A Contribution to the Microwave Double Resonance Technique and Measurements of Collision Induced Transitions

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A construction for a versatile absorption cell is presented, which may be used for a large variety of double resonance experiments in the radiofrequency, microwave and millimeter wave region. Some measurements of collision induced transitions are reported.

For some years double resonance [1—4] spectroscopy in the microwave[1] region proved to be a very useful technique both for three and four level experiments.

For the assignment of dense and complicated rotational spectra microwave double resonance (MWDR) in three level systems is as important as the Stark effect [5]. For the study of collisional induced transitions and rotational energy transfer four level systems have been investigated [6, 7].

The experimental technique is to irradiate a sample with two microwaves of different frequency, one of it, the pump microwave, ν_p, is of much stronger intensity ($\sim$ Watt) than the signal microwave, ν_s ($\sim \mu$Watt).

For a successful experiment, the microwaves have to be combined in the absorption cell and the detector must be shielded from the strong modulated pump microwave. Because of the severe filtering problem most experiments are made for $\nu_s > \nu_p$, which limits the application of MWDR. In this case waveguide cut off and low pass filters provide a simple means for the separation of the pump from the signal radiation.

In the course of our experiments we developed an absorption cell, by which we overcome this limitation in a simple way.

This cell can be used for $\nu_s > \nu_p$- and for $\nu_p > \nu_s$-experiments in a similar simple arrangement and over a very broad frequency range.

The pump and signal modes in the cell as shown in Fig. 1 are very different in type. In the waveguide the microwave propagates in an usual waveguide mode, along the septum corresponding to a stripline mode. A mode transition seems rather unlikely. According to our experience it is simpler to separate signal and pump radiation in the "stripline"-cell than in a former arrangement [5]. If the signal source is of weak intensity, as it is common for $\nu_s > 40$ GHz, the direct feed into the cell waveguide helps to get a higher detector current than using directional couplers[2].

The construction is given in Figure 1. The "stripline"-cell is in principal a Stark-cell with two connectors. The septum has been modified to a stripline like inner conductor. A vacuum tight SMA connector (1) is soldered into the narrow wall of an oversized waveguide and connected to the septum, which is in its first part a 50 Ω stripline (2) between two parallel grounded plates [9] formed by the broader walls of the waveguide. To minimize a deadjustment of the septum by the Teflon strips (3) especially during the cooling of the cell, the Teflon strips have been cut into two parts. In addition a Teflon rod (4) is pressed to the septum.

The transmission in the stripline mode is attenuated by 1.5 db from DC to 2.4 GHz. In the region up to 18 GHz the transmission fluctuated with frequency, but it proved always sufficient for the experiments. For the waveguide mode the cell of 4 m length was used to 40 GHz. In a second version with X-band waveguide[3] with a length of 1.50 m transmission in the waveguide mode is sufficient to frequencies above 100 GHz.

The cell is used in configurations of the spectrometer given in Figs. 5 and 6. Figures 2—4 give the details for the signal and pump sources. Signal and

[1] Here "microwave" means the region from radiofrequency to millimeter waves.

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[2] The new cell has a superior performance than that, we published some years ago [8].

[3] Here Omni Spectra connector TNC part No. 3152-5006-10 is used.

