Time-resolved Microwave Double Resonance in Four Level Systems: H_2CO * **

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Experiments have been performed using time-resolved spectroscopy techniques in a four-level double resonance scheme. The time-resolved variations of radiation probing the populations of a K-type doublet of H_2CO have been studied as pump radiation suddenly switched on and off induces population changes between levels of another K-doublet. Non-exponential behavior with characteristic times longer than the relaxation time associated with pressure broadening has been exhibited. A theoretical treatment of this effect, using a generalized density matrix equation, is proposed. It gives reasonable agreement with the observed time dependences.

1. Introduction

Microwave spectroscopy has been extensively used as a tool in studies on the complicated rotational relaxation problem. Most studies have been based on lineshape and lineshift measurements as a function of pressure or foreign gases [1]. These methods, however, give only *average* relaxation parameters: in most cases the average molecule-field interaction time is obtained. More information is obtained from measurements of the evolution of the lineshape as a function of the microwave power [2], since these lead to two distinct relaxation times: T_2, caracterizing relaxation of coherence between two levels connected by the microwave radiation, and T_1, being related to relaxation of the population difference between these two levels.

Microwave double resonance studies on systems which do not share a common level lead to a considerable improvement of our knowledge of rotational relaxation mechanisms. Using this technique, not only preferred collisional transfer has been exhibited but also some quantitative information about various rotational relaxation mechanisms has been obtained [3].

Time-resolved spectroscopy has recently been developed in the microwave [4, 5] and infrared ranges [6]. While in the infrared range it has been especially useful to measure the average velocity change in molecular collisions [7], in the microwave range it has mainly been used to measure some T_1 [8, 9, 10] and T_2 [11] values or some ,,diffusion'' properties.

In principle, time-resolved spectroscopy gives at least as much information as steady state measurements. This is obvious when the observed signal comes from different processes with very different time constants (see for example [12]).

The main aim of this work is therefore to study the possibilities of time-resolved microwave double resonance on systems which do not share any common level and to report the new information that this technique provides. As many different time dependences have been assumed for these signals [13, 14], it is also interesting to observe the actual shape of these signals in order to give a better basis for theoretical calculations of collision-induced signals. In the next part of this paper (Sect. 2) we shall discuss the principle of these Time-resolved Microwave Double Resonance experiments. The experimental set-up is presented in Section 3. In the following section, the experimental results are reported. In particular, the influence of parameters such as the pressure and probe power has been studied, yielding some characteristics of the collisionally transferred physical quantities. A theoretical calculation of the signal time dependence is given in Sect. 5 while the results are discussed in a final section with special emphasis on the new information about collisions.

Furthermore, a few papers have been recently published about infrared microwave double resonance [15]. The question whether the observed

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signals are due to inversion-inversion or vibration-vibration energy transfer is not well established. Different arguments using time-resolved spectroscopy have been used. It is therefore interesting to know the time dependence of pure rotation-rotation energy transfer signals.

2. Principle of the Experiment

In these experiments, strong radiation („pump" radiation) is sent into the gas sample. Its frequency is in coincidence with that of a molecular transition ($2' \leftarrow 1'$, for instance). It introduces a deviation from Boltzmann equilibrium between the populations of the levels of the pumped transition. This deviation is transferred to the populations of the other levels (1 and 2, for example) through intermolecular collisions (see Figure 1). These population changes, which depend on the strength of collision transfer, are easily monitored by measuring the intensity variations of the $2 \leftarrow 1$ transition, since this absorption is directly proportional to the population difference between levels 1 and 2. Up to now, the experiments have been performed in the steady state regime [3] except in a recently published experiment by Mäder et al. [16]. They obtained results similar to those presented here but attention was paid to the variation of the signals with quantum number M. M is the quantum number associated with the projection of the angular momentum J on a space fixed axis.

Time-resolved variations of the absorption of the $2 \leftarrow 1$ transition can be observed by square-wave modulating the pump power. This pump switching method is much more suitable for our experiments than the Stark switching method. By the latter, we can only observe pump-induced variations on Stark-induced transients. But, as the maximum amplitude variations only reach 30% in the steady state experiments that give the maximum intensity variations (3), the pump-induced variations would always be obscured by Stark transients induced in the probe levels. The method of switching pump power avoids this difficulty since only the signal due to pump-induced absorption variations is observed.

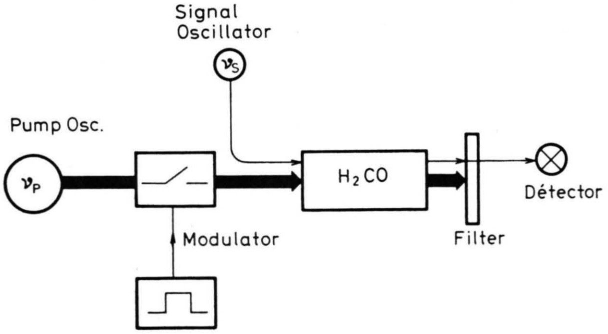

Fig. 1. Schematic diagram of time-resolved experiments on a four level system.

