On the Influence of a Finite Pump Width in IR-MW Double Resonance Experiments

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We have numerically checked the influence of a finite pump width in a three-level microwave-infrared double-rseonance system by extending an equation given earlier by Shimizu and Oka. The influence of IR-pumping on MW absorption intensity is calculated as a function of pressure. Results are compared with experiments.

1. Introduction

Infrared pumping of a molecular rovibrational transition provides a potentially powerful tool of greatly enhancing the intensity of rotational transitions, say, in the vibrational ground state. Due to the depletion of a rotational level by the application of the pump radiation, all rotational transitions beginning or ending on this level can be observed with greatly increased intensity; to the present the method is handicapped only by the lack of a sufficiently versatile tunable c. w. infrared laser with adequate power output. However, the effect has been observed also with fixed frequency lasers. Experiments of this type have been performed by several groups [1–4] using the coincidence of the P(13) line of the N_2O laser with the $\nu_2 [a^q Q(8,7)]$ vibrational transition of ammonia. In this case the microwave transition whose intensity increase is observed is not a rotational but an inversion transition characteristic of ammonia. In the following we shall investigate the effect of the infrared pump on the $J=8$, $K=7$, $+ \longleftrightarrow -$ inversion transition in the vibrational ground state at 23,232.24 MHz, see Figure 1.

The relative change in MW absorption intensity, $\Delta I/I$, due to IR pumping decreases with increasing sample pressure due to collisional relaxation processes which tend to restore the thermal equilibrium. Shimizu and Oka [1] have calculated the relative change in MW absorption intensity $\Delta I/I$ of the above $Q(8,7)$ line using Karplus and Schwinger's formula on saturated absorption. They have assumed that (a) the spectral width of the laser pump is negligible and (b) the Boltzmann distribution is disturbed only in the pumped levels. They have obtained satisfactory agreement with experimental values at pressures near and above 10 mTorr. However, at lower pressures the experimental values lie far above the calculated ones [1, 3].

It is the purpose of this note to show that that the calculated dependence of $\Delta I/I$ on pressure qualitatively agrees with the experimental results also in the low-pressure region when the assumption (a) is abandoned and a finite spectral width of the laser pump or an equivalent laser instability is instead assumed.

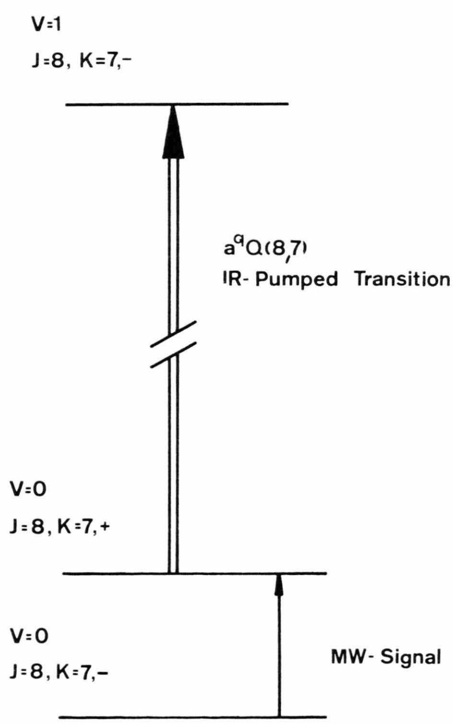

Fig. 1. Level scheme in NH_3 double-resonance experiment.

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2. Experimental

The instrumentation has been described in Reference [3]. It consists of a Stark modulated microwave spectrometer and a N_2O IR-laser. A 3-m X-band waveguide ($22.83 \times 10.16\ mm^2$) with a middle septum serves as the absorption cell. MW and IR power are coupled into the cell through two arms of a magic T of K-band dimensions ($10.67 \times 4.32\ mm^2$) with a tapered connection to the cell. The IR beam is focussed into the cell by a BaF_2-lens.

3. Calculations

Assumption (b) above appears to be confirmed by the observation that the intensities of all NH_3 ground state microwave transitions other than the $Q(8,7)$, which has the upper level in common with the pump transition, change by less than 3% [5] upon pumping. However, one might doubt that assumption (b) holds sufficiently well also for the lower (8,7) level, because it is apparent from extensive studies of collisionally induced transitions of NH_3 that this lower (8,7) level is affected more than any other non-pumped level by the presence of the pump [5, 6]. If collisional energy transfer between the two (8,7) levels does play a dominant part, disproportionate values of $\Delta I/I$ at medium pressures where these collisions are significant and at low pressures where they are negible could indeed be expected. While not excluding in principle this explanation we notice that the disagreement between experimental and theoretical $\Delta I/I$ values is largest at extremely low pressures where intermolecular collisions are rare and assumption (b) above should hold best. We have therefore retained (b) in the following calculations where we show that the introduction of a finite effective pump width could well account for the $\Delta I/I$ trend observed. However, at present we must leave it open wether this is the only contribution. Following [1] the relative change in microwave intensity of the $Q(8,7)$ line is

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

where

ν_M	MW-frequency,
$\gamma = \lvert\mu E_r\rvert/h$	power broadening parameter, 200 KHz in this experiment,
$\delta\nu$	Doppler width of the IR transition $\nu_2\, a\, {}^qQ(8,7)$ of NH_3,
$1/(2\pi\tau)$	pressure broadening, 26 kHz at 1 mTor, τ mean time between collisions,
$\nu_L - \nu_0$	coincidence mismatch of the laser pump, 7.4 ± 1 MHz in this case [7].

