

# Pulsed Microwave Microwave Double Resonance Spectroscopy with Fourier Transform Technique

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We present a new three and four level double resonance spectroscopy in the microwave region. A pulsed pump radiation and Fourier transform technique for detection of the signal radiation is used. This method is complementary to that using continuous microwave pump radiation.

## 1. Introduction

Recently we showed that microwave (MW) double resonance experiments can be performed with microwave Fourier transform (MWFT) techniques [1]. In our first experiments we used a continuous microwave (CW) pump radiation. One observation is that the transient emission signal in the presence of a CW pump radiation decays faster. This results in an additional line broadening, as can be seen in Fig. 3 of [1].

In this paper we present an extension to pulsed MW pump radiation. Switching off the pump radiation during the period of polarization of the molecular ensemble and the measuring time of the transient emission signal the additional line broadening can be avoided. So the high resolution of the MWFT spectroscopy can be maintained.

## 2. Experimental

The construction of our standard MWFT spectrometer was reported in detail in [2–4]. For microwave microwave double resonance spectroscopy we made some changes in our experimental set up.

The MW switch control has to be modified for the double resonance technique. Other changes and the general set up are given in Figure 1.

We use also a new averaging system with a maximum repetition rate of 26 kHz for the experiments collecting 1024 data points during each measuring cycle.

### a) Pump pulse generation

The phase stabilized K-band MW source (**1** in Fig. 1\*) was pulse modulated by a MW switch **17** and amplified to a maximum level of about + 30 dBm. The MW switch is specified for frequencies up to 18 GHz, but it was used in the whole K-band up to 26.5 GHz without deterioration of the pulse shape. The pump pulse reaches the sample cell via a special X-band coax to waveguide transition **12**. A K-band waveguide was introduced on its back side as shown in Figure 2. The X-band isolator **22** did not disturb the experiment.

### b) Signal pulse generation

The phase stabilized X-band MW source **13** was pulse modulated by a special technique called phase alternating pulse sequence (PAPS) **18, 19** (see also Figure 3). By this technique the phase of the transient emission signal is alternated by 180 degrees. Alternating also additions and subtractions in the signal averaging system samples only the emission signal and cancels coherent disturbances to a large extent. By using sequences of pulse pairs of each phase an influence of the transient emission signal following the foregoing pulse is eliminated. This method is used in NMR spectroscopy and described in more detail below.

### Signal detection

Because the pump radiation may damage the MW preamplifier **24** we inserted one (or two) low-pass filters **23** in front of the detection system. The

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\* Numbers refer to Fig. 1 or 4 respectively.

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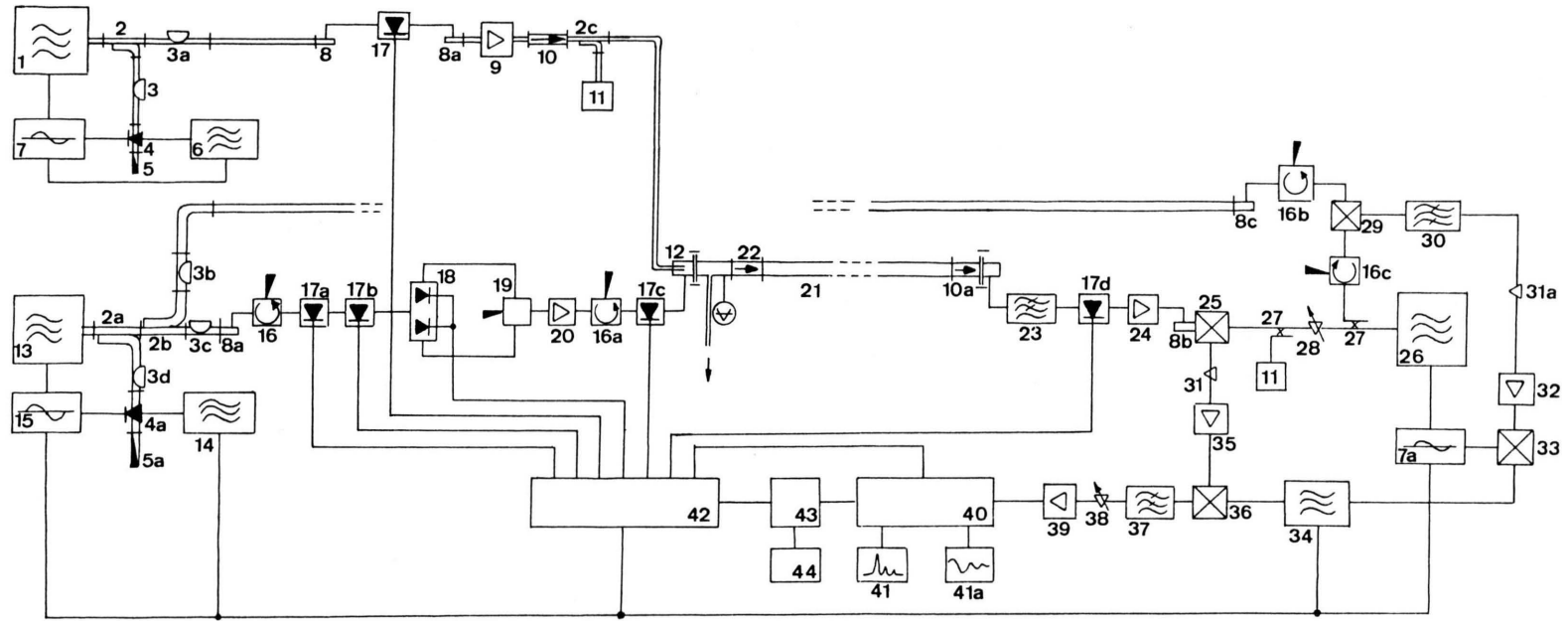