The formaldehyde molecule (H_2CO) has been chosen for this study for two reasons: (a) collision-induced signals are very strong and very well known through the work of Oka [17]; (b) formaldehyde is a molecule of astrophysical interest since the rotation transition $J_{K_a K_c} = 1_{10} \leftarrow 1_{11}$ has been observed in absorption against the galactic radiation [18] and many processes including collision transfer [19] have been proposed to explain the population excess in the lower level (1_{11}).

Rotational energy levels of formaldehyde are mainly K-type doublets. The K-type doubling transitions are typically in the centimeter region while transitions between different doublets fall in the millimetre and submillimetre ranges. We follow the experimental procedure of Oka. The pump radiation is resonant with the K-doubling transition of the doublet with angular momentum quantum number J while absorption variations are monitored on the adjacent doublets i.e. doublets with the same K_a quantum number but with angular momentum quantum number $J-1, J-2, \ldots$. In spite of intensity variations in the following scheme smaller than in other ones, we have chosen to pump the $7_{2,5} \leftarrow 7_{2,6}$ transitions (8.884 GHz) and to monitor the $8_{2,6} \leftarrow 8_{2,7}$ (14.726 GHz), mainly for experimental reasons as discussed below.

3. Experimental Set-Up

The experimental set-up is very similar to that used in our study of time-resolved double resonance on a three-level system in OCS [20]. The modifications are due to the fact that the filtering problem is still more difficult in the present experiment since the pump power may propagate through the standard waveguide for the probe frequency, especially into the probe source. The main changes (Fig. 2) are: (a) counter propagation of the pump and probe radiations; (b) probe oscillator and detection protection by waveguides below cut-off; (c) pump protection by a resonant iris with a cut off of

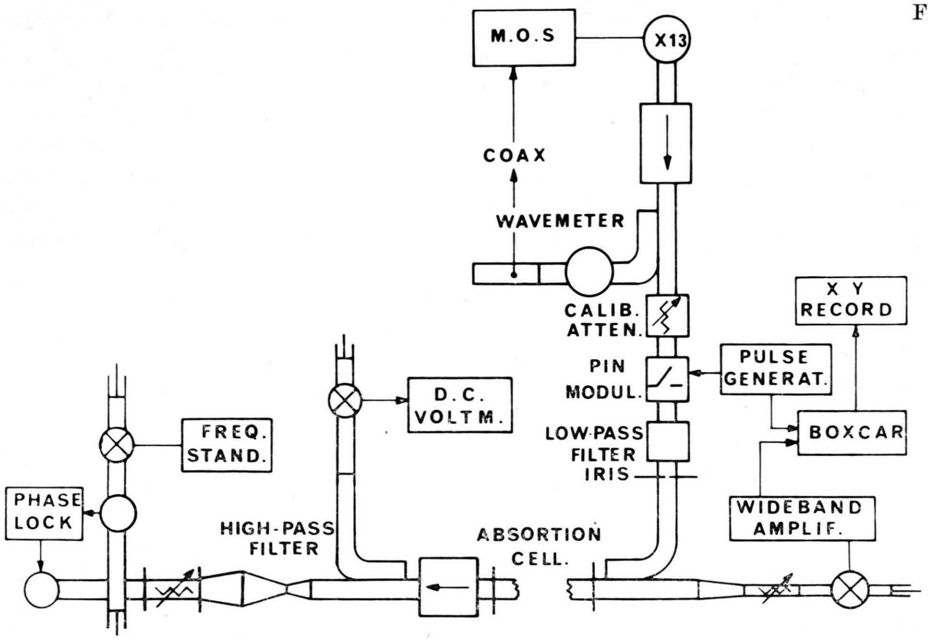

Fig. 2. Experimental set-up.

~ 20 dB; (d) introduction of an X-band isolator to reduce the pump standing waves. Second harmonic generation of the pump radiation creates signals that can propagate through the detection system. In order to prevent this, frequency selective couplers have proved useful.

It should be noted that these filtering problems are more drastic than in steady state experiments, since in such experiments the detection of a small amount of pump power only gives a shift from zero signal while in time-resolved experiments the effect of pump switching leakage into the detection is superimposed as a square wave on the observed signal. This completely spoils the observed signal. However spoiled signals may be used for qualitative comparison if much care is taken to substract the actual pump leakage signal from the recorded signal.

Pressure measurements have been made using a temperature-compensated Pirani gauge head (Edwards 65 C 2). In order to maintain high purity, sample was flown at low rate through the cell, the pressure being measured both at the input and in the middle of the cell to correct for pressure gradients.

4. Experimental Results

Steady state experiments show that only the amplitude of probe signals is changed by a frequency shift of the pump radiation and that the lineshape is always lorentzian in the pressure range used [21]. This leads us to study only the case where both probe and pump radiations are in exact coincidence with the corresponding transitions since a small frequency mismatch does not introduce any new feature, other than a decrease of the signal amplitude. The experimental parameters which are varied are the probe and pump powers and the gas pressure.

a) Pressure Dependence of the Signals

From steady state experiments [3], it has been found that at high pressures, the efficiency of the pumping is reduced and the signal amplitude is decreased. Such behavior has been observed at pressures above 55 mtorr as can be seen from the difference of steady state signals in the recordings of Figure 3. Of course the time characteristics of the onset and offset of the absorption are decreasing with the pressure but the most striking feature is the relatively long time constant of these absorption variations: in the conditions of Fig. 3 at a pressure of 12 mtorr, the $1/e$ time is 6 μs while the relaxation time deduced from collision broadening is 10 times faster (~ 0.6 μs).

