A Contribution to the Investigation of $T_2$-Relaxation: 
Rotational Transitions of OCS and SO$_2$

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With use of a Fourier transform microwave spectrometer in the range of 4 GHz to 18 GHz, the pressure dependence of collisional coherence dephasing times $T_2$, at room temperature has been determined for (a) the transition $J=0 \rightarrow J=1$ of OCS, $^{16}$OCS, and OC$^{34}$S, (b) nine transitions of SO$_2$ in ground state having $13 \leq J \leq 59$, and (c) eight transitions of SO$_2$ having $12 \leq J \leq 55$ in the first excited bending vibrational state, where $J$ is the rotational quantum number of the lower state.

1. Introduction

The relaxation of the radiation-induced polarization in the pure rotational transitions of carbonyl sulphide, OCS, is well understood on the basis of perturbative collisional theories [1, 2] by using electrostatic, inductive and dispersive long range interaction forces [3, 4]. It is useful to see the effect of isotopes on the relaxation which is expected to be small, because of the small changes in energy spacings and reduced mass. In the paper, an attempt was made to measure the pressure dependence of $T_2$ for the transitions $J=0 \rightarrow J=1$ of OCS, $^{16}$OCS and OC$^{34}$S in natural isotopic abundances. The results are also compared with the modified Murphy-Boggs theory [4].

The study of the second system reported here is sulphur dioxide SO$_2$. Because of the large number of closely spaced energy levels, the system is more complicated to understand theoretically. However, previous experimental and theoretical studies [5–11] reveal that the curve for the $J$-dependence of $1/T_2$, where $J$ is the rotational quantum number of the lower state, shows a maxima at some value $J_{\text{max}}$. Krishnaji et al. [5] have found from linewidth studies that the values of $J_{\text{max}}$ are different for the R- and P-transitions and are 18 and 20 respectively. Yang et al. [8] have also reported frequency domain linewidths measurements exhibiting a similar trend.

Transient emission techniques were used to determine $1/T_2$ by Dobbs et al. [9], Bestmann et al. [10] and Bomsdorf et al. [11]. From these studies, a similar behaviour of the $J$-dependence of $1/T_2$ was observed. However, due to the limited number of measurements, there was no further attempt to find the precise values of $J_{\text{max}}$ for P- and R-branch separately. In the present paper, we report the values of $1/T_2$ for more transitions of SO$_2$ in the ground as well as in the first excited bending vibrational state $v_2$.

2. Experimental

Fourier transform microwave spectrometers in J, X, and Ku-bands described earlier [12, 13, 14] have been used for the detection of the transient emission signal of the molecular sample following an intense microwave pulse. The frequency of the pulsed microwave radiation was chosen to be near resonant to the transitions of considerations and the molecular emission signal was observed at a beat frequency of about 30 MHz by frequency down conversion. 1024 data points were sampled at an interval of 10 ns starting after a delay of 500 to 1000 ns after the offset of the microwave pulse to eliminate perturbations by the reflected microwave pulse. OCS and SO$_2$ were used after vacuum distillation. Pressure measurements were made using a MKS Baratron 310 B capacitance manometer. The pressure ranges were from 1 mT to 40 mT for OCS and 1 mT to 25 mT for SO$_2$. All measurements were done at room temperature.

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Table 1. Measurement of the pressure dependence of the collisional dephasing rotational relaxation time $T_2$ ($= \sqrt{\beta}$) for the transition $J = 1 \rightarrow 0$ of different isotopes of OCS in natural abundances. Temperature: $300 \pm 2$ K, error in the double standard.

<table>
<thead>
<tr>
<th>System</th>
<th>$v_{FT}$ (MHz)</th>
<th>$v_{FfT}$ (MHz)</th>
<th>$\beta$ (µs$^{-1}$ mT$^{-1}$)</th>
<th>$\alpha$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCS–OCS</td>
<td>12162.971</td>
<td>12162.9803 (4)</td>
<td>0.0368 (8)</td>
<td>0.0089 (56)</td>
</tr>
<tr>
<td>OCS$^{18}$–OCS</td>
<td>11865.666</td>
<td>11865.6663 (6)</td>
<td>0.0377 (2)</td>
<td>0.0077 (18)</td>
</tr>
<tr>
<td>OCS$^{18}$–OCS</td>
<td>11409.711</td>
<td>11409.7155 (8)</td>
<td>0.0383 (4)</td>
<td>0.0121 (30)</td>
</tr>
</tbody>
</table>

Table 2. Measurement of the pressure dependence of the collisional dephasing rotational relaxation time $T_2$ for different rotational transitions of SO$_2$ at $300 \pm 2$ K, error in the double standard, $n$: normal species, $v_2$: first excited bending vibrational state (519 cm$^{-1}$) of $n$-species. $J'$ and $J$ denote upper and lower rotational states of transitions, respectively.

