Investigation of T_1 and T_2 Relaxation for Ethylene Oxide Rotational Transitions *

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The dependence of rotational relaxation times T_1 and T_2 on pressure and temperature has been determined for various rotational transitions of ethylene oxide by using transient microwave techniques.

In this paper we report on the analysis of transient microwave experiments to determine the relaxation times T_1 and T_2 for ethylene oxide (C_2H_4O) rotational transitions. In recent years time resolved microwave techniques have primarily been applied to the study of T_1 and T_2 relaxation of OCS and NH_3 [1]. To our knowledge ethylene oxide is with the exception of SO_2 [2] the only asymmetric top molecule for which transient effects have been investigated quantitatively. The relaxation time T_1 which phenomenologically describes the decay of two-level population difference has been determined by means of a π, τ, $\pi/2$ pulse sequence method as described previously [3], [4]. The analysis of transient emission signals has been carried out to investigate the relaxation time T_2 [5] which accounts for the decay of macroscopic polarization of the coherently prepared sample. We present here results for the pressure and temperature dependence of T_1 and T_1 for various rotational transitions of C_2H_4O.

Details on the experimental set up have been given recently [4, 6] and only some additional remarks are made here. For both transient experiments the Stark switching technique has been used to bring the molecular energy level difference into or out of resonance with the microwave radiation field which requires high voltage Stark pulses of short duration and fast rise and fall times. To fulfill this demand a four stage pulse amplifier with conventional vacuum tubes was constructed, see circuit diagram Fig. 1, to amplify single or double pulses from TTL level. The last stage of the amplifier consists of a parallel circuitry of eight tubes in order to deliver a sufficient high charging and dicharging current for the capacity of the Stark system. So Stark cell capacities of about 1000 pF * were loaded by a single our double pulse signal up to 600 volts with rise and fall times in the range of 100 nsec.

For temperature variation the absorption cell was cooled with methanol flowing through a cooling jacket. For the interpretation of relaxation data the temperature of the investigated gases should be known accurately. Therefore, the temperature readings of a thermometer which was in contact with the brass sample cell were calibrated with respect to a spectroscopically determined "in situ" mean gas temperature, as discussed in detail in the appendix. The temperatures were in the range from 200 K to 300 K.

The ethylene oxide sample was purchased from J. T. Baker Chemical Co. with a purity of 99.7% and used in the experiments after vacuum distillation. The sample pressure was varied from about 0.5 mTorr to 25 mTorr for the T_2 experiment. Lower pressures (< 6 mTorr) had to be used for the T_1 experiment.

From the analysis of transient emission and π, τ, $\pi/2$ pulse sequence signals at different pressures the pressure dependence of $1/T_2$ and $1/T_1$, respectively, has been determined for several rotational transitions which were in the available frequency range from 8 to 40 GHz. The details of data analysis have been reported recently [4, 6]. The resulting coefficients for the linear pressure dependence of inverse relaxation times $1/T_2$ and $1/T_1$ (slopes β) are given in Table 1 and 2. By using the

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* A 5 m conventional X-band Stark cell was used in the experiments.

