op} which makes pure *ortho* levels mix with pure *para* states and vice versa can make the *"ortho-para"* transition possible. As an example, if the initial state in a transition is *ortho* $|\varphi_O^i\rangle$ and the final state is the superimpose of a *para* state $|\varphi_P^f\rangle$ and an *ortho* state $|\varphi_O^f\rangle$, we can estimate intensity of the forbidden transition by the equation as below [1]:

$$I = \left|\langle(c_1\varphi_P^f + c_2\varphi_O^f)|\mu|\varphi_O^i\rangle\right|^2 = |c_2|^2\left|\langle\varphi_O^f|\mu|\varphi_O^i\rangle\right|^2 = \frac{\left|\langle\varphi_P^f|H_{op}|\varphi_O^f\rangle\right|^2}{\left|E_O^f - E_P^f\right|^2}\left|\langle\varphi_O^f|\mu|\varphi_O^i\rangle\right|^2$$

It means that forbidden transition intensity can be obtained from the intensity borrowing from the corresponding allowed transition; $\langle\varphi_O^f|\mu|\varphi_O^i\rangle$ by a factor of $|c_2|^2$.

Until now such kind of *"ortho-para"* transition has not been experimentally observed [1] and the final goal in our research is experimental observation of *"ortho-para"* transition.

Mizoguchi et al. in 2008 [2] observed hyperfine splitting in FTMW spectrum of S_2Cl_2 for $J < 11$ quantum numbers. In the hyperfine structure analysis by considering diagonal hyperfine terms, unexpected splitting of order of 50 kHz was observed. For explanation of these splitting patterns off-diagonal quadruple hyperfine terms were introduced. As the off-diagonal hyperfine terms can be an origin of *"ortho-para"* mixing, so we can expect *"ortho-para"* transition in S_2Cl_2.

For estimating the possibility of experimental observation of an *"ortho-para"* transition, precise calculation of factors $\left|\langle\varphi_P^f|H_{op}|\varphi_O^f\rangle\right|^2$ and $\left|E_O^f - E_P^f\right|^2$ of various rotational states are necessary and for knowing these factors microwave spectroscopy of S_2Cl_2 is indispensable. Generally as by increasing the transition frequency makes the detection sensitivity higher, going to higher frequencies is desirable. In the previous cm microwave spectroscopy of S_2Cl_2, rotational states were limited to $J < 11$. We decided to extend the spectroscopy measurements in mm wave regions in order to get more information on *"ortho-para"* mixing coefficients of high J and K rotational states. By using these information we can choose an *"ortho-para"* transition with the highest probability of experimental observation.

2. Experiment

We could extend observation of S_2Cl_2 up to 100 GHz by using a millimeter-wave spectrometer combined with a pulsed jet nozzle with frequency of 10Hz and 0.5 atm Ar as the buffer gas. The experiment temperature is estimated to be about 5K by assigning band head of the observed Q branch transitions. A gating system with frequency modulation technic was used. The InSb microwave detector cooled by liquid Helium was used. The typical example of observed spectrum is shown in figure 1. We also used lines observed by another gas cell experiment with a temperature of 200K in order to get information about higher rotational states.

3. Result, Discussion and Conclusion

We observed 70 transitions for $S_2^{35}Cl_2$ and 80 transitions for $S_2^{35}Cl^{37}Cl$ in the frequency region of 75GHz to 100GHz and for quantum numbers less than $J = 37$. Based on these observation we obtained new rotational molecular constants including fourth and sixth order centrifugal distortion

constants, as shown in Table 1. Figure 1 shows improvement of rotational transitions prediction relative to the previous work. The fourth-order centrifugal distortion constant δ_K and sixth-order centrifugal distortion constants are necessary for the determination of calculating the term energy for high-K levels. By these new molecular constant the $\left|E_O^f - E_P^f\right|$ values can be calculated more precisely. Also we have the chance of investigation of "*ortho-para*" transitions for high frequencies and high rotational quantum numbers. We observed triplet patterns Q branches as shown in figure 2. These triplet patterns are in good agreement with the hyperfine patterns that calculated by the reported hyperfine constants. This result means the hyperfine constants determined in the cm spectroscopy are accurate enough for calculating the mixing coefficients between *ortho* and *para* levels in the mm regions. By increasing the transition frequency the each hyperfine component is not resolved within Doppler limited spectroscopy, however, it does not matter in searching "*ortho-para*" transitions. So based on these constant we can calculate effect of off-diagonal terms in for high quantum numbers.