Fig. 1. Microwave microwave double resonance Fourier transform spectrometer, X- and K-band. List of devices and parts.

- |                                                                                                     |                                                                                                               |                                                    |
|-----------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------|----------------------------------------------------|
| 1 Backward wave oscillator, Hewlett Packard, 8690B with 8696A (18–26.5 GHz);                        | 15 Synchronizer, Rhode and Schwarz, XKG;                                                                      | 28 Attenuator, coax;                               |
| 2 Directional coupler, 20 dB;                                                                       | 16 Isolator, coax;                                                                                            | 29 Microwave mixer, Watkins Johnson, M17C;         |
| 3 Waveguide attenuator;                                                                             | 17 Microwave switch, Hewlett Packard, 33144A, with driver 33190B;                                             | 30 Bandpass filter, 160 MHz;                       |
| 4 Waveguide mixer;                                                                                  | 18 Microwave switch, SPDT, General Microwave, F8928;                                                          | 31 Attenuator;                                     |
| 5 Termination;                                                                                      | 19 Hybrid 3 dB, TRM, HS 510, 8–12.4 GHz;                                                                      | 32 Amplifier, 160 MHz;                             |
| 6 Frequency standard, Rhode and Schwarz, XUC and interpolation oscillator, Rhode and Schwarz, SMDH; | 20 TWT amplifier, Hughes, 1177H, X/Ku-band;                                                                   | 33 IF mixer;                                       |
| 7 Synchronizer, Schomandl, FDS 30;                                                                  | 21 Square X-band sample cell, 25 × 25 mm with taper, mode filter, gas inlet system and capacitance manometer; | 34 Frequency multiplier, 10 to 130 MHz;            |
| 8 Waveguide to coax transition;                                                                     | 22 Waveguide isolator, Pamtech XHG 2001;                                                                      | 35 Amplifier, 160 MHz;                             |
| 9 TWT amplifier, Hughes, 1077H, K-band;                                                             | 23 Microwave lowpass filter, 18 GHz;                                                                          | 36 IF mixer;                                       |
| 10 Waveguide isolator;                                                                              | 24 Microwave preamplifier, AvanteK, AMT-12435, 37 dB gain, 4 dB noise figure;                                 | 37 Lowpass filter, 50 MHz;                         |
| 11 Microwave power meter;                                                                           | 25 Orthoguide double balanced mixer, RHG, WMP12CO6EC;                                                         | 38 Variable attenuator;                            |
| 12 Special coax to X-band transition with K-band coupling;                                          | 26 Backward wave oscillator, CSF, CO521 with power supply;                                                    | 39 Amplifier;                                      |
| 13 Backward wave oscillator, Hewlett Packard, 8690B with 8694A (8–12.4 GHz);                        | 27 Directional coupler, coax;                                                                                 | 40 Transient recorder and signal averaging system; |
| 14 Frequency standard, Hewlett Packard, 8656A, 0.1–990 MHz;                                         |                                                                                                               | 41 Display unit;                                   |
|                                                                                                     |                                                                                                               | 42 Microwave switch control unit;                  |
|                                                                                                     |                                                                                                               | 43 Minicomputer Texas Instruments, DS 990/10;      |
|                                                                                                     |                                                                                                               | 44 Terminal.                                       |

