Contributions to Microwave Spectroscopy by the group at the University of Kiel, Germany

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In March 1969, U.Andresen, H.Dreizler, A.Guarnieri, H.Legell, H.Mäder and D.H.Sutter (Fig.1) moved to the Institute of Physical Chemistry of the University of Kiel (Fig.2). Fortunately, the equipment for a microwave (MW)-spectrometer could be transferred from Freiburg. Within a week, the spectrometer was installed in a laboratory, which had been planned by Prof.Dr.W.Zeil who moved to the University of Ulm.

It was intended to continue the work in the field of MW-spectroscopy which originally began in Freiburg. The topics were: Structure of molecules in the gas phase, hindering potential of internal rotation, internal rotation vibration interaction (Fig.3), dipole moments, nuclear quadrupole constants first of ^{14}N, later with improved spectrometers of D, ^{35}Cl, ^{37} Cl ^{17}O, ^{10}B, ^{11}B, ^{33}S, ^{79}Br, ^{81}Br, ^{127}I . D.H.Sutter initiated the investigation of the rotational Zeeman effect and A.Guarnieri extended the frequency range beyond 40 GHz. The first step in such investigations is the assignment of the rotational spectra first by the Stark effect assisted later by RF-MW and MW-MW double resonance spectroscopy. Later followed investigations of relaxation effects, line shape analyses and the construction of waveguide (WG) and molecular beam (MB) microwave Fourier transform spectrometers (MWFT) with different types of resonators and their extensive use. A number of van der Waals complexes and free radicals were studied. All experimental work was accompanied by theoretical considerations and later by quantum chemical calculations. Many programs were written to evaluate the spectra.

As the number of investigated molecules is large, only some specific examples will be described below, including details about advances in spectroscopic instrumentation. Additional details are given in the respective papers, see *Kiel publication list*

1969: Planning and construction of a laboratory for the accommodation of a 20 t magnet manufactured by Bruker, Karlsruhe with magnetic fields up to 21 kGauss over a gap of 6 cm and 31 kGauss over a gap of 0.6 cm width and 2.5 m length.

1970: Development of instrumentation for frequency sweeps of carcinotrons (BWO) under stabilized conditions (51). Installation of MW- and millimeter (MMW)-spectrometers for the investigation of the rotational Zeeman effect (Figs.4,5) (50,56,59,96). (The numbers refer to the *Kiel publication list*).

1972: RF-MW double resonance experiment (66,94)

1975: Observation of collision-induced transitions (95,131).

1979: Begin of waveguide microwave Fourier transform (WG MWFT)-spectroscopy first in the range of 12- 18 GHz (147,151) with a home made control and averaging system, extended later down to 2 and up to 40 GHz (422,328,194, 313, 351). Studies of rotational relaxation (143,145).

1980: Observation of transient dispersion and absorption with a superheterodyne MW-spectrometer (153).

1981: Measurement of deuterium nuclear quadrupole hyperfine structure (D-hfs) with MWFT spectroscopy (171).

1982: Introduction of mini computers (178,181) for controlling a MWFT-spectrometer. MW-MW double resonance experiments with the FT technique (189, 200).

1983: Ku band (12.4-18 GHz) bridge superheterodyne spectrometer for the study of the rotational Zeeman effect (199).
Severe damage of the institute by a winter storm (Fig.6).

1984: Two dimensional WG MWFT-spectroscopy (220). Determination of dipole moments with MWFT spectroscopy (223).

1985: Linewidth measurements (227).

1986: Rotational spectrum of Germane, GeH_4 (248).

1987: Measurement of the dipole moment of C_6H_5D by MWFT spectroscopy (261).
Spin-rotation and spin-spin interaction (274,277).

1988: Improved control and averaging system for MWFT spectrometers (299).
Presentation of the technical developments at the Hannover industrial fair (Fig.7).
RF-MW double resonance with the MWFT technique (286).
A.Guarnieri starts cooperation with Prof. Dr. J. L.Alonso in Valladolid for the set up of a MMW- and sub-MMW-spectrometer.
First result from cooperation with Valladolid (428a).

