POWER CONSIDERATIONS IN
THE COLLISION - INDUCED
DOUBLE RESONANCE

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POWER CONSIDERATIONS IN THE
COLLISION - INDUCED DOUBLE RESONANCE

by

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Submitted in partial fulfilment
of the requirements for the degree of Master of science,
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CONTENTS

ABSTRACT

Two pairs of energy levels of a molecule are considered. Optical transitions among each of these two pairs are coupled by the molecular binary collision. The case where the collision keeps the velocity of the molecule constant while reorienting it and maintaining the rotational energy is considered. Since the velocity is maintained constant, the molecules undergoing both the optical transitions belong to the same velocity group. This condition may be satisfied by tuning the molecular level structure by a varying Stark field. In short, we are considering coupling of two optical transitions due to the velocity-maintaining collisions.

An expression for the energy absorbed in the molecular system when the collision - induced double resonance occurs is found. This leads to the expression for the signal absorption in any molecular system in general. The treatment begins with the phenomenological equation of motion for the velocity - dependent density matrix of the two level molecular system. This is obtained by adding the phenomenological terms to the usual equation of motion in the Heisenberg picture. A two level molecular system can be represented by a 2X2 density matrix. Since the system under consideration consists of two pairs of levels, two 2X2 density matrices are dealt with. The effect of collisions is taken care of by introducing the collision kernel in the equation of motion. The equation of motion for the diagonal and the off-diagonal elements are obtained from the equation of motion for the general

density matrix. The expression for the difference in the diagonal elements is obtained in terms of the difference in the off - diagonal elements and vice versa. From these two equations, an expression for the difference in the off - diagonal elements is obtained in terms of measurable quantities. This difference along with the expectation value of the component of the dipole moment between the molecular energy states of interest is introduced in an expression for the energy absorbed in the molecular system. This expression involves the time derivative of the polarisation induced in the molecules by the field. Since the molecular system exhibits dynamic behaviour, the energy expression is time averaged. Also, since different molecular velocity groups of the Maxwell velocity distribution curve are involved in the collision, the energy expression is velocity averaged over the Maxwellian velocity range.

Two cases are considered. First, energy expression is found in the general case, i.e., when the velocity changes during the collision. Secondly, energy is calculated when the velocity is maintained constant during the collision. This expression shows that the energy depends linearly and quadratically upon the collision constants. This is shown to be a general expression for the particular energy expression obtained by Shoemaker et al.

Numerical evaluation for the signal absorption in the molecule methyl fluoride is done. The value is found to be $\Delta I = 1.323 \times 10^{-2}$ ergs/sec cm^2. The contribution due to the linear terms in the collision constants is 1.15×10^{-2} ergs/sec cm^2 and the contribution due to the quadratic terms is 1.73×10^{-3} ergs/sec cm^2. The meaning of this is that the quadratic contribution is 13·1 % of the total contribution, which is a considerable proportion. This contribution will be larger for a molecule with larger collision constants. This fact argues in favour of the general expression obtained.

CHAPTER I

INTRODUCTION

The study of collision induced double resonance is in its early stages of development. In the past few years, some experimental methods have been devised, with which to compare the probabilities of collision induced transitions. However, a universal method to measure the individual transition probabilities is still lacking, even though Pressure Broadening measurements provide useful data in revealing individual collisional transition probabilities.

Molecular transitions occurring in the vibrational-rotational region are considered. The symmetric top molecules are suitable for the study of double resonance, because they do not have quadrupole moment and hence are a good subject for Stark effect measurement.

In the double resonance case there are two independent radiations. One is the pumping radiation which perturbs the molecular level system and the other one is the signal radiation which monitors the system.

Consider the collision induced transitions, say between rotational levels. The typical four level energy diagram for OCS (carbonyl sulfide) is shown schematically in Fig. 1.1

A dc electric field is applied so that the degeneracy of the rotational level is lifted and the rotational levels are split into M components. Two microwave radiations (ν_p and ν_s) are applied simultaneously to the molecule. The radiations have their electric fields parallel to the dc field so that only $\Delta M = 0$ radiative transitions occur. The pumping radiation ν_p is stronger than the signal radiation

