The Pressure Dependence of T_2-Relaxation Rates for Rotational Transitions of Sulfur Dioxide in Mixtures with Oxygen and Nitrogen

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The transient emission technique in the time domain has been used to determine the pressure dependence of the coherent dephasing time T_2 of sulfur dioxide in mixtures with O_2 and N_2 for several rotational transitions in the vibrational ground state. From these data line broadening parameters $\Delta\nu/p$ and collisional cross-sections are calculated.

Introduction

Besides the fundamental interest for intermolecular interactions, the investigation of the pressure dependence of T_2-relaxation rates for rotational transitions of gaseous molecules provides information about pressure broadening of spectral lines in the microwave and optical region. Such data are particularly important for models to interprete the results of spectroscopic technique of monitoring trace gases in the terrestrial atmosphere.

Sulfur dioxide plays an important role as an air pollutant which contributes predominantly to the environmental problem of acid rain when being converted to sulfuric acid in the atmosphere. Therefore the capability of detecting and quantifying sulfur dioxide in the air is the first important step to avoid its emission into the environment.

Line broadening parameters of spectral lines ($\sim 1/T_2$) of SO_2 broadened by the major constituents of the air (N_2 and O_2) are essential for the interpretation of remote sensing techniques like atmospheric laser probing [1].

Experimental

We report on the pressure dependence of T_2-relaxation for several rotational transitions of SO_2 in the ground vibrational state in mixtures with O_2 and N_2. The experiments were carried out in the frequency range from 7 to 25 GHz with microwave Fourier transform (MWFT) spectrometers in J- and in X-band and with a MW-bridge type pulse spectrometer in K-band. Experimental details and setup's are given elsewhere [2–4]. Pressure measurements were done with a MKS-Baratron capacitance manometer. The partial pressure fo SO_2 was maintained at about 3 mTorr, the partial pressures of the foreign gases were varied from 0–60 mTorr. SO_2 was purchased from J. T. Baker, Nitrogen and Oxygen from Messer-Griesheim, respectively.

The mixtures were established by adding small amounts of the perturbing gases into the sample cell, which was previously filled with a certain amount of SO_2. Some measurements were performed with ternary systems consisting of sulfur dioxide and the buffer gases N_2 and O_2. In this case the sample cell was filled with certain amounts of SO_2 and one of the foreign gases. The partial pressure of the other perturber was varied in the range given above. The results did not differ significantly from those obtained in binary mixtures. All measurements were done at room temperature (295 ± 3 K).

Analysis and Results

The transient emission decay signals $S(t)$ at each pressure, being detected after pulse excitation and frequency down conversion, were analysed by comparison with a theoretical expression. In case of the measurements in J- and in X-band the down conversion leads to a centre frequency of about 30 MHz (exactly 30 MHz in case of resonant excitation), and the equa-

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tion used is

$$S(t) = S_0 \exp[-t^2/4q^2] \exp[-t/T_2] \cos(\Omega t + \varphi). \quad (1)$$

The analysis was carried out with a least squares fitting program with S_0, T_2, Ω and φ as fitting parameters. The term $\exp[-t^2/4q^2]$, related to the doppler dephasing of the transient signal, was held fixed; the constant q is given by the Doppler half-width ($\Delta\nu_D = (\ln 2)^{1/2}/2\pi q$). No significant pressure dependence of the angular beat frequency Ω was observed.

The measurements in K-band were done with a bridge-type spectrometer with down conversion of the microwave frequency to DC. In this case the equation

$$S(t) = S_0 \exp[-t^2/4q^2] \exp[-t/T_2] + C \quad (2)$$

was used to analyse the recorded transient signals with C being an arbitrary offset.

The pressure dependence of $1/T_2$ was obtained by a linear least squares analysis of the fit results for $1/T_2$ at each sample pressure according to the expression

$$1/T_2 = \alpha + \beta p, \quad (3)$$

with α containing contributions from wall collisions as well as from self-broadening of SO_2, and p being the partial pressure of the foreign gas. In case of the ternary mixtures with one of the foreign gases maintained at a fixed partial pressure, α also contains the contributions from those collisions.