1989: MWFT measurements of CH_4 (321).
D-hfs measurements and quantum chemical calculations.
Two-dimensional radiofrequency (RF) MWFT spectroscopy (338).
Ethylene-O_3 complex in cooperation with NBS, Washington (342).
Construction of a Zeeman MWFT spectrometer (309).
PC-controlled phase-stabilized MMW-spectrometer (317).

1990: Set-up of a molecular beam (MB MWFT) spectrometer. Beam parallel to the Fabry-Perot resonator axis increased resolution and sensitivity considerably in comparison to a beam perpendicular to the axis. Many isotopologues could be investigated in natural abundance (362). Implementation of automatic scan for the beam spectrometer. One microwave source for the spectrometer by using single sideband modulators (353,368,443,517).

1991: MWFT-spectrometer with a circular waveguide of 36 m length. Measurement of CH_4 (375), SO_3 (387), mono-substituted CO_2 (483). Use of a discharge in the beam nozzle to produce unstable species (393). First use of quantum chemical calculations to assist spectroscopy (390).

1992: Construction of first MMWFT-spectrometer (420). Beginning of measurements of rare gas containing complexes (C_6H_5F-Ar) (412). J.-U. Grabow developed new computer

programs to control MB MWFT- spectrometers. These are now used in many laboratories worldwide.

1993: Automatic scan WG MWFT developed (443).
Construction of a MB MWFT spectrometer for the detection of air pollution in the atmosphere (464, 520), Fig.8, presented at the Hannover industrial fair.
H.Mäder and A.Guarnieri begin a cooperation with scientists of the Institute of Applied Physics of the Russian Academy of Sciences in Nizhnii Novgorod (Russia) (510,553,590,610,612,619).

1994: MB MWFT spectroscopy extended to 40 GHz (458). MWFT-spectrometer for measuring the Stark-effect, $D_2C=C=CH_2$ (441). Investigation of van der Waals complexes (467,473).
Measurements of perturbation-allowed transitions (468, 536, 579, 632).

H. Dreizler retired, but was able to continue his work in the laboratory.

1995: Investigation of the Zeeman effect with WG MWFT, pyrolysis (479,537).

1996: Laser vaporisation for MB MWFT, Urea $(NH_2)_2CO$, (499). Use of CH_4 as carrier gas for the beam (516). MB MWFT spectrometer in the 1-4 GHz range with a H_{01} resonator (505). Three methyl top internal rotation (500).

A.Guarnieri retired. He was able to continue his work in a new laboratory of the technical faculty.

1997: MB MWFT-spectrometer was built for the MW group in Valladolid (526).

1998: Investigation of DC_6H_4F in natural abundance (547), Aniline-Water, $C_6H_5NH_2$-H_2O, complex (543). First results obtained with a newly constructed MB MWFT spectrometer equipped with a semi confocal Fabry-Perot cavity to allow production of free radicals in the expanding beam by laser photolysis (542).

1999: D.H. Sutter retired.

2000: Extended use of a discharge nozzle for the production of unstable species (569,576,583,594,599).

2004: Structure of phenylacetylene, C_6H_5 CCH determined with the measurement of 39 isotopologues, extended structure and quantum chemical calculations (589).

2005: Set up of a MMW- and sub-MMW-spectrometer for investigations of Lamb Dip spectra (610,612).

2006: Structure of phenylacetylene-argon, C_6H_5CCH-Ar, determined with 24 isotopologues, extended structural and quantum chemical calculations (611).

2007: H.Mäder retired.

Invited papers, review papers:
38 in Publication list Dreizler (Freiburg), 63,104,256,403,488,536.

