



Detection of Microwave Transitions between Ortho and Para States in a Free Isolated Molecule

Hideto Kanamori,^{1,*} Zeinab. T. Dehghani,¹ Asao Mizoguchi,¹ and Yasuki Endo²

¹*Department of Physics, Tokyo Institute of Technology, Tokyo 152-8551, Japan*

²*Department of Applied Chemistry, National Chiao Tung University, Hsinchu 30010, Taiwan*

(Received 9 August 2017; published 25 October 2017)

Microwave transitions between the ortho and para states of the S_2Cl_2 molecule in a free isolated condition are observed for the first time. In the theoretical treatment, we derive eigenfunctions of an effective Hamiltonian including the ortho-para interaction to calculate the intensities and frequencies of forbidden ortho-para transitions in the cm-wave region and pick up some promising candidates for the spectroscopic detection. In the experiment, transitions of the S_2Cl_2 molecule under a supersonic jet condition are observed with a Fourier transform microwave spectrometer. Seven hyperfine resolved rotational transitions including the lowest rotational level are detected as the ortho-para transitions at the predicted frequencies within the experimental errors. The observed intensities are about 10^{-3} times the allowed transitions, which are consistent with the predictions based on the intensity-borrowing model. This result suggests that the ortho-para conversion of this molecule occurs in a few thousand years through spontaneous emission even in a circumstance where molecular collisions occur rarely like in interstellar space.

DOI: 10.1103/PhysRevLett.119.173401

The ortho-para symmetry in molecular systems has its origin in the permutation symmetry of identical particles. A complete wave function should change (not change) sign by an interchange of two identical fermions (bosons) in the system, and it is one of the most fundamental postulates in quantum mechanics [1–3]. Every molecule with a C_2 symmetry axis has ortho-para symmetry if the identical nucleus has nonzero spin. In order to exchange a complete wave function between the ortho and para states, it is necessary to swap the symmetry of the rotational part and nuclear spin part of the wave function simultaneously. It is rigorously forbidden for free isolated molecules to exchange their symmetry by an interaction with electromagnetic radiation [4]. There are a few reports on the experimental observations of ortho-para transitions in the IR region. One is an observation of IR ortho-para transitions of methane, but it was done under an external magnetic field [5]. Most other phenomena associated with the ortho-para transitions are nuclear spin conversion by molecular collisions [6–8] or surface interactions [9].

Real molecular states may not be necessarily pure ortho nor para [10]. Especially, radicals and ions with an unpaired electron have large intrinsic ortho-para mixing, and a possibility of the radiative ortho-para transition was discussed [11,12]. However, it has never been observed yet except for the rotational transition of H_2^+ in an exotic state [13]. It was the $N = 1 \leftarrow 0$ rotational transition in the highest vibrational level ($v = 19$) of the dissociation limit of the ground electronic state, for which the first dissociative electronic state is mixed.

Besides the radicals and ions, even singlet molecules could mix slightly with each other through internal

interactions between the end-over-end rotation and the nuclear spin angular momenta [14]. We picked the S_2Cl_2 molecule as a possible molecule to observe such a mixing for the following reason. This molecule drew our attention because it is a candidate molecule for detecting the energy difference between enantiomers due to the parity violation [15]. With this idea in mind, we performed a high-resolution spectroscopic study of this molecule by Fourier transform microwave (FTMW) spectroscopy [16], where we have confirmed that this molecule has C_2 symmetry through the analysis of hyperfine resolved rotational spectra of $S_2^{35}Cl_2$ and $S_2^{35}Cl^{37}Cl$. The existence of two identical ^{35}Cl nuclei with $I = 3/2$ in $S_2^{35}Cl_2$ shows ten or six hyperfine components according to the ortho or para state.

An important discovery in this molecule was that unexpected energy shifts for the hyperfine levels with $I_{total} = 0$ and 2 were found in the lowest rotational level, $J_{Ka,Kc} = 0_{0,0}$. In order to explain these shifts, we considered off-diagonal terms of the nuclear quadrupole interaction, which mix the ortho and para states. Essentially, electric dipole transitions between pure ortho and para states are strictly forbidden under the Pauli principle. However, the existence of not a small amount of ortho-para mixing in this molecule suggests a possibility of observing optical transitions between the ortho and para states.

Here, we report a theoretical prediction of ortho-para MW transitions based on an intensity-borrowing model and experimental results of the first detection of such transitions.

