

Infrared-Microwave Double Resonance Experiments with NH_3

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Infrared-microwave double resonance experiments have been performed with ammonia. The experimental equipment consists of a microwave spectrometer and an N_2O -laser. First results are in general agreement with previous experiments of other authors. Higher resolution reveals more details of the IR-pumped $\nu_2[a^qQ(8, 7)]$ transition. Several four-level systems were observed.

1. Introduction

Since the advent of infrared lasers, infrared-microwave double resonance (IR-MW-DR) experiments have been carried out by several groups^{1–9}. The effect of resonant laser pumping on a MW absorption line has been first clearly observed by Shimizu and Oka⁷, although weak effects due to non-resonant pumping had been found earlier. These authors studied double resonance effects in some three-level and four-level systems of ammonia. In a similar experiment⁹ double resonance in a three-level system of formaldehyde has been observed using a $3.5\ \mu$ He-Xe laser and millimeter waves. Microwave-optical double resonance has been reported by Field et al.¹⁰.

In an IR-MW-DR experiment IR laser radiation pumps molecules from a certain rotational level of the ground vibrational state into a rotational level of an excited vibrational state. The resulting non-Boltzmann rotational distribution in the ground state is monitored by MW absorption lines.

The use of a laser to pump molecular ro-vibrational transitions is limited by the degree of coincidence of the laser line with a particular transition. Conventional IR absorption spectra provide only approximate information on the expected degree of coincidence due to the limited resolution of IR grating spectrometers. Although CO_2 or N_2O lasers emit a multitude of lines^{11,12}, the tunability of a single line is limited to the Doppler width of the laser transition (≈ 60 MHz).

Before tunable IR lasers such as spin-flip Raman-lasers^{13–16} or Pb:Sn:Te diode lasers^{17,18} can be extensively used for spectroscopic purposes, recently developed methods like laser Stark spectroscopy^{19,20}, laser magnetic resonance spectro-

scopy^{21,22} and two-photon spectroscopy²³ are able to give very precise data now, but so far only few molecules have been investigated in those ways. For $^{14}\text{NH}_3$ a nearly exact coincidence with the P(13) line of the N_2O laser was found by F. Shimizu²⁰. In our experiments we made use of this coincidence.

2. Experimental

The experimental setup consists of two parts, an IR laser and a MW spectrometer (Figure 1). The laser tube of 1.8 m length and a diameter of 22 mm is sealed with KCl-Brewster windows at both ends and cooled by water. Nitrous oxide (N_2O) or carbon dioxide is used as the active gas, to which N_2 and He is added, giving a total pressure of about 5 or 9 Torr, respectively. A stabilized discharge current of about 30 mA is used.

The laser cavity consists of a blazed grating (71 l/mm) and a partially transmitting germanium mirror through which the power is coupled out.

The DR-measurements were performed with a concave mirror (radius of curvature 10 m, reflectivity 80 percent) and a flat one with a reflectivity of 95 percent. The IR power level inside the cell lay typically between 80 and 500 mW. Higher output power, which could be delivered by the laser, was avoided in the DR measurements with respect to the thermal sensibility of the grating (replica!). The laser spectrum was analyzed with a grating monochromator (Hilger & Watts, D 300). A chopper wheel inside the resonator provides square wave intensity modulation of the beam with a frequency of 1180 Hz. CW-power is measured by a thermopile (Coherent Radiation Lab., model 201 power meter). To isolate the laser from floor vibrations it is mounted on a concrete slab ($300 \times 25 \times 15\ \text{cm}^3$) which is sitting on three soft rubber pieces. Stabilizing the laser output by piezoelectrically tuning the cavity was not attempted so far.