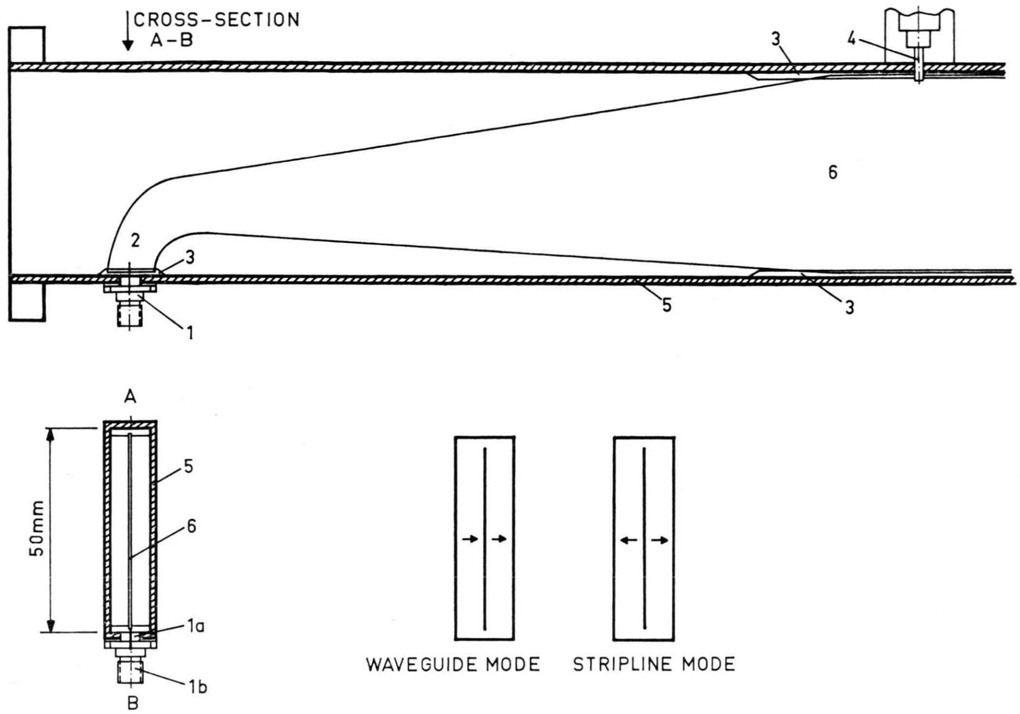

Fig. 1. Construction of the DR-absorption cell. The other end of the cell is of the same form with the SMA connector on the opposite side.

1, 1a, 1b SMA connector, Fa. ECM part no. 64HS-80-0 and 6540.
2 Stripline nose of septum 50 Ω, 11 × 0.5 mm.
3 Teflon strip 10 × 1,5 mm, groove 0.5 × 0.75 mm.
4 Teflon rod ⌀ 2 mm pressed to the septum. Rod holder connected to the vaccum line.
5 Oversized waveguide 50 × 10 mm inner, 53 × 13 mm outer cross section.
6 Septum 48.5 × 0.5 mm.

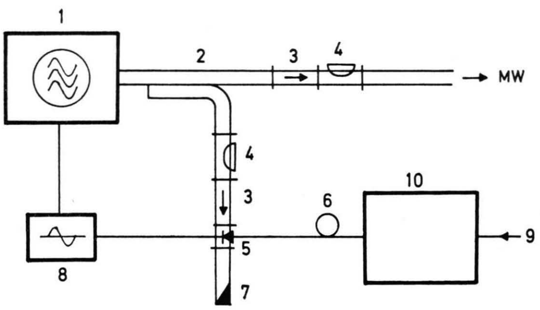

Fig. 2. Phase locked MW-signal source for DR-spectrometer.

1 BWO-sweeper (Hewlett-Packard 8690 B),
2 Directional coupler 10 db,
3 Waveguide isolator,
4 Variable attenuator,
5 Mixer,
6 Tuner,
7 Termination,
8 Synchronizer (Schomandl FDS 30),
9 Input of normal frequency,
10 Frequency standard with digital sweep (Rohde and Schwarz XUC, SMDH and digital sweep generator [12]).

pump sweeps are possible. It should be pointed out that for the KU-band the replacement of the pump-source BWO by a YIG-Tuned Gunn Oscillator was tested. It was phase locked to the frequency standard by a special interface[4].

The DR-spectrometer was successfully applied to the assignment of rotational lines in torsional excited states of dimethylselenide $(CH_3)_2Se$, using three level double resonances. Here the pump frequencies were near 6.7 GHz on the stripline for the $1_{01}-1_{20}$ transitions, the signal frequencies were near 24.9 and 38.4 GHz in the waveguide for the $1_{01}-2_{12}$ and $1_{10}-2_{21}$ transitions, respectively. Detailed results will be given in a later paper, when the analysis of the torsional fine structure will have been performed.

For hydrogen cyanide, HCN, we performed four level DR-experiments, which are labeled by (a) in

[4] See appendix.