In the theoretical treatment for the $S_2^{35}Cl_2$ molecule, the following rotational Hamiltonian including the hyperfine interaction [16,17] was employed:

$$\mathbf{H} = \mathbf{H}_{\text{rot}} + \mathbf{H}_{\text{hf}}, \quad (1)$$

where \mathbf{H}_{rot} is the asymmetric rotor Hamiltonian including the sixth-order centrifugal distortion terms with its eigenlevels denoted as J_{K_a, K_c} and eigenfunctions as $|J_{K_a, K_c}\rangle$. \mathbf{H}_{hf} is the hyperfine interaction term involving the nuclear spins of two equivalent Cl nuclei. The nuclear spins of the two Cl nuclei are denoted \mathbf{I}_1 and \mathbf{I}_2 with their magnitude 3/2, and the total nuclear spin is defined as $\mathbf{I} = \mathbf{I}_1 + \mathbf{I}_2$, whose magnitude is 0, 1, 2, and 3. The total angular momentum \mathbf{F} is defined as $\mathbf{F} = \mathbf{J} + \mathbf{I}$, and the eigenlevels of the total Hamiltonian are denoted as J_{K_a, K_c}, I, F with the total wave function as $|J_{K_a, K_c}, I, F\rangle$. Since the number of the nuclear spin function of the identical $^{35}\text{S}(I = 0)$ nuclei is only one, the discussion about the ortho or para symmetry is limited to the Cl nuclei. The molecular states of $\text{S}_2^{35}\text{Cl}_2$ are classified into the ortho or para state depending on odd ($I = 1, 3$) or even ($I = 0, 2$) quantum numbers of the total nuclear spin according to Fermi-Dirac statistics. In this Letter, the ortho or para rotational levels are denoted as $(^{o/p})J_{K_a, K_c}, I, F$, and their corresponding wave functions are represented as $(^{o/p})|J_{K_a, K_c}, I, F\rangle$.

Concerning the ortho-para symmetry, the Hamiltonian (1) can be divided into two parts: diagonal and off-diagonal parts for the ortho-para symmetry,

$$\mathbf{H} = \mathbf{H}_{(0)} + \mathbf{H}_{\text{op}}. \quad (2)$$

It means that the Hamiltonian matrix consists of ortho and para blocks and the first term has matrix elements only within each block. The ortho block consists of levels with $^oJ_{K_a, K_c}, I = 1, F$ and $^oJ_{K_a, K_c}, I = 3, F$, and the other, the para block, consists of $^pJ_{K_a, K_c}, I = 0, F$ and $^pJ_{K_a, K_c}, I = 2, F$. The second term \mathbf{H}_{op} in Eq. (2) has matrix elements connecting the two blocks. Generally speaking, the \mathbf{H}_{op} term should be considered when the operator $(\mathbf{I}_1 - \mathbf{I}_2)$ cannot be ignored. In the case of S_2Cl_2 , the terms in \mathbf{H}_{op} consist of off-diagonal terms of the Cl nuclear quadrupole interaction involving χ_{ab} and χ_{bc} , which have previously been determined to be $-49.24(8)$ and $-30.27(3)$ MHz, respectively [16]. The Hamiltonian matrices are diagonalized to obtain eigenenergies and eigenfunctions, where the eigenlevels have nonzero contributions from opposite ortho or para levels, whose amount is represented by the square of the mixing coefficient, $|c_{\text{op}}|^2$.

Once an ortho level is mixed with a nearby para level, an electric dipole transition from another para level becomes possible by intensity borrowing from the nearby allowed para-para transition [3]. The intensity of the ortho-para transition, I_{op} , is proportional to the square of the product of the transition moment and the mixing coefficient as shown below:

$$I_{\text{op}} \propto |\langle ^p\psi' | \mu | ^o\psi'' \rangle|^2 = |c_{\text{op}}|^2 \cdot |\langle ^p\psi_{(0)'} | \mu | ^p\psi_{(0)''} \rangle|^2, \quad (3)$$

