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A Study on possibility of observing “*ortho-para*” microwave transition in Disulfur Dichloride, S₂Cl₂

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1. Introduction

One of the special properties of S₂Cl₂ is being a candidate for observing “*ortho-para*” transition. As two identical Cl atoms in S₂Cl₂ have $I_i = \frac{3}{2}$ nuclear spin, the total nuclear spin angular momentum can be $I = 0, 1, 2, 3$. According to Pauli principle, molecular levels in S₂Cl₂ are classified to *ortho* or *para* levels. The former is $K_a K_c = oe, eo$ rotational states coupled with odd- I nuclear spin states and the latter is $K_a K_c = oo, ee$ and even- I . In general, the transition between *ortho* and *para* states is strictly forbidden. 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 an initial *ortho* state; $|\varphi_o^i\rangle$ in a transition is superimposed with a *para* state; $|\varphi_p^i\rangle$ and the final state is an *ortho*; $|\varphi_o^f\rangle$ state, we can estimate the intensity of the forbidden transition by the equation as below [1]:

$$I = |\langle (c_1 \varphi_p^i + c_2 \varphi_o^i) | \mu | \varphi_p^f \rangle|^2 = |c_1|^2 |\langle \varphi_p^i | \mu | \varphi_p^f \rangle|^2 = \frac{|\langle \varphi_p^i | H_{op} | \varphi_o^i \rangle|^2}{|E_o^i - E_p^i|^2} |\langle \varphi_p^i | \mu | \varphi_p^f \rangle|^2$$

It means that the forbidden transition intensity can be obtained from an intensity borrowing from the corresponding allowed transition; $\langle \varphi_p^i | \mu | \varphi_p^f \rangle$ by a factor of $|c_1|^2$.

Until now such a kind of “*ortho-para*” transition has never been experimentally observed [1]. Recently, Mizoguchi *et al.* studied cm-FTMW spectroscopy of S₂Cl₂ for $J < 11$ quantum numbers and found some evidences of *ortho-para* mixing due to quadrupole hyperfine interaction [2]. However, the mixing ratio is not so large enough to detect the “*ortho-para*” transition in the cm-MW region. Generally speaking, spectral intensity becomes stronger as increase of the transition frequency, the searching the forbidden transition at higher frequencies is advantageous. So we extended the MW spectroscopic measurements of S₂Cl₂ from cm to mm wave regions in order to get more information on the *ortho-para* mixing coefficients of higher J and K rotational states. Using our new rotational molecular constants, we can calculate the *ortho-para* mixing coefficients for all the states and found the best candidates for detecting “*ortho-para*” transitions.

2. Experiment

We extend the observation of S₂Cl₂ up to 100 GHz by using a mm-MW spectrometer combined with a pulsed jet nozzle with a repetition frequency of 10 Hz. To make the rotational temperature as low as 10 K, 0.5 atm Ar was used as the buffer gas. The MW form a multiplied synthesiser was detected by an InSb detector cooled by liquid Helium. A gated data acquisition system with source frequency modulation technic was used. We also observed some lines by gas cell experiment with a temperature of 200 K in order to get information about higher rotational states.

3. Result and Discussion

We observed 70 transitions for S₂³⁵Cl₂ and 80 transitions for S₂³⁵Cl³⁷Cl in the frequency region of 75 GHz to 100 GHz and for quantum numbers less than $J = 37$. Based on these observation we determined new rotational molecular constants including the fourth and sixth order centrifugal distortion constants by a least square method, as shown in Table 1.

By these new molecular constants we had the chance of investigating interactions between levels with different *ortho* or *para* symmetry. As the total angular quantum number; $F = |J + I|, \dots, |J - I|$ is always good quantum number, we finding out the largest mixing states by hitting every Eigen vectors in each F block. Our study shows the highest *ortho-para* mixing coefficients belongs to K doubling levels with $\Delta J = 0, \Delta K_a = 0$. The next considerable *ortho-para* mixing coefficients were found between levels with $\Delta J = 0, \Delta K_a = \pm 2$. We also found *ortho-para* mixing between levels with accidental relationships between their rotational quantum numbers. Table 2 shows the examples from these three groups of mixed levels.

Figure 1 shows our candidate for “*ortho-para*” transition which starts from mostly “*ortho*” state; $|c_1\phi_P^i + c_2\phi_O^i\rangle = |J_{K_a K_c} I F\rangle = |9_{6,3} 1 9\rangle_O^*$. This “*ortho*” state is mixed with a *para* state; $|\phi_P^i\rangle = |9_{6,4} 0 9\rangle_P$ with the mixing coefficient; $|c_1|^2 = 0.17$. So if we calculate a R -transition between this state and $|\phi_P^f\rangle = |10_{7,3} 0 10\rangle_P$, which is very little mixed with *ortho* states, the “*ortho-para*” transition between $|10_{7,3} 0 10\rangle_P$ and $|9_{6,3} 1 9\rangle_O^*$ by intensity equal to 0.17 of that of the allowed transition of $|10_{7,3} 0 10\rangle_P \leftarrow |9_{6,4} 0 10\rangle_P$. The result is drawn in red stick line in Figure 1. However, there are several allowed transitions located around the “*ortho-para*” transition. The transition frequency is about 1.4MHz away from the nearest allowed transition which shown in the figure1. This value is larger than Doppler broadening (1MHz) in our experimental condition. So detection of this “*ortho-para*” transition seems feasible with normal spectroscopic technics.

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)	

Table 2. Example of three types of mixed levels

Relation between interacting levels	Main part of wave function, $ J_{K_a K_c} I F\rangle$	Mixed part of wave function, $ J_{K_a K_c} I F\rangle$	Mixing coefficient, $ c_1 ^2$	$ E_O - E_P /MHz$
$\Delta J = 0, \Delta K_a = 0$	$ 9_{6,3} 1 9\rangle_O$	$ 9_{6,4} 0 9\rangle_P$	0.17	1.1249
$\Delta J = 0, \Delta K_a = \pm 2$	$ 22_{7,15} 2 20\rangle_P$	$ 22_{5,18} 3 20\rangle_O$	0.008	100312.8397
accidental	$ 11_{3,8} 3 8\rangle_O$	$ 10_{4,6} 2 8\rangle_P$	0.002	256.7134

References

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)

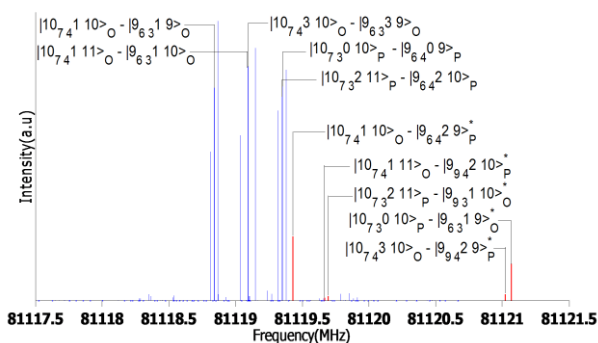


Figure 1. predicted spectrum pattern of one of the candidates for observing “*ortho-para*” transitions. blue lines shows normal transitions and red lines shows “*ortho-para*” transition.