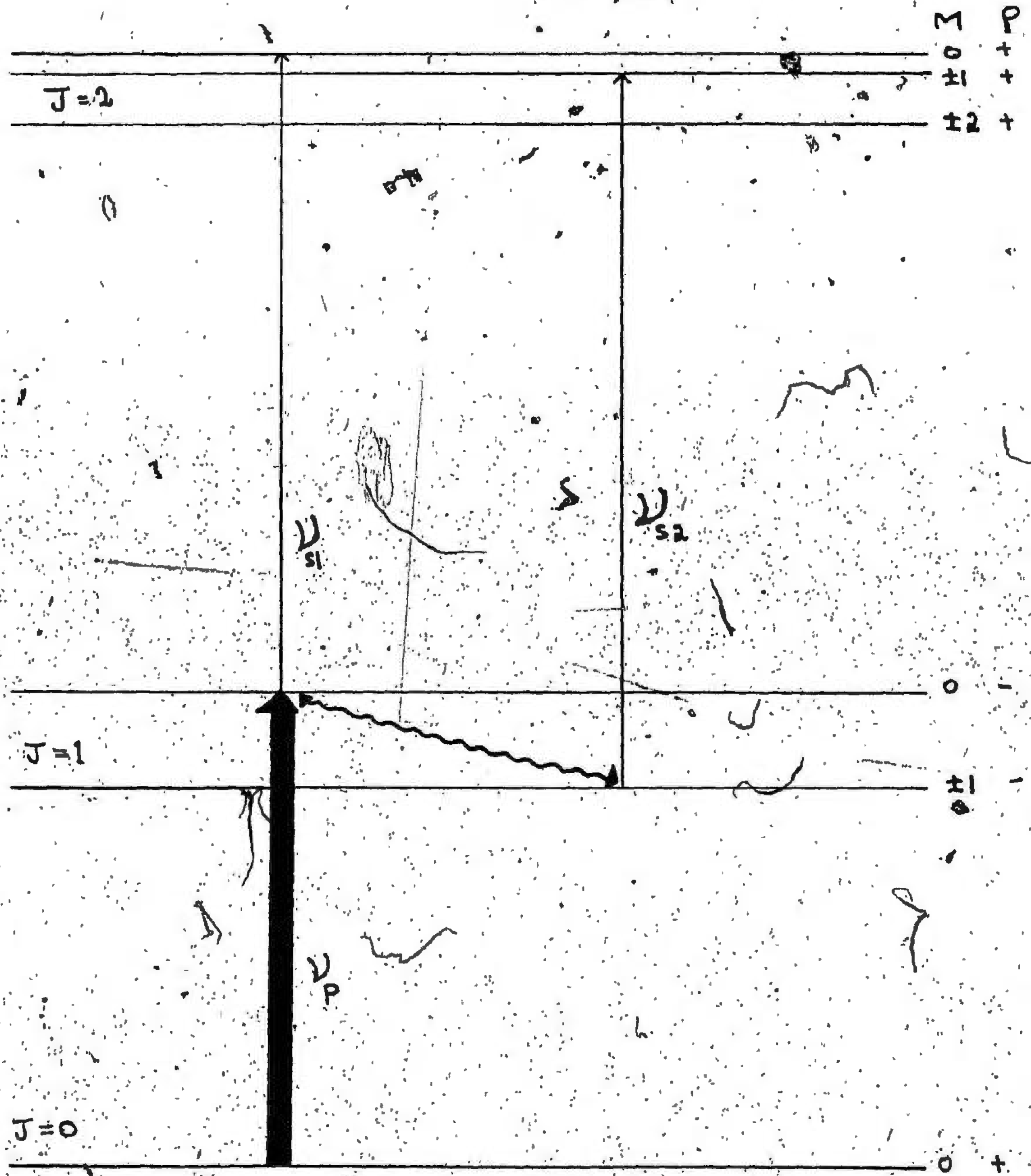


Fig. 1.1. The four level energy diagram for Carbonyl Sulfide.

ν_s. The pumping radiation pumps the molecule from the J = 0, M = 0 level to the J = 1, M = 0 level. The signal radiation monitors the resultant change in other rotational levels. The transition ν_{s1} which is directly connected to the pumping transition shows an increase in the intensity. This is because the population of the level J = 1, M = 0 is increased because of the pumping. In the typical experiment on OCS, the transitions ν_{s2} and ν_{s1} were monitored. Since ν_{s2} is not directly connected to ν_p, any effect on ν_{s2} due to the pumping radiation should arise from the collisional transfer of molecules from the state J = 1, M = ± 1. This experiment indicated the possibility of the transfer of molecular population from one level to another due to collision for a properly chosen rotational energy system. In other words, it indicated the possibility of studying the rotational energy transfer due to the double resonance. Cox et al. tried to find this sort of resonance in OCS, but were not successful. However this experiment encouraged this sort of investigation in other molecules.

The rotational level system in CH_2CH_2O provided the first successful observation of this kind. This was achieved by T. Oka.[1] The particular energy level structure of this molecule is schematically shown in Fig. 1.2.

Here the pumping transition ν_p is $2_{21} \leftarrow 2_{12}$ at frequency 34157 Mc/s. The signal transitions $3_{30} \leftarrow 3_{21}$ and $3_{21} \leftarrow 3_{12}$ are at frequencies 23135.5 Mc/s and 23611.5 Mc/s respectively. As is evident from the diagram, ν_{s1} and ν_{s2} are not directly associated with ν_p. Thus, the only way by which the intensities of ν_{s1} and ν_{s2} are changed is through the collisional transfer as shown by wavy arrows in Fig. 1.2. When