Alexander von Humboldt, Deutsche Forschungsgemeinschaft und DAAD fellows: J.L.Alonso, S.Antolinez, S. Blanco, D.P.Consalvo, M.C.L.Gerry, G. Golubiatnikov, Z.Kisiel, M.Kreglewski, A. Lapinov, A. Lesarri, F.Lorenzo, J.C.Lopez, V.N. Markov, S.C. Mehrotra, G.K.Pandey, F.Rohart, M.E. Sanz, K.V.L.N. Sastry, F. Scappini, M.Suzuki.

Many coworkers working for their diploma, doctor and habilitation theses and guests from Germany and abroad contributed to the results. Among the guests were Alexander von Humboldt and Deutscher Akademischer Austauschdienst fellows. An extended cooperation with laboratories within Germany and abroad took place. A.Guarnieri and H. Dreizler spent several periods in Valladolid with Prof Dr. J. Alonso and in Lille with Prof.Dr J. Demaison, H.Mäder visited several times Bologna (Dr. F.Scappini), Lille (Prof.Dr. F.Rohart) and Edmonton (Prof. Dr. W. Jäger) for scientific collaboration. D.Sutter and H.Mäder were postdoctoral fellows at the University of Urbana with Prof. Dr.W. H. Flygare.

The work would not have been possible without the expertise of the mechanics and electronics workshops of the institute.

W.Stahl took up a faculty position at the Technische Hochschule Aachen, E. Hamer at the Hochschule Ravensburg-Weingarten, H.Bomsdorf at the Bergische Universität Wuppertal, and W.Jäger at the University of Alberta, Edmonton. J.U. Grabow has presently a position at the University of Hannover. H.M.Heise obtained an honorary professorship from the University of Applied Sciences Südwestfalen, Germany.

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Fig.1. First members of the Kiel group who moved from Freiburg (1969).
Top (from left) : H.Legell, U.Andresen, D.H.Sutter.
Bottom (from left) : A.Guarnieri, H.Dreizler, H.Mäder