in which $|^{o/p}\psi_{(0)}\rangle$ denotes the zeroth-order eigenfunction of the Hamiltonian (2) ignoring the contributions of \mathbf{H}_{op} . The last term of Eq. (3) consists of the square of the mixing coefficient and the transition dipole moment of the allowed transition. In general, $|c_{\text{op}}|^2$ becomes larger as the energy difference between nearby levels is smaller. However, in order to detect a very weak ortho-para transition clearly, it should be well isolated from a nearby strong allowed transition, so that the energy difference between them should be sufficiently larger than their spectral linewidth. The spectral linewidth in the cm-wave region is usually determined by the Doppler effect, and the skirt of the line profile of a strong peak extends as large as a few hundred kilohertz. Therefore, a level with a large mixing coefficient but a sufficiently large energy separation from the lender state is desirable. As the C_2 symmetry axis of this molecule is along the b axis, asymmetry doublets have opposite ortho or para symmetry. From the rotational constants of S_2Cl_2 , Ray's asymmetric parameter κ is -0.925 , indicating that this molecule is close to a prolate top. As a result, energy separations between asymmetry doublets decrease rapidly as K_a increases. There are, thus, many chances to have appropriate nearby pairs with opposite ortho-para symmetries for this molecule.

The discussion so far given is a simplified one considering only a perturbation with a single opposite symmetry level, but an actual level is often mixed with several opposite symmetry components at the same time. Therefore, in order to estimate intensities properly, transition moments should be directly calculated using the eigenfunctions of the Hamiltonian given in Eq. (2).

As an example, the calculated results for the $2_2 - 2_1$ asymmetry doublets are shown in Fig. 1. This pair consists of the allowed para-para transition $2_{2,0} - 2_{1,1}$ and the ortho-ortho transition $2_{2,1} - 2_{1,2}$. Each transition consists of a few tens of hyperfine components as shown in the enlarged plots in Fig. 1(b). Besides these allowed transitions, there exist forbidden transitions of ortho-para, $2_{2,1} - 2_{1,1}$, and para-ortho, $2_{2,0} - 2_{1,2}$. Among these forbidden transitions, the $^p2_{2,0}, 2, 4 - ^o2_{1,2}, 3, 3$ transition is the strongest and is located farthest away from any of the allowed transitions, so that it is expected to be less disturbed by strong allowed transitions. This transition is, thus, nominated as a candidate for the experimental detection in this region. Similarly, other candidates were selected from among all the possible transitions in the cm-wave region.

In order to predict the intensities of such transitions whether their detections are experimentally feasible or not, we also calculated the permanent dipole moment at the CCSD(T)/aug-cc-pVTZ level, yielding μ_b to be 0.928 D, using the program package MOLPRO 2012.1 [18]. The intensities of the candidate transitions were then calculated to be about one-thousandth of the intensity of the allowed transitions as shown in the last column in Table I. These values were well within the detectable level of our FTMW spectrometer.

