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Analysis of the nuclear quadrupole interaction of Disulfur Dichloride, S_2Cl_2

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ABSTRACT

Pure rotational spectra of $S_2{}^{35}Cl_2$ and $S_2{}^{35}Cl^{37}Cl$ have been observed using a Fourier-transform microwave spectrometer. An analysis of the hyperfine structure made by considering the nuclear spin statistics showed that S_2Cl_2 has C_2 symmetry, where the hyperfine splittings due to the two Cl nuclei were analyzed precisely. The nuclear quadrupole coupling constants including the off-diagonal ($\chi_{ab}, \chi_{ac}, \chi_{bc}$) components and the nuclear spin–rotation interaction constants associated with the two Cl nuclei have been determined for the first time. We have shown that the nuclear quadrupole interaction plays an important role in the *ortho–para* mixing.

1. Introduction

A number of spectroscopic studies for S_2X_2 (X = H, F, Cl, Br) have been performed since 1930s to determine their most stable structures [1–12]. In these studies, two types of most stable structures have been observed. One is a skew XSSX-type of configuration (Fig. 1a), and the other is a pyramidal S=SX_2-type of configuration (Fig. 1b). For disulfur difluoride (S_2F_2), two kinds of stable isomers were observed by microwave spectroscopy [1]. Rotational analyses of isotope species which consisted of ^{32}S and ^{34}S determined the molecular structures of the two isomers to be skew FSSF with C_2 symmetry and pyramidal S=SF_2 with C_s symmetry, respectively. Of these two, the S=SF_2 isomer is slightly more stable than the FSSF isomer, because the latter slowly isomerizes to the former at temperatures above −100 °C [2]. On the other hand, for S_2X_2 (X = H, Cl, Br), only the skew XSSX-type of configurations have been observed experimentally [3–10]. However, only S_2H_2 has been confirmed to have the C_2 symmetry about the *c*-axis by the observation of intensity alternation due to the nuclear spin statistics by microwave spectroscopy [3]. No experimental evidence has been obtained so far to prove that S_2Cl_2 [4–10] or S_2Br_2 [8] has C_2 symmetry.

Recently, S_2Cl_2 has received much attention as it is one of the best systems to achieve an experimental confirmation of parity violation in molecules [13]. Parity violation has already been confirmed in elementary particle physics [14,15] and in atoms [16], but has never been observed experimentally in a molecular system. Berger et al. [13] theoretically showed that the effect due to parity violation could be observed as a tiny energy difference between two enantiomers of S_2Cl_2, using their multiconfiguration linear response approach to electroweak quantum chemistry in the limit of the random phase approximation in combination with high level *ab initio* calculations. In order to confirm parity violation, we must prove that S_2Cl_2 has C_2 symmetry and that two enantiomers exist. We have to obtain detailed information on the energy levels before the observation of parity violation to distinguish whether a shift or splitting of a spectrum is caused by parity violation with an order of $\Delta E_{pv}/hc \sim 10^{-12}$ cm^{-1}, or by other effects such as the hyperfine interaction or a tunneling splitting.

As S_2Cl_2 has two Cl atoms with nuclear spin $I = 3/2$, complicated hyperfine splittings are expected due to the nuclear quadrupole interaction. In a previous study, Marsden et al. [10] have observed partly resolved hyperfine structures in the rotational transitions, and have determined the diagonal ($\chi_{aa}, \chi_{bb}, \chi_{cc}$) components of the nuclear quadrupole coupling constants of each Cl atom. The effect of the off-diagonal ($\chi_{ab}, \chi_{bc}, \chi_{ac}$) components of the nuclear quadrupole coupling constants was too small to be observed by their spectrometer. However, we cannot ignore the influence of the off-diagonal components because the shift or splitting is expected to be much larger than that due to parity violation. So far, a determination of the complete quadrupole coupling tensor including all the three off-diagonal components has been obtained for several molecules with a single coupling nucleus. In the case of molecules with two coupling nuclei, complete analysis with the off-diagonal nuclear quadrupole interaction terms have been done only for $SOCl_2$ [17] and CHBrClF [18].