The DR-cell is built from a 4 m long waveguide of dimensions $58.17 \times 29.083\ \text{mm}^2$. This cross

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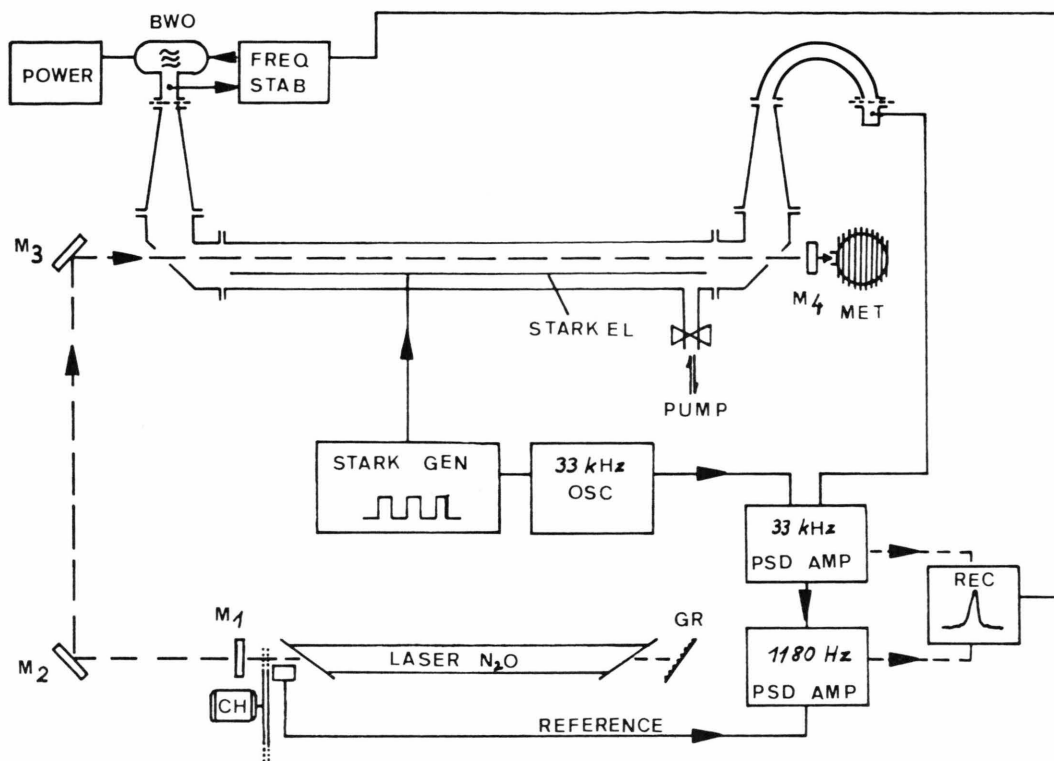


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ARRANGEMENT FOR MW IR DOUBLE RESONANCE

Fig. 1. Double Resonance Apparatus.

AMP amplifier
BWO backward wave oscillator
Ch chopper
GR grating
M 1, M 2, M 3, M 4 mirrors

MET power meter
PSD phase sensitive detector
REC recorder
STARK EL Stark-electrode
STARK GEN Stark voltage generator.

section, which is oversized compared with the (free space) wavelength around 1.3 cm used in this experiment, was chosen to reduce wall collisions. A Stark electrode was asymmetrically positioned in the cell to prevent it from being hit by the laser beam. The parallel IR-beam was coupled in and out of the cell by 90°-bends (E-corner), made of waveguide material, which were sealed by NaCl-windows of 6 mm thickness. The coupling knees showed serious reflections of the MW-radiation. As an alternative solution an oversized 3-dB-K-band directional coupler²⁴ was constructed, by the use of which the reflections could be reduced, but not avoided. The cell temperature can be lowered from room temperature to -90°C to increase sensitivity.

Phase-stabilized backward wave oscillators (CSF and Varian) serve as MW-sources. 33 kHz Stark-modulation can be used in addition to IR modulation (1180 Hz).

The sensitivity of the MW spectrometer part of the apparatus was tested with the well-known $\text{O}^{16}\text{C}^{13}\text{S}^{34}$ -isotope line ($0 \rightarrow 1$) at 11.82347 GHz. This line could be recorded with a S/N ratio of about 10. Two hyperfine components (209 kHz apart) of a particular transition of allylamine ($1_{1,0} \rightarrow 1_{0,1}$ at 19.802 GHz)²⁵ were used to test the resolution, which was found to be better than 200 kHz. The double resonance spectrometer was tested with ammonia as shown in the following chapter.