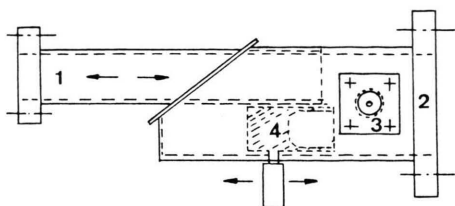


Fig. 2. Special coax to X-band transition with K-band coupling. 1. Adjustable K-band waveguide; 2. X-band waveguide; 3. SMA connector; 4. Adjustable short.

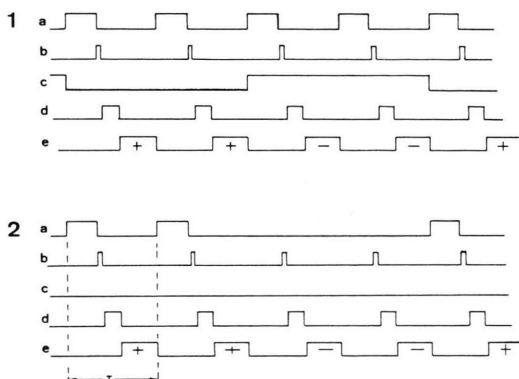


Fig. 3. Simplified diagram of pulse generation and signal averaging for pulsed microwave double resonance experiments. 1. Pulsed pump experiment, 2. Sequential pulsed pump experiment. a) Microwave pump pulse (K-band) 1 to 18  $\mu$ s. b) Microwave signal pulse (X-band) 0.1 to 0.3  $\mu$ s. c) Phase alternation of the signal pulse. d) Data collection. e) Signal averaging (+ addition, - subtraction). Experiment time  $\tau = 40$  to 60  $\mu$ s, depending on pump pulse length.

transient emission signal is amplified **24** and frequency converted downwards in two steps **25**, **36**. For experiments with pulsed pump radiation one may omit the lowpass filter if the MW switch **17d** is closed during the pump and polarizing signal pulses. This may allow double resonance experiments with neighbouring pump and signal frequencies.

#### Signal averaging system

The speed of our new signal averager **40** was increased by use of faster digital circuitry and averaging the sampled data points by four channels in parallel as shown in Figure 4. Because most of the transient emission signals have a signal to noise ratio less than 1/2 we use a one bit digital transient

recorder with a 1024 data points memory and sample rates of 10, 20, 50 or 100 ns. The sample rate circuitry is synchronized to the 10 MHz system frequency by frequency multiplying. The signal averaging system and the microwave switch controller **42** are connected to a minicomputer controlling the whole system.

#### Pulse sequences for double resonance experiments

A simplified diagram of the pulse sequences and signal averaging modes is shown in Figure 3. The first experiment was made with a pump pulse train as shown in line **1a**. The pump pulse length is adjustable from 1  $\mu$ s to 18  $\mu$ s. Approximately 0.1  $\mu$ s after the end of each pump pulse the signal pulse for preparing the molecular ensemble was generated **1b** and phase alternated according to **1c**. After collecting the data from one transient emission signal an averaging by adding or subtracting synchronized to the phase alternation starts. Depending on the pump pulse length one experiment takes a time between 40 and 60  $\mu$ s. The following four equations give the recorded signals.  $f_p(t)$  is the transient emission signal under measurement,  $\bar{f}_p(t + \tau)$  is that remaining from the foregoing pulse, the index p indicates that the MW pump pulse was generated and  $\tau$  is the experiment repetition time:

$$\begin{array}{rcl} f_p(t) - \bar{f}_p(t + \tau) & & + \\ f_p(t) + \bar{f}_p(t + \tau) & & + \\ -f_p(t) + \bar{f}_p(t + \tau) & & - \\ -f_p(t) - \bar{f}_p(t + \tau) & & - \end{array} \quad (1)$$

Adding and subtracting the signals results in  $4f_p(t)$ .

The second experiment was made by omitting each second pulse pair and the phase changes as given in Fig. 3 (**2a**, **2c**). The data collection results with a consideration similar to **1** in a signal of  $2(f_p(t) - f(t))$ , where  $f(t)$  is the decay function without pump pulse influence.