<table>
<thead>
<tr>
<th>Transitions $J' - J$</th>
<th>$v_{FT}$ (MHz)</th>
<th>$v_{FfT}$ (MHz)</th>
<th>$\beta$ (µs$^{-1}$ mT$^{-1}$)</th>
<th>$\alpha$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$1_{2,10} - 1_{3,13}$</td>
<td>8420.266</td>
<td>8420.280 (40)</td>
<td>0.1020 (50)</td>
<td>-0.020 (9)</td>
</tr>
<tr>
<td>$1_{4,12} - 1_{3,15}$</td>
<td>14587.770</td>
<td>14587.7663 (12)</td>
<td>0.1025 (6)</td>
<td>-0.0316 (92)</td>
</tr>
<tr>
<td>$1_{5,14} - 1_{4,11}$</td>
<td>7169.611</td>
<td>7169.6126 (4)</td>
<td>0.1007 (8)</td>
<td>0.0119 (13)</td>
</tr>
<tr>
<td>$1_{8,15} - 1_{7,14}$</td>
<td>9403.252</td>
<td>9403.242 (12)</td>
<td>0.1070 (20)</td>
<td>-0.027 (22)</td>
</tr>
<tr>
<td>$1_{7,22} - 1_{6,23}$</td>
<td>8911.130</td>
<td>8911.166 (104)</td>
<td>0.0970 (50)</td>
<td>0.048 (70)</td>
</tr>
<tr>
<td>$4_{8,38} - 4_{9,41}$</td>
<td>7503.438</td>
<td>7503.4402 (2)</td>
<td>0.0823 (6)</td>
<td>0.0118 (9)</td>
</tr>
<tr>
<td>$5_{1,43} - 5_{1,44}$</td>
<td>11472.333</td>
<td>11472.3381 (18)</td>
<td>0.0712 (16)</td>
<td>0.0321 (78)</td>
</tr>
<tr>
<td>$5_{5,46} - 5_{4,43}$</td>
<td>9240.706</td>
<td>9240.7373 (40)</td>
<td>0.0760 (20)</td>
<td>0.041 (2)</td>
</tr>
<tr>
<td>$6_{0,49} - 5_{9,48}$</td>
<td>5189.245</td>
<td>5189.2453 (4)</td>
<td>0.0756 (4)</td>
<td>0.0168 (36)</td>
</tr>
<tr>
<td>$v_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$1_{11,9} - 1_{2,10}$</td>
<td>10527.634</td>
<td>10527.6354 (8)</td>
<td>0.0923 (44)</td>
<td>0.0121 (129)</td>
</tr>
<tr>
<td>$2_{4,20} - 2_{3,19}$</td>
<td>11457.038</td>
<td>11457.0430 (8)</td>
<td>0.0931 (30)</td>
<td>0.0122 (105)</td>
</tr>
<tr>
<td>$2_{8,22} - 2_{7,21}$</td>
<td>6326.685</td>
<td>6326.6875 (4)</td>
<td>0.1028 (14)</td>
<td>0.0141 (24)</td>
</tr>
<tr>
<td>$3_{3,25} - 3_{2,24}$</td>
<td>8797.393</td>
<td>8797.3916 (18)</td>
<td>0.0983 (14)</td>
<td>0.0063 (50)</td>
</tr>
<tr>
<td>$3_{6,30} - 3_{4,27}$</td>
<td>9509.683</td>
<td>9509.671 (8)</td>
<td>0.1020 (40)</td>
<td>0.021 (12)</td>
</tr>
<tr>
<td>$4_{0,33} - 3_{9,32}$</td>
<td>5086.252</td>
<td>5086.2522 (6)</td>
<td>0.0939 (14)</td>
<td>0.0135 (44)</td>
</tr>
<tr>
<td>$5_{1,43} - 5_{0,40}$</td>
<td>11994.413</td>
<td>11994.4177 (5)</td>
<td>0.0834 (11)</td>
<td>-0.0051 (71)</td>
</tr>
<tr>
<td>$5_{6,46} - 5_{5,43}$</td>
<td>5636.827</td>
<td>5636.8258 (24)</td>
<td>0.0791 (26)</td>
<td>0.0202 (102)</td>
</tr>
</tbody>
</table>

