Investigation of T_2-relaxation with a Microwave Pulse Spectrometer Rotational Lines of Formaldehyde and Sulfurdioxide

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We discuss the features of a MW-pulse spectrometer as applied to time-resolved investigation of T_2-relaxation of rotational transitions. The pressure dependence of $1/T_2$ of various transitions of formaldehyde, HCHO, and sulphurdioxide, SO_2, has been studied at room temperature. Results are given for different isotopic species and vibrational states and compared with earlier linewidth studies and theoretical calculations.

In the recent years collisional relaxation was of great interest. Although many researchers contributed to that field many questions are open and more measurements should be provided. In addition the methods of measurement should be complemented. Hitherto the determination of the linewidth and application of the Stark switch method to produce transient phenomena were the source of experimental data in the microwave region [1, 2].

We constructed a MW-pulse spectrometer [3]* which is equally suited to supply data in the time and frequency domain. The measurements of the transient signals in the time domain may be converted to the frequency domain by a Fourier transformation with a dedicated computer.

The pulse method has several features complementary to the other methods.

As a transient emission signal is observed saturation effects are excluded. In performing line width measurements saturation must be carefully considered as a certain microwave power is necessary for detection [4].

Modulation broadening is avoided by the pulse method. For line width measurements modulation techniques are commonly used to increase the sensitivity.

It is possible to polarize transitions with high rotational quantum numbers J. With the transient Stark switch technique only low J-lines may be investigated, as the magnitude of the Stark pulse is practically limited. Hence switching on and off resonance is not feasible for high J-lines.

In our present set up it is not possible to polarize single M-satellites, as can be done by the Stark switching method for low J-lines, sometimes with the help of a DC-bias. By a special cell this disadvantage of the pulse method may be overcome.

The movement of the molecule in the inhomogeneous field of the microwave pulse may be neglected, as the pulse length is typically 50 ns. The pulses of the Stark switch are typically 1000 ns as lower MW-power is used.

A dispersion of the MW-pulse travelling down the waveguide could not be observed.

The difficulty to produce an exact $\pi/2$-puls for all molecules in a certain cross section is common to both the pulse and Stark switch method, as the waveguide mode produces an inhomogeneous field.

The most striking advantage of the pulse method is the increase of sensitivity with respect to the Stark switch method. Comparison within our laboratory shows an increase of at least one order of magnitude. Lines with an absorption coefficient of $5 \cdot 10^{-8}$ cm^{-1} may be investigated now.

Presently our spectrometer is designed for the Ku-band (12–18 GHz). Extension to lower frequencies seems to be straightforward. For higher frequencies certain microwave components, as switches and TWT's, are still not available.

We measured the pressure dependence of the dephasing rotational relaxation time T_2 of formaldehyde, HCHO, and Sulfurdioxide SO_2 at room temperature. Lines of isotopic species of an excited

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* Details of the construction and performance will be published later.

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Table 1. Measurement of the pressure dependence of the dephasing rotational relaxation time T_2. Formaldehyde. Temperature 300 ± 2 K, error is the double standard error of the fit. *n*: normal species $H^{12}CHO$. ^{13}C: $H^{13}CHO$ in natural abundance.

$J_{K_-K_+} - J'_{K'_-K'_+}$		Frequency[a] [MHz]	β_{exp} [μsec^{-1} mTorr^{-1}]		β_{calc}	Estimated absorption coefficient [cm^{-1}]
$2_{1,1} - 2_{1,2}$	*n*	14 488.481	.141 ± .004	.138[b]	.165[c]	5.5 E-5
$8_{2,6} - 8_{2,7}$		14 726.639	.157 ± .008			1.3 E-5
$15_{3,12} - 15_{3,13}$		11 753.132	.124 ± .003[d]			9.2 E-6
$16_{3,13} - 16_{3,14}$		17 027.477	.125 ± .004			1.5 E-5
$24_{4,20} - 24_{4,21}$		14 360.930	.080 ± .004			4.7 E-5
$33_{5,28} - 33_{5,29}$		14 211.797	.0438 ± .0014			5.2 E-8
$2_{1,1} - 2_{1,2}$	^{13}C	13 778.810	.150 ± .002			5.5 E-7
$8_{2,6} - 8_{2,7}$		13 287.325	.164 ± .005			1.2 E-7
$16_{3,13} - 16_{3,14}$		14 592.409	.133 ± .008			1.3 E-7

[a] Frequencies remeasured. They fit better to the predicted frequencies of [11] than the measured frequencies of [11].
[b] From line width measurement $\Delta\nu_p = 22$ MHz/Torr of [7].
[c] From [9]. [d] The anomally reported in [8] was not observed.

