A Contribution to the Investigation of T_2-Relaxation with a Pulse Spectrometer

G. Bestmann and H. Dreizler

Abt. Chemische Physik im Institut für Physikalische Chemie der Universität Kiel

Z. Naturforsch. **35 a**, 564 – 565 (1980);
received March 24, 1980

We investigated the pressure dependence of the T_2-relaxation time for several rotational transitions of acetaldehyde, CH_3CHO. No difference in the relaxation of A- and E-species transitions could be detected. The analysis was performed in the time and frequency domain.

As part of our studies on the rotational relaxation of astrophysically interesting molecules [1 – 4] we present measurements of the coefficient β of the linear pressure dependence of $1/T_2$ of acetaldehyde, CH_3CHO. This molecule has a methyl-group as internal rotor. An additional reason to investigate this molecule was the question if the A- and E-species lines behave differently. By internal rotation the level scheme of this molecule splits into two parts, the A- and E-scheme. There are no transitions allowed between these levels of different symmetry species induced by an electromagnetic field.

The measurements were made with a microwave pulse and Fourier transform spectrometer [5]. Acetaldehyde was supplied by Merck, Darmstadt, with a purity of 99% after vacuum distillation. As checked by gaschromatography the sample contained less than 0.5% volite impurities. Our Fourier transform spectrometer measures the decay of the transient emission * in the time domain. The data are stored in a computer for further analysis. After making a Doppler correction the data points were fitted to a cosine-function with exponential decay

$$f(m\,\Delta t) = A \cdot \exp(-m\,\Delta t/T_2) \cdot \cos(2\,\pi\,\nu_c\,m\,\Delta t + \varphi) \tag{1}$$

with A, T_2, ν_c and φ as fitting parameters. The number of data points m is in the range of 80 to 300. As sometimes the baseline of the decay is exponentially deformed and additional lines are in the range of the frequency band of our measuring system we got a complicated decay.

By making a fast Fourier transformation of the Doppler corrected time domain signal (1) and evaluating the power spectrum we got a Lorentzian line shape without a saturation term

$$p_k^2 = \frac{A_0}{(1/T_2)^2 + ((k-c)\,2\,\pi/T)^2}$$

with T the measuring time for the time domain signal and $(2\,\pi/T)$. $c = 2\,\pi\,\nu_c$ the center frequency of the line. A_0, $(1/T_2)^2$ and c are now the fitting parameters. With a number of data points k in the range of 20 we got a filtering of the data points cutting off the low frequencies related to the deformed baseline and cutting off the additional lines.

The power spectrum of the Fourier transformed emission signal is nearly independent of the phase angle, which reduces the number of fitting parameters by one. A comparison of the results shows no differences in the evaluation of $1/T_2$ if we optimise the standard error of $1/T_2$ for a certain pressure by choosing an optimal Fourier transform length.

The results given in Table 1 are evaluated with both methods. For $1/T_2$ we notice for some lines differences outside the standard error as a result of a disturbance of the baseline.

An estimation of the absolute error of our measurements was given in [3]**.

In Table 1 we also give the frequencies of the line measured by our Fourier transform spectrometer. They agree well with those measured by Stark spectroscopy [6]. From the T_2-results it may be seen that there is no reliable difference of A- and E-species lines.

The range of $J_{K_-K_+}$ is too limited in the presently accessible band from 12 – 18 GHz to state a correlation to J [3]. No measurements of line widths were found in the literature.

We thank the Deutsche Forschungsgemeinschaft and Fonds der Chemie for funds, the members of our group for discussions, Mr. M. Adolfatto for the purification of the substance and the gaschromatogram.

---

* See for example Figs. 1 and 2 of [4].

Reprint requests to Prof. Dr. H. Dreizler, Institut für Physikalische Chemie, Abt. Chemische Physik, Olshausenstr. 40 bis 60, D-2300 Kiel.

** *Erratum:* In [3] Table 1 and 2 and [4] Table 1 we gave erroneously the single standard error.

Table 1. Measurement of the pressure dependence β [μs^{-1} mTorr^{-1}] of the relaxation time T_2 of acetaldehyde, CH_3CHO. $1/T_2 = \beta\, p + \alpha$, p pressure, temperature 298 K. β_t and β_ν calculated from data in the time and frequency domain. ν_{St} and ν_{FT} [MHz] frequency of lines measured by Stark- and FT-spectroscopy, Γ symmetry species, a) forbidden transition, b) overlapping lines, in brackets uncertainty or standard error. For FT-spectroscopy uncertainty 20 to 30 kHz. Additional uncertainty for β_t and β_ν 4⁰/₀ from pressure and temperature.

Transition $J_{K_- K_+} - J'_{K'_- K'_+}$	Γ	ν_{cal} [6]	ν_{St} [6]	ν_{FT}	β_t	β_ν
$3_{03} - 2_{12}$	A	12 013.447 (726)	12 014.999 (20)	12 014.97	0.262 (3)	0.251 (4)
	E	12 637.481 (840)	12 635.228 (20)	12 635.22	0.263 (4)	0.258 (6)
$5_{14} - 5_{15}$	A	15 967.402 (982)	15 968.452 (20)	15 968.45	0.220 (8)	0.220 (9)
	E	15 989.459 (1001)	15 988.730 (20)	15 988.71	0.207 (3)	0.227 (4)
$5_{24} - 6_{15}$	A	15 166.872 (1554)	15 164.478 (20)	15 164.46	0.240 (4)	0.237 (4)
	E	13 142.547 (1818)	13 145.877 (50)	13 145.96	b)	b)
$5_{23} - 6_{15}$ a)	E	15 525.986 (1865)	15 525.099 (50)	15 526.44	0.247 (8)	0.244 (8)
$10_{1.10} - 9_{27}$	A	14 770.506 (1541)	14 766.065 (20)	14 766.06	0.229 (4)	0.230 (4)
	E	15 723.049 (1543)	15 727.190 (20)	15 727.20	0.230 (6)	0.223 (5)
$10_{38} - 11_{29}$	A	14 688.737 (1949)	14 691.111 (20)	14 691.10	0.268 (5)	0.270 (6)
	E	12 495.404 (2169)	12 492.973 (50)	12 493.03	0.267 (4)	0.290 (5)
$10_{37} - 11_{29}$ a)	E	14 457.415 (2436)	14 456.726 (20)	14 456.88	b)	b)
$11_{29} - 11_{2.10}$	A	12 158.260 (1512)	12 158.059 (20)	12 158.05	0.232 (4)	0.238 (5)
	E	12 366.322 (1509)	13 366.328 (20)	12 366.33	0.231 (4)	0.247 (4)
$12_{2.10} - 12_{2.11}$	A	16 682.601 (2110)	16 682.008 (20)	16 681.98	0.270 (6)	0.270 (6)
	E	16 846.391 (2065)	16 846.003 (20)	16 845.99	0.245 (8)	0.241 (5)
$19_{3.16} - 19_{3.17}$	A	—	12 873.798 (20)	12 873.79	0.258 (2)	0.260 (4)
	E	—	13 025.707 (20)	13 025.70	b)	b)
$20_{3.17} - 20_{3.18}$	A	—	17 018.103 (20)	17 018.14	0.254 (4)	0.267 (5)
	E	—	17 163.112 (20)	17 163.09	0.252 (3)	0.262 (6)

[1] H. Mäder, Z. Naturforsch. **34 a,** 1170 (1979).

[2] H. Mäder, W. Lalowski, and R. Schwarz, Z. Naturforsch. **34 a,** 1184 (1979).

[3] G. Bestmann, H. Dreizler, and H. Mäder, Z. Naturforsch. **34 a,** 1330 (1979).

[4] W. Schrepp, G. Bestmann, and H. Dreizler, Z. Naturforsch. **34 a,** 1467 (1979).

[5] G. Bestmann, H. Dreizler, H. Mäder, and U. Andresen, **35 a,** 392 (1980).

[6] A. Bauder, F. J. Lovas, and D. R. Johnson, J. Phys. Chem. Ref. Data **5,** 53 (1976).