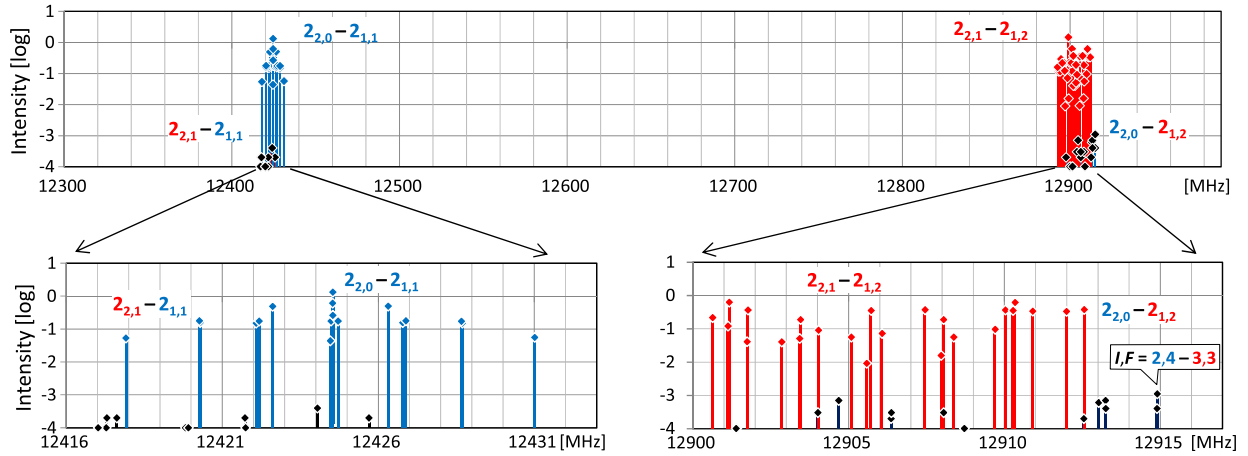


FIG. 1. The calculated spectrum of the hyperfine resolved rotational transitions of $2_{2,0} - 2_{1,1}$ and $2_{2,1} - 2_{1,2}$ including the forbidden transitions. (a) Para-para and ortho-ortho transitions are shown in blue and red, respectively. (b) Enlarged spectrum including the ortho-para transitions in black color, whose intensities are less than one-thousandth of those of the allowed transitions. Among these forbidden transitions, ${}^p2_{2,0}, 4 - {}^o2_{1,2}, 3$ at 12 915 MHz is the strongest and is located furthest away from the allowed transitions.

A Balle-Flygare-type FTMW spectrometer at National Chiao Tung University [19] operating in the frequency region of 4–40 GHz was used for the observation of ortho-para transitions of $S_2^{35}Cl_2$. Commercially available reagent S_2Cl_2 was used without any purification and was diluted with Ar to 0.1%. This sample gas was ejected into the FTMW chamber by a pulsed valve (General Valve Co; 0.7 mm ϕ) with 1.2×10^5 Pa stagnation pressure and a 5 Hz repetition rate. The pressure in the vacuum chamber was kept at 4.0×10^{-3} Pa during the measurement. The rotational temperature of the molecule in the jet was estimated to be 3 K. Since the direction of the molecular jet was set parallel to the optical axis of the MW cavity, a spectral peak has a doublet profile due to the Doppler effect of the standing wave in the cavity. The power of the pumping MW was set to be as large as possible (more than 30 mW) for observations of transitions with very small transition moments. Even so, since lines were expected to be very weak, free induction decay signals with the sample gas pulse on and off were alternatively obtained and subtracted in order to eliminate a systematic noise. The difference signals were accumulated

and Fourier transformed in a computer. It took 40 min for accumulating 10000 difference signals.

With this FTMW spectrometer, we searched for the ortho-para transitions based on the predicted frequencies of the candidate transitions. Figure 2 shows a result of the ${}^p2_{2,0}, 2, 4 - {}^o2_{1,2}, 3, 3$ transition obtained after 40 000 accumulations. The predicted frequency is 12 914.9 MHz as indicated in the figure with a dotted line, where a doublet peak was observed. The separation of the doublet was consistent with the Doppler effect due to the standing wave in the MW cavity. In fact, this peak is accidentally overlapped with another para-ortho transition, ${}^p2_{2,0}, 2, 3 - {}^o2_{1,2}, 3, 3$, at 0.005 MHz lower frequency with the intensity of one-third of that of ${}^p2_{2,0}, 2, 4 - {}^o2_{1,2}, 3, 3$, which was not detected separately. Meanwhile, the peak appearing at 12 914.7 MHz is not a signal but a zero frequency spurious noise at the frequency of the incident microwave.

Another example of the observed ortho-para transition is the lowest rotational transition of $1_{1,0} - 0_{0,0}$. As seen in the predicted spectrum in Fig. 3, this transition has no asymmetry pair because the lower K_a is zero. Four hyperfine

TABLE I. Observed ortho-para transitions.

J'	K'_a	K'_c	I'	F'	o/p	J''	K''_a	K''_c	I''	F''	o/p	Obs. [MHz]	O-C ^a [MHz]	Intensity ^b
1	1	0	1	1	<i>o</i>	0	0	0	2	2	<i>p</i>	6923.5126	0.0046	0.0028
1	1	0	1	2	<i>o</i>	0	0	0	2	2	<i>p</i>	6932.1175	0.0001	0.0039
1	1	0	3	2	<i>o</i>	0	0	0	2	2	<i>p</i>	6919.0508	0.0046	0.0026
1	1	0	3	3	<i>o</i>	0	0	0	2	2	<i>p</i>	6934.8680	0.0005	0.0026
2	2	0	2	3	<i>p</i>	2	1	2	3	3	<i>o</i>	12914.8991	0.0066	0.0004
2	2	0	2	4	<i>p</i>	2	1	2	3	3	<i>o</i>	12914.8991	0.0018	0.0010
2	2	1	3	2	<i>o</i>	1	1	1	2	2	<i>p</i>	17996.0412	0.0068	0.0013
1	1	1	2	3	<i>p</i>	0	0	0	2	2	<i>p</i>	6766.3760	0.0005	2.0068 ^c

^aObserved frequency—calculated frequency.