As will be discussed below, other parameters may influence this risetime but it is always larger than the meantime between collisions.

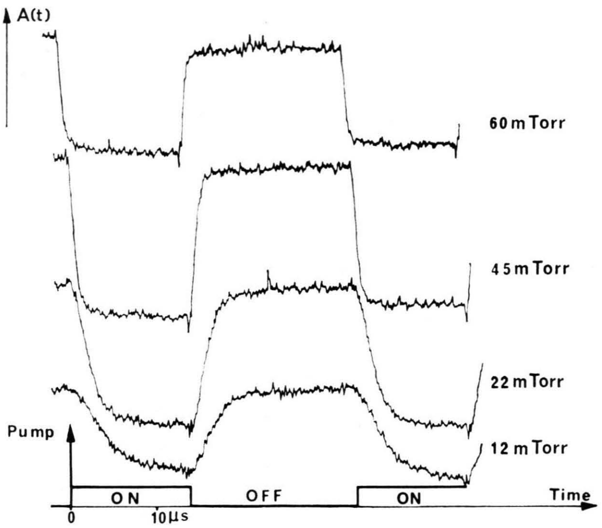

Fig. 3. Time evolution of the double resonance signal on a four-level system as the pump power is switched off and on (lower trace) for various H_2CO pressures (a) 60 mtorrs (b) 45 mtorrs, (c) 22 mtorrs, (d) 12 mtorrs.

b) Probe Power Dependence

The evolution of the signal lineshapes with the probe power is demonstrated on Figure 4. The probe power has been increased from a to d but the DC level on the probe detector has been kept at a constant level so as to observe a signal directly proportional to the absorption-coefficient variation. Only the sensitivity of the integrator has been changed to give measurable signals.

The effect of increasing probe power is to reduce the rise and fall times of the modulated signal. Moreover for the recordings obtained at relatively high probe power (Fig. 4d), it can be seen that the signal is faster when the pump is turned on. This can be attributed to a competition effect between the pump-induced and the probe-induced population variations. As this effect also depends on relaxation effects, i.e. the gas sample pressure, a more general study has been undertaken of which the main results are given in the following paragraph.

c) Results of the Simultaneous Study

A systematic simultaneous study of the influence of probe power, pump power and pressure has been made by recording signals for 3 different probe powers, 3 different pump powers at each pressure point. The time dependence of these signals has been investigated by plotting on a logarithmic scale the quantity $10 \times \frac{A(t) - A(\infty)}{A(\infty)}$ where $A(\infty)$ is the steady state value of the absorption and $A(t)$ is the signal amplitude at time t. A typical plot is presented on Figure 5. It calls for the following comments:

(i) In the limits of high pump power (i.e. the plateau in the pressure variation of $\Delta I/I$) and very

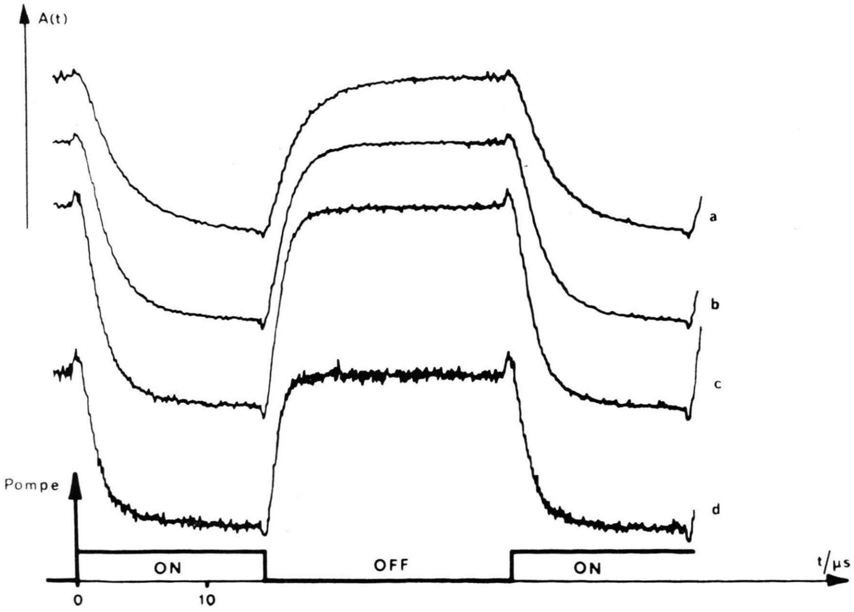

Fig. 4. Time evolution of the double resonance signal on a four-level system as the pump power is switched on and off (lower trace) for probe power increasing from a to d. H_2CO pressure 15 mtorrs. The DC level on the detector has been kept at a constant value in order to keep a constant sensitivity.