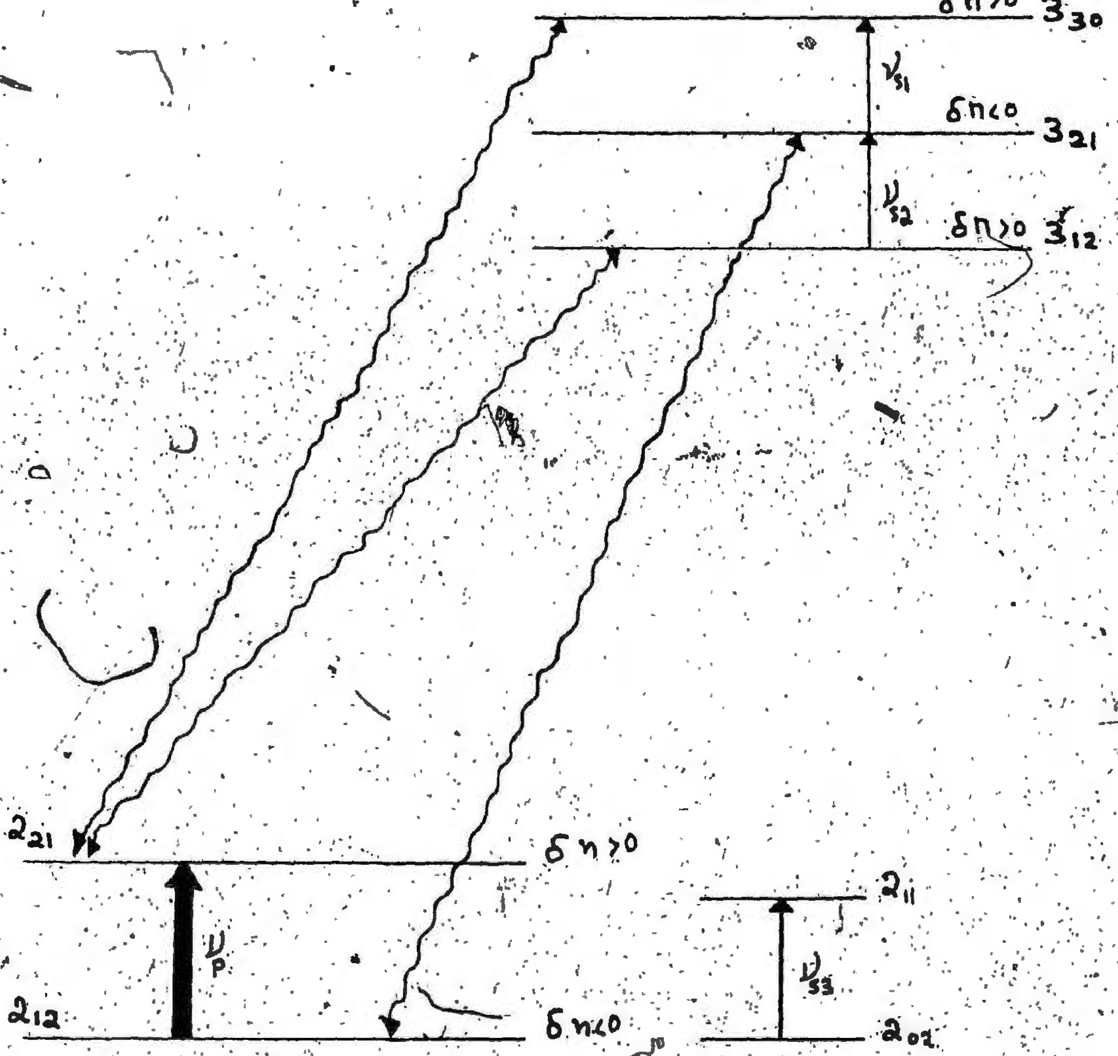


Fig. 1.2. The rotational level structure of ethylene oxide.

ν_p was applied, the signal ν_{s1} decreased (by about 12%) and the signal ν_{s2} increased (by about 7%). This is because the population of 3_{21} was decreased and that of 3_{12} was increased. The increase in the molecular population of the 2_{21} level due to pumping is selectively transferred to the 3_{12} and 3_{30} levels and the depletion in the population of 2_{12} is reflected in the decrease in the population of 3_{21}. This is why the population difference, and hence, the intensity of absorption for the transitions ν_{s1} and ν_{s2} decrease and increase, respectively. The transition ν_{s3} $(2_{11} \leftarrow 2_{02})$ was monitored simultaneously and it was found there is no change in the intensity of this transition. Even though these latter levels are energetically close to the pumped levels, they are unaffected by the pumping because of the dipole selection rules. Collision induced transitions follow dipole selection rules according to Anderson[2].

Next let us consider the simplest 4 level system shown in Fig. 1.3. The pumping levels are (1, 2) and the signal levels are (3, 4). The efficiency of saturation ϕ (due to pumping) has been given by Karplus and Schwinger[3] as

$$\phi = \frac{(n_2^0 - n_2) - (n_1^0 - n_1)}{(n_2^0 - n_1^0)} = \frac{(\mu_{12}E_p/\hbar)^2}{(\omega_o - \omega_0)^2 + (1/T)^2 + (\mu_{12}E_p/\hbar)^2} \qquad \ldots\ldots(1.1)$$

where n_i $(i = 1, 2)$ denotes the molecular populations under pumping, n_i^0 the equilibrium Boltzman population, μ_{12} the transition dipole matrix element, E_p the electric field of the pumping radiation and T