^bCalculated value by using the eigenfunctions.

^cAn example of a typical allowed transition for the comparison of the intensity.

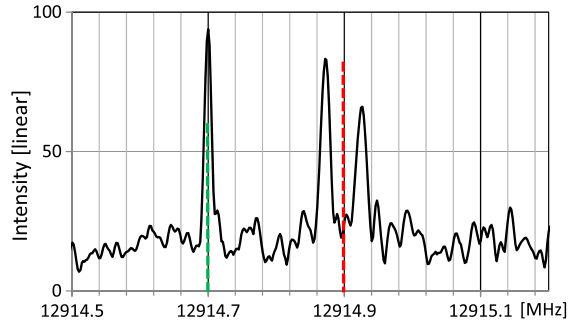


FIG. 2. The observed spectrum of the $P_{2,0,2,4} - O_{1,2,3,3}$ transition with a doublet profile due to the Doppler effect. A red dotted line indicates the predicted frequency. The singlet peak at 12914.7 MHz indicated by the green dotted line is an artificial peak due to the zero frequency spurious noise.

resolved transitions from the lower $(I, F) = (2, 2)$ para level to the upper $(I, F) = (3, 2)$, $(1, 1)$, $(1, 2)$, and $(3, 3)$ ortho levels were observed as shown in the bottom panel in Fig. 3. All the transitions were observed as doublets with the same Doppler profiles. The unequal intensity of the doublets may be due to the fact that the background noise suppression is not sufficient. However, their center frequencies agree very well with the predictions within 5 kHz. Finally, we could observe seven ortho-para transitions for three rotational transitions. All the observed ortho-para transitions are listed in Table I with the observed frequencies and the predicted intensities considering the Hönl-London factor. The observed transitions are also shown in Fig. 4 of the rotational level diagram without the hyperfine structures.

The intensities of the observed ortho-para transitions are 3 orders of magnitude smaller than that of a typical allowed transition as shown in Table I. As seen in Fig. 4, the ortho-para transition $o_{1,0,1,1} - p_{0,0,2,2}$ borrows its intensity mainly from the allowed transition of $p_{1,1,0,1} - p_{0,0,2,2}$, in which the upper level is located at 168 MHz below the $1_{1,0}$ level. The square of the mixing coefficient between the two upper states is calculated to be 1.3×10^{-3} . Another case of mixing is between the asymmetry doublet, $2_{2,0}$ and $2_{2,1}$. The difference of their rotational term energies is calculated to be only 2 MHz, if the hyperfine interaction is ignored. When the hyperfine interaction is taken into account, the $P_{2,0,2,4}$ level is mixed with the $O_{2,1,3,4}$ level with the squared coefficient of 1.9×10^{-3} . Thus, the forbidden transition $P_{2,0,2,4} - O_{1,2,3,3}$ could be observed.

The linewidth of the observed spectra is only 5 kHz as seen in Fig. 3. This means that the collision rate in the MW cavity is no more than 5×10^3 /s. Such a small collision rate suggests what we observed is not a collision-induced radiative transition but a transition due to the intrinsic transition moment of the molecule in free space.

The key to the successful observation of the radiative ortho-para transitions is that the S_2Cl_2 molecule has especially large ortho-para mixing. There are two reasons why the mixing is so large. One is that the matrix elements in H_{op} are large, since the off-diagonal terms of the quadrupole interaction are nearly the same order of magnitude as the diagonal terms [16]. This fact comes from its molecular structure, in which Cl-S-S-Cl is helically