Table 2. Measurement of the pressure dependence of the dephasing rotational relaxation time T_2. Sulfurdioxide. Temperature 300 ± 2 K, error is the double standard error. *n*: normal species $^{32}SO_2$. ν_2: first excited vibrational state (519 cm^{-1}) of $^{32}SO_2$. ^{34}S: $^{34}SO_2$ in natural abundance.

$J_{K_-K_+} - J'_{K'_-K'_+}$		Frequency[a, b] [MHz]	β_{exp} [μsec^{-1} mTorr^{-1}]		β_{calc}[f]	Estimated[g] absorption coefficient [cm^{-1}]
$1_{1,1} - 2_{0,2}$	*n*	12 256.64	.084 ± .002	.082[c]	.088	1.5 E-6
$10_{2,8} - 11_{1,11}$		11 788.80	.096 ± .002	.107[c]	.100	2.0 E-6
$14_{2,12} - 15_{1,15}$		14 587.60	.098 ± .005	.094[c]	.100	1.8 E-6
$22_{5,17} - 23_{4,20}$		12 132.40	.101 ± .008			3.6 E-6
$32_{7,25} - 33_{6,28}$		16 681.03	.107 ± .002			3.4 E-6
$45_{8,38} - 44_{9,35}$		17 539.94	.087 ± .002			9.4 E-7
$50_{9,41} - 49_{10,40}$		13 599.50	.089 ± .002			2.6 E-7
$58_{12,46} - 59_{11,49}$		15 470.40	.082 ± .005			
$1_{1,1} - 2_{0,2}$	ν_2	13 457.50	.086 ± .002		(.088)	1.5 E-7
$10_{2,8} - 11_{1,11}$		16 126.89	.091 ± .002		(.100)	3.1 E-7
$12_{2,10} - 13_{1,13}$		13 084.10	.101 ± .003		(.100)	1.6 E-7
$25_{4,22} - 24_{5,19}$		16 048.54	.108 ± .003	(0.101)[d]		5.1 E-7
$5_{2,4} - 6_{1,5}$	^{34}S	17 970.40	.097 ± .003	(.073)[e]	(.093)	2.2 E-7
$12_{3,9} - 13_{2,12}$		13 208.10	.112 ± .003	(.096)[e]	(.107)	1.8 E-7
$15_{2,14} - 14_{3,11}$		13 184.80	.110 ± .003		(.102)	1.8 E-7
$14_{2,12} - 15_{1,15}$		15 994.10	.096 ± .002		(.100)	7.2 E-8
$19_{3,17} - 18_{4,14}$		14 754.70	.101 ± .003		(.102)	2.5 E-7
$26_{6,20} - 27_{5,23}$		14 850.40	.102 ± .004			1.8 E-7
$31_{7,25} - 32_{6,26}$		12 567.30	.093 ± .002			8.3 E-8
$36_{8,28} - 37_{7,31}$		14 547.10	.097 ± .004			6.7 E-8

[a, b] Frequencies from [12] for *n* and ν_2 and [13] for ^{34}S.
[d] From line width measurement of ground state [15].
[f] Calculated for normal species ground state [6] and [16].

[c] from line width measurements [10] and [14].
[e] From line width measurement of normal species [15].
[g] From or estimated from [17].

vibrational state are included. The results are given in Tables 1 and 2.

For formaldehyde the samples were taken after repeated pumping off residuals over liquid nitrogen.

SO_2 was supplied by Baker Chemikalien Groß-Gerau, with a purity of 99.98%. It was used after a vacuum distillation.

Pressure measurements were made using a MKS-Baratron 310 B capacitance manometer. The pressure range was from 3 to 25 mT.