#### 3. Three level double resonance

We tested the spectrometer with carbonyl sulfide, OCS, its isotopic species and allyl cyanide-gauche,  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CN}$ . We demonstrate the performance with spectra of the latter substance. The level system is shown in Figure 5a.

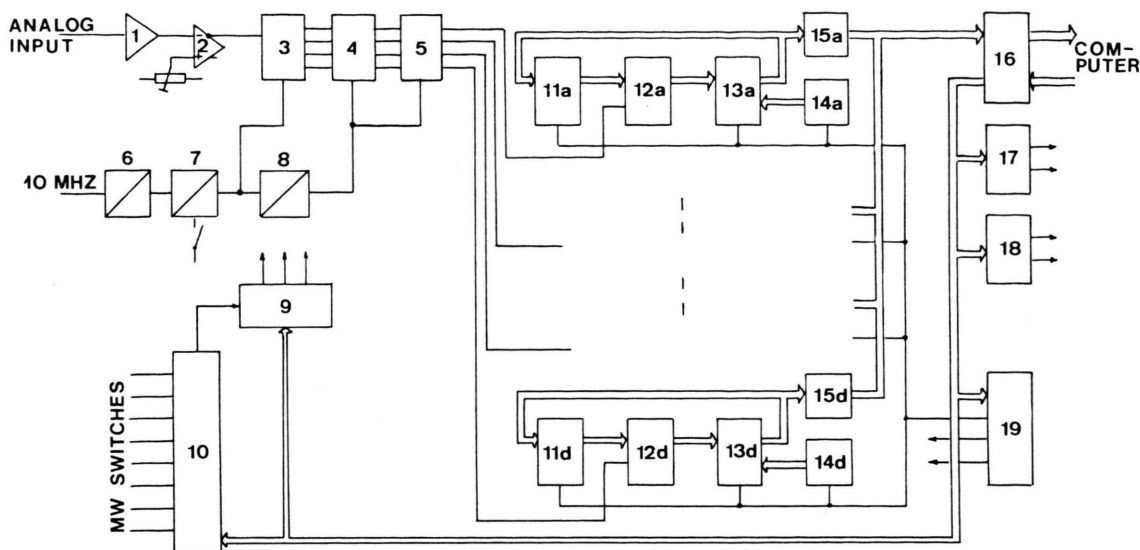


Fig. 4. Simplified block diagram of transient recorder and signal averaging system.

- |                                      |                                    |
|--------------------------------------|------------------------------------|
| 1 Input buffer;                      | 9 Data record control and synchro- |
| 2 1 bit analog to digital conversion | nization;                          |
| (comparator);                        | 10 MW switch control circuit;      |
| 3 4 bit shift register;              | 11 a-d: 16 bit register;           |
| 4 4 bit register;                    | 12 a-d: 16 bit adder/subtractor;   |
| 5 256 × 4 bit random access memory   | 13 a-d: 256 × 16 bit RAM;          |
| (RAM);                               | 14 a-d: Address counter;           |
| 6 Frequency multiplier 10 MHz to     | 15 a-d: Output bus buffer;         |
| 100 MHz;                             | 16 Computer interface buffer;      |
| 7 Divide by N counter,               | 17 Analog data output;             |
| N = 1, ..., 16;                      | 18 Analog data output;             |
| 8 Divide by 4 counter;               | 19 Signal averaging control.       |

In Fig. 6a a 20 MHz section out of the rotational spectrum recorded with the usual MWFT technique [2-4] is given. For comparison in Fig. 6b a three level double resonance spectrum is shown. A CW pump radiation of 19459.480 MHz, 100 mW, near resonant to the  $\nu_p = 8_{17} - 8_{08}$  transition was applied. It is observed, that the  $\nu_s = 7_{26} - 8_{17}$  transition (8326.200 MHz) splits and decreases in intensity. The other unassigned transitions (8312.91, 8327.34, 8330.27 and 8332.77 MHz) are unchanged. We conclude that they are negligibly influenced by the pump radiation.

In Fig. 7a the measurement of Fig. 6a was repeated with a different length of the polarizing signal pulse. The double resonance spectrum of Fig. 7b resulted by applying a pump pulse with 19459.480 MHz and 100 mW of 18  $\mu$ s length ending 0.1  $\mu$ s prior to the polarizing signal pulse (see Figure 3a). The transition  $7_{26} - 8_{17}$  increases by a

factor 2.5, which was calculated by referring to the other four lines.