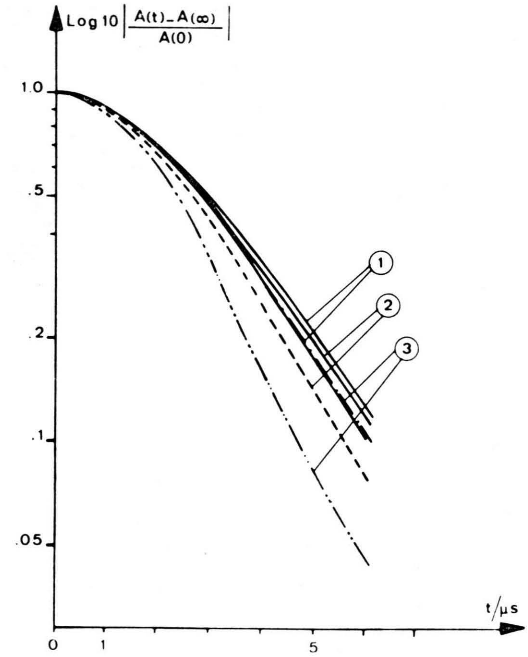

Fig. 5. Logarithmic plot of amplitudes deduced from recordings such as in Fig. 3 and 4. The signal as the pump is turned on and off is in dotted and full lines, respectively. The uncertainties are typically 5% of the maximum amplitude. Probe power attentuation is (1) 6 dB, (2) 3 dB, (3) 0 dB, respectively.

low probe power (probe-induced population variation much smaller than that due to collisions) the signal has a standard time-dependence which is represented by a near coincidence of all the full lines and one dashed line in Figure 5.

(ii) The most striking feature is the clearly non-exponential behavior of the signals. Due to the limited signal-to-noise ratio, many different kinds of analytic behavior may be fitted to the time-dependence of the signals, for instance the $(1+Kt)\exp(-t/\tau)$ shape calculated by Oka for transients in NH_3 would be as adequate as a sum of exponentials with different time constants;

(iii) as probe power increases, the steady state is reached more and more quickly and this effect is as obvious when the pump is turned off as when it is turned on;

(iv) it should also be mentioned that, at the onset of the pump power, the pump nutation features (i.e. oscillations of the pump populations as the pump is switched on) have no observable effect on the probe signal. This may be due to the weakness of the coupling between the energy levels of each transition that delay and damp such transferred oscillations. An auxiliary cause of smearing out of the effect is the inhomogeneity of the pump power through the waveguide cell.

5. Theory

Using the same rate equation formalism as Gordon [13], Oka has calculated the time dependence of the NH_3 collision-induced signals [3]. His results were obtained assuming: (i) the transition probability due to the probe signal to be much smaller than any transition probability involved in this process, (ii) some symmetries or propensity rules for the different rates of the collision-induced transitions and (iii) instantaneous changes for the pump induced population changes of the levels directly connected by the pump radiation. The time dependence found using these approximations can be described by a function of the kind $e^{-t/\theta}(1+t/\theta)$. Although this result is in qualitative agreement with our experimental results, assuming a value for θ which would depend on the probe power, we want to improve Gordon's formalism by taking into account two effects which have been shown to be of some experimental importance. The first of these consists of various nutation effects: Stark modulated or double resonance modulated microwave absorption experiments have shown that, whatever the microwave power may be, the long-term population change for the levels connected by this microwave radiation is not instantaneous but it established through damped oscillations which are known as „transient nutation". The second type of effect is due to probe saturation which cannot be neglected in our experiments.

In this calculation we shall first put the master equation of the density matrix into a simplified form suitable for time-resolved experiments. Then we shall derive the basic differential equations describing the time evolution of the four level system. In the last part, we shall solve these equations in some limiting cases.

Master Equation of the Density Matrix

We shall start from the density matrix equation as used by Redfield in magnetic resonance [22]

$$i\hbar\frac{d\varrho_{ab}}{dt} = [H,\varrho]_{ab} + i\hbar\sum_{c,d} R_{abcd}\,\varrho_{cd}\,, \qquad (1)$$

where H is the hamiltonian of the atomic or molecular system, R a time-independent supermatrix and ϱ_{ab} the density matrix elements between states a and b. The conditions under which this equation is valid, as discussed in [23], are as follows:

(i) multiple interactions with the thermal reservoir have to be neglected;

(ii) the correlation time τ_c of the reservoir is much smaller than the relaxation times and the other times, such as the nutation times, describing the evolution of the system.