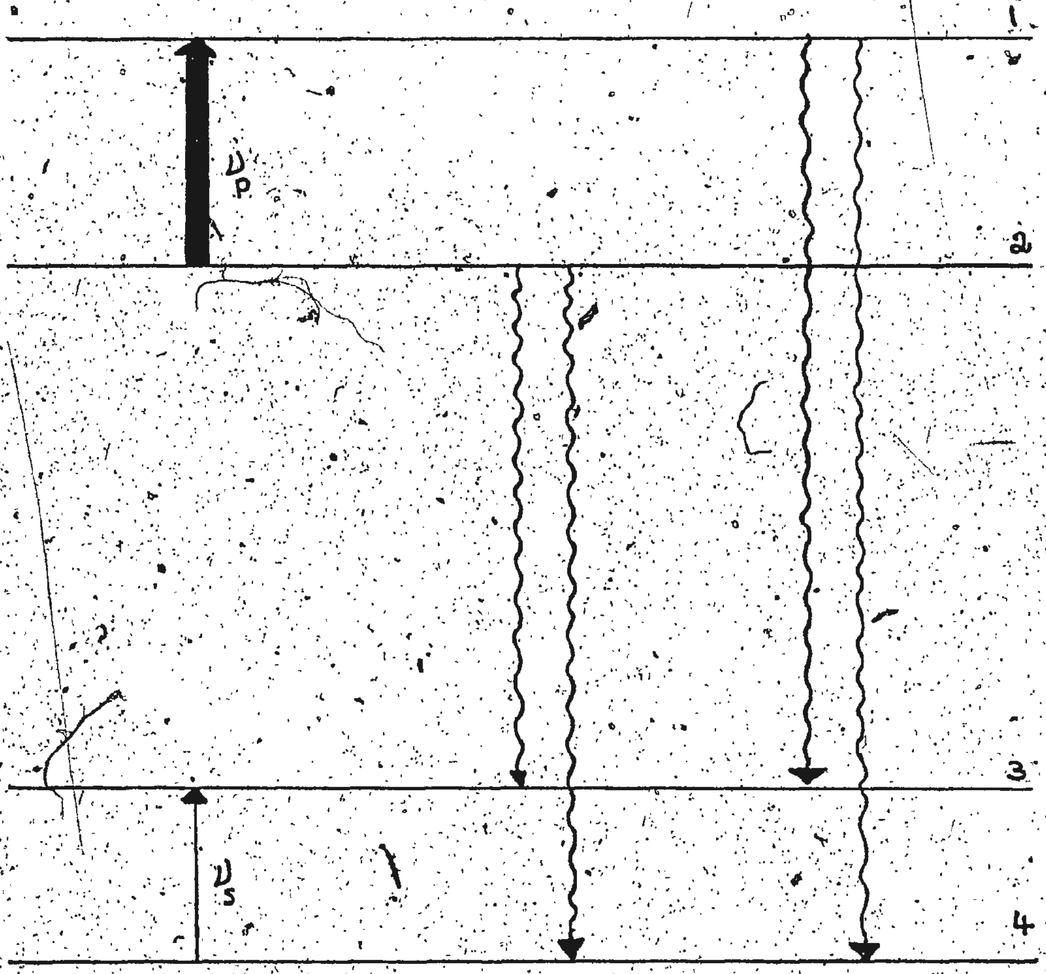


Fig. 1.3. Typical four level structure.

the relaxation time for the transition 1 ⟷ 2.

From Eqn. (1.1) it is clear that when resonant radiation is used for pumping ($\omega = \omega_0$) efficient saturation is achieved if

$$\mu_{12}E_p/\hbar >> \frac{2\pi}{T} \quad \text{.................................} \quad 1.2$$

Since the relaxation time, T, can be obtained from the pressure broadening experiments, one can choose E_p to satisfy Eqn. (1.2). Depending upon the value of μ_{12}, one can choose the proper pumping field to satisfy the maximum efficiency condition. If the saturation condition (1.2) is satisfied, the deviations of the molecular populations from the normal Boltzman distribution n_i^0 are given by

$$\delta n_1 = -\delta n_2 = (n_2^0 - n_1^0)/2 \quad \text{..................} \quad 1.3$$

That is, under unit efficiency, population transferred is half the difference in populations of 1 &2. The signal radiation monitors the collisionally transferred population deviations in levels 3 and 4. The relative change in the intensity of the signal absorption may be expressed as

$$\eta = \frac{\Delta I}{I} = (\delta n_4 - \delta n_3) \ / \ (n_4^0 - n_3^0) \quad \text{..................} \quad 1.4$$

where we have assumed that the population deviations δn_i due to the pumping are small compared to n_i because $h\nu_p << kT$ (refer to the eq 1.3). The denominator of eq (1.4) is also small. Hence η can be relatively large. For example, for H_2CO, $\eta = 0.307$. The intensity of the signal radiation should be small because we want the signal radiation to monitor the population difference without affecting it. Normally a signal radiation power of the order of 1μW is used so that the signal power is about one million times smaller than the pumping power. In other words, ϕ_{34} should be as small as possible. Thus in analogy with eq.(1.2) we can write $\mu_{34} E_s/h << 1/\tau$.

In the present work, an expression has been derived for the energy absorbed in the molecular system when collision induced double resonance occurs. This follows from the equation of motion for the velocity dependent density matrix. Expressions for the diagonal and off - diagonal elements of the density matrix are obtained, from which the double resonance term is extracted. Polarization induced in the molecules by the field is found and incorporated in the expression for the energy absorbed.

The following chapter gives the theoretical description of the energy level system considered in the work.

CHAPTER 2

THEORY

Experiments on collision - induced double resonance in $^{13}CH_3F$ were done by R. G. Brewer, R.L. Shoemaker and S. Stenholm[4]. The level structure for this molecule is schematically shown in Fig. 2.1. The relevant vibration rotation levels are denoted by a,b,c and d. The transitions $a \leftarrow b$ and $c \leftarrow d$ are caused by the monochromatic laser radiations of angular frequencies Ω_1 and Ω_2 . These two transitions are coupled by the collisions $a - c$ and $b - d$. It is found that these coupling collisions have certain characteristics as mentioned below:

(i) They preserve the molecular velocity. For example, the average velocity change for a binary collision in methyl fluoride is about 85 cm/sec. This was experimentally found by Shoemaker et al. This is very small compared to the molecular velocity which is about 10^4 cm/sec for methyl fluoride. Thus collisions shift the velocity group within the Doppler profile. Consequently the velocity can be considered to be the same before and after the collision.