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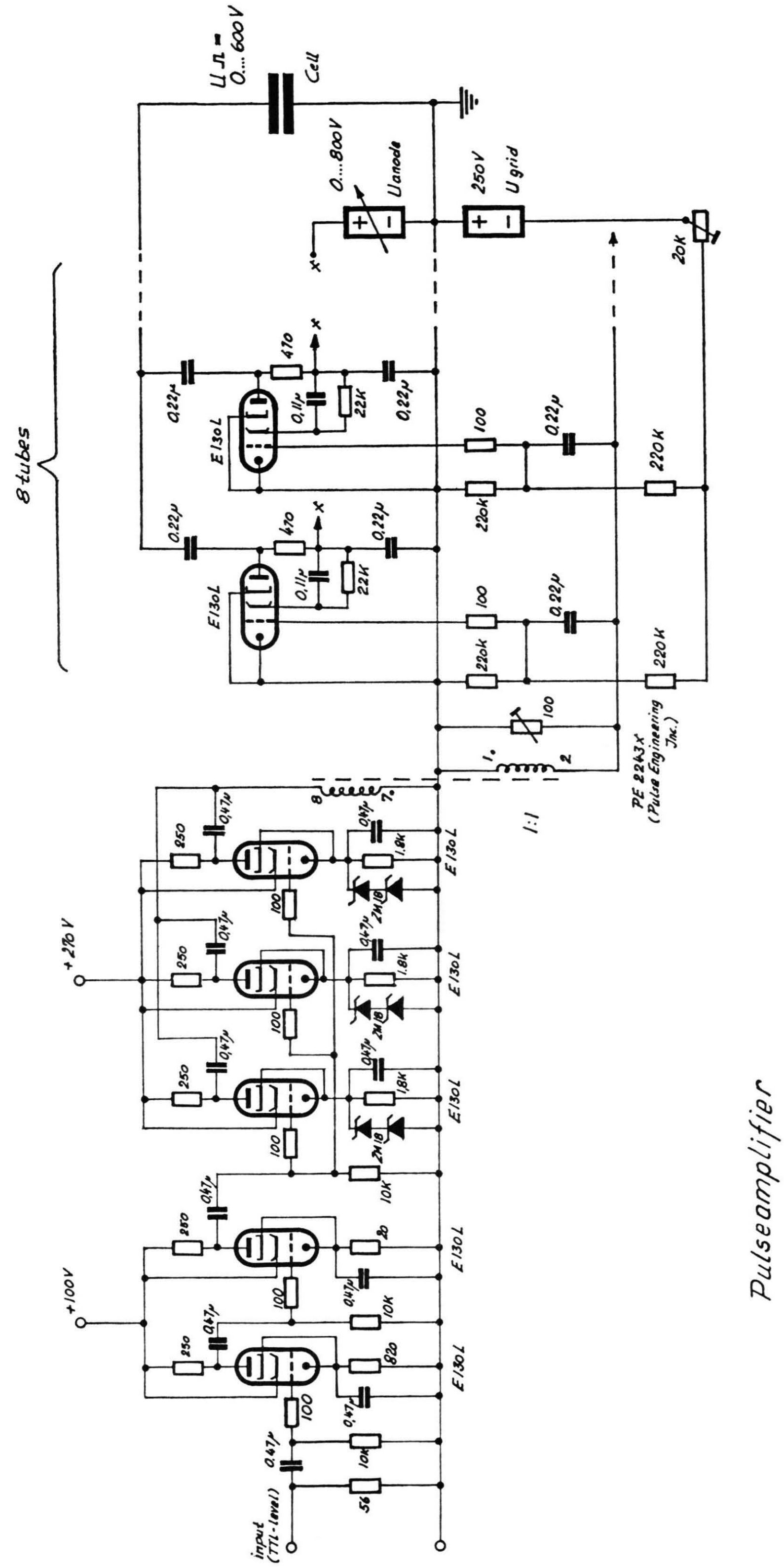

Fig. 1. Circuit diagram of the pulse amplifier for single and double pulse transient Stark switch experiments.

Table 1. Pressure dependence of $1/T_2$ (β) for C_2H_4O rotational transitions.

Transition[a] $J_{K_-K_+}-J'_{K_-K_+}$	Frequency[b] [GHz]	T [K]	β [μsec^{-1} mTorr^{-1}]
$1_{01}-1_{10}$	11.3859	213	0.1786 (12)[c]
$2_{11}-2_{20}$	15.6036	213	0.1854 (16)
$2_{02}-2_{11}$	24.9237	213	0.1755 (14)
$2_{12}-2_{21}$	34.1571	213	0.1978 (16)
$3_{21}-3_{30}$	23.1343	213	0.1948 (8)
$3_{12}-3_{21}$	23.6104	213	0.1914 (12)
$3_{22}-3_{31}$	39.6801	213	0.2063 (12)
$4_{22}-4_{31}$	24.8344	213	0.1900 (12)
$4_{31}-4_{40}$	34.1477	213	0.1929 (32)
$0_{00}-1_{11}$	39.5816	213	0.1742 (6)
		233	0.1664 (8)
		253	0.1474 (8)
		273	0.1431 (8)
		294	0.1317 (10)

[a] $|M| = J$ component polarized.
[b] Zero Stark field transition frequency.
[c] Errors in paranthesis are in the last digit given and twice the standard deviations.

Table 2. Pressure dependence of $1/T_1$ (β) for C_2H_4O rotational transitions.

Transition[a] $J_{K_-K_+}-J'_{K'_-K'_+}$	Frequency[b] [GHz]	T [K]	β [μsec^{-1} mTorr^{-1}]
$1_{01}-1_{10}$	11.3859	213	0.161 (2)[c]
$2_{11}-2_{20}$	15.6036	213	0.162 (6)
$0_{00}-1_{11}$	39.5816	213	0.170 (6)
		233	0.169 (4)
		253	0.158 (4)
		273	0.150 (6)
		300	0.144 (6)

[a] $|M| = J$ component polarized.
[b] Zero Stark field transition frequency.
[c] Errors in paranthesis are in the last digit given and twice the standard deviations.