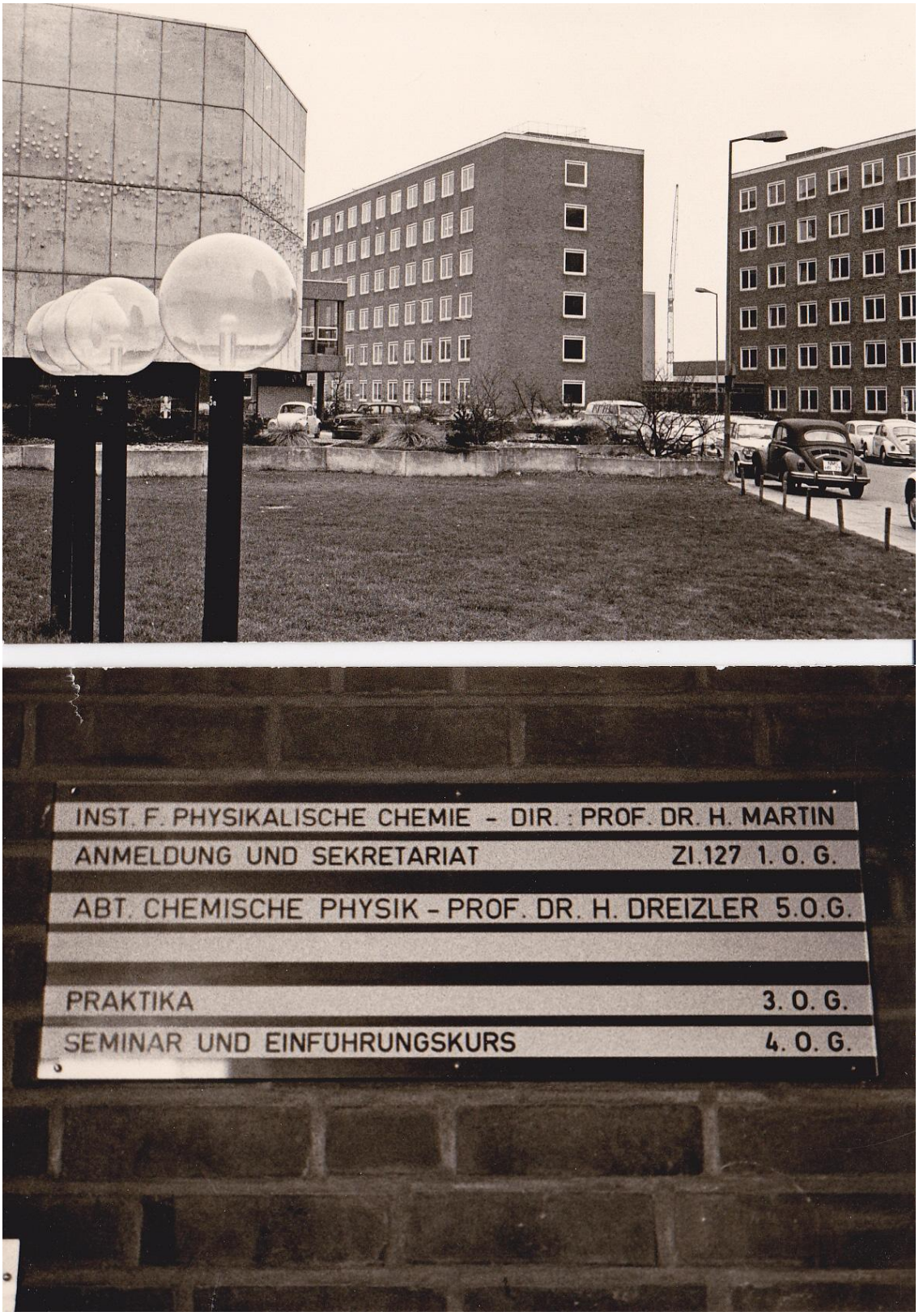

Fig.2. Move to Kiel (1969). In the top picture the central building is the Institute of Physical Chemistry and the main part of the microwave laboratory was based on the fifth (=top) floor, while the Zeeman spectrometer was located in the basement.