For our type of experiment and pressure range, the impact approximation [24] is known to give good results, so that we can consider the condition (ii) to be fulfilled. It has been shown that when the second approximation is valid the first one also holds [23]. There is therefore no problem in using Redfield's equation to describe our experiment. In the experiments described in this paper, the energy levels are degenerate with respect to the magnetic quantum number. The problem of the M-dependence of the various relaxation rates has been considered theoretically by Pickett [25]. He showed that in time resolved double resonance experiments, the basic equations are essentially the same, except that the population differences have to be replaced by an intensity weighted sum of population differences for M states. In their experimental study of collision induced transitions between M resolved rotational levels of the $J = 0, 1, 2$ and 3 of OCS, Mader et al. showed that M dependence of collision induced transitions have to be explicitely considered [16]. However as our experiments are made on relatively high J levels, we can consider that a kind of quasi classical limit in which M degeneracy is only considered as a population factor and M independent relaxation times are assumed, gives a first approximation of the relaxation matrix. Even with this assumption the use of Redfield's supermatrix may seen very complicated. Fortunately many elements of R are zero. Moreover using the unitary and symmetries of the scattering matrix S and its relation to R, the elements of R are shown to fulfill the relations [25, 26]

$$\sum_a R_{aacd} = 0\,, \quad R^*_{abcd} = R_{badc}\,. \tag{2}$$

Using the thermal equilibrium density matrix and Eq. (1), we have

$$\sum_c R_{abcc} \exp(-E_c/kT) = 0\,. \tag{3}$$

The detailed balance principle (or relaxation microreversibility) gives

$$R_{aabb} = R_{bbaa} \exp - (E_a - E_b/kT)\,. \tag{4}$$

As microwave energies are much smaller than thermal kinetic energies ($E_a - E_b \ll kT \sim 200\ \mathrm{cm}^{-1}$ at room temperature), this can be approximated as

$$R_{aabb} = R_{bbaa}\,.$$

Using the interaction picture, it is easily shown that the only elements which are coupled together are those whose frequencies are nearly the same: R_{abcd} is non zero if

$$\hbar\,\omega_{ab} = E_a - E_b \cong E_c - E_d = \hbar\,\omega_{cd}\,.$$

This is the secular approximation [23] which brings in an error on ϱ_{ab} of the order of

$$[(\omega_{ab} - \omega_{cd})\,\tau]^{-1} \ll 1\,,$$

where τ is a time of the order of the rotational relaxation times.

Substracting from both sides of Eq. (1) the thermal equilibrium density matrix $\varrho^{(0)}_{ab}$ the master equation of our system may be written

$$\frac{\mathrm{d}}{\mathrm{d}t}\,\varrho_{ab} = -\frac{i}{\hbar}\,[H, \varrho)_{a,b} + \sum_{c,d} R_{abcd}\,(\varrho_{cd} - \varrho^{(0)}_{cd})\,, \tag{5}$$

where the $\sum$ is extended over c and d such as $|\omega_{ab} - \omega_{cd}| < \tau^{-1}$.

Before developping these equations it is appropriate to make a few remarks about the meaning of some elements of the relaxation supermatrix.

- R_{aaaa} is the relaxation rate into the state a. It is similar to the NMR relaxation rate $(T_1)^{-1}$. The elements like R_{aabb} are related to the relaxation rate from b to a through collisions and are analogous to the usual coefficients of the rate equations.
- The elements of R coupling off diagonal (coherence) elements of g to themselves are similar to the parameter $(T_2)^{-1}$ of NMR.
- The elements of R coupling coherences to different coherences or to populations are usually zero except in some very special cases of degeneracy. They are responsible for the coherence transfer recently discussed in [27].

Development of the Master Equation in the Case of Four Level Double Resonance Experiments

To solve our problem, the density matrix is restricted to the subspace generated by the levels connected by the pump and probe radiation. They are written 1′ and 2′ and 1, 2 respectively. The other states are assumed to be a part of the thermal bath. We also assumed the lifetime of each level to be the same, which is consistent with previous line width studies:

$$R_{iiii} = -\tau^{-1}\,.$$

According to the above remark on the physical significance of the R_{ijij}, the same relaxation time will be assumed for all coherences since the microwave lines involved in the problem have almost the same pressure broadened line width [28].

The transitions $1 \to 1'$ and $2 \to 2'$ have the same characteristics: both involve a change of parity, have almost the same frequency and are such that $\Delta J = 1$, $\Delta K_c = 1$. Together with the detailed balance, this leads us to

$$R_{111'1'} = R_{1'1'11} = R_{2'2'22} = R_{222'2'} = k_\alpha/\tau\,.$$

Using similar arguments, we assume for parity forbidden transitions

$$R_{112'2'} = R_{2'2'11} = R_{221'1'} = R_{1'1'22} = k_\gamma/\tau$$

and for transitions inside one doublet

$$R_{1122} = R_{2211} = R_{1'1'2'2'} = R_{2'2'1'1'} = k_\beta/\tau\,.$$

These last approximations are similar to these used by Oka [3] to derive population transfer coefficients. All the notations are summarized on Figure 6.