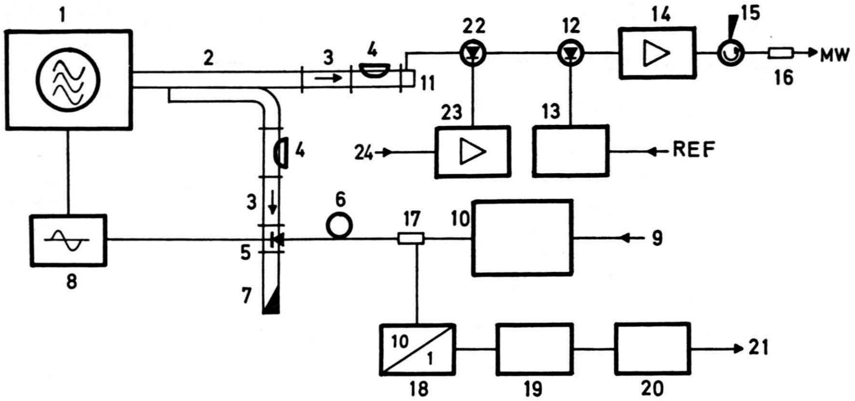

Fig. 3. Phase locked and levelled MW-Pump source for DR-spectrometer.

1–9 see Fig. 2.
1 The BWO may be replaced by a YIG-Tuned Gunn Oscillator.
10 Frequency standard (Rohde and Schwarz XUC with motor drive).
11 Waveguide to coax transition.
12 Pinswitch (Hewlett-Packard, Alpha-Industries, General Microwave).
13 Pin power supply and TTL-Pulse former.
14 TWT-amplifier (Hughes 1277 H 09, 1–2 GHz, 20 W; 1177 H 03, 8–12 GHz, 10 W; 1177 H 04, 12–18 GHz, 10 W; Varian VTC-6160 B 1, 4–8 GHz, 20 W).
15 Circulator with termination.
16 Low pass filter (Sage, K + L, RYT).
17 Directional coupler.
18 High speed frequency divider for frequencies up to 1.2 GHz (Plessey Sp 8667 B).
19 Frequency counter (Fluke 1953 A with parallel BCD output).
20 Marker generator.
21 Output to recorder.
22 Pin attenuator (General Microwave).
23 Leveling amplifier.
24 Input from detector 14 Fig. 5.

Table 1. The other experiments (b) were made with a cell in the arrangement described in [5]. From the signal to noise ratio of the measured signal transitions we state that also all transitions may be found easily as collisionally induced signals, which are in frequency between the pump and observed signal transition.

From these experiments it may be deduced that a collisional energy transfer is observable at least to a J value differing by 7 from that of the pump transition. Hithertoo only a difference of 4 was reported [10]. The stepwidth ΔJ of a single collision cannot be derived from this experiment.

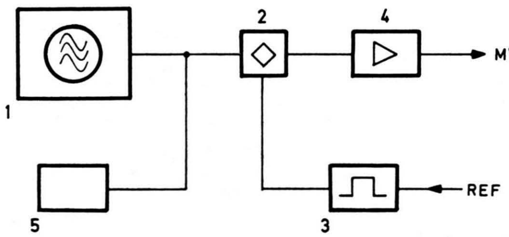

Fig. 4. RF-Pump source for DR-spectrometer.

1 RF-Oscillator,
2 Double balanced mixer,
3 Square wave generator,
4 Power amplifier (Hughes 46148 H, 0.5–1 GHz, 10 W),
5 Counter.

Table 1. Four level DR-experiments for HCN l-doublet-transitions, bending vibrational state $v_l = 1$, $l = \pm 1$. For $\nu_s > \nu_p$ see Fig. 5, for $\nu_p > \nu_s$ see Figure 6. Transition frequencies:

J	5	6	7
ν [MHz]	6731.89[c]	9423.32	12562.32
J	8	9	10
ν [MHz]	16562.32	20181.40	24660.31
J	11	12	13
ν [MHz]	29584.66	34953.76	40766.90

Pump transition	Signal transition			
$J = 5$	$J = 7$[a]	$J = 9$[a, b]	$J = 10$[b]	$J = 11$[b, d]
$J = 6$	$J = 10$[b]	$J = 11$[b]	$J = 12$[b]	$J = 13$[b]
$J = 7$	$J = 5$[a, e]	$J = 8$[b]	$J = 9$[b]	
$J = 8$	$J = 5$[a]	$J = 9$[a, b]		

[a] Performed with the set up reported in this work.
[b] Performed with the set up of 5.
[c] Frequencies from 10.
[d] S/N approx. 10, $p = 30$ mT, $RC = 1.25$ sec.
[e] S/N better than 25, $p = 20$ mT, $RC = 1.25$ sec.