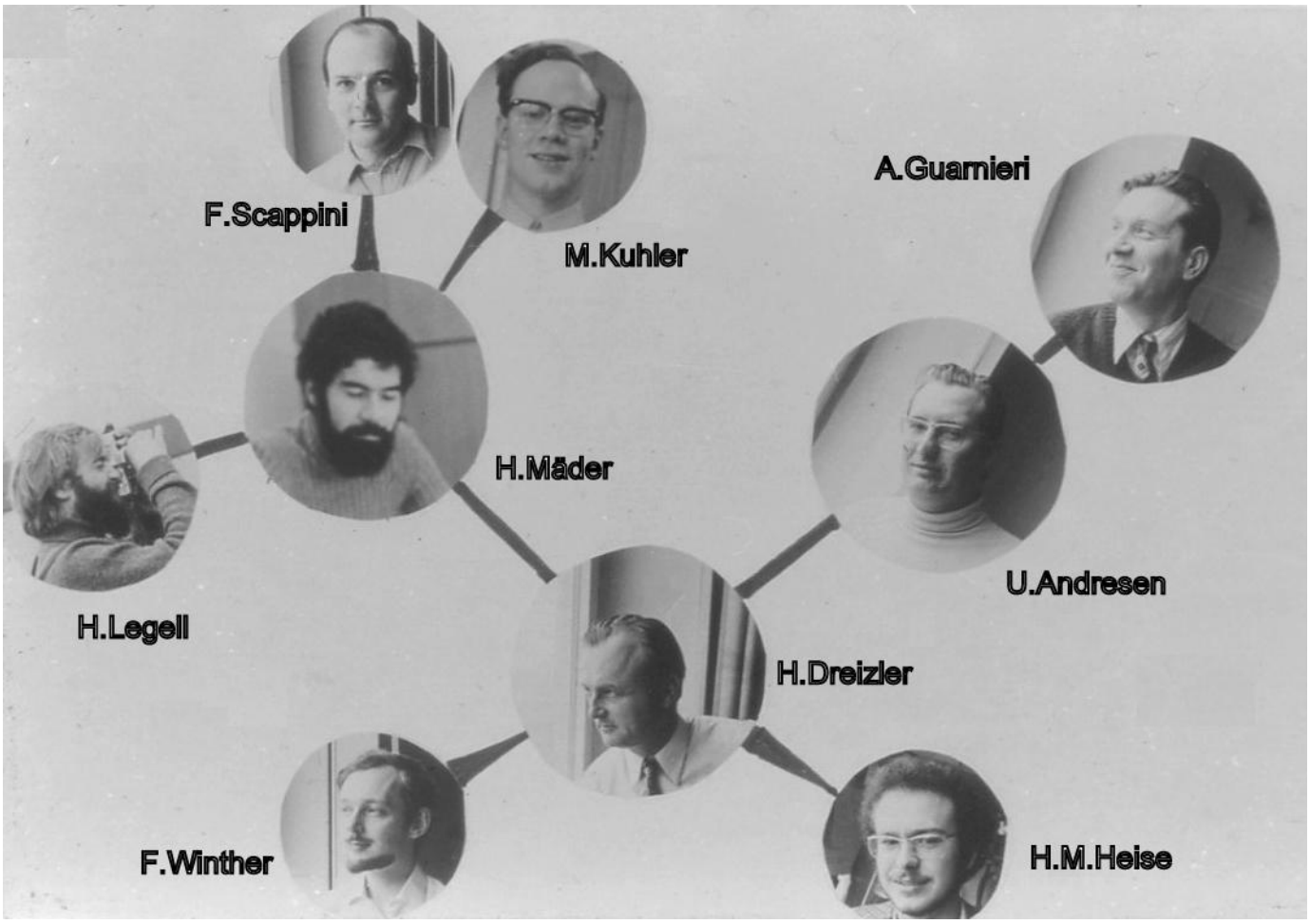

Fig.3. "Molecular example", CH_3CH_2CN, for the investigation of internal rotation and internal rotation vibration interaction with principal investigators (1974).