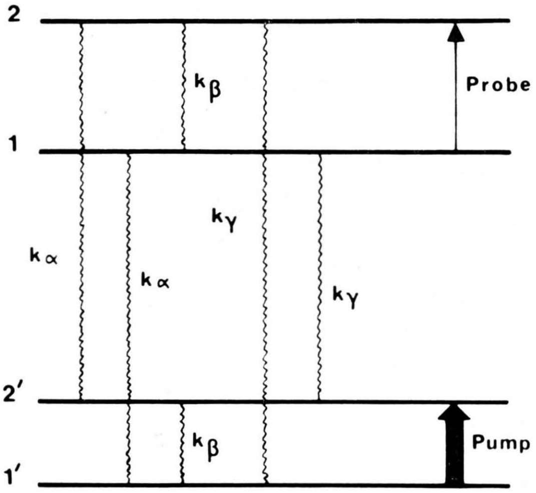

Fig. 6. Relative position of probe and pump transitions. α- and β-type transitions are electric dipole allowed. The wavy arrows indicate the various collision-induced transitions considered in this paper.

Eventually, Eq. (5) may be developed as:

$$\frac{\mathrm{d}\varrho_{11}}{\mathrm{d}t} = -\frac{i}{\hbar}\left(H'_{12}\varrho_{21} - \varrho_{12}H'_{21}\right) - \left(\frac{\varrho_{11} - \varrho_{11}^{(0)}}{\tau}\right) + \frac{k_\alpha}{\tau}\left(\varrho_{1'1'} - \varrho_{1'1'}^{(0)}\right) + \frac{k_\beta}{\tau}\left(\varrho_{22} - \varrho_{22}^{(0)}\right) + \frac{k_\gamma}{\tau}\left(\varrho_{2'2'} - \varrho_{2'2'}^{(0)}\right),$$

$$\frac{\mathrm{d}\varrho_{12}}{\mathrm{d}t} = -\left(\frac{1}{\tau} + i\,\omega_{12}\right)\varrho_{12} - \frac{i}{\hbar}\left(H'_{12}\,\varrho_{22} - \varrho_{11}\,H'_{12}\right),$$

$$\frac{\mathrm{d}\varrho_{22}}{\mathrm{d}t} = -\frac{i}{\hbar}\left(H'_{21}\,\varrho_{12} - \varrho_{21}\,H'_{12}\right) - \left(\frac{\varrho_{22} - \varrho_{22}^{(0)}}{\tau}\right) + \frac{k_\alpha}{\tau}\left(\varrho_{2'2'} - \varrho_{2'2'}^{(0)}\right) + \frac{k_\beta}{\tau}\left(\varrho_{11} - \varrho_{11}^{(0)}\right) + \frac{k_\gamma}{\tau}\left(\varrho_{1'1'} - \varrho_{1'1'}^{(0)}\right),$$

$$\frac{\mathrm{d}\varrho_{21}}{\mathrm{d}t} = \left(\frac{\mathrm{d}\varrho_{12}}{\mathrm{d}t}\right)^{*},$$

$$\frac{\mathrm{d}\varrho_{1'1'}}{\mathrm{d}t} = -\frac{i}{\hbar}\left(H'_{1'2'}\,\varrho_{2'1'} - \varrho_{1'2'}\,H'_{2'1'}\right) - \left(\frac{\varrho_{1'1'} - \varrho_{1'1'}^{(0)}}{\tau}\right) + \frac{k_\alpha}{\tau}\left(\varrho_{11} - \varrho_{11}^{(0)}\right) + \frac{k_\beta}{\tau}\left(\varrho_{2'2'} - \varrho_{2'2'}^{(0)}\right) + \frac{k_\gamma}{\tau}\left(\varrho_{22} - \varrho_{22}^{(0)}\right),$$

$$\begin{aligned}
\frac{\mathrm{d}\varrho_{1'2'}}{\mathrm{d}t} &= -\left(\frac{1}{\tau} + i\,\omega_{1'2'}\right)\varrho_{1'2'} - \frac{i}{\hbar}\,(H'_{1'2'}\,\varrho_{2'2'} - \varrho_{1'1'}\,H'_{1'2'})\,,\\
\frac{\mathrm{d}\varrho_{2'2'}}{\mathrm{d}t} &= -\frac{i}{\hbar}\,(H'_{2'2'}\,\varrho_{1'2'} - \varrho_{2'1'}\,H'_{2'2'}) - \left(\frac{\varrho_{2'2'} - \varrho^{(0)}_{2'2'}}{\tau}\right)\\
&\quad + \frac{k_\alpha}{\tau}\,(\varrho_{22} - \varrho^{(0)}_{22}) + \frac{k_\beta}{\tau}\,(\varrho_{1'1'} - \varrho^{(0)}_{1'1'}) + \frac{k_\gamma}{\tau}\,(\varrho_{11} - \varrho^{(0)}_{11})\,, \qquad (6)\\
\frac{\mathrm{d}\varrho_{2'1'}}{\mathrm{d}t} &= \left(\frac{\mathrm{d}\varrho_{1'2'}}{\mathrm{d}t}\right)^{*},
\end{aligned}$$

with $H' = \mu\,E\sin\omega\,t + \mu'\,E'\sin\omega'\,t$ and $\omega_{ij} = \dfrac{E_i - E_j}{\hbar}$.