Further four level double resonances were observed for formaldehyde, H_2CO. The transitions are given in Table 2.

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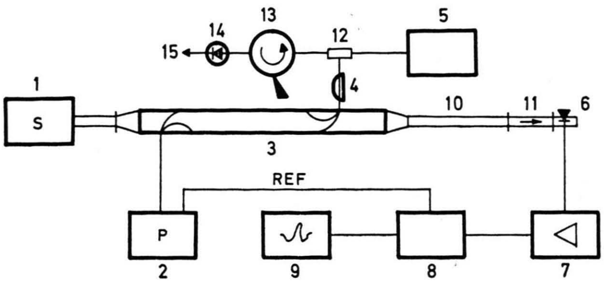

Fig. 5. DR-Spectrometer for $\nu_s > \nu_p$.
1 Signal source see Fig. 2,
2 Pump source see Fig. 3 or 4,
3 Cell,
4 Attenuator,
5 Power meter,
6 Detector for ν_s,
7 Amplifier,
8 Phase sensitive detector,
9 Reocrder,
10 Cut off filter,
11 Waveguide isolator,
12 Directional coupler 10 db,
13 Circulator,
14 Detector for pump leveling,
15 Output to leveling amplifier Fig. 3,
12–15 When Pump source Fig. 3 is used.

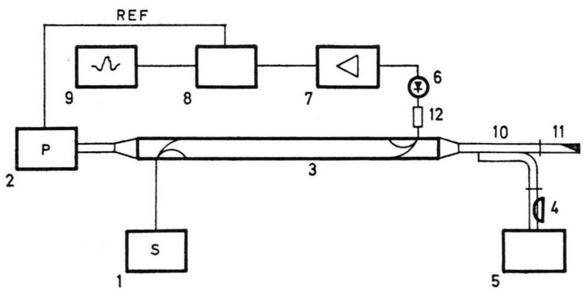

Fig. 6. DR-Spectrometer for $\nu_p > \nu_s$.
1 Signal source see Fig. 2,
2 Pump source see Fig. 3 or 4,
3 Cell,
4 Attenuator,
5 Power meter,
6 Detector for ν_s,
7 Amplifier,
8 Phase sensitive detector,
9 Recorder,
10 Directional coupler 10 dB,
11 Termination,
12 Low pass filter.

Table 2. Four level DR-experiments for H_2CO. For $\nu_s > \nu_p$ see Fig. 5, for $\nu_p > \nu_s$ see Figure 6.

Pump transition $J_{K_-K_+}-J'_{K'_-K'_+}$	Pump frequency ν_p [MHz]	Signal transition $J_{K_-K_+}-J'_{K'_-K'_+}$	Signal frequency ν_s [MHz]
$1_{11}-1_{10}$	4829.73	$2_{12}-2_{11}$	14488.65
$2_{12}-2_{11}$	14488.65	$1_{11}-1_{10}$	4829.73

equipment in other applications, Mr. H. Feldmeier for preparing the drawings, the Deutsche Forschungsgemeinschaft and the Fonds der Chemie for financial support.

Appendix

To test the replacement of BWO sources by YIG-Tuned-Gunn Oscillators (YTGO) in a MW-spectrometer we constructed a phase locked YTGO source using a Systron-Donner Mod. SDYX-3001, 12.4–18 GHz, 25 mW YTGO.

Comparison of Stark spectra recorded with phase locked BWO-and YTGO-sources showed a signal to noise ratio better by approximately a factor of two for the BWO-source. For cases where an extrem sensitivity is not required, YTGO's may be used in Stark spectroscopy.

For DR-experiments no difference between phase locked BWO- and YTGO-pump source have been noticed, presumably because a TWT-amplifier is rather noisy. In this case the full advantage of the low voltage power supply, the claimed longer life time and lower price of a YTGO may be taken without sacrifying sensitivity.

Details of the construction may be obtained from the authors upon request.

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