Assuming saturation of the  $8_{17} - 8_{08}$  transition, which was checked experimentally by increasing the pump power, a factor of  $(1 + \nu_s/2\nu_p)^2 = 4.7$  may be

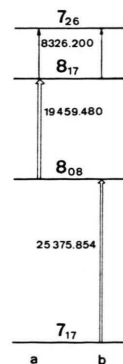


Fig. 5. Level scheme of 3- and 4-level double resonance experiments (frequencies in MHz).

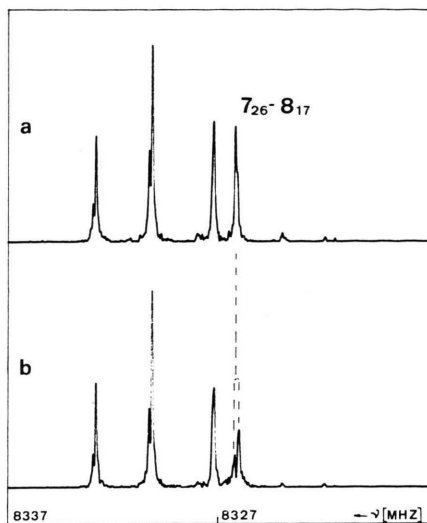


Fig. 6. 20 MHz scan out of the rotational spectrum of allyl-cyanide-gauche, transition  $7_{26}-8_{17}$ ,  $\nu = 8326.200$  MHz. The other transitions are unassigned. Data acquisition: 1024 data points, expanded to 4096 data points prior to Fourier transform, 10 ns sample interval, 256 K averaging cycles ( $K = 1024$ ),  $p = 0.3$  mTorr,  $T = 240$  K. a) Standard spectrum without pump radiation. b) 3-level double resonance experiment with continuous pump radiation,  $\nu_p = 19459.480$  MHz,  $P = 100$  mW. Transition frequencies of the splitted  $7_{26}-8_{17}$  transition:  $\nu_1 = 8326.050$  MHz,  $\nu_2 = 8326.247$  MHz.

calculated assuming Boltzmann distribution before the onset of the pump pulse. As a power spectrum is recorded, the relative change in occupation number difference has to be squared. The calculated value must be considered as an upper limit, as there is a delay between the pump and polarizing pulse. It may be mentioned that the signal transition does not change in line width.

Under certain conditions the pulse method may be superior to the CW method [1]. This is demonstrated in Figure 8. In Fig. 8a a CW pump radiation was applied at a higher sample pressure of 1.2 mT. The  $7_{26}-8_{17}$  transition cannot be observed clearly. As a decrease of pump power (Fig. 8b) to 30 mW increases the intensity of the  $7_{26}-8_{17}$  transition, we assume, that the additional relaxation due to inhomogeneous pump field makes the transient emission unobservable, before its measurement starts.

Figure 9 demonstrates a method for determination of the resonant pump frequency  $\nu_p$ . By varying  $\nu_p$  and observing the intensity of the signal transition  $7_{26}-8_{17}$  relative to the uninfluenced lines one gets a maximum for the signal transition for a pump fre-

quency of 19459.480 MHz. By interpolation from Figs. 9a and 9c one gets 19459.478 MHz. The transition  $8_{17}-8_{08}$  was calculated at 19459.488 MHz [5].

Figure 7c demonstrates another variation of the double resonance experiment. It should be compared with Figs. 7a and 7b. A pump and signal pulse sequence, as given in Fig. 3, part 2, was used. Only the  $7_{26}-8_{17}$  transition can be observed. The three other lines are eliminated, which ensures again that they are not influenced by the pump.

We like to remark that the difference spectrum is weaker as it may be estimated from the signal to noise ratio in Figs. 7a and 7b. But calculating the relative amplitude of the power spectrum of the difference signal using the measured value of  $f_p(t)/f(t) = \sqrt{2.5}$  (see above) one gets with  $2(f_p(t) - f(t)/4f(t))^2$  a value of 8.5% in good agreement with the measured signal.