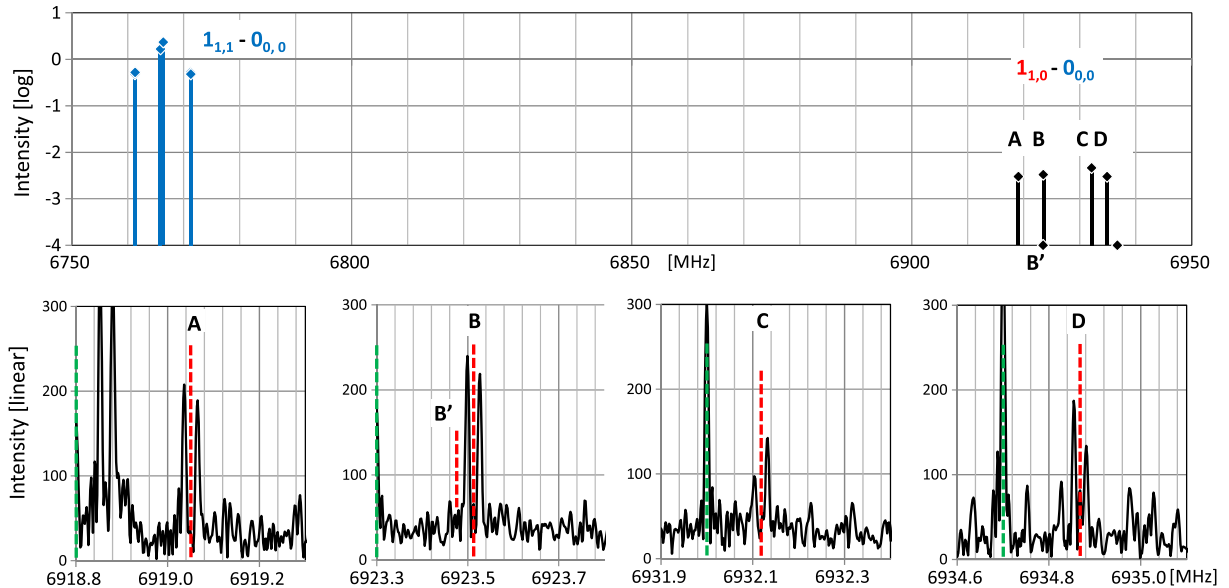


FIG. 3. The predicted and observed spectra of the ortho-para transitions from the lowest rotational level $0_{0,0}$. Top panel: Predicted positions and intensities of para-para and ortho-para transitions from the lowest rotational level $0_{0,0}$. Four hyperfine components from the lower $(I, F) = (2, 2)$ level in $0_{0,0}$ to the upper $(I, F) = (3, 2)$, $(1, 1)$, $(1, 2)$, and $(3, 3)$ levels in $1_{1,0}$ are labeled with A–D, respectively. Bottom panels: Observed spectra of the ortho-para transitions after the accumulation of 10 000 shots. The position of the predicted frequency is shown as a red dotted line, and the zero frequency spurious peak is indicated by the green dotted line in each panel. A stronger doublet peak at 6918.86 MHz in panel (a) is not assigned yet.

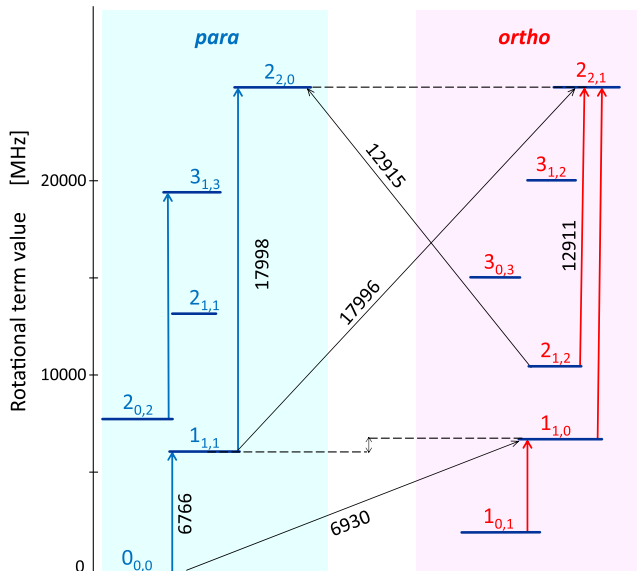


FIG. 4. The level diagram of several lowest rotational levels without hyperfine structure. The normal para-para and ortho-ortho transitions reported in Ref. [1] and ortho-ortho transitions observed in this work are shown with the transition frequencies in megahertz units. The energy separations of $2_{20}-2_{21}$ and $1_{10}-1_{11}$ are 2 and 168 MHz, respectively.

twisted. The bonding axis between Cl and S nuclei, which is almost parallel to the direction of the electric field gradient of the quadrupole interaction, is not parallel to any principal axis of the moment of inertia.

The other reason is that it is easy to have interacting partner levels nearby. Since this molecule is a near prolate asymmetric top with Ray's asymmetric parameter κ of -0.925 and has the permanent electric dipole moment along the b axis, each asymmetry K doublet has opposite ortho-para symmetry, and the energy separation of the pair reduces rapidly with the increase of K_a .

