

A Contribution to the Investigation of Collision-Induced Transitions in the Microwave Range

H. Mäder, H. Dreizler and A. Guarnieri

Abteilung Chemische Physik im Institut für
Physikalische Chemie der Universität Kiel

(Z. Naturforsch. 30 a, 693 – 694 [1975];
received April 11, 1975)

A MW-MW-double resonance spectrometer for the investigation of collision-induced transitions is described and tested with some rotational transitions of ethylene oxide.

Collision-induced transitions between rotational levels have recently been investigated with MW-MW-double resonance technique, employing continuous MW-radiation and Stark-effect modulation^{1, 2}, or frequency modulated MW-pump radiation^{3, 4}. We have used in our experiment a square-wave amplitude modulation of the pump radiation. The experimental set-up is shown in Figure 1. The continuous microwave of a phase stabilized BWO is on-off-modulated by a PIN-modulator and is amplified by a TWT in order to obtain a maximum pump power of about 2 W. The rise and fall times of the microwave bursts as obtained from the PIN-modulator were less than 100 nsec and not noticeably modified by the TWT. In order to prevent the harmonics which are generated by the TWT to reach the signal detector, it was necessary to use a low pass filter. Up to now we have applied pump frequencies from 8 to 12.4 GHz and signal frequencies from 20 to 40 GHz. A special directional coupler⁵ turned out to be useful for the coupling of the signal radiation into the absorption waveguide.

The signal was recorded by means of a phase sensitive detector which was tuned to the modulation frequency of the pump radiation. The spectrometer was tested with the following rotational transitions of ethylene oxide.

Pump	Signal	
$1_{01}-1_{10}$	$2_{12}-2_{21}$	μ_b
11 385.71 MHz	34 157.10 MHz	
$1_{01}-1_{10}$	$0_{00}-1_{11}$	*
	39 581.6 MHz	
$1_{01}-1_{10}$	$4_{40}-4_{31}$	*
	34 148.3 MHz	

μ_b indicates that collisional “selection rules” of the type μ_b connect the levels of the pump-and signal transitions. Such connections are not present for the transition pairs labeled with *. For the first transition pair the signal is power and pressure dependent.

For the other transition pairs the signal form was different as shown in Figure 2. In this case the

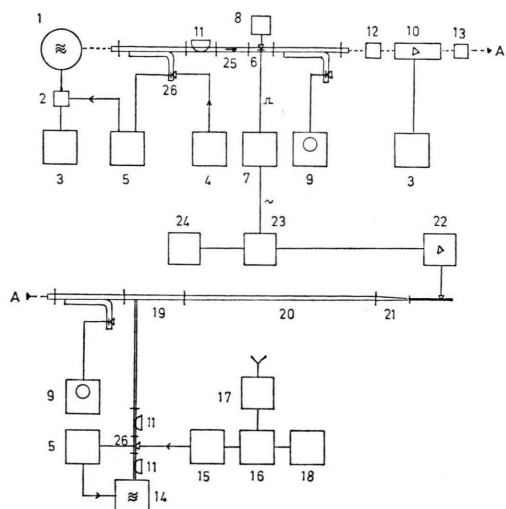


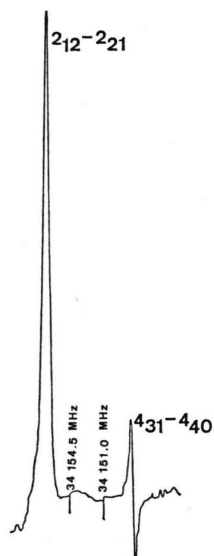
Fig. 1. Schematic of the MW-MW-double resonance spectrometer.

- 1 BWO, CSF 4032 B, 8–16 GHz,
- 2 Modulator for beam voltage correction,
- 3 Power supply, FXR Z 817 A,
- 4 Frequency decade, Schomandl FD 3, 300–1000 MHz,
- 5 Synchronizer, Schomandl, FDS 30, 30 MHz,
- 6 Pinmodulator, hp 8735 A,
- 7 Pulse generator, Amritsu MG 412 A,
- 8 Bias power supply, Philips PE 1507,
- 9 Oscilloscope, Tektronix 585,
- 10 TWT, Varian VTX 6084, 8–12.4 GHz,
- 11 Variable attenuator,
- 12 Attenuator 3 db,
- 13 Low pass filter, Sage, L 12 MA 049,
- 14 MW-sweeper, hp 8690 B, 8697 B, 26–40 GHz,
- 15 Frequency standard, Rohde & Schwarz XUC, 460–1000 MHz,
- 16 Frequency synthesizer, Rohde & Schwarz SMDH, 20–30 MHz,
- 17 Standard frequency receiver, DK Instruments, DX –10–9 D, 5 MHz reference,
- 18 Digital sweeper,
- 19 Directional coupler⁵, 10 db,
- 20 X-band absorption cell, 7 m,
- 21 Taper X to Q-Band,
- 22 Preamplifier 100 kHz,
- 23 Phase sensitive detector, Ithaco Dynatrac 391 A,
- 24 Recorder,
- 25 Uniline,
- 26 Mixer,
- MW-coaxial cable

modulation of the signal is most probably due to the high power effects of the pump radiation. The strong nonresonant radiation gives primarily rise to a second-order Stark-shift $\Delta\nu_M$ of each M-component of the signal line⁶. $\Delta\nu_M$ denotes the DC Stark shift corresponding to the pump radiation field amplitude which is about 40 V/cm for a radiation power density of 1 W/cm².

In order to control the result as found for the first transition pair we have used a different experi-





mental arrangement which allowed to pump the transition $2_{12}-2_{21}$ and to monitor the transition $1_{01}-1_{10}$. An OKI 30 V 12 Klystron was used as the frequency modulated pump and a BWO as the signal source. As modification to double resonance spectrometers described elsewhere^{1,4}, it turned out to be useful to apply a coaxial detector. The attenuation of the coaxial cable at 34 GHz and coaxial low pass filters provide a simple means to prevent the MW-pump radiation from reaching the detector. The result of the first experiment was confirmed.

We thank the Deutsche Forschungsgemeinschaft and Fonds der Chemie for funds.

Fig. 2. A portion of the MW-MW-DR spectrum of ethylene oxide, The $1_{01}-1_{10}$ MW transition at 11 385.7 MHz is pumped.

¹ T. Oka, J. Chem. Phys. **45**, 754 [1966].

² T. Oka, J. Chem. Phys. **48**, 4919 [1968].

³ A. M. Ronn and E. B. Wilson jr., J. Chem. Phys. **46**, 3262 [1967].

⁴ P. J. Seibt, J. Chem. Phys. **57**, 1343 [1972].

⁵ J. Ekkers, A. Bauder, and Hs. H. Günthard, Rev. Sci. Instrum. **45**, 311 [1974].

⁶ C. H. Townes and A. L. Schawlow, Microwave Spectroscopy, McGraw Hill Book Comp., New York 1955, Chap. 10-8.

⁷ R. C. Woods, III, A. M. Ronn, and E. B. Wilson jr., Rev. Sci. Instrum. **37**, 927 [1966].