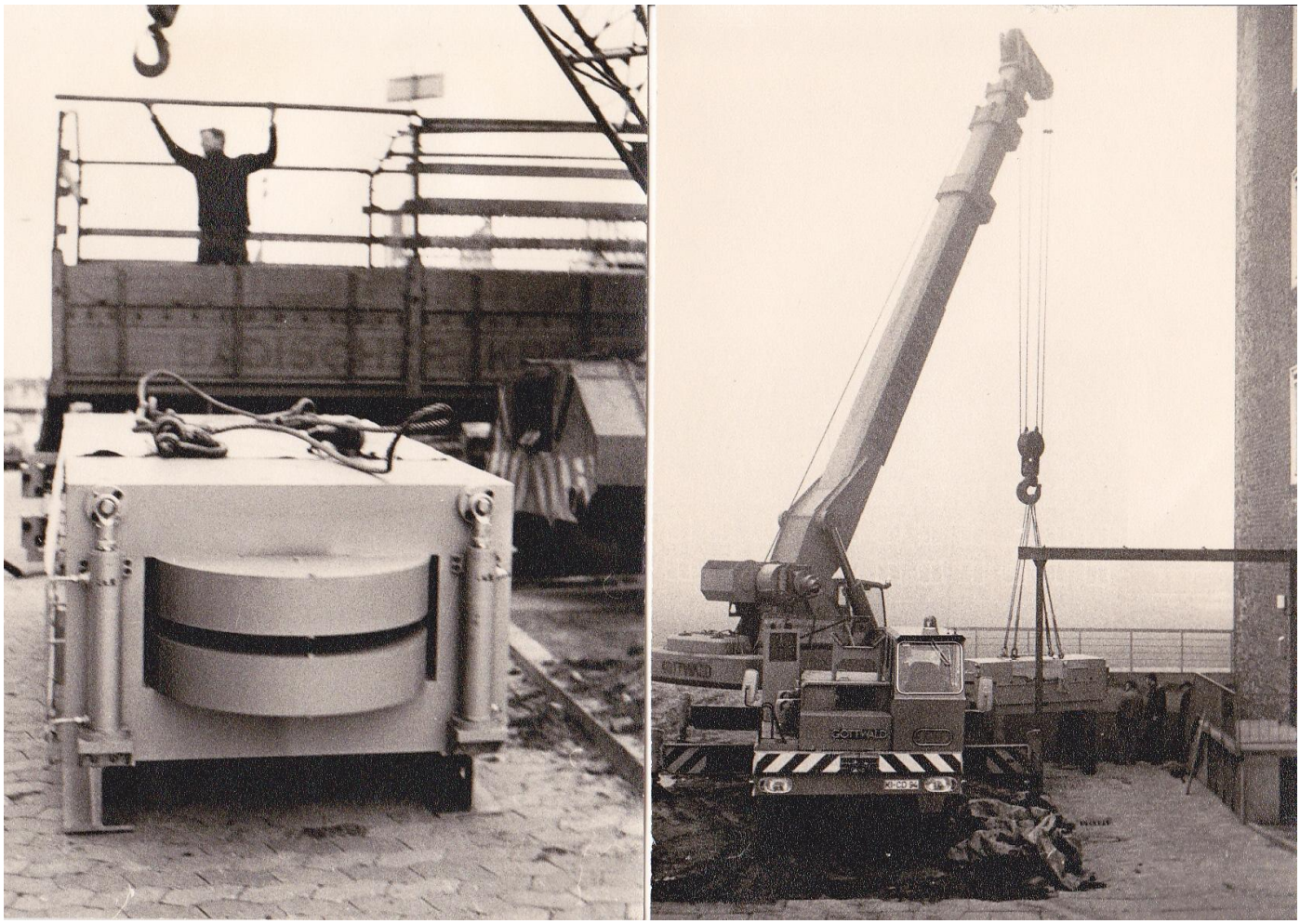

Fig.4. Installation of the 20 ton magnet for the Zeeman MW spectrometer (1970). The magnet was manufactured by Bruker, Karlsruhe and its installation in the basement of the building required heavy transport equipment.