It should be noticed that the difference between observed and predicted frequencies is less than 7 kHz. Since the latter frequencies were determined by the separate spectral analyses of the ortho-ortho and para-para transitions, the energy offset between the ortho and para system was not directly determined. It may be an *a priori* assumption that there is no offset between the two states. The present experimental result ensures that, if there exists an energy offset between them, it should be smaller than this experimental value.

Finally, we have to make sure that what we observed is not the breakdown of the permutation symmetry but the direct experimental verification of ortho-para mixings in a molecule due to the hyperfine interaction. That is to say, this mixing gives us a chance to observe the radiative ortho-para transitions with about one-thousandth of the intensity of allowed transitions.

Using the formula of Einstein's A coefficient, this result concludes that the ortho-para conversion occurs in a few

thousand years through spontaneous emission even in circumstances where the temperature is cool and molecular collisions occur rarely like in interstellar space. Indeed, the features described above for the S_2Cl_2 molecule have an advantage for the detection of the ortho-para transitions. Since any molecule that has the C_2 symmetry axis has more or less the same character, it should be recognized that this is a common feature of such molecules.

The authors acknowledge many helpful discussions with Professor Takeshi Oka. This research was supported by the Ministry of Science and Technology of Taiwan under Grant No. MOST 104- 2113-M-009-020 (Y. E.) and a Grant-in-Aid for Scientific Research of the Ministry of Education, Science, Culture, and Sports of Japan [19654060].

*Corresponding author.

kanamori@phys.titech.ac.jp

- [1] P. A. M. Dirac, *Proc. R. Soc. A* **112**, 661 (1926).
- [2] W. Heisenberg, *Z. Phys.* **38**, 411 (1926).
- [3] P. R. Bunker and P. Jensen, *Fundamentals of Molecular Symmetry* (IOP, London, 2005).
- [4] G. Herzberg, *Spectra of Diatomic Molecules, Molecular Spectra and Molecular Structure Vol. 1* (Van Nostrand Reinhold, New York, 1950).
- [5] I. Ozier, P. Yi, A. Khosla, and N. F. Ramsey, *Phys. Rev. Lett.* **24**, 642 (1970).
- [6] R. F. Curl, J. V. V. Kasper, and K. S. Pitzer, *J. Chem. Phys.* **46**, 3220 (1967).
- [7] P. L. Chapovsky and L. J. F. Hermans, *Annu. Rev. Phys. Chem.* **50**, 315 (1999).
- [8] Z. D. Sun, K. Takagi, and F. Matsushima, *Science* **310**, 1938 (2005).
- [9] K. Fukutani and T. Sugimoto, *Prog. Surf. Sci.* **88**, 279 (2013).
- [10] T. Oka, *Orders of Magnitude and Symmetry in Molecular Spectroscopy; Handbook of High-Resolution Spectroscopy* (Wiley, New York, 2011).
- [11] M. Hayashi, K. Harada, R. Kavrach, T. Tanaka, and K. Tanaka, *J. Chem. Phys.* **133**, 154303 (2010).
- [12] K. Tanaka, K. Harada, and T. Oka, *J. Phys. Chem. A* **117**, 9584 (2013).
- [13] A. D. J. Critchley, A. N. Hughes, and I. R. McNab, *Phys. Rev. Lett.* **86**, 1725 (2001).
- [14] A. Miani and J. Tennyson, *J. Chem. Phys.* **120**, 2732 (2004).
- [15] R. Berger, M. Gottselig, M. Quack, and M. Willeke, *Angew. Chem., Int. Ed.* **40**, 4195 (2001).
- [16] A. Mizoguchi, S. Ota, H. Kanamori, Y. Sumiyoshi, and Y. Endo, *J. Mol. Spectrosc.*, **250**, 86 (2008).
- [17] Z. T. Dehghani, S. Ota, A. Mizoguchi, and H. Kanamori, *J. Phys. Chem. A* **117**, 10041 (2013).
- [18] H.-J. Werner *et al.*, MOLPRO version 2012.1, a package of *ab initio* programs, 2012; see <http://www.molpro.net>.
- [19] C. Cabezas, J.-C. Guillemin, and Y. Endo, *J. Chem. Phys.* **145**, 184304 (2016).