Our next step is calculating $\left|\langle\varphi_P^f|H_{op}|\varphi_O^f\rangle\right|^2$ coefficients by considering off diagonal hyperfine constants for finding the best candidates for observing "*ortho-para*" transitions and finally designing a suitable experiment for observing the interested line.

Table 1. The rotational constants and centrifugal distortion constants of S_2Cl_2

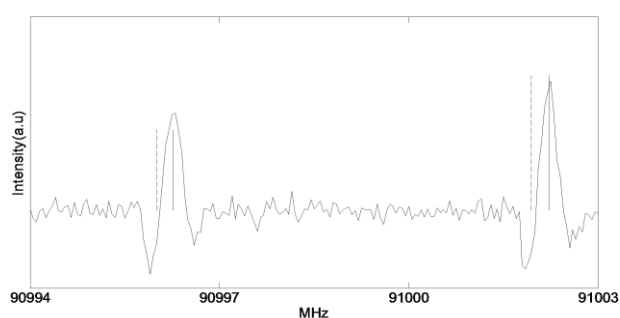|		$S_2^{35}Cl^{35}Cl$	
		This work	Ref. [2]
A	/MHz	5533.8933 (15)[a]	5533.8964 (11)
B	/MHz	1393.8509 (14)	1393.8436 (3)
C	/MHz	1232.6642 (16)	1232.6728 (2)
Δ_J	/kHz	0.584 (5)	0.556 (3)
Δ_{JK}	/kHz	-5.217 (40)	-5.115 (28)
Δ_K	/kHz	24.01 (5)	24.70 (25)
δ_J	/kHz	0.123 (5)	0.144 (2)
δ_K	/kHz	4.7 (8)	
H_J	/Hz	0.032 (4)	
H_{JK}	/Hz	-1.3 (6)	
H_{KJ}	/Hz	4 (2)	
H_K	/Hz	-4 (2)	
h_J	/Hz	-0.014 (3)	
h_{JK}	/Hz	3.6 (4)	
h_K	/Hz	-41(21)	

Figure. 1. Comparing spectrum prediction by new and old molecular constants for $S_2^{35}Cl_2$. Dash lines shows spectrum prediction by old molecular constants [2] and solid lines shows the prediction with molecular constants of result of our experiment. The spectrum with lower frequency is for $J = 17_{6\,12} - 16_{5\,11}$ and the spectrum with higher frequency is for $J = 17_{6\,11} - 16_{5\,12}$
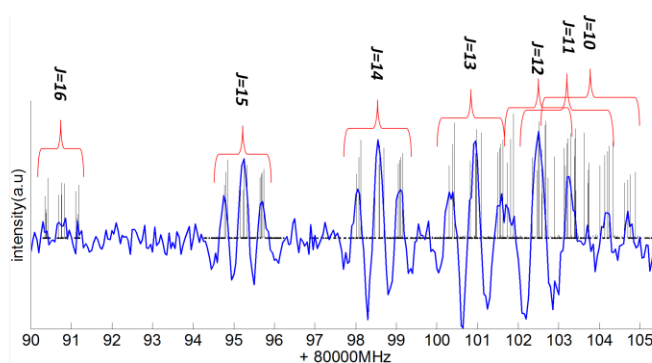

Figure 2. $^rQ_{K=9}(J)$ branch series for $S_2^{35}Cl_2$. We observed hyperfine splitting that is in good agreement with hyperfine patterns which produce according to the reported hyperfine constants [2].

Refrences
1. A.Miani,J.Tennyson, J.Chem.Phys.120,2732,(2004)
2. A.Mizoguchi,Sh.Ota, H.Kanamori,Y.Sumiyoshi, Y.Endo, J.Mol.Spect, 250,86,(2008)