The most interesting experimental case occurs when both radiation frequencies are exactly resonant ($\omega = \omega_0$, $\omega' = \omega_0'$). We use the following changes of variable:

$$\begin{aligned}
a &= \varrho_{21}\exp(i\,\omega_0\,t)\,, & D &= \varrho_{11} - \varrho_{22}\,,\\
& & D_0 &= \overset{0}{\varrho}_{11} - \overset{0}{\varrho}_{22}\,,\\
a' &= \varrho_{2'1'}\exp(i\,\omega_0'\,t), & D' &= \varrho_{1'1'} - \varrho_{2'2'}\,,\\
& & D_0' &= \overset{0}{\varrho}_{1'1'} - \overset{0}{\varrho}_{2'2'}\,,
\end{aligned}$$

which is the equivalent, for a four level system, to the rotating frame transformations. Neglecting, as in the two level rotating wave approximation, the rapidly varying terms, these equations may be written

$$\begin{aligned}
\frac{\mathrm{d}D}{\mathrm{d}t} &= -\frac{\mu\,E}{\hbar}\,(a + a^{+}) - \left(\frac{D - D_0}{T_1}\right)\\
&\quad + \frac{1}{T_1{}'}\,(D' - D_0')\,,\\
\frac{\mathrm{d}D'}{\mathrm{d}t} &= -\frac{\mu'\,E'}{\hbar}\,(a' + a'^{+}) - \left(\frac{D' - D_0'}{T_1}\right)\\
&\quad + \frac{1}{T_1{}'}\,(D - D_0)\,, \qquad (7)\\
\frac{\mathrm{d}a}{\mathrm{d}t} &= -\frac{1}{T_2}\,a + \frac{\mu\,E}{2\hbar}\,D\,,\\
\frac{\mathrm{d}a'}{\mathrm{d}t} &= -\frac{1}{T_2}\,a' + \frac{\mu'\,E'}{2\hbar}\,D'\,,
\end{aligned}$$

where we have used

$$T_2 = \tau\,, \quad T_1 = \frac{\tau}{1 + k_\beta}\,, \quad T_1{}' = \frac{\tau}{k_\alpha - k_\gamma}\,.$$

The parameter τ is in fact the relaxation time of the coherences, $\tau/(1 + k_\beta)$ is the relaxation time of the population differences inside one doublet and can then be considered as an analog of the T_1 relaxation time in NMR, $T_1{}' = \tau/(k_\alpha - k_\gamma)$ may be considered as characteristing the way a population difference inside one doublet is transferred to the other doublet. This is also consistent with the fact that the measured differences between T_1 and T_2 have been attributed to the strong relative importance of k_β transitions with respect to the other types of transitions ($k_\beta \sim 1$) as it is the case for the inversion doublets of ammonia [29, 30]. However, for H_2CO, the large observed value of the intensity change indicates that the collisional transfer for low K_a, high J levels through dipole-type α-transitions are very efficient. That is very easily understood by considering that the value of the dipole matrix element for $\Delta J = 1$ α-transition is proportional to $(J^2 - K_a{}^2)^{1/2}$ while that for $\Delta J = 0$ β-transition it is proportional to K_a.

Before solving these equations in the transient regime, it is interesting to know the steady state resolutions since they provide the limit conditions for the transient case.

Steady State Solution

Taking into account in ϱ_{ij} only the terms oscillating at an angular frequency ω_{ij}, we get

$$D = \frac{D_0(1 - X^2) - X^2\,4x'^2\,T_1\,T_2\,D_0'}{1 + 4x^2\,T_1\,T_2 - X^2}$$

with

$$X^2 = \frac{T_1{}^2}{T_1{}'^2} \times \frac{1}{1 + 4x'^2\,T_1\,T_2}\,.$$

The X^2 term in the denominator may be interpreted as a feedback: the population change due to pump power is transferred to the probe levels. This changes the rate of population transfer from the probe levels to the pump ones since the probe level populations are not the same as at thermal equilibrium.

The oscillating component of the dipole moment is then easily deduced from

$$\langle\mu\rangle = \mathrm{Tr}(\varrho\,\mu) = 2\mu\,\mathrm{Re}\,\varrho_{21} = \mu\cos\omega t\,\frac{\mu E T_2}{\hbar}\,D\,.$$

Note that in the steady state regime, the oscillating dipole is directly proportional to the population difference D. In the case of practical interest, the pumping is very strong ($x'^2 T_1 T_2 \gg 1$), so that

$$D = \frac{1}{1 + 4x^2 T_1 T_2}\left[D_0 - \frac{T_1}{T_1'}\,D_0'\right].$$

The first term is the population difference taking into account the probe saturation, while the second one is due to the collision-induced transitions. It works as a transfer of the pump population difference to the probe levels with an efficiency equal to

$$\frac{T_1}{T_1'} = \frac{k_\alpha - k_\beta}{1 + k_\beta}\,,$$

which is consistent with the interpretation given in the previous paragraph.