Stark-switching technique only the $|M| = J$ component of the Q-branch transitions was investigated. The temperature dependence of both T_1 and T_2 was examined for the $M=0$ component of the R-branch $J_{K_-K_+}-J'_{K'_-K'_+}=0_{00}-1_{11}$ transition.

As seen from the error limits given in Table 1 and 2, the pressure dependence of $1/T_2$ is more accurately given which is primarily due to the larger pressure range as involved in the analysis of transient emission signals. Systematic deviations of the experimental conditions due to shifts in pressure (<0.1 mTorr) and temperature (<1 K) may account for about 1% additional inaccuracy in the pressure dependence of both $1/T_2$ and $1/T_1$.

Only few linewidth data were found in the literature — mainly taken at room temperature — which may be compared with our measurements for the pressure dependence of $1/T_2$. Our result for the $J_{K_-K_+}-J'_{K'_-K'_+}=0_{00}-1_{11}$ transition at room temperature (see Table 1) is about 15% larger than the value from linewidth measurements given by Srivastava et al. [7] ($\beta=0.112$ μsec^{-1} mTorr^{-1}). The deviation is approximately within the 10% to 15% uncertainty quoted by the authors. Using the temperature dependence of this transition to extrapolate our other $1/T_2$ data to room temperature gives good agreement with the results of linewidth investigations of Gilbert [8].

The results of Table 1 and 2 indicate a small difference in pressure and temperature dependence of the relaxation times T_1 and T_2. No detailed theory has been worked out so far to allow for an explanation of this observation in terms of intermolecular collision dynamics. Additional experimental information seems to be necessary to get a better insight in details of the collisional process such as collisional transition rates and pathways.

Ethylene oxide is a molecule which exhibits rather strong collision-induced transitions between rotational levels as found from microwave four-level double resonance experiments [9, 10]. Such investigation complement the results from two-level transient experiments. Studies which involve a more complete set of rotational levels of ethylene oxide and combine results from two- and four level microwave experiments are now in progress in our laboratory [11].

Appendix

The sample cell cooling system is not ideally isolated and may allow for small temperature variations of the sample gas. An "in situ" mean gas temperature may be defined spectroscopically from the intensity ratio of two rotational lines. For peak intensity comparison at different temperatures we used the $J=0-1$ rotational lines of the OCS normal and ^{13}C-species in the vibrational states $(v_1v_2v_3)=(100)$ and (000), respectively, which are close in frequency ($\nu=12126.715$ MHz and 12123.845 MHz). Figure 2 shows the recordings from a conventional MW-Stark spectrometer at two different temperatures. The peak absorption coefficients are related to the population difference of the considered

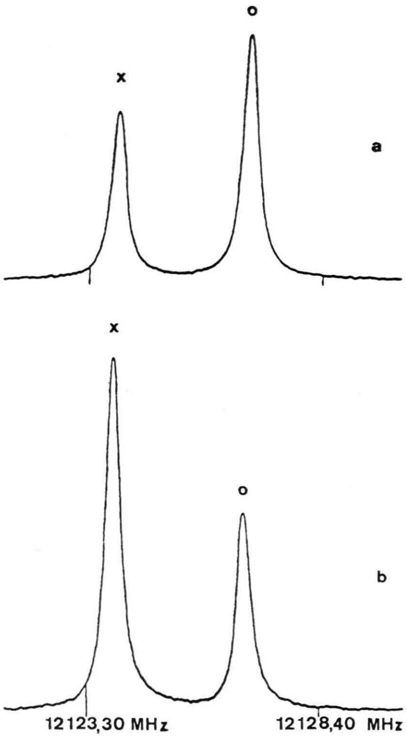

Fig. 2. Recordings of OCS $J = 0 \leftarrow 1$ transitions at different temperatures; a) $T = 295$ K, b) $T = 240$ K. × ground vibrational state $(v_1 v_2 v_3) = (000)$, $O^{13}CS$, ○ vibrational state $(v_1 v_2 v_3) = (100)$, $O^{12}CS$.

transitions and thereby to the rotation-vibration partition function* at a given temperature and to the isotope abundancies. The derivation of mean gas temperature from the observed line intensity ratio is straightforward and the resulting values were compared with the thermometer reading in the range of investigated temperatures (200 K – 300 K). The latter temperature values were found to be systematically too high which is most probably due to insufficient contact of the thermometer with the sample cell. Corrections up to 6 K at low temperatures had to be made and the corrected values — estimated to be accurate within 1 K — are given in the analysis.

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* Calculated for a rigid rotor-harmonic oscillator energy level scheme.

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