The resulting rate coefficients of the investigated systems may be converted to the more familiar pressure broadening parameters ($\Delta\nu/p = \beta/2\pi$), which characterize the pressure dependence of the half-width of the lines.

According to gas kinetic considerations for a hard sphere collisional model, effective cross sections may be evaluated from the experimental results with the expression

$$\sigma_{\mathrm{eff}} = \beta(\pi k T \mu/8)^{1/2}, \quad (4)$$

where μ is the reduced mass of the collision partners.

The results of our investigations are compiled in Tables 1 and 2. Table 1 contains the quantum numbers and frequencies of the investigated transitions, together with a labeling number to identify them in the following tables. The pressure broadening parameters and effective collisional cross sections are given for the binary systems SO_2–N_2 and SO_2–O_2 in Table 2.

Theoretical calculations [5] based on an Anderson-Tsao-Curnutte theory of line-broadening were avail-

Table 1. Investigated rotational transitions of SO_2 in the vibrational ground state.

Nr.	Transition $J(K_-, K_+)$–$J'(K'_-, K'_+)$	Frequency [MHz]
1	2 (0, 2) – 1 (1, 1)	12 256.583
2	10 (2, 8) – 11 (1, 11)	11 788.728
3	12 (2, 10) – 13 (1, 13)	8 420.275
4	15 (2, 14) – 14 (3, 11)	7 169.613
5	18 (3, 15) – 17 (4, 14)	9 403.232
6	22 (5, 17) – 23 (4, 20)	12 132.464
7	24 (4, 40) – 23 (5, 19)	22 482.513
8	27 (6, 22) – 28 (5, 23)	8 911.115
9	29 (5, 25) – 28 (6, 22)	6 837.404
10	34 (6, 28) – 33 (7, 27)	6 848.444
11	35 (6, 30) – 34 (7, 27)	25 049.399
12	37 (18, 30) – 38 (7, 31)	19 637.021
13	48 (10, 38) – 49 (9, 41)	7 503.440

Table 2. Experimental and theoretical [5] values of the T_2-relaxation parameter β, line broadening parameter $(\Delta\nu/p)$ and collisional cross section σ_{eff} for rotational transitions of SO_2 in mixtures with N_2 (**A**) and O_2 (**B**) at 295 ± 3 K. The errors in parentheses are the single standard deviation and given in units of the last digit. The labeling numbers of the transitions refer to Table 1.

Trans. Nr.	β_{exp} [μs^{-1} mTorr^{-1}]	β_{theor}	$\Delta\nu/p$ [MHz Torr^{-1}]	σ_{eff} [nm^2]
A				
1	0.0294 (3)	0.0295	4.68 (5)	1.131 (12)
2	0.0268 (4)	0.0305	4.27 (6)	1.031 (16)
3	0.0271 (1)	0.0302	4.13 (2)	1.042 (4)
4	0.0267 (3)	0.0285	4.25 (5)	1.027 (12)
5	0.0271 (5)	0.0273	4.27 (6)	1.042 (20)
6	0.0248 (2)		3.95 (3)	0.954 (8)
7	0.0265 (6)		4.22 (10)	1.019 (24)
8	0.0235 (2)		3.74 (3)	0.904 (8)
9	0.0261 (3)		4.15 (5)	1.004 (12)
10	0.0250 (2)		3.98 (3)	0.962 (8)
11	0.0255 (4)		4.06 (6)	0.981 (16)
12	0.0278 (3)		4.42 (5)	1.059 (12)
13	0.0243 (2)		3.87 (3)	0.945 (8)
B				
1	0.0222 (1)	0.0126	3.53 (2)	0.916 (4)
2	0.0182 (2)	0.0134	2.90 (3)	0.751 (8)
3	0.0188 (2)	0.0131	2.99 (3)	0.776 (8)
4	0.0187 (1)	0.0129	2.98 (2)	0.771 (4)
5	0.0174 (22)	0.0123	2.77 (35)	0.718 (91)
6	0.0178 (1)		2.83 (2)	0.735 (4)
7	0.0230 (6)		3.66 (9)	0.949 (24)
8	0.0173 (1)		2.75 (2)	0.714 (4)
9	0.0178 (1)		2.83 (2)	0.735 (4)
10	0.0177 (1)		2.82 (2)	0.730 (4)
11	0.0195 (2)		3.10 (3)	0.805 (8)
12	0.0196 (3)		3.12 (5)	0.809 (12)
13	0.0173 (1)		2.75 (2)	0.714 (4)

