***J*-Dependence of T_2 -Parameters for Rotational Transitions of SO₂ and CH₃OH in *K*-Band**

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With the help of a microwave Fourier transform spectrometer in the range from 18 GHz to 26 GHz, the coefficients β for the linear pressure dependence of collisional dephasing rates $1/T_2$ have been determined by the transient emission technique for fourteen pure rotational transitions of SO₂ with $5 \leq J' \leq 66$ in the ground vibrational state, twelve transitions with $8 \leq J' \leq 62$ in the first excited bending vibrational state, and twelve transitions of methanol with $2 \leq J' \leq 11$, where J' is the rotational quantum number of the upper level of a transition. The T_2 -parameter β for the transition $J(K_-, K_+) = 49(4, 46) - 48(5, 43)$ of SO₂ in the ground state shows an anomalous behaviour, whereas the values for all other transitions show a J -dependence in accordance with previous results. No significant variation of T_2 -parameters with J has been found for the rotational transitions of CH₃OH.

The objective of the present note is to report the pressure dependence of T_2 -relaxation for several rotational transitions of SO₂ and CH₃OH in the frequency range from 19 GHz to 26 GHz by the microwave transient emission technique [1] with the help of a *K*-band microwave Fourier transform spectrometer [2]. Details of the experimental method are given in [1].

SO₂ (purity 99.98%) and CH₃OH (purity >99.5%) were purchased from J.T. Baker Co. and Merck-Schuchardt Co., respectively, and used without further purification. The pressures were measured with a MKS baratron 310 B capacitance manometer and were in the range from 1 mTorr to 25 mTorr for SO₂ and 1 mTorr to 15 mTorr for CH₃OH. All measurements were done at room temperature.

The transient emission decay signals were analyzed by least squares fitting the expression

$$S(t) = \sum_{i=1}^N S_i(0) \exp(-t/T_{2i} - t^2/4p_i^2) \cos(\omega_i t + \phi_i) \quad (1)$$

to account for several transitions in the observed frequency range (50 MHz). $S(t)$ is the value of the signal at time t and N is the number of observed transitions excited by the microwave pulse. For the

i -th observed transition, $S_i(0)$ gives the signal amplitude at the offset of the microwave pulse, q_i is related to the Doppler half width $\Delta\nu_{D,i} (= \sqrt{\ln 2/2\pi} q_i)$, T_{2i} is the collisional dephasing time, ω_i the angular beat frequency and ϕ_i the phase, with $S_i(0)$, $1/T_{2i}$, ω_i and ϕ_i as fitting parameters for all N transitions.

The pressure dependence of $1/T_{2i}$ for the i -th transition is described by the slope β_i obtained from the linear least squares fit of the expression

$$1/T_{2i} = \alpha_i + \beta_i p, \quad (2)$$

where α_i is the intercept and p is the pressure.

The results for the slopes β are denoted by " T_2 -parameters" here and are given for rotational transitions of SO₂ and CH₃OH in Table 1 and 2, respectively, along with the results from previous studies. In addition, the tables give the resonance frequencies of the transitions (ν_{FIT}) as obtained from the extrapolated beat frequency fit procedure at zero pressure [1]. These frequencies are in good agreement with the values reported earlier [3, 4]. The given uncertainties for ν_{FIT} are smaller than the usual frequency errors in MWFT spectroscopy and do not reflect systematic deviations.

The J -dependence of T_2 -parameters for rotational transitions of SO₂ in the ground as well as in the first excited bending vibrational state is similar to the trend as reported earlier [1] with the exception of the ground state rotational transition $J(K_-, K_+) = 49(4, 46) - 48(5, 43)$. The reason for this anomalous behaviour of this transition is not clear.

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Table 1. Values of T_2 -parameters β for different rotational transitions of SO₂ normal species at (300 ± 5) K. Errors in parantheses are in the last digit given and twice the standard deviation. ν_{FIT} : Zero pressure resonance frequency.