3. Results

The P(13) line of N_2O at 927.7425 cm^{-1} ¹² coincides almost exactly with the infrared transition $\nu_2[a^q Q(8, 7)]$ of ammonia²⁰ (Figure 2). Together with the (8, 7) inversion transition of the ground vibrational state it forms a three-level system. Due

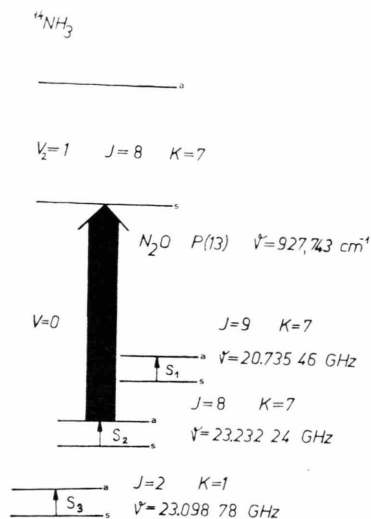


Fig. 2. Energy level-scheme of $^{14}\text{NH}_3$ showing three MW-transitions (S_1 , S_2 , S_3), forming one three-level (S_2) and two four-level systems (S_1 , S_3) together with the pumped transition.

to the IR pumping, the population in the common intermediate level decreases and thus the intensity of the microwave transition between the lowest two levels of the system increases. This increase in MW intensity was observed in the range of a factor of 1 to 15 of the original intensity, depending on the gas pressure. Extensive measurements of the pressure dependence of the relative change in the Stark-modulated MW absorption signal, (8, 7) of NH_3 , have been made, using a cw IR pump radiation. A change in MW absorption intensity of $1 \cdot 10^{-3}$ due to IR pumping was still detectable.

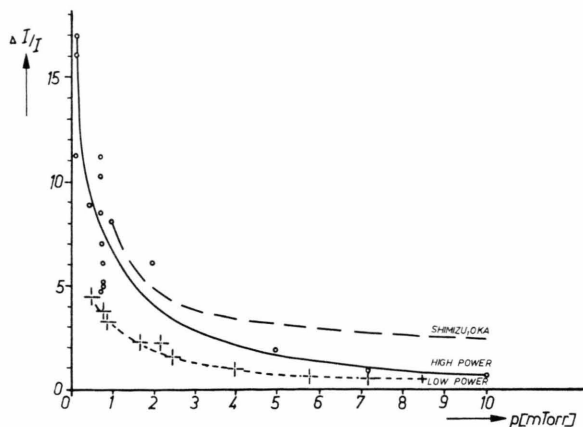


Fig. 3. Observed pressure dependence of $\Delta I/I$ due to IR-pumping in the three-level system of $^{14}\text{NH}_3$ of Fig. 2 and comparison with the results of Shimizu and Oka.

Our results of the pressure dependence of $\Delta I/I$ come close to those reported by Shimizu and Oka (upper curve in Figure 3)⁸. The designation "high power" and "low power" corresponds to IR-power densities of about 300 and 100 $\text{mW} \cdot \text{cm}^{-2}$, respectively. With a "high power" radiation and a sample pressure of 10 mTorr an increase in line intensity of approximately 60% was observed. At lower pressures the ratio $\Delta I/I$ increases steadily. At pressures below 0.5 mTorr the pumping becomes very efficient. To compare our curves with those of Shimizu we must take into account an uncertainty in our pressure measurement up to a factor of 3. Our seemingly lower efficiency at higher pressures can be accounted for by the fact that in contrast to Shimizu's arrangement our IR beam pumps only about 1/5 to 1/7 of the molecules interacting with the microwaves. Figure 4 shows a comparison between a normal microwave absorption line and the laser pumped absorption line. Pressure is below 0.5 mTorr.

Although the IR beam, which has a diameter of 12 mm at the cell entrance, diverges slightly within the cell, a considerable part of the power can be coupled out at the end of the cell for measurement purposes (alignment, control of laser operation, rough check of molecular absorption) and to prevent the MW-diode from being irradiated by too much IR power. If the power meter is replaced by a plane mirror the beam can be reflected for a second pass through the cell, thus enhancing the IR power in the interaction region. Figure 5 shows a comparison between three recordings: MW absorption without IR, the signal pumped by one pass of the IR beam, and the signal pumped with a reflected double-pass beam.