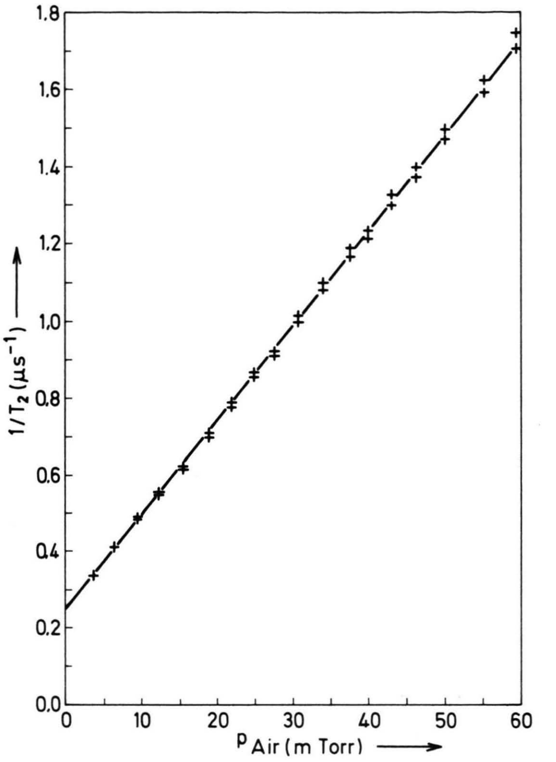

Fig. 1. Experimental results for the air partial pressure dependence of $1/T_2$ for the rotational transition $J(K_-, K_+)-J'(K'_-, K'_+) = 15(2, 14) - 14(3, 11)$ of SO_2 in mixture with air at 295 K together with the fitted straight line. The error bars denote twice the standard deviations from fit results of the transient emission signals. – The partial pressure of SO_2 was held fixed at 3.3 mTorr. – The error bars are indicated with double-crosses.

able for nitrogen- and oxygen-broadening of some microwave lines of sulfur dioxide with lower J-values. They are also compiled in the corresponding tables. The accordance with the empirical values is rather poor, especially in case of oxygen-broadening.

Table 3. Experimental and calculated values of the T_2-relaxation parameter β and the line broadening parameter $(\Delta\nu/p)$ for the rotational transition $J(K_-, K_+)-J'(K'_-, K'_+) = 15(2, 14) - 14(3, 11)$ (Nr. 4 in Table 1) of SO_2 in mixtures with air at 295 K. The errors in parentheses are the single standard deviation and given in units of the last digit. – The calculation was done according to Equation (5).

	β_{air} [μs^{-1} mTorr^{-1}]	$\Delta\nu/p$ [MHz Torr^{-1}]
Experimental	0.0249 (1)	3.96 (2)
Calculated	0.0250 (3)	3.98 (5)

Line broadening parameters for mixtures of sulfur dioxide with air may be calculated from the corresponding data for mixtures with nitrogen and oxygen according to

$$\beta(\text{Air}) = 0.79\,\beta(N_2) + 0.21\,\beta(O_2) \tag{5}$$

because the individual contributions of both buffer gas components do not depend on each other. As a test of (5), the air broadening parameter of one transition of SO_2 (Nr. 4 in Table 1) in mixtures with air was analysed with the partial pressure of the air being varied in the range from 0 to 60 mTorr. The air was taken from a lecture bottle purchased from Messer-Griesheim. The result given in Table 3 confirms the value predicted by (5). Figure 1 shows the pressure dependence of the relaxation rate $1/T_2$ for the investigated rotational transition of SO_2 together with the fitted straight line according to (3).

Acknowledgements

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