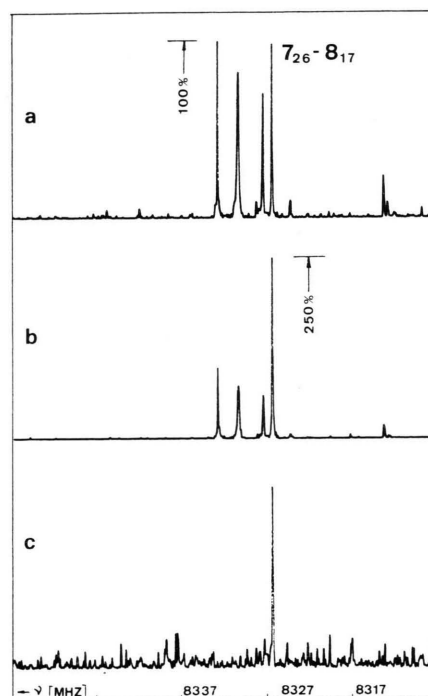


Fig. 7. 50 MHz scan out of the rotational spectrum of allyl-cyanide-gauche, transition  $7_{26}-8_{17}$ , ( $\nu = 8326.20$  MHz). The other transitions ( $\nu = 8312.91, 8327.34, 8330.27, 8332.77$  MHz) are unassigned. Data acquisition: 1024 data points, 10 ns sample interval, 256 K averaging cycles ( $K = 1024$ ),  $p = 0.5$  mTorr,  $T = 240$  K. a) Standard spectrum without pump radiation. b) 3-level double resonance experiment with pulsed pump radiation,  $\nu_p = 19459.480$  MHz,  $P = 100$  mW and  $t = 18 \mu s$ . c) Measurements of the difference spectrum as described in the text.

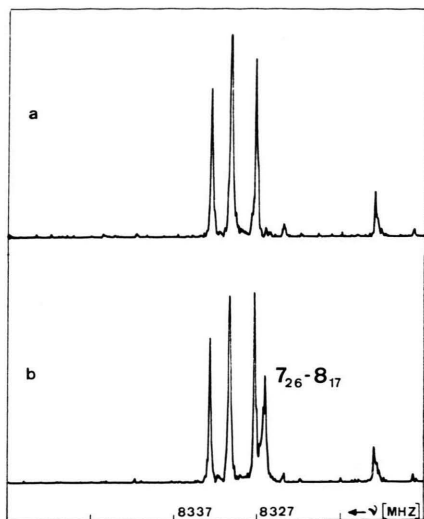


Fig. 8. Same as Fig. 7 except pressure.  $p = 1.2$  mTorr. a) 3-level double resonance experiment with continuous pump radiation,  $\nu_p = 19459.480$  MHz,  $P = 100$  mW. b) Same as a) except  $P = 30$  mW.

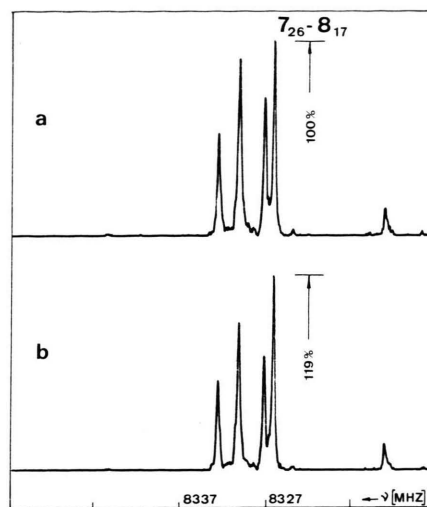


Fig. 10. Same as Fig. 7 except pressure.  $p = 1.4$  mTorr. a) Standard spectrum without pump radiation. b) 4-level double resonance experiment with pulsed pump radiation  $\nu_p = 25375.854$  MHz,  $P = 100$  mW,  $t = 18$   $\mu$ s.

#### 4. Four level double resonance

Four level double resonance experiments were performed with the  $7_{26}-8_{17}$  signal and the  $8_{08}-7_{17}$  pump transition, as indicated in Figure 5b. Only first order dipolar collision induced transitions of  $\mu_b$ -type are present within these four levels.

As can be seen from Fig. 10 the intensity increases by approximately 19% by applying the pump radiation. The resonant pump frequency may also be found by variation of  $\nu_p$ . The value is near to the value measured by Stark spectroscopy to 25375.854 MHz [5] for the  $8_{08}-7_{17}$  transition. The difference spectrum could not be observed clearly in this case.