Transient Regime: witching off of the Pump Power

The simplest transient case is that which occurs when the pump power is switched off ($x' = 0$). Then the set of equations (7) is simplified since the fourth equation has a trivial solution

$$\begin{aligned} a' &= a_0' \exp(-t/T_2) \\ &= x'\,T_2\,D'(t=0)\exp(-t/T_2)\,. \end{aligned}$$

The corresponding coherence corresponds to the free emission signal which occurs at the pump frequency. This is coupled to no other term and leads to the obvious conclusion that the pump-free emission does not change the probe transient effects. Although the system of differential equations is simpler in that case its general analytical solution is rather complicated since it needs the diagonalization of a 3×3 matrix. However, simple solutions may be obtained in some particular cases of physical interest:

a) $T_1 = T_2 = \tau$

Using the same relaxation time for coherences and populations is a reasonable assumption since most of the measurements of these quantities indicate that they are equal, except for ammonia [29, 30]. It is then easily shown that the population difference D evolves in the following way

$$D = D_t\,e^{-t/T_1}\sin\left(\left(4x^2 - \frac{1}{T'^2_1}\right)^{1/2} t + \varphi\right) + \frac{D_0\left(\frac{1}{T_1^2} - \frac{1}{T_1'^2}\right)}{4x^2 + \frac{1}{T_1^2} - \frac{1}{T_1'^2}}\,,$$

where D_t is the transient amplitude given by

$$D_t = D_{ss} - \frac{D_0\left(\frac{1}{T_1^2} - \frac{1}{T_1'^2}\right)}{4x^2 + \frac{1}{T_1^2} - \frac{1}{T_1'^2}}$$

and D_{ss} is the steady state amplitude as given in the preceeding paragraph.

In the transient regime, the absorption variations (i.e. the oscillating dipole) are no longer proportional to the population difference but rather to the coherence, that is obtained by integrating the last equation of (7)

$$\begin{aligned} \langle\mu\rangle = {} & 2\mu\exp(-t/T_2) \\ & \cdot\exp(-i\,\omega_0 t)\int x\,D\exp(t/T_2)\,\mathrm{d}t\,. \end{aligned}$$

From which it comes that the time dependence of the oscillating component of the average electric dipole moment behaves like

$$e^{-t/T_1}\cos\left[\left(4x^2 - \frac{1}{T_1'^2}\right)^{1/2} + \varphi\right].$$

b) Very Weak Probe Power

When the Rabi period associated with the probe transition is much longer than the relaxation times involved in the experiment, an analytic solution of (7) may be deduced: the dipole is simply decaying with a time constant T_2 while the populations exhibit the same behaviour as a system of couple oscillators with a feedback T_1'/T_1. It should be noticed that in this case the master equation reduces to the rate equation since we neglect any coupling between diagonal and off-diagonal elements of the density matrix.

Transient Regime: Onset of the Pump Power

The solution of the differential equation system is obviously more complicated in this case. However a very simple result may be obtained in the case of weak probe power. Then the third equation of (7) is completely uncoupled leading to the result that the dipole moment at the probe frequency evolves towards its equilibrium value with a time constant T_2. This seems contradictory to the low power results. However, our statement of a low power was probably not fulfilled especially for the short term behavior when $D_0 < 1$. Note that the condition $\frac{\mu E}{2\hbar} D \ll T_2^{-1}$ is much more restrictive than the usual non saturation condition $\mu E/\hbar \ll T_1^{-1}, T_2^{-2}$ since the amount of population transfer comes in. Using lower probe power is not feasible because of signal to noise ratio problems.

The general solution in this case is similar to that of the preceeding section since we have to calculate the behaviour of the four-level system when coupled only with one field. As many approximations have to be made in order to get on analytical solution of these differential equations, it is not appropriate to solve the most complicated case, a task which may be undertaken numerically when definite values of the R_{iijj} are available [31].

6. Conclusion

The formalism introduced here has allowed us to find analytical solutions corresponding to the limiting cases where T_1 is equal to T_2 or when the probe power is very weak. It also gives the general frame of the equations which have to be solved numerically if no assumption is made about the relative strengths of the microwave fields and about the various relaxation times. Another approach to an analytical result is the perturbation solution of the master equation. However, if one comes to a more rigorous solution of (7), the description of relaxation also has to be improved at least in two ways: (i) by including more rotational levels in the basis set for the density matrix since $\Delta J = 2$ or 3 transitions are very likely to occur [3] and should be taken into account in a more refined treatment; (ii) by considering the M-degeneracy of the energy levels so as to include relaxation times of the various irreducible tensor components, i.e. not only population and polarization relaxation times but also alignment and orientation [32, 33, 34].

This is beyond the scope of this work which is concerned with experimental results on the time dependence of absorption due to collision-induced population transfer and with exploring the possibilities of that method. Our experiments have provided the first observation of such time-resolved signals. Their time dependence has been shown to be not strictly exponential. Another noteworthly result is that pseudo-rise times and fall times of the absorption signals are usually larger than the relaxation time associated with the line width at the same pressure. In particular, even if one neglects the nutation effects it cannot be considered that the effect of the switching on of the pump power is to establish instantaneously the long-term change in population. This result is also of interest in relation to the experimental determination of various relaxation rates by modulated microwave double resonance [35].

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