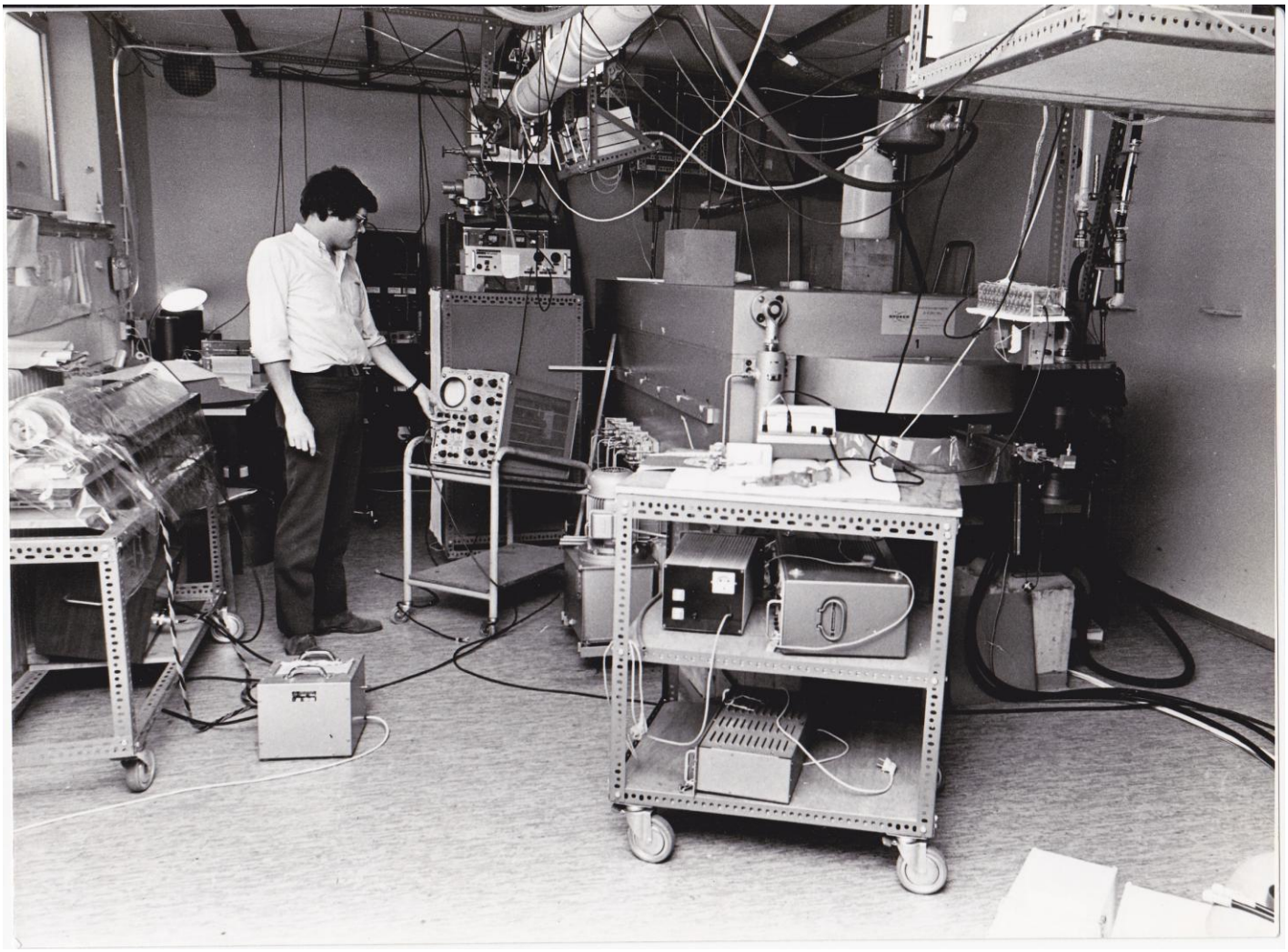

Fig.5. Zeeman MW spectrometer with E.Hamer (1970). The magnet pole distance could be changed by lifting the top pole with four hydraulic jacks and changing spacers. The achievable magnetic field could was 21 kG for 6 cm pole spacing. The detector end of a J-band sample cell is visible in the magnet. Measurements with this cell were made over the 5.3-40 GHz frequency region.

Fig.6. After a heavy storm, the Institute labs, especially in the fifth floor, were severely damaged (January 1983).

Fig. 7. Various achievements of the Kiel group were presented several times at the Hannover industrial fair (top). The bottom picture records presentation of the homemade transient digitizer for the extraction of weak periodic signals from the noise (1988). The digitiser was especially designed for waveguide Fourier-transform spectroscopy and could average up to 25k records per second, each up to 4096 points and 40 microseconds long.
Several MW group members are in attendance: U.Andresen (1st left), Ch.Keussen (4th from left), H.Dreizler (5th from left).

