Theoretical and Experimental Study of the Radiative Ortho-Para Transition in Disulfur Dichloride, S_2Cl_2

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Abstract:

Ortho-para transition in disulfur dichloride is studied theoretically and experimentally. Our calculation based on intensity borrowing from the opposite symmetric state shows that direct observation of the *ortho-para* transition in millimeter wave region could be possible. The *ortho-para* transition of $|10_{7\,3}\ 2\ 10\rangle^P$ - $|9_{6\,3}\ 1\ 9\rangle^O$ and $|10_{7\,4}\ 1\ 10\rangle^O$ - $|9_{6\,4}\ 2\ 9\rangle^P$ were surveyed by using supersonic jet spectroscopy.

Introduction:

Disulfur Dichloride (S_2Cl_2) has two Chlorine atoms with nuclear spin I = 3/2. As a result of coupling of two Cl nuclei, total nuclear spin of S_2Cl_2 is equal to I = 0,1,2,3. According to the Pauli Exclusion Principle there are restrictions on symmetry properties of molecular wave functions. By these restrictions the total molecular wave functions of the molecule are divided to *ortho* and *para* states. Although the conversion process between *ortho* and *para* states is known to be extremely small, it attracts researcher's attention. Most of studies have been done through collisional processes; however the studies of the radiative transition have been very limited. Essentially, the electric dipole transition moment between pure *ortho* and *para* states is zero. Nevertheless, hyperfine interactions can change the pure symmetric property of the molecular wave functions to be impure. It means that the total molecular wave function is mixture of both *ortho* and *para* states. By perturbation theory, the mixing coefficient of the molecular wave functions is represented by an equation

$$\langle \Psi^O |\, H_{O\text{-}P}\, | \Psi^P \rangle \ / \ (E_O - E_P),$$

where $H_{O\text{-}P}$ shows the interaction term between *ortho* and *para* states. Then *ortho-para* transition could have the transition moment through intensity borrowing. The collisional *ortho-para* transitions originated by nuclear spin - rotation interaction have been studied in some molecules theoretically and experimentally[1]. In case of S_2Cl_2, the nuclear electric quadruple interaction is the most important interaction that makes *ortho-para* mixing. The nuclear quadruple coupling constant of S_2Cl_2 has been determined by FTMW spectroscopy[2]. The off-diagonal χ_{ab} andχ_{ac} coupling constants which play the main role in the *ortho-para* interactions bring large off-diagonal elements among mostly degenerated *K*-doubling states which have the different symmetry. . This leads to appearing the *ortho-para* mixing coefficients in the molecular wave function.

Discussion and Results:

Using the hyperfine constants determined by FTMW[2] and rotational constants including up to sixth order centrifugal constants determined by millimeter microwave spectroscopy[3], the *ortho*-*para* mixing ratio of all molecular levels with quantum numbers up to F = 30 are calculated. The results show the rotational states with K_a larger than six are no more pure symmetric but are mixed with the opposite symmetry. The results also show intensity borrowing coefficients for the K_a-doubling states in the millimeter wave transition are so high that direct observation of the radiative *ortho*-*para* transition could be possible. As an example, the K_a-doubling states of $|9_{6\,3}\ 1\ 9>^{O}$ and $|9_{6\,4}\ 2\ 9>^{P}$, which denotes $|J_{KaKc}\ I\ F>^{O/P}$, are mixed with each other by squared coefficient of 0.4. Figure 1-a shows the predicted spectrum pattern corresponding to these two mixed *ortho*-*para* states. The pattern plotted by solid line is the spectra profile considering the *ortho*-*para* transition and the pattern in dashed line is the profile without it. Figure 1-b shows the direct absorption spectrum measured by supersonic jet spectroscopy in 81118 - 81121 MHz region. In this stage, the observed spectrum does not prove the theoretical prediction yet. As seen in the figures, the measured spectra profile is different from the predicted pattern. The broadening of two patterns looks different and there are unpredicted wings on both side of the measured spectrum. These differences might correspond to how to simulate the line profile. The line shape is assumed as Gaussian with FWHM of 0.2 MHz, but the actual line profile in the supersonic jet condition may be different from it. Anyway further improvement in the prediction of the candidate transition and more measurements are necessary for this work.

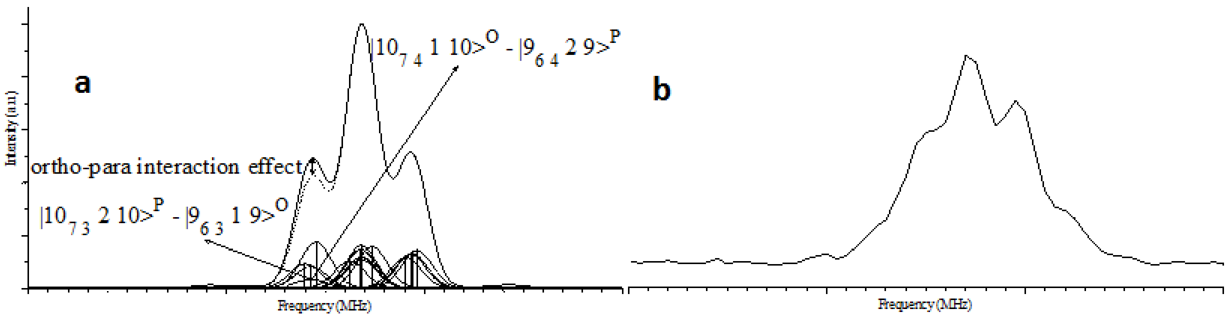

Figure1. a) Predicted pattern by *ortho*-*para* transition (solid) and without *ortho*-*para* transition (dashed). b) Measured spectrum by supersonic jet experiment. The frequency range is 81118 -81121 MHz with notching of 0.1MHz

References:

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