In this work, we aimed at a complete analysis of the hyperfine structure for the rotational energy levels of the ground vibrational state of S_2Cl_2 using a Fourier-transform microwave spectrometer,

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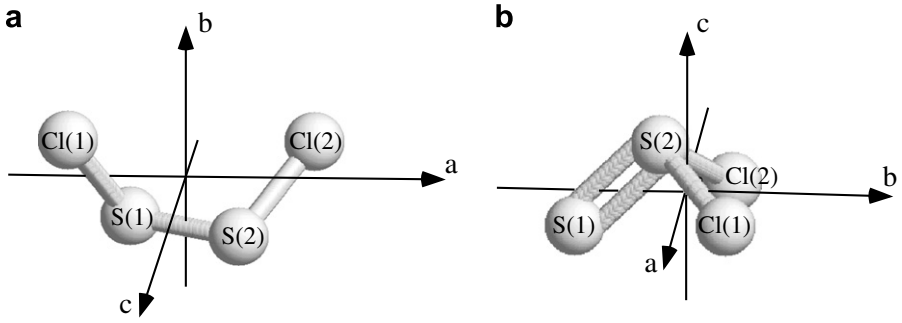

Fig. 1. Two S_2Cl_2 isomers. The numbers in parentheses are labeled for convenience to distinguish two equivalent atoms.

which has a higher resolution than that used in the previous measurement [10]. Observed transitions, with complicated splittings due to the hyperfine interaction, have been least-squares analyzed using an effective Hamiltonian including the nuclear quadrupole interaction and the nuclear spin–rotation interaction. The determined hyperfine constants, including all the off-diagonal components of the nuclear quadrupole coupling constants, reproduced the observed spectral patterns perfectly. Furthermore, the hyperfine resolved spectra confirm that the structure of S_2Cl_2 has C_2 symmetry. We also have shown that the nuclear quadrupole interaction played an important role in the *ortho–para* mixing.

2. Experimental

Rotational transitions of S_2Cl_2 have been measured using a Fourier-transform microwave spectrometer [19]. Details of the spectrometer have been described previously [20]. A commercial sample of S_2Cl_2 was used without purification. The Ar buffer gas was passed through a reservoir containing cotton, soaked in the liquid S_2Cl_2, just before the pulsed valve. The S_2Cl_2 vapor was expanded into a vacuum chamber with the Ar buffer gas at a stagnation pressure of 0.7 atm. A conical guide block was attached in front of the pulsed valve, so as not to produce splittings due to the Doppler effect. Molecules in the supersonic jet were polarized by a microwave pulse at 20 cm downstream from the pulsed valve. The FID signal from the molecule was detected and down-converted to signals with frequency about 1 MHz. The signal was accumulated for 100–500 shots at each frequency point. Fourier-transformation of the time domain signal yielded the spectrum of S_2Cl_2. The experimental accuracy of the frequency measurement is better than 10 kHz.