Shimizu and Oka have calculated the pumping effect on the MW line (8, 7) assuming that the Boltzmann distribution is disturbed only in the pumped levels and that the spectral width of the pump is small compared with the Doppler width. They derived⁸:

$$\frac{\Delta I}{I} = \frac{1}{2} \left(\frac{kT}{h\nu_M} \right) \sqrt{\pi} \gamma^2 (\delta\nu)^{-1} \left[\left(\frac{1}{2\pi\tau} \right)^2 + \gamma^2 \right]^{-\frac{1}{2}} \cdot \exp \left[\frac{-(\nu_L - \nu_0)^2}{(\delta\nu)^2} \right]$$

ν_M MW frequency,
 $\gamma = |\mu E_p|/h$ 900 kHz in this experiment,

$\delta\nu$	Doppler width of the IR transition $\nu_2[a^qQ(8, 7)]$ of NH_3 ,
$1/2\pi\tau$	relaxation frequency, 26 kHz at 1 mTorr,
$\nu_L - \nu_0$	difference between laser and transition frequency, 7.4 ± 1 MHz in this case ²⁶ .

General agreement with experimental values is found only at pressures above 5 mTorr, using the values mentioned above. At pressures below 1 mTorr the experimental values lie far above those calculated.

When the IR beam is chopped at 1180 Hz, the signal obtained by phase sensitive detection without Stark-modulation corresponds to the absolute change in MW absorption intensity due to IR pumping. Figure 6 shows a recording of the same line as on Figs. 4 and 5 but with IR instead of Stark modulation. The advantage of this method, compared with Stark modulation, is that no Stark lobes disturb the line shape and only the effect of the IR pumping is observed.

As the separation of the different hyperfine levels of the (8, 7) rotational state of NH_3 does not exceed 2 MHz, which is small compared to the Doppler width of the IR transition $\nu_2[a^qQ(8, 7)]$, all those levels are pumped by the laser radiation. Therefore hyperfine components should be expected in the DR spectrum. Resolution and sensitivity of our spectrometer are high enough that two pairs of hfs components, sitting symmetrically on each

side of the main line at a distance of approximately 1.5 and 1.8 MHz, can be clearly seen in double resonance. Figure 6 shows three of them. This hfs pattern was also observed in the pure MW-spectrum at the same frequencies which agree, within experimental errors, with the calculated values²⁷.

Considerations different from those of three-level systems apply to experiments with "four-level" systems. Here, a rotational transition is monitored which has no level in common with the pump transition. However, the two rotational levels monitored are connected with the pumped levels by relaxation processes. For reasons which have collectively been termed "collisional selection rules"^{28,29} the relaxation rates are in general different for different pairs of rotational levels. Therefore, applying the pump radiation will in many cases change the intensity of even those rotational transitions which are not directly connected with the pumping transition.

Again the $\nu_2[a^qQ(8, 7)]$ IR transition was pumped by the P(13) laser line for the investigation of four-level systems. The change in intensity upon pumping is of course not nearly as large as had been observed in the three-level system. The collision induced (9, 7) and (7, 7) transitions had been observed earlier by Shimizu and Oka⁸. In addition to these we have found several other 4-level systems³⁰. So far we have tested 20 transitions between 18 and 24 GHz by IR modulation and phase sensitive detection at 1180 Hz. Among these we found 14 lines which show an effect upon pump-

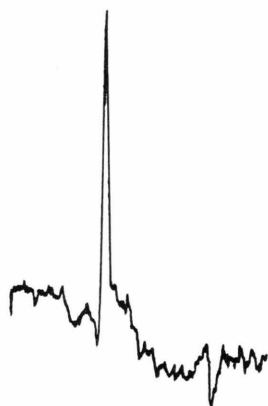


Fig. 4. Influence of the IR-pump on MW-absorption intensity on the (8, 7) line at low pressures (below 0.5 mTorr). Left: laser pumped line. Right: no laser power. Stark effect modulation (33 kHz) in both cases. Power density is about $300 \text{ mW} \cdot \text{cm}^{-2}$.