Using the values shown, Shimizu and Oka [1] have obtained general agreement with the experiment only at pressures above approx. 5 mTorr. Based on Eq. (1) we calculate the influence of a finite laser line width by a simple qualitative argument. We replace the laser line of width L by n closely spaced monochromatic lines each having one nth of the total power. Their frequency spacing is so chosen that the molecules absorbing energy from each individual line occupy adjacent portions, each of width $2\,[(\frac{1}{2}\pi\tau)^2 + \gamma^2/n]^{1/2}$ in the much wider Doppler profile of the pumped transition. Note that the saturation broadening term has appropriately been assumed to be only one nth of that present in Equation (1). The number n of portions into which L can be subdivided is then found by evaluating

$$n = L\frac{1}{2}\left[\left(\frac{1}{2\pi\tau}\right)^2 + \frac{\gamma^2}{n}\right]^{-\frac{1}{2}} + 1\,. \quad (2)$$

(For L approaching $0, n$ tends to 1 as it should.) The total microwave signal enhancement $\Delta I/I$ is taken to be the sum of that due to each of the n individual lines. Each individual contribution is given by an Eq. (1) where however, γ^2 has been replaced everywhere by γ^2/n. If the variation of the exponential "coincidence mismatch factor" of Eq. (1) over the laser line width L can be neglected, the individual contributions are easily summed to give

$$\frac{\Delta I}{I} = \frac{1}{2}\left(\frac{kT}{h\,\nu_M}\right)\sqrt{\pi}\,\gamma^2 \times \left[\left(\frac{1}{2\pi\tau}\right)^2 + \frac{\gamma^2}{n}\right]^{-1/2} \exp\left[\frac{-(\nu_L-\nu_0)^2}{(\delta\nu)^2}\right] \quad (3)$$

where n is to be evaluated from Equation (2). For $L=0$ Eq. (3) reduces to Equation (1). However, for a finite laser line width L Eq. (3) will yield a considerably larger ratio $\Delta I/I$ than Eq. (1) whenever saturation dominates over collision broadening, i. e. in the low-pressure region. For the 3-level system of the experiment presented in Fig. 1, Fig. 2

shows the influence of a finite pump width calculated from Eqs. (2) and (3). The curve which fits our experiment best is the one for $L = 4$ MHz. This appears to be a rather high value for a laser line width, however, it could be accounted for by short term laser instabilities which would have the same

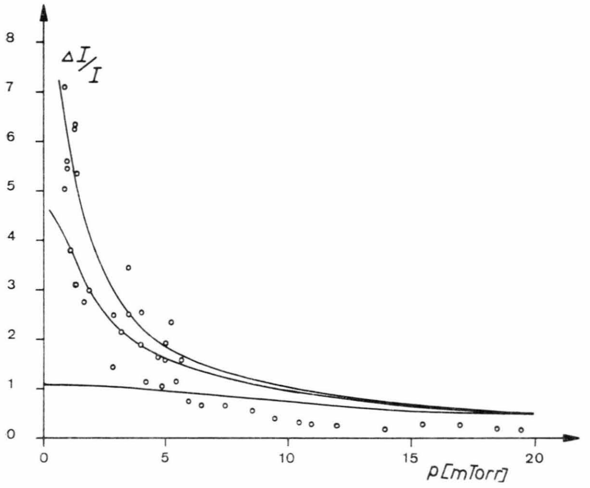

Fig. 2. Relative change of the intensity $\Delta I/I$ of the microwave transition Q (8,7) of NH_3 upon laser pumping vs. pressure. ○ experimental points (note that for pressures near 1 mTorr, the pressure readings taken may be in error by a factor of 2). —— curves calculated by Eqs. (3) and (2) with power density of 15 mW/cm^2 and $\mu = 0.2$ D (yielding $\gamma = 0.239$ MHz), and pressure parameter $1/(2\pi\tau p) = 26$ MHz/Torr [1]. Parameter is laser line width $L = 0, 2, 4$ MHz (from bottom to top).

effect. The amplitude of the frequency fluctuations of the laser used in our experiment is estimated to be of the order of 3 MHz. The fluctuation is rapid compared with the mean time between collisions particularly at low sample pressures. Additionally, mode structure might contribute to the laser line width. At pressures above 10 mTorr the experimental values of Fig. 2 lie below the calculated ones. This could be explained by the fact that laser power is reduced appreciably by molecular absorption. Calculation shows that reduction of one third in laser power, which agrees with absorption measurements, gives satisfactory results. The quantitative application of Eq. (1) or (3) is complicated by the fact that the laser power distribution within the cell is not well known. At any rate, from Fig. 2 it is seen that the arguments leading to Eqs. (2) and (3) suggest a mechanism which (alone or with contributory effects) could indeed account for the sharp increase of $\Delta I/I$ observed for low pressures.

Acknowledgements

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