Different techniques were used to record and analyze the transient emission signals which were decaying with the relaxation time T_2 and oscillating at an IF of about 30 MHz. The broadband amplified signals were A/D converted, then digitally averaged and the final results stored in the memory of a Digital Equipment Corp. PDP 11 or Texas Instruments 990/10 computer for further analysis. For strong signals with low noise a 6 bit A/D conversion was carried out in steps of 5 nsec by means of a transient digitizer (Biomation Mod. 6500). For subsequent averaging a 1024 channel digital averager (Fabri-Tek Mod. 1072) was used. More efficient recording and averaging for weak signals with small signal-to-noise ratios ($\lesssim 1$) was obtained by employing a homemade 1 bit 10 nsec-A/D-converter and digital averager* (1024 channels). So, up to 98304 average cycles could be achieved in about 21 seconds.

Different computer programs were written to analyze the stored data. After baseline subtraction the data points were corrected for Doppler-contributions which is a standard procedure in the pressure broadened limit [5].

The time dependence of the corrected data was assumed to be of the form

$$S(t) = A\, e^{-t/T_2} \cos(B\,t + D)\,. \qquad (1)$$

Expression (1) was least squares fitted to the data points as stored in the TI-990/10 computer with A, T_2, B and D as fitting parameters. The analysis with the PDP-11 computer was somewhat simplified by linear least squares fitting a semilogarithmic plot of the absolute values of maxima-minima data points with respect to time in order to determine only the decay constant T_2. From the results for T_2 at different sample pressures from both fitting procedures the coefficient β of the linear pressure dependence (slope) is then evaluated by using a linear least squares fit and weighting the $1/T_2$ data points with their standard deviations. As an example for the plot of $1/T_2$ versus pressure, data points for the $J_{K_-K_+} - J'_{K_-'K_+'} = 1_{1,1} - 2_{0,2}$ transition of $^{32}SO_2$ are shown in Figure 1.

The doubled standard errors of the results for β which are given in Tables 1 and 2 do not reflect systematic deviations in the experimental conditions which are primarily shifts in pressure (<0.5 mTorr) and temperature (< 2 K). These additional inaccuracies are estimated to be about 4% in relative magnitude.

In Table 1 and 2 we compare our results with those from linewidth measurements. For the isotopic species and excited vibrational states we enclosed the values in brackets to indicate that they refer to the normal species in vibrational ground state.

For $2_{1,1} - 2_{1,2}$ of HCHO and $14_{2,12} - 15_{1,15}$ of SO_2 the agreement is within the error limits.

The β_{calc} were calculated by Tejwani [6] using the Anderson-Tsao-Curnutte-theory. The agreement is roughly within 10%.

The formaldehyde data for both normal and ^{13}C-species indicate no significant dependence of T_2 relaxation times on the molecular mass. It is found that the pressure coefficients strongly decrease with increasing rotational quantum number J. Such J-dependence behaviour has also been found from linewidth studies of other transitions [7, 8] and is predicted theoretically [9].

For sulphus, dioxide only two transitions for the ground state and the first excited ν_2-vibrational state ($1_{1,1} - 2_{0,2}$ and $10_{2,8} - 11_{1,11}$) of the $^{32}SO_2$ species were in the available range of frequencies to allow for comparison of the results. No significant change of slope coefficient β with vibrational state

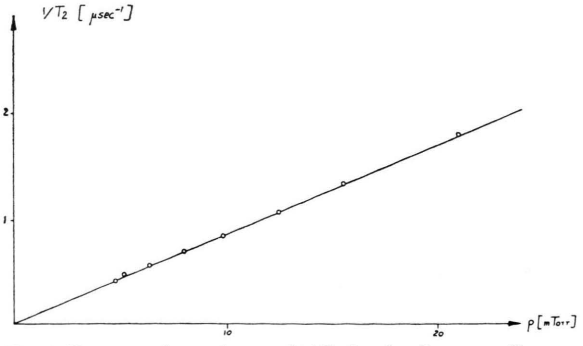

Fig. 1. Pressure dependence of $1/T_2$ for the $J_{K_-K_+} - J'_{K_-'K_+'} = 1_{1,1} - 2_{0,2}$ transition of $^{32}SO_2$ from pulse-induced transient emission.

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* Details on construction will be published separately

was observed. The results for the $14_{2,12}-15_{1,15}$ transition of both isotopic species in the ground vibrational state are in good agreement. A qualitative trend of the linewidth parameters ($\sim \beta$) with the quantum number J has been reported elsewhere [10] indicating an increase of β with increasing J for small J-values ($\lesssim 20$) as was also found in this investigation, see Table 2. The observed tendency of decrease in linewidth parameters with increase in quantum number J for larger J-values has also been confirmed by the present study.

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