#### 5. Theory

A theoretical expression for the transient emission signal can easily be derived for the three level double resonance from [1], Chapter 3\*. The Eqs. (5) of [1] modify to

$$\varepsilon_p \neq 0, \quad \varepsilon_s = 0 \quad \text{for } t \leq 0 \quad (\text{period A}), \quad (2a)$$

$$\varepsilon_p = 0, \quad \varepsilon_s \neq 0 \quad \text{for } 0 \leq t \leq t_1 \quad (\text{period B}), \quad (2b)$$

$$\varepsilon_p = 0, \quad \varepsilon_s = 0 \quad \text{for } t \geq t_1 \quad (\text{period C}), \quad (2c)$$

\* Definition of symbols are given there.

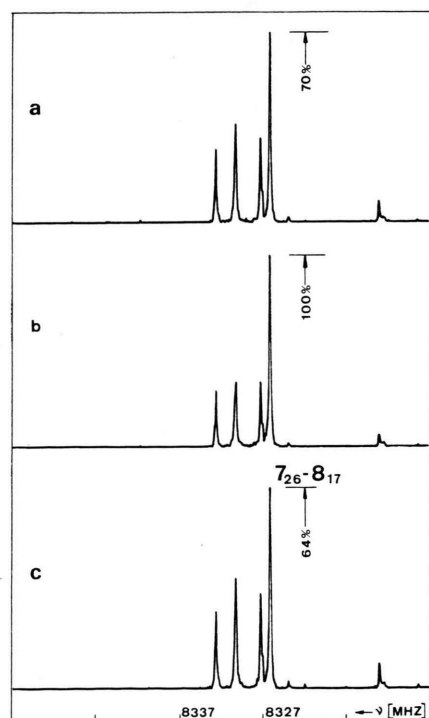


Fig. 9. Same as Fig. 7 except pressure.  $p = 1.4$  mTorr. a) 3-level double resonance experiment with off resonant pulsed pump radiation,  $\nu_p = 19459.000$  MHz,  $P = 100$  mW,  $t = 18$   $\mu$ s. b) 3-level double resonance experiment with resonant pulsed pump radiation,  $\nu_p = 19459.480$  MHz,  $P = 100$  mW,  $t = 18$   $\mu$ s. c) 3-level double resonance experiment with off resonant pulsed pump radiation,  $\nu_p = 19460.000$  MHz,  $P = 100$  mW,  $t = 18$   $\mu$ s.



neglecting the short period between the end of the pump and the beginning of the signal pulse.

The results for period A are identical to Eqs. (9) of [1]\*. In our present experiments  $\varepsilon_p = 0$  and  $\kappa_p = 0$  in the periods B and C. This experimental condition cancels some terms in (10) of [1], especially the two photon term  $U(t)$ . The simple condition for a  $\pi/2$ -pulse results from

$$V_s(t) = -\frac{\chi_s^3}{8\Omega^3} W_s(0) \sin 2\Omega t \quad (3)$$

which is again a special form of (10) of [1].

The polarization (14) of [1] which is proportional to the detected signal modifies to:

$$P(t') = -N_{\mu_{ab}} \exp(-\alpha t') V_s(t_1) \sin \omega_s t'. \quad (4)$$

For a signal pulse with  $2\Omega t_1 = \pi/2$  one obtains:

$$V_s(t_{\pi/2}) = -(W_s^0 + W_p^0/2). \quad (5)$$

One gets finally:

$$P(t') = N_{\mu_{ab}} (W_s^0 + W_p^0/2) \exp(-\alpha t') \sin \omega_s t'. \quad (6)$$

For the arrangement of levels as given in Fig. 5a the signal increases by saturation of the pump transition. With other arrangements of the levels the signal may decrease.

\* Equation (8 d) of [1] should be corrected to  $W_s(0) = W_s^0 + \chi_p^2 W_p^0/2(\alpha^2 + \chi_p^2)$ .

If it is possible to produce a pump  $\pi$ -pulse the initial condition (5) of the transient emission changes to

$$V_s(t_\pi) = -(W_s^0 + W_p^0) \quad (7)$$

which should give an increased effect.

From the above equations it is obvious that there is the possibility to increase the sensitivity of the spectrometer by transferring higher occupation number difference from high frequency transitions by applying high frequency pump pulses.

## 6. Summary

We think that pulsed microwave microwave double resonance spectroscopy is feasible. The pulsed pump and continuous pump technique need further development to be as useful a tool as double resonance in normal microwave spectroscopy.

## Acknowledgement

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