(ii) The molecular angular momentum vector for the molecule changes direction, i.e., the collision makes the molecule go from one space quantized M state to another M state. In summary, we can say that the double resonance we are interested in is that which involves a group of molecules having the same velocity and undergoing two transitions that do not share a common level and involving changes in M value. The intensity of this double resonance scheme is comparable to that of the traditional double resonance effect where the two

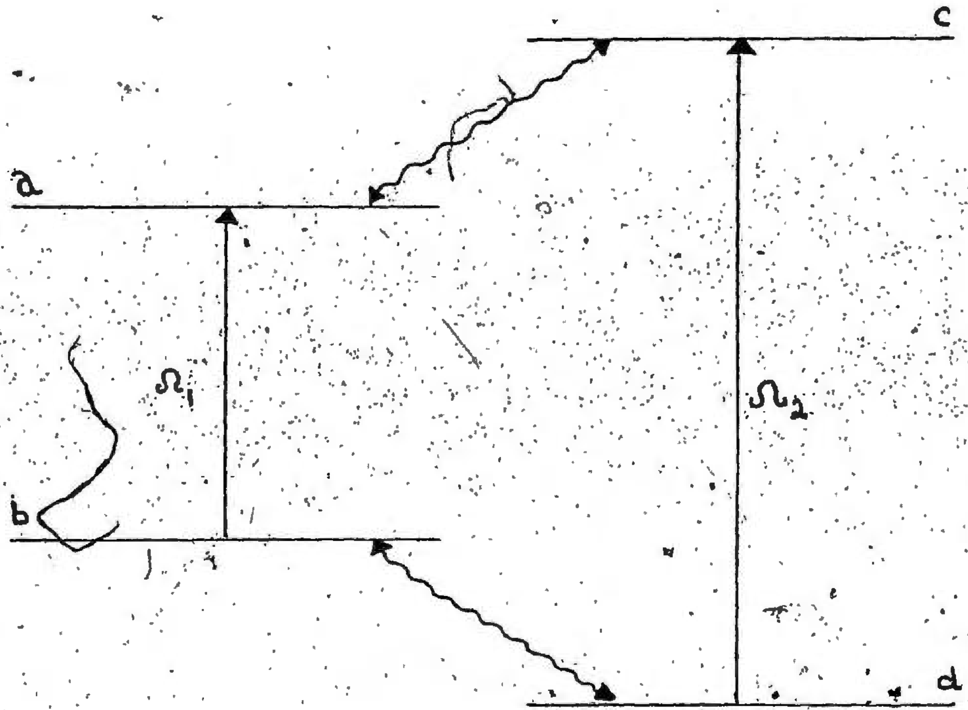


Fig. 2.1. The level structure for Methyl fluoride ($^{13}CH_3F$).

transitions are connected by an intermediate level as shown in Fig. 2.2. Referring to Fig. 2.1, the two laser fields select the resonant velocity groups (groups of molecules having the same velocity) according to $\Omega_1 = \omega_{ab}(1+v_z/c)$ and $\Omega_2 = \omega_{cd}(1 + v_z/c)$ where Ω_1 and Ω_2 are the angular frequencies of the fields 1 and 2 respectively, ω_{ab} and ω_{cd} are the transition angular frequencies for the transitions a – b and c – d respectively and v_{z1} and v_{z2} are the components of the molecular velocities along the field axis for the transitions a – b and c – d respectively. The angular frequency corresponding to the doppler effect is denoted by

$$k_1 v_{z1} = \frac{\omega_{ab}}{c} v_{z1} \simeq \frac{\Omega_1}{c} v_{z1}$$

where k_1 is the amplitude of the propagation vector for the field 1. Similarly,

$$k_2 v_{z2} = \frac{\omega_{cd}}{c} v_{z2} \simeq \frac{\Omega_2}{c} v_{z2}$$

where k_2 is the amplitude of the propagation vector for the field 2. Since Ω_1 and Ω_2 are nearly the same,

$$k_1 = k_2 = k$$

hence we get:

$$\Omega_1 - \Omega_2 = \omega_{ab} - \omega_{cd} + k(v_{z1} - v_{z2})$$

We saw that the velocity is maintained constant during the collision. That is,

$$v_{z1} = v_{z2}$$

Hence

$$\Omega_1 - \Omega_2 = \omega_{ab} - \omega_{cd} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 2.1$$

This is the collision - induced double resonance condition.

The levels a and c are the magnetic sublevels of the rotational level J_1. Similarly b and d are the magnetic sublevels of the rotational level J_2. Hence the levels a and c are very near to each other compared to the separation a – b, or c – d. Therefore the separations a – b and c – d are not much different. So there is no reason why we should distinguish between a – b and c – d. This means that there is no distinction between the pumping radiation and the signal radiation. In other words, the laser fields of angular frequencies Ω_1 and Ω_2 are of the same power.

When a dc Stark field is applied to the molecular gas, it interracts with the molecular electric dipole moment, causing a splitting of the rotational energy levels and resulting in the appearance of fine structure in the rotational spectrum. In considering the molecular Stark effect, the relative directions of the dipole moment and the angular momentum vector for a molecule must be taken into account.

For linear molecules, the dipole moment is perpendicular to $\vec{J}$ provided that the molecule is not in an excited vibrational bending

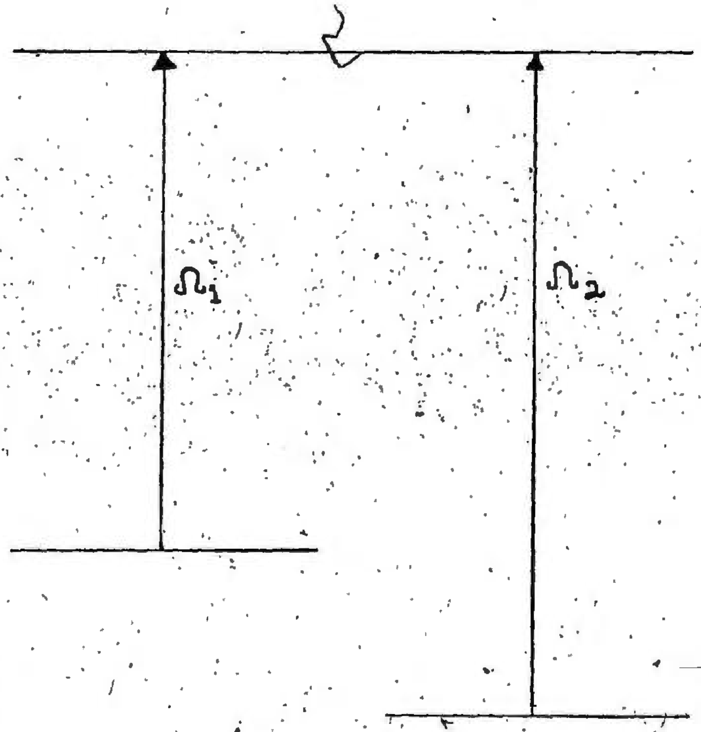


Fig. 2.2. The traditional double resonance level structure.

