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Infrared-microwave double resonance: signal dependence on microwave radiation strength

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ABSTRACT

The influence of MW radiation on the magnitude of double resonance signals is studied in the case of steady-state 3-level IR-MW double resonance, using IR or MW radiation as probe field. The measurements reveal a strong signal dependence on the microwave power level. Changes in the absorption factor of more than 50% occur. They can be explained only if higher order effects are taken into account: the Takami theory is in good agreement with the measurements for both cases of probe field.

INTRODUCTION

In recent years a large number of double-resonance experiments has been performed. These are mainly used to extract structural data from complex spectra and for the investigation of relaxation phenomena.

In this paper we describe a few experiments on NH_3 where the influence of the microwave power level on the magnitude of the probe absorption in three-level infrared-microwave double-resonance experiments is investigated. Both infrared and microwave radiation have been used as probe fields. Each radiation field can be so strong that saturating of the corresponding transition occurs.

EXPERIMENTAL SET-UP

In the IR-MW double-resonance set-up a home-built tunable CO_2-laser is used as infrared source. Standard K-band microwave apparatus has been used except for the absorption cell. The number of coincidences between gas absorption frequencies and laser transition frequencies can be increased largely by the application of a strong external electric field (ref. 1). Therefore an open Stark cavity (ref. 2) is used for IR- and MW-absorption, since it allows for the introduction of electric fields with a high homogeneity ($3 \cdot 10^3$) and it offers a long microwave absorption path length (15 m). As the irradiated volumes of IR and MW are not identical, the observed changes in infrared and microwave absorption must be corrected to allow for a comparison with theoretical predictions. These corrections have been performed on the data presented below. The gas pressure range was limited at high pressure (above a few Pa) by sparking and at low pressure (less than 0.1 Pa) by the detection SNR.

THEORY

Relevant parameters in IR-MW double-resonance are the infrared and microwave transition rates given by $x = \mu_{IR}E_{IR}/h$ and $x_m = \mu_m E_m/h$ respectively and the collision transition rate γ. $\mu_{IR}(\mu_m)$ is the transition dipole moment for the infrared (microwave) transition with a radiation electric field vector E_i. In many cases one single relaxation rate is used which is of the order of the collision frequency and therefore proportional to the gas pressure p.

The first theoretical relation for steady-state 3-level IR-MW DR with microwave detection has been given by Oka (ref. 3). He assumed that the population of only one velocity class was changed by monochromatic infrared pumping and that microwave radiation did not influence the population distribution. The relative change $\Delta\alpha/\alpha$ induced in the microwave absorption α depends in a simple way on x and γ.

A much more advanced theory has been presented by Takami (refs. 4-5) using a density matrix model in which both radiation fields interact with the molecules simultaneously. By omitting the off-diagonal terms a rate equation model remains. The general theory is applicable for infrared as well as microwave detection, but the relevant formulas are very complicated.

RESULTS

Microwave detection

As an example we present measurements on the following system: infrared radiation at 27.96946 THz (CO_2 - P(32))) pumps the ammonia transition (v_2=0→1; J=5, K=3, M=5,sym→J=5, K=3, M=5,asym) at 1.235 MV/m. Microwave radiation at ν = 22833 MHz is then absorbed by the transition J=5, K=3, M= 4⇄5. The common level is the (J=5, K=3, M=5, asymm)-level.

We measured the dependence of the relative change $\Delta\alpha/\alpha$ induced in the microwave absorption due to laser pumping as a function of pressure (see fig. 1) using various microwave densities at one infrared power density.

As indicated (curve A) a good fit between the data and the Oka relation can be obtained, yielding values for x and γ. Such fits can also be made for the other series. However it results in different values for x! (A: 0.25 MHz; B:0.29 MHz; C: 0.41 MHz; D: 0.49 MHz).

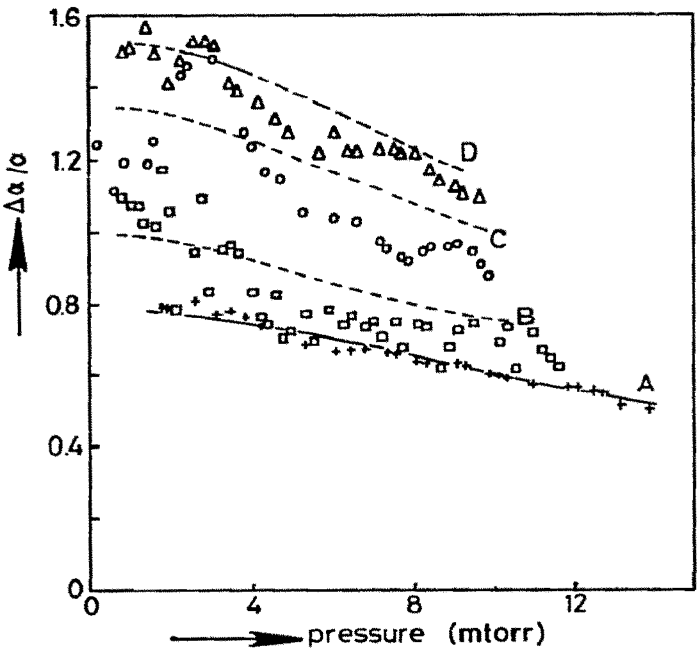

Fig. 1. The relative change ($\Delta\alpha/\alpha$) induced by laser pumping in the microwave absorption as a function of pressure. The solid curve A refers to the best fit according to the Oka theory ($\to$ x = 250 kHz and γ = 20 kHz/m/Torr). The broken curves refer to calculations of the Takami theory (experimental conditions x = 0.4 MHz, x_m = 350 kHz (B), 700 (C), 1400 kHz (D) and γ = 20 kHz/mTorr).