Transition	ν_{FIT}	β [μs^{-1} mTorr $^{-1}$]		
$J'(K'_-, K'_+) - J(K_-, K_+)$	[MHz]	this work	others	
g = ground vibrational state				
5 (2, 4) – 6 (1, 5)	23414.2493 (4)	0.0933(14)	0.0910(20) [7]	0.0880(30) [8]
8 (2, 6) – 9 (1, 9)	24083.4781 (2)	0.0960(10)	0.0940(10) [7]	0.0940(30) [8]
8 (1, 7) – 7 (2, 6)	25392.8195 (4)	0.0917(26)	0.0930(10) [7]	
12 (3, 9) – 13 (2, 12)	20335.4053 (2)	0.1068(10)	0.1070(30) [8]	0.1108(32) [2]
21 (5, 17) – 22 (4, 18)	24309.5913(22)	0.1088(22)	0.1030(10) [7]	0.1070(30) [8]
24 (4, 20) – 23 (5, 19)	22482.5595 (6)	0.1082(24)	0.1050(10) [7]	0.1070(30) [8]
35 (6, 30) – 34 (7, 27)	25049.4513 (2)	0.1077(10)	0.0940(20) [7]	
37 (8, 30) – 38 (7, 31)	19637.0642 (2)	0.0932 (6)	0.0952(10) [2]	
40 (7, 33) – 39 (8, 32)	23034.8144 (6)	0.0947(16)	0.0910(10) [7]	0.0940(30) [8]
42 (9, 33) – 43 (8, 36)	24319.6578 (2)	0.0886 (6)	0.0890(20) [7]	
49 (4, 46) – 48 (5, 43)	24915.7487 (6)	0.1069(20)		
61 (11, 51) – 60(12, 48)	25883.6060 (6)	0.0764(14)		
63 (13, 51) – 64(12, 52)	19306.2054(10)	0.0718(10)		
66 (12, 54) – 65 (13, 53)	21761.3840(500)	0.0779(120) *, a		
ν_2 = first excited bending vibrational state				
8 (1, 7) – 7 (2, 6)	22065.6835(10)	0.0991(12)		
14 (2, 12) – 15 (1, 15)	19681.1302 (4)	0.1045 (6)		
17 (2, 16) – 16 (3, 13)	22733.9652 (4)	0.1080(12)		
22 (5, 17) – 23 (4, 20)	22904.9041 (6)	0.1124(16)		
25 (2, 24) – 24 (3, 21)	21264.3251(10)	0.1122(12)		
27 (6, 22) – 28 (5, 23)	22220.3635(12)	0.1094(22)		
30 (5, 25) – 29 (6, 24)	22928.5795 (4)	0.1047(14)		
41 (7, 35) – 40 (8, 32)	24796.9407 (4)	0.0960(14)		
43 (9, 35) – 44 (8, 36)	23206.2937 (6)	0.0894(12)		
46 (8, 38) – 45 (9, 37)	19229.6291(180)	0.0859(36) *, b		
59 (12, 48) – 60 (11, 49)	21479.4035(40)	0.0763(42)		
62 (11, 51) – 61 (12, 50)	20031.0165(50)	0.0666(64) *, c		

* Fitted with an expression having two exponential terms, i.e. $N = 2$ in (1). For all other transitions, $N = 1$ was used.^a The transition 12(3, 9)–13(2, 12) in the vibrational state (1, 0, 0) with the resonance frequency 21 768.64 MHz was also observed with a signal intensity of about 60% of the transition given in the table. The T_2 -parameter for this additional transition was determined to 0.0728(208) μs^{-1} mTorr $^{-1}$.^b The transition 24(4, 20)–23(5, 19) in the vibrational state (1, 0, 0) with the resonance frequency 19 226.75 MHz was also observed with a signal intensity of about 15% of the transition given in the table. The T_2 -parameter for this additional transition was determined to 0.0984(124) μs^{-1} mTorr $^{-1}$.^c Additional transition at frequency 20046.36 MHz observed (not assigned).Table 2. Values of T_2 -parameters β for different rotational transitions of CH₃OH in the ground vibrational state at (300 ± 5) K. Errors in parantheses are in the last digit given and twice the standard deviation.

Transition $J', K' - J, K$	ν_{FIT} [MHz]	β [μs^{-1} mTorr $^{-1}$]	
		this work	Ref. [5]
2, 1 – 3, 0(E)	19967.3961(2)	0.1048(16)	
5, 2 – 5, 1(E)	24959.0789(4)	0.1092(14)	0.1131(13)
6, 2 – 6, 1(E)	25018.1225(4)	0.1135(42)	
7, 1 – 7, 1(A)	23346.9558(6)	0.1134(14)	
7, 2 – 7, 1(E)	25124.8719(4)	0.1125(16)	
8, 2 – 8, 1(E)	25294.4165(2)	0.1095(16)	0.1219(13)
9, 2 – 9, 1(E)	25541.3979(4)	0.1131(20)	
9, 2 – 10, 1(A+)	23121.0242(5)	0.1142(16)	
10, 2 – 10, 1(E)	25878.2661(4)	0.1105(28)	
10, 1 – 9, 2(A–)	23444.7783(6)	0.1141(16)	
11, 2 – 11, 1(E)	26313.1239(4)	0.1096(34)	
11, 1 – 10, 2(A+)	20171.0891(4)	0.1091(30)	

From Table 2 it can be seen that the T_2 -parameters for rotational transitions of CH₃OH do not change significantly with the rotational quantum number J . The values of T_2 -parameters for two transitions reported earlier from linewidth studies with a microwave saturation spectrometer [5] are larger than the corresponding values obtained from the present method. This difference may be because of the two different techniques used: the transient emission technique involves the detection of the molecular signal in absence of an external radiation, which is present in the saturation spectroscopic technique. Only in the limit of low power the results for the pressure dependence of collisional dephasing times will be the same for the two techniques [6]. It

may also important to note that a larger pressure range from 10 mTorr to 200 mTorr was used in [5].

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