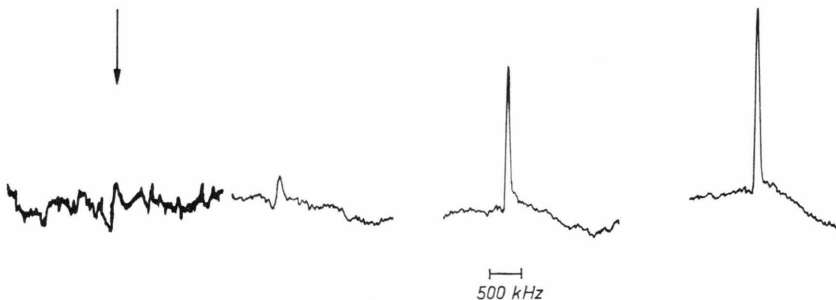


Fig. 5. Increase of $\Delta I/I$ due to double-pass IR-pumping. From left to right: no laser power, single-pass, double-pass pumping. Pressure is about 1 mTorr. Other conditions are the same as in Figure 4.

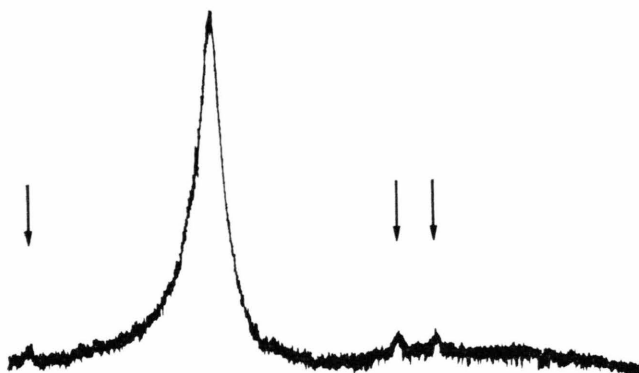


Fig. 6. Recording of the (8, 7) IR-MW double resonance signal obtained by applying IR-modulation at 1180 Hz and phase-sensitive detection of the MW-absorption signal. Hyperfine structure components were also observed (arrows). Power density is about $100 \text{ mW} \cdot \text{cm}^{-2}$.

ing. Figure 7 shows the recording of the lines (2, 1) at 23.09878 GHz and (9, 7) at 20.73546 GHz. The lines are recorded below the base line due to phase-sensitive detection. This shows that the microwave absorption intensity is decreased by IR pumping.

The relative change in MW absorption intensity, $\Delta I/I$, is strongly different for different collision-induced transitions. At 10 mTorr the highest value of $\Delta I/I$ between 18 and 24 GHz was found for the (9, 7) line ($\Delta I/I \approx 3\%$). This is about 40 times larger than the highest value of $\Delta I/I$ found for the other lines at this pressure. This seems to support the validity of the $\Delta J = 1$, $\Delta K = 0$ and parity ($+$ \leftrightarrow $-$) collisional selection rules govern-

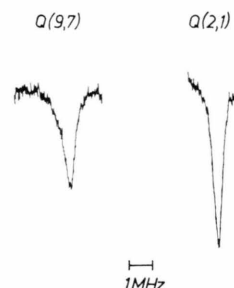


Fig. 7. Recording of the MW-transitions (2, 1) and (9, 7) of $^{14}\text{NH}_3$, not directly connected with the pumped transition (4-level systems) in double resonance applying pure IR-modulation at 1180 Hz. Power density is about $300 \text{ mW} \cdot \text{cm}^{-2}$. Pressure is about 10 mTorr. Scale is not the same for both recordings. The (9, 7) line is about 20 times larger than the (2, 1) line.

ing the transitions induced by NH_3 — NH_3 collisions²⁹. However, although ΔJ and ΔK is large for some lines — see for example the (2, 1) line — these lines have also been clearly observed. Measurements are in progress. Results will be published elsewhere³¹.

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