Takami derived a simple relation for $\Delta\alpha/\alpha$ if $x^2 >> \gamma^2$ and $x_m^2 >> \gamma^2$; namely: $\Delta\alpha/\alpha$ (:) $(x_m^2 + \gamma^2)^{\frac{1}{2}}$. Although these conditions are fulfilled in our experiments, the data do not show such behaviour.

The complete Takami theory leads to a much better result (see the broken curves in fig. 1 for the other series of data). In these calculations we use the experimental values for x and x_m.

Infrared detection

We present measurements on the following system: Microwave radiation at ν = 24667 MHz pumps the ammonia transition J=3, K=3, M=2$\leftrightarrows$3 at 0.611 MV/m. Then the infrared transition v_2=0, J=3, K=3, M=3,symm $\to$ v_2=1, J=3, K=3, M=3,asymm. absorbs the CO_2 – R(11) laser radiation (29.00085 THz). The lowest level is the common one.

The dependence of the relative change in infrared absorption $\Delta\alpha/\alpha$ as a function of the microwave power level is presented in fig. 2. The sign of $\Delta\alpha/\alpha$ is independent of x, x_m and γ for all situations we investigated, although the infrared power could be varied in such a way that DR with MW-detection under the same conditions would shown emission instead of absorption of microwave radiation. A rate equation model yields that then a change of sign for $\Delta\alpha$ must occur for DR with an IR probe signal and that $\Delta\alpha/\alpha$ due to microwave pumping can not be larger than $h\nu/2kT$ ($\approx$ 0.0025); this is much less than we find experimentally.

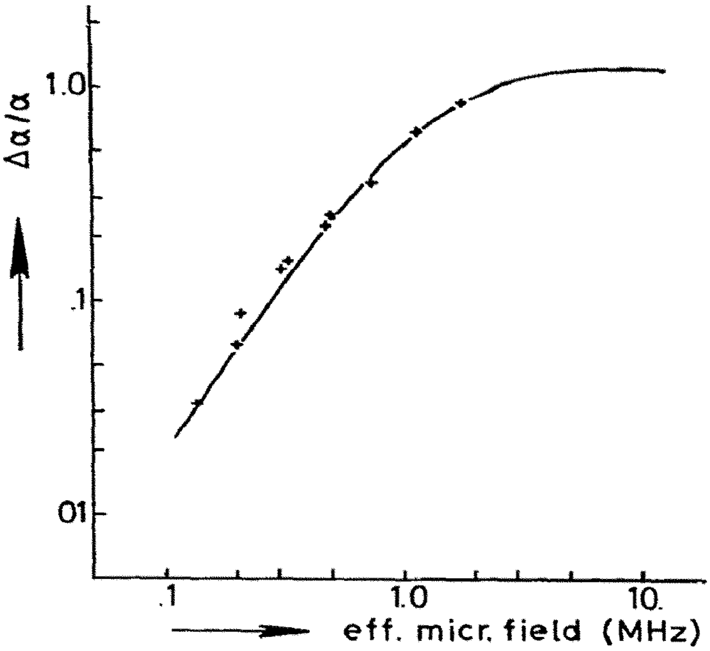

Fig. 2. The relative change ($\Delta\alpha/\alpha$) induced by microwave pumping in the infrared absorption as a function of the microwave power. The pressure used is about 1 Pa. The solid curve is the theoretical relation according to the Takami formulation and is nearly independent of pressure for this value of x ($\sim$ 0.8 MHz).

A similar system has been investigated by Takami (ref. 6) who found a change of sign for $\Delta\alpha$ at increasing pressure.

The complete Takami theory for IR detection shows that this occurs when $x^2/\gamma^2 \sim 2\ h\nu/kT$, a condition which we can not achieve in our system. The Takami formulism shows further that higher order effects are much more important that the small effects according to a rate equation model. In fig. 2 the theoretical curve calculated with the Takami formulism using parameters based upon our own experimental conditions show a good fit with our experimental data. Calculations show that the relation between $\Delta\alpha/\alpha$ and x_m is almost independent of pressure for the given infrared level.

CONCLUSIONS

In IR-MW DR both IR and MW detection signals are strongly dependent on the microwave power level in a complicated way due to high order and multi photon processes. The complete Takami theory gives a good description of the experimental data. Therefore a simple relation between induced change in absorption and induced change in population exists only for infrared pumping and microwave detection with very low microwave power.

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