3. Results

Spectra of S_2Cl_2 have been observed easily in the region of 4–18.5 GHz based on the rotational constants determined by the previous microwave experiment [10]. Since spectra were observed with large S/N ratios, two isotopic species, $S_2{}^{35}Cl_2$ (56%) and $S_2{}^{35}Cl^{37}Cl$ (38%) were observed in their natural abundances. However, we did not observe transitions of $S_2{}^{37}Cl_2$ (6%) in the present experiment because of its low relative abundance. We observed 10 rotational transitions (7 for the *R*-branch and 3 for the *Q*-branch) for $S_2{}^{35}Cl_2$ and 11 rotational transitions (8 for the *R*-branch and 3 for the *Q*-branch) for $S_2{}^{35}Cl^{37}Cl$. The observed transition frequencies for $S_2{}^{35}Cl_2$ and $S_2{}^{35}Cl^{37}Cl$ are listed in Tables 1 and 2, respectively. Typical examples of the observed spectra are shown in Figs. 2 and 3a for $S_2{}^{35}Cl_2$ and Fig. 3b and 4 for $S_2{}^{35}Cl^{37}Cl$, in which the observed rotational lines were split by the nuclear quadrupole interaction of the two Cl nuclei. The number of lines for $S_2{}^{35}Cl_2$ (Fig. 2) are less than that of $S_2{}^{35}Cl^{37}Cl$ (Fig. 4) for the same rotational transition. This result strongly suggests the existence of the nuclear spin statistics due to the two equivalent Cl nuclei in $S_2{}^{35}Cl_2$. In this work, the following coupling scheme of the angular momenta is used. At first, two nuclear spin angular momenta $\mathbf{I}(1)$ and $\mathbf{I}(2)$ are coupled to give the total nuclear spin angular momentum $\mathbf{I}$, where I should be 0, 1, 2, 3 because $I(1)$ and $I(2)$ are 3/2. Then, $\mathbf{I}$ is coupled to the overall rotation $\mathbf{J}$, to give the total angular momentum $\mathbf{F}$. Hereafter, numbers in parentheses after the atomic symbol or the nuclear spin operator are used to distinguish two equivalent atoms as shown in Fig. 1(a). If $S_2{}^{35}Cl_2$ has C_2 symmetry, the nuclear spin statistics requires that a rotational level can couple only with a nuclear spin state with even resultant angular momentum ($I = 0, 2$) or odd ($I = 1, 3$). Since the symmetry axis is along the *b*-axis, the rotational levels can be classified into two; those with $K_aK_c = ee$, oo couple with even-I, and those with eo, oe couple with odd-I. In general, the former is referred as *para*-levels and the latter is referred as *ortho*-levels. We observed six lines for the lowest rotational transition, $J = 1_{11}–0_{00}$. If the nuclear spin angular momentum I is a *good* quantum number, the selection rule $\Delta I = 0$ allows only four transitions for $J = 1_{11}–0_{00}$ to be observed. However, the fact that two more lines with $\Delta I \neq 0$ were observed distinctly indicates that I is not strictly a *good* quantum number. Therefore, we have to use only $\Delta F = 0, \pm 1$ as a more general selection rule for the spectral assignment. By using the combination differences, consistent assignments of the quantum number F were obtained to all the hyperfine components of three rotational transitions, $J = 1_{11}–0_{00}$, $2_{20}–1_{11}$, and $1_{10}–1_{01}$.

The observed transitions were fitted to the following Hamiltonian,

$$\mathbf{H} = \mathbf{H}_{\text{rot.}} + \mathbf{H}_{\text{Q}} + \mathbf{H}_{\text{NSR}}, \tag{1}$$

where $\mathbf{H}_{\text{rot.}}$, $\mathbf{H}_{\text{Q}}$, and $\mathbf{H}_{\text{NSR}}$ correspond to the rotational term including the quartic centrifugal distortion effect, the nuclear quadrupole coupling term, and the nuclear spin–rotation interaction term, respectively. The $\mathbf{H}_{\text{rot.}}$ term is written in the Watson *A*-reduced form [21]. The $\mathbf{H}_{\text{Q}}$ and $\mathbf{H}_{\text{NSR}}$ terms consist of the sum of the nuclear hyperfine interaction terms due to the two Cl nuclei, *i.e.*

$$\mathbf{H}_{\text{Q}} = \sum_{i=1,2} \mathbf{Q}^{(2)}(i) \cdot \mathbf{V}^{(2)}(i),$$

$$\mathbf{H}_{\text{NSR}} = \sum_{i=1,2} \tfrac{1}{2} \sum_{k=0}^{2} [\mathbf{T}^{(k)}(\mathbf{C}(i)) \cdot \mathbf{T}^{(k)}(\mathbf{J}, \mathbf{I}(i)) + \mathbf{T}^{(k)}(\mathbf{J}, \mathbf{I}(i)) \cdot \mathbf{T}^{(k)}(\mathbf{C}(i))], \tag{2}$$

where the symbol i denotes each Cl nucleus. The nuclear quadrupole coupling constant χ_{ij} is expressed as the tensor product between the nuclear quadrupole moment tensor $\mathbf{Q}^{(2)}$ and the electric field gradient tensor $\mathbf{V}^{(2)}$. To calculate the matrix elements of these effective Hamiltonian terms, the Wang-transformed basis functions $|JK, (I(1)I(2))I, FM_F, \gamma\rangle$ were used, where γ is the parameter indicating the parity symmetry in a rotational state. If these basis functions are used, the matrix of $\mathbf{H}_{\text{rot.}}$ is divided into four blocks, which are classified as E^+, E^-, O^+, and O^- [21]. It should be noticed