The transient decay emission signal was fitted by a least square fit program to the following expression

$$S(t) = S(0) \exp(-t^2/4\beta^2)$$

- $\exp(-t/T_2) \cos(\omega t + \Phi)$, (1)

where $S(t)$ is the value of the signal at time $t$, $S(0)$ is the value of the emitted signal at the offset of the microwave pulse, $q$ is related to the Doppler half width $\Delta v_D = \sqrt{\ln 2/2\pi q}$, $T_2$ is the collisional dephasing time, $\omega$ is the angular beat frequency of the oscillating signal and $\Phi$ is the phase with $S(0)$, $1/T_2$, $\omega$ and $\Phi$ as fitting parameters. Within the experimental accuracy, expression (1) for $S(t)$ was found to be sufficient to describe the observed transient emission signals and no attempt was made to account for non-exponential decay behaviour [15, 16] besides the Doppler factor in (1).

The pressure dependence of $1/T_2$ was obtained by the linear least square fit of the following expression

$$1/T_2 = \chi + \beta p,$$

where $\chi$ is the intercept and $p$ is the pressure. A fit similar to (2) was done to obtain the pressure dependence of the frequency of oscillation. However, the effect in the most cases was found to be negligible within experimental errors. $v_{FfT}$ shown in Tables 1 and 2 is the extrapolated frequency at zero pressure, as obtained from the intercept $\chi$ of the beat frequency fit procedure.
3. Results and Discussions

The results obtained for OCS and SO$_2$ are given in Tables 1 and 2, respectively. It can be seen from the Tables that the transition frequency $v_{FIT}$ obtained by the fit method mentioned above is in agreement with the value $v_{FT}$ obtained by line-shape analysis after transformation from time to frequency domain (using a Cooley-Tukey fast Fourier transform algorithm). That some values of the intercepts $x$ for the SO$_2$–SO$_2$ system are negative indicates uncertainties of absolute pressure measurements, in particular the zero pressure meter setting.

The ratios of $1/T_2$ for OC$^{34}$S and $^{18}$OCS to the corresponding value of OCS are 1.02 (3) and 1.04 (3) respectively, where the values in the parentheses are the double standard deviations of the fit in the last significant digits. The ratio for the transition $J = 1 \rightarrow J = 2$ of OC$^{34}$S has been found previously to be 0.987 (3) [17] and 0.95 (6) [11]. Considering additional inaccuracies in our and previous results which may be partly due to pressure and temperature variations indicate that the isotopic effects on $T_2$-relaxation are negligible. This has been confirmed by recent theoretical calculations, using a modified Murphy-Boggs-theory [4], of the width parameters of the $J = 0 \rightarrow 1$ transition for the $^{18}$OCS–OCS and the OC$^{34}$S–OCS systems. These theoretical ratios for the transition $J = 0 \rightarrow 1$ are found to be 0.99 in the both cases.

The experimental values of $1/T_2$ for the R- and P-transitions of SO$_2$ versus $J'$ where $J'$ is rotational quantum number of upper state are shown in Fig. 1 along with earlier results. The $J$-dependence has a similar trend as reported earlier [8, 9, 10, 11]. The Boltzmann-factor averaged over all $K_-$ and $K_+$ for SO$_2$ has a maximum at $J = 18$, from which a maximum value of $1/T_2$ is expected to be around $J = 18$. The measurements for the transitions with $J$ quantum number close to the expected maximum at $J = 18$ for both P and R-branch would be required for the more accurate determination of the maximum. The value of $1/T_2$ for the transition $^{18}$S$_{3,15}$ $\leftrightarrow$ $^{17}$S$_{4,14}$ of SO$_2$ in the ground state shows the maximum for the R-branch [10]. It is not possible to determine the value of $J_{max}$ for P-branch because no value has been reported around $J = 18$. However, the available experimental values indicate the value of $J_{max}$ between $J = 15$ to $J = 23$. Although it is not possible to determine the value of $J_{max}$ for P- and R-transitions of SO$_2$ in the excited state due to the nonavailability of data around the expected value of $J_{max} = 18$, the available data indicate the similar $J$-dependence as in the case of the ground state. An extension to an upper frequency range of the Fourier transform microwave spectrometer will be useful to provide data in the considered range.

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