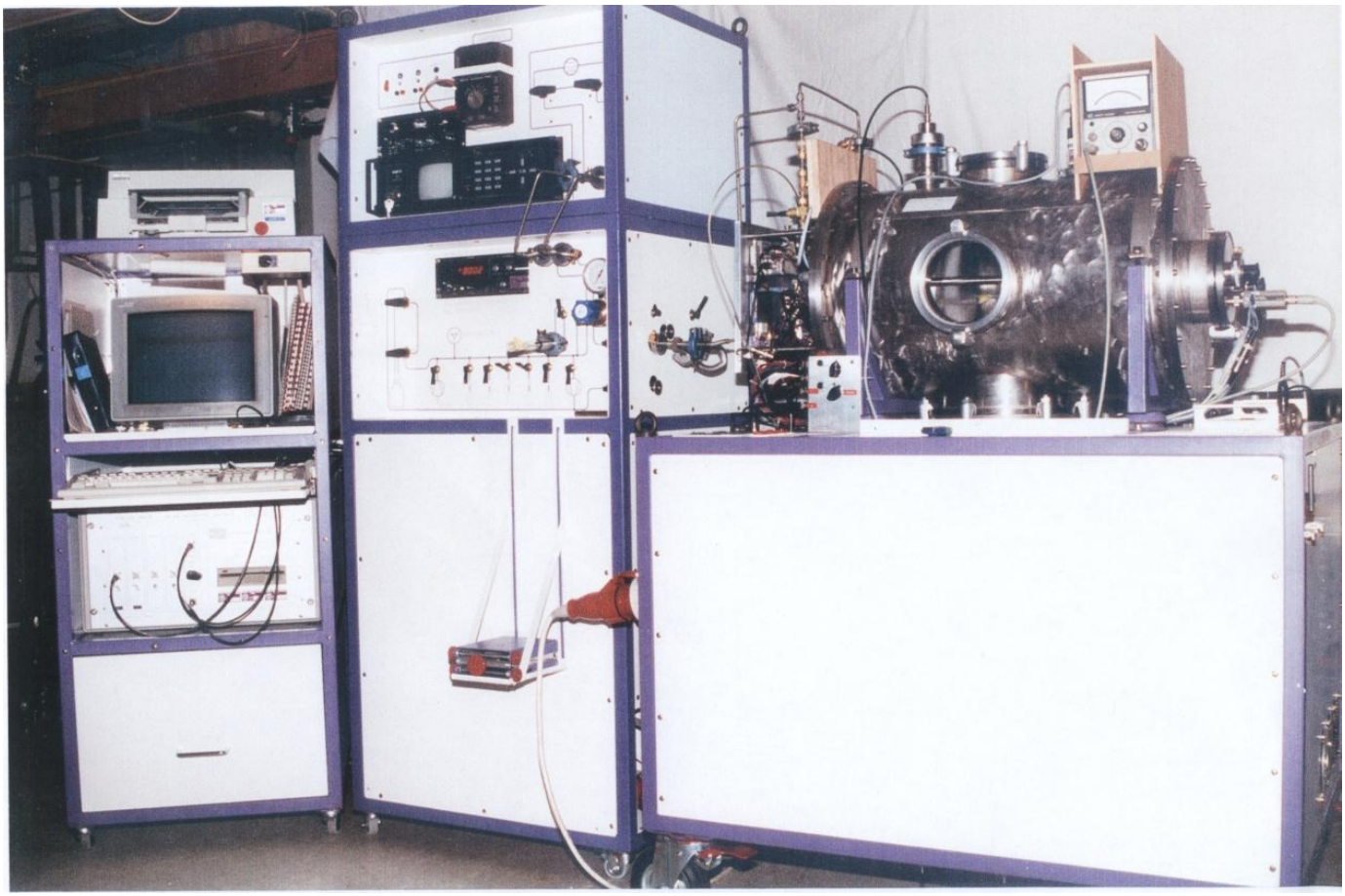

Fig.8 The commercialised MB MWFT spectrometer designed for detection of air pollution in the atmosphere. The spectrometer was described in detail in Andresen et al., Fresenius *J. Anal. Chem*., **349**,272-276(1994), and was covered by several patents including US patent 5124653 granted in 1992. The operational frequency range was 6-26.4 GHz and detection performance at the ppm level was demonstrated. The spectrometer was exhibited in 1993 at the Hannover industrial fair.