mode, and that it is in a $^1\Sigma$ electronic state. The great majority of stable molecules are normally in such an electronic state since their electons are fully paired. In symmetric top molecules (eg. CH_3F) which is the case we are interested in, the dipole moment is necessarily directed along the figure axis and hence it has a component along J except when K = 0. In the case when the dipole moment μ is perpendicular to J, the splitting of the rotational levels by an electric field depends on the square of the field intensity E. This is the so called second order stark effect. On the other hand, if μ has a component along the direction of J, the splitting is proportional to E. This is referred to as first order stark effect.

First order stark effect is most important for symmetric tops. In such a molecule, the total angular momentum $\vec{J} = \hbar\sqrt{J(J+1)}$ has a component $\vec{K} = \hbar K$ along the figure axis.

Refer to Fig. 2.3. This shows that the dipole moment μ which is directed along the figure axis. This has a component μ_J along the direction of J, of magnitude

$$\mu_J = \frac{\mu K}{\sqrt{J(J+1)}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.2$$

The direction of J is fixed in space and consequently the direction of μ_J is also fixed. If now an electric field E is applied as shown, μ_J will interract with it, and the energy of interraction is given by

$$W = -\mu_J E \cos\theta \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.3$$

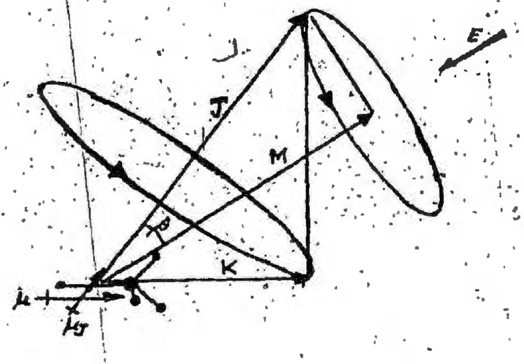


Fig. 2.3. Vector model for the first-order Stark effect of a symmetric top molecule, showing the component of the electric dipole along the total angular momentum J, and the precession of J about the electric field E.

The angular momentum $\vec{J}$ and with it μ_J will process about the direction of $\vec{E}$ as shown in the figure. This motion will be quantized, since θ is determined by the permitted projections, M of J along the direction of the field.

$$M = J, J-1, J-2, \ldots\ldots\ldots -J$$

$$\vec{M} = M\hbar$$

$$\cos\theta = \frac{M}{\sqrt{J(J+1)}}$$

Substitute this in eq. (2.3). Using eq. (2.2) we get

$$W = \frac{\mu K}{\sqrt{J(J+1)}} E \frac{M}{\sqrt{J(J+1)}}$$

i.e., $$W = \frac{\mu EMK}{J(J+1)} \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.4$$

Thus each level typified by JK is split by the field into 2J+1 components, provided $K \neq 0$. If μ is measured in debyes (1 Debye = 10^{-18} e.s.u.cm) and E in volts/cm, then

$$W_1 \text{ (Mc/s)} = -0.50348 EMK\mu \;/\; \{J(J+1)\}$$

For $J = K = M = 2$ and $\mu = 1$ debye and field strength of 50 volts/cm, W_1 = 17Mc/sec

Thus the level JK which is (2J+1) - fold degenerate from the spatial point of view (M) in the absence of a field, has this degeneracy completely removed by a field, splitting into 2J+1 levels for M ranging from J to -J.

The optical selection rules governing transitions between different rotational levels are $\Delta J = \pm 1$, $\Delta K = 0$ together with $\Delta M = 0$ if the electric field vector of the radiation is parallel to the stark field, and $\Delta M = \pm 1$ if it is perpendicular to the stark field.

In the double resonance experiment on $^{13}CH_3F$ (see reference 3), the radiations had their electric fields parallel to the stark field so that the optical selection rules $\Delta J = \pm 1$, $\Delta K = 0$, $\Delta M = 0$ were observed. If W_1 is the energy corresponding to the level splitting in the lower rotational energy level and if W_2 is the energy corresponding to the level splitting in the upper rotational level, then

$$\omega_{ab} - \omega_{cd} = \frac{|W_1| - |W_2|}{\hbar} \tag{2.5}$$

from (2.4),

$$W_1 = \frac{-\mu E M_1 K}{J(J+1)} \tag{2.6}$$

Similarly

$$W_2 = \frac{-\mu E M_2 K}{(J+1)\ (J+2)} \tag{2.7}$$

Eq. (2.7) follows from the selection rule $\Delta J = \pm 1$

Substituting (2.6) and (2.7) in (2.5) we get

$$\omega_{ab} - \omega_{cd} = \frac{1}{\hbar}\left\{\frac{-\mu E M_1 K}{J(J+1)} + \frac{\mu E M_2 K}{(J+1)\ (J+2)}\right\}$$

i.e.,

$$\omega_{ab} - \omega_{cd} = (M_1\Delta_\ell - M_2\Delta_u)E \tag{2.8}$$

where $\Delta_\ell = \dfrac{\mu K}{\hbar J(J+1)}$ and $\Delta_u = \dfrac{\mu K}{\hbar(J+1)\ (J+2)}$

Here Δ_ℓ is the angular frequency corresponding to the energy shift per unit stark field per unit magnetic moment quantum number change for the lower rotational energy level and Δ_u is the same quantity for the upper rotational energy level.

Substitute eq. (2.8) in eq. (2.1); we get

$$\Omega_1 - \Omega_2 = (M_1\Delta_\ell - M_2\Delta_u)E \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.9$$

The vibration rotation transition investigated in $^{13}CH_3F$ is the fundamental ν_3 band line (J, K) = (4, 3) - (5, 3). The spectrum as shown in Fig. 2.4 was obtained by Shoemaker, Stenholm and Brewer. This spectrum can be explained in terms of the eq. (2.9). The quantity $(\Omega_1 - \Omega_2)$ is kept at a constant value 30.008 Mc/sec. to satisfy the double resonance condition. Since this is kept constant, $(M_1\Delta_\ell - M_2\Delta_u)$ decreases as E increases, according to eq. (2.9). From eq. (2.4) it follows that $\Delta_\ell > \Delta_u$ and hence $(\Delta_\ell - \Delta_u)$ is positive. Resonances occur in such a way that $(\Omega_1 - \Omega_2)/E$ is less by $(\Delta_\ell - \Delta_u)$ for a particular resonance than for the previous resonance. It is found that the lines a, b, c, d, e, f satisfy the resonance condition eq. (2.9) if they have M_1 and M_2 values as shown below:

Line	M_1	M_2
a	4	2
b	3	1
c	2	0
d	1	-1
e	0	-2
f	-1	-3

Table 2.1

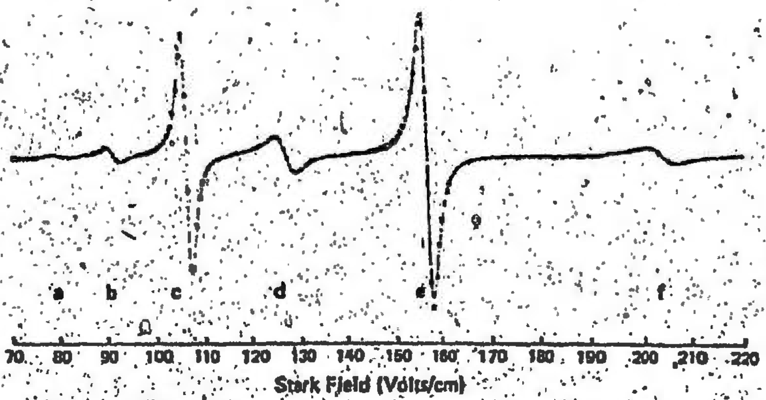


Fig. 2.4. Double resonance spectrum for methyl fluoride. This was obtained by Shoemaker et al. (see ref. no. 4)

These can be pictorially represented as shown in Fig. 2.5 (schematical representation). Here the lines c and e correspond to the ordinary double resonance where the two transitions are connected by an intermediate level. As may be seen from Fig. 2.6, c and e are more intense than other lines. The linewidth of each of them is half that of the lines corresponding to the collision induced double resonance. From Fig. 2.5 we can also see that the ordinary double resonance is a particular case of the collision induced double resonance.

The experimental set up used is shown in Fig. 2.6. Two continuous wave lasers are locked to a fixed frequency difference $(\Omega_1 - \Omega_2)$ and their light enters the Stark cell from the same direction. The coherent electric field $E_1 \exp\left[i(\Omega_1 t - k_1 z)\right]$ (where z is the direction of the optical beam) is in resonance with the transition a - b_1. This is for the narrow velocity group v_z which is the longitudinal velocity. The second transition c - d involving the resonant field $E_2 \exp\left[i(\Omega_z t - k_2 z)\right]$ communicates with the first transition only if it is turned to the same velocity group and if velocity preserving collisions cause the transitions c - a and b - d. The effective field in the cell is

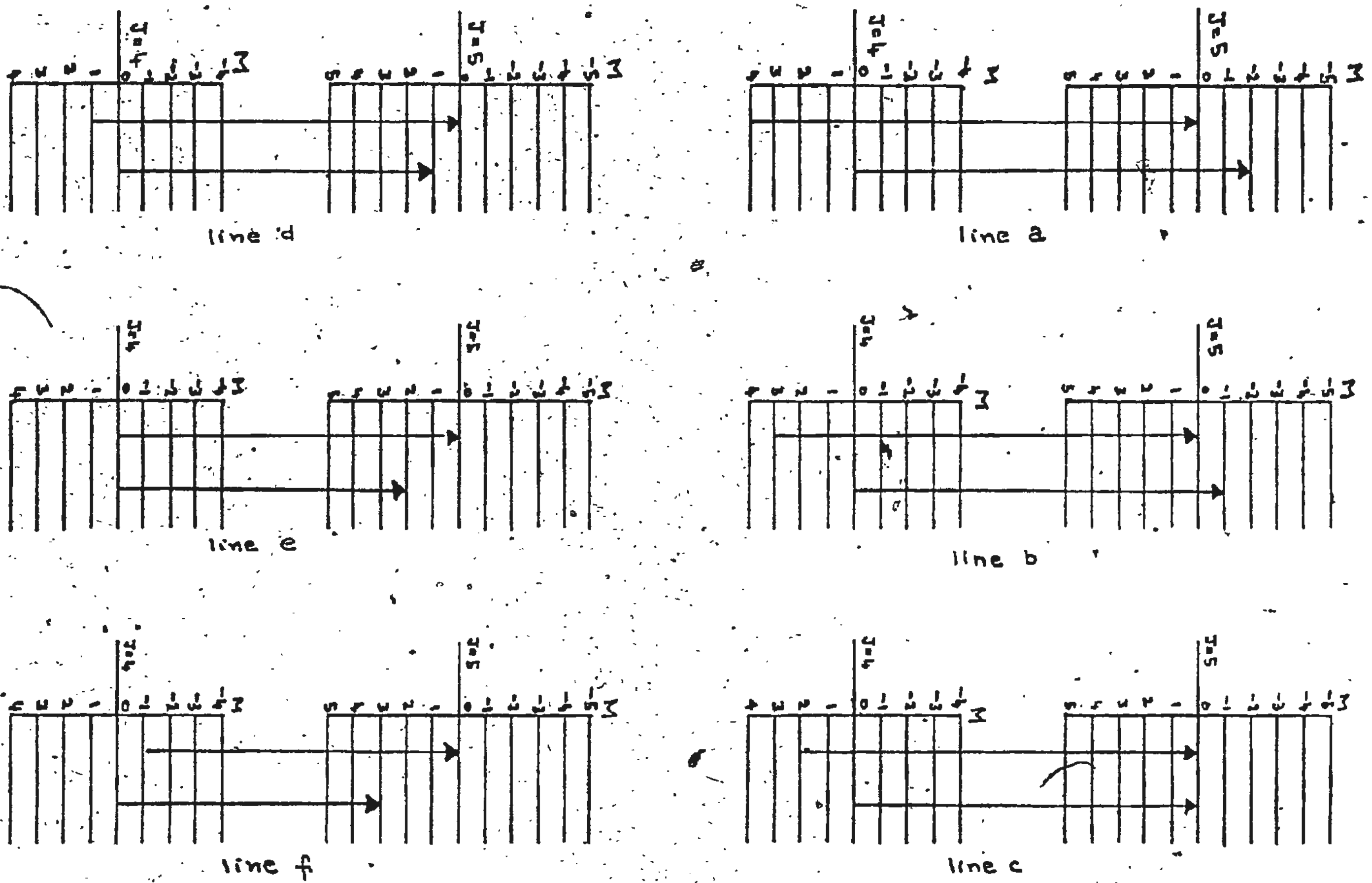


Fig. 2.5. Energy level diagram of $^{13}CH_3F$. The transitions shown are for the lines a, b, c, d, e and f of Fig. 2.4.

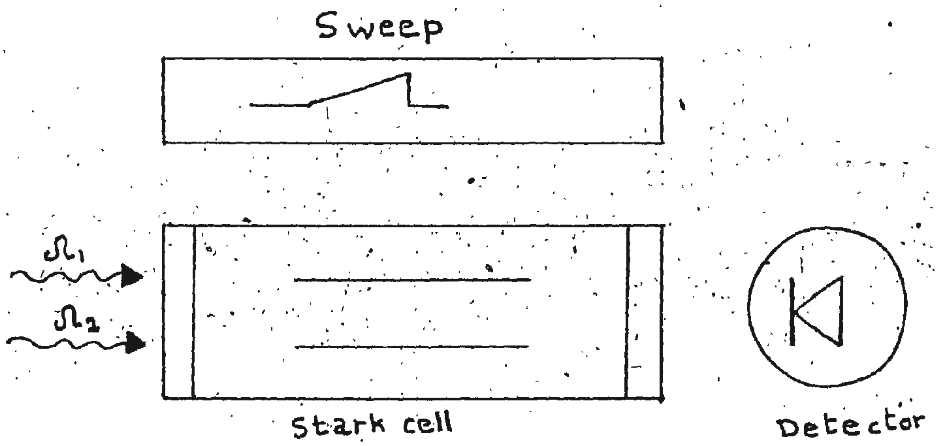


Fig. 2.6. Simplified experimental set up for the collision induced double resonance.

$$E_x(z,\ t) = E_1 \mathrm{Cos}(\Omega_1 t - kz) + E_2 \mathrm{Cos}(\Omega_2 t - kz) \ \ldots\ldots\ldots \ 2.10$$

This is because $k_1 \simeq k_2$, i.e., $\frac{\Omega_1}{C} \simeq \frac{\Omega_2}{C}$. This is again because $\Omega_1 - \Omega_2 << \Omega_1$ or Ω_2. The levels are optically coupled by

$$H_I = -\mu_x E_x(z,\ t)$$

The selection rules are such that

$$\langle a|\mu_x|b\rangle = \mu_{ab} \neq 0; \quad \langle c|\mu_x|d\rangle = \mu_{cd} \neq 0$$

$$\langle a|\mu_x|d\rangle = \langle b|\mu_x|c\rangle = 0$$

The last two relations are because there is no cross coupling, i.e., Ω_1 induces transition in a - b only and Ω_2 in c - d only.

The intensity change of both the laser beams is a measure of the energy absorbed in the system. This is the subject of interest in this work.

The following chapter gives the experimental procedure of the collision induced double resonance phenomenon.

CHAPTER 3

THE CONVENTIONAL EXPERIMENTAL PROCEDURE

The conventional experimental arrangement [†] used in the collision induced double resonance is described in this chapter. Block diagram of the experimental set up is given in Fig. 3.1.

Two collinear laser beams propagate in the same direction through a stark cell. The stark cell is a rectangular waveguide of standard design. The stark electrode is fitted in the cell, along its length, and parallel to and equidistant from the wide faces of the guide. The electrode is well insulated from the walls of the guide. This is achieved by means of polystyrene strips. The stark cells are limited to between three and five meters in length because of the attenuation effects. The stark cell contains the sample under study. Two CO_2 lasers provide the radiation. The frequency of both the laser beams may be chosen to tally with the transition frequency in question.

The difference in frequency of the two lasers have to be kept constant in