

A Contribution to the Stark-Spectroscopy at Low Microwave Frequencies

W. Schrepp and H. Dreizler

Abteilung Chemische Physik im Institut für
Physikalische Chemie der Universität Kiel

Z. Naturforsch. **34a**, 903–905 (1979);
received June 6, 1979

Recently we published a construction of a microwave-microwave double resonance spectrometer [1], which allows a variety of experiments. An essential part of it is a "stripline" absorption cell.

Although Stark-Spectroscopy [2] gave a very important impetus to the investigation of rotation spectra and is in use for three decades, measurements below 6.5 GHz are few in number compared to the frequency region above 6.5 GHz.

The reason is that generally the line intensity decreases at lower frequencies and the cross sections of the standard waveguides are larger. If one does not use special waveguides * a higher Stark voltage has to be applied to produce the necessary Stark field for modulation. This requires a rather powerful Stark square wave generator ** to load and unload the capacity of the absorption cell.

Measurements in the low frequency region may be useful since at these lower frequencies the density of rotational spectra is sometimes considerably lower than at higher frequencies, which facilitates the assignment.

We noticed that the stripline cell, which transmits from DC to 18 GHz in a coaxial type mode, may be used for Stark-Spektroscopy by feeding the Stark voltage and the microwave simultaneously to the septum. After having finished our experiments, we

noticed that S. Weisbaum [4] et al. measured the transitions 3_2-3_3 and 5_2-5_3 of HDO at 486.50 and 824.64 MHz, respectively, by a similar technique. The radiofrequency was connected together with the Stark voltage to the septum of a conventional Stark cell.

In Fig. 1 we give the details of the set up. To combine the microwave and the square wave we use "monitor tees" *. The square wave is fed into the monitor port which transmits a 100 kHz square wave. For example, a residual square wave of 140 V is observed at the microwave port when applying a 400 V square wave. To prevent any influence of the square wave on the microwave source we use a piece of waveguide as a high pass filter. At the output of the absorption cell another piece of waveguide acting as a high pass filter protects the detector crystal. The cell we used for the measurements presented in Table 1 and Fig. 2 is made of an X-band waveguide R 100 (cut off for the TE_{10} -mode 6.56 GHz). The construction is similar to that given in Fig. 1 of the previous paper [1], but TNC connectors ** are used. The cell has been tested for a voltage of 2500 V between septum and the waveguide walls. The attenuation of the microwave on the stripline between 0.4 and 2.4 GHz is about 1.5 dB.

Table 1. Rotational lines of Acetaldehyde, CH_3CHO , in the region of 4.5 to 6.6 GHz. Frequencies in MHz.

$J_K - K_+ - J'_K - K'_+$	Γ	$\nu_{exp.}^a$	$\nu_{calc.}^b$
$3_{12}-3_{13}$	A	6390.085	6389.492 (0.485)
	E	6545.420	6546.454 (0.519)
$9_{27}-9_{28}$	A	5778.030	5777.759 (0.889)
	E	6187.027	6186.582 (0.948)

^a experimental uncertainty ± 40 kHz.

^b from [5], standard errors in brackets.

Γ symmetry species.

Formaldehyde, CH_2O , and acetaldehyde, CH_3CHO , have been used for tests. The lines of acetaldehyde in Table 1 have not been measured yet. The calculated frequencies were taken from [5]. In Fig. 3 we present a test measurement of the Stark effect of the line $1_{10}-1_{11}$ of CH_2O at 4829.73 MHz. Here we

* Tees manufactured by Microlab-FXR, for 4 to 8 GHz type HW60N.

** Omni Spectra connector TNC part No. 3152-5006-10.

Reprint requests to Prof. Dr. Helmut Dreizler, Abteilung Chemische Physik, Institut für Physikalische Chemie, Universität Kiel, Olshausenstr. 40–60, D-2300 Kiel.

* We use in many applications a waveguide with 10×47 mm inner cross section [3].

** For a field of 4000 V/cm in a waveguide R 48, 3.94–5.99 GHz, with 47×22 mm inner cross section approximately 4000 V are necessary. For a waveguide R 22, 1.72–2.61 GHz, with 109×55 mm cross section approximately 10 000 V must be applied.

0340-4811 / 79 / 0700-0903 \$ 01.00/0

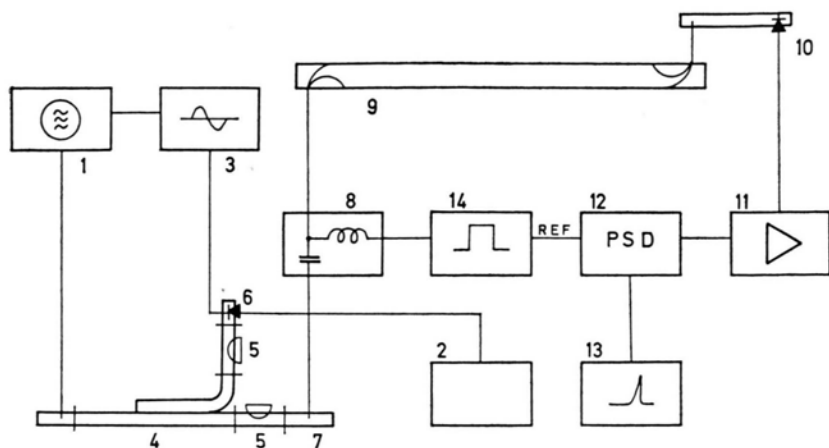


Fig. 1. Scheme of the Spectrometer. 1 Backward Wave Oscillator (BWO) Carcinotron CSF CO 63A with FXR Z817A power supply, 2 Frequency standard XUC and SMDH, Rhode und Schwarz, digital ramp generator [6], 3 Synchriminator FDS 30, Schomandl, 4 Directional coupler 10 dB, 5 variable attenuator, 6 Mixer, 7 waveguide R 70, 5.38–8.17 GHz used as high pass filter, cut off 4.285 GHz, 8 Monitor tee Microlab-FXR, HW60N, 4–8 GHz, 9 Absorption cell, X-band waveguide with stripline septum, 10 detector, Microwave Assoc. MA 40074, 11 Pramplifier 100 kHz, 12 Phase sensitive detector, Ithaco Dynatrac 391 A, 13 Recorder, 14 Stark square wave generator.

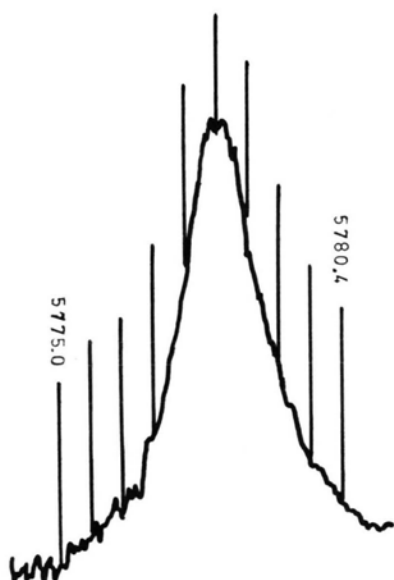


Fig. 2. Rotational transition $9_{27}-9_{28}$, A at 5778.03 MHz of CH_3CHO measured with the X-band stripline cell. Frequencies in MHz, pressure 40 mT, temperature -40°C , time constant 4 sec.

used the cell described in [1] with an inner cross section of 10×47 mm. It has a Stark field which is more homogeneous than that in the cell made of the X-band waveguide ***.

The measurements at still lower frequencies are limited presently by the lack of microwave sources and filters in our laboratory. To overcome the sensitivity problem a longer absorption cell and signal averaging may be used.

*** The Stark lobes are narrow enough to allow polarisation for measurements of the relaxation times T_1 and T_2 .

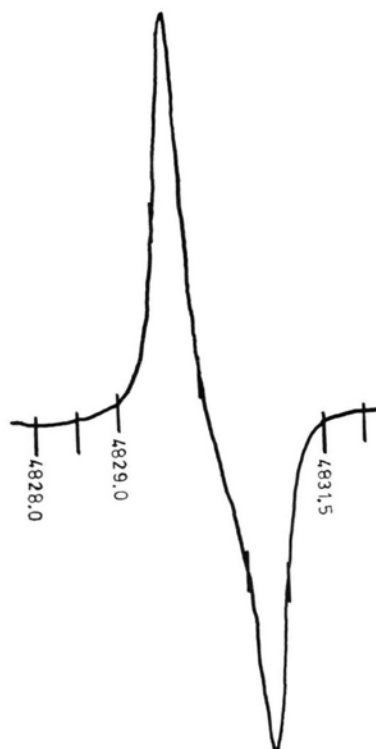


Fig. 3. Stark effect of the transition $1_{10}-1_{11}$ at 4829.73 MHz of CH_2O measured with the stripline cell of 4 m length and 47×10 mm cross section. Frequencies in MHz, pressure 6 mT, temperature -30°C , time constant 1.25 sec, Stark field 90 V/cm.

Acknowledgements

We thank the workshop of the Institute of Physical Chemistry for the workmanship, the members of the group for many discussions and the Deutsche Forschungsgemeinschaft and Fonds der Chemie for financial support.

- [1] H. Dreizler, W. Schrepp, and R. Schwarz, Z. Naturforsch. **34a**, 571 (1979).
- [2] R. H. Hughes and E. B. Wilson jr., Phys. Rev. **71**, 562 (1947); K. B. McAfee jr., R. H. Hughes, and E. B. Wilson jr., Rev. Sci. Instr. **20**, 821 (1949).
- [3] F. Mönnig, Dipl. Thesis, Freiburg 1963.
- [4] S. Weisbaum, Y. Beers, and G. Herrmann, J. Chem. Phys. **23**, 1601 (1955).
- [5] A. Bauder, F. J. Lovas, and D. R. Johnson, J. Phys. chem. Ref. Data **5**, 53 (1976).
- [6] U. Andresen and H. Dreizler, Z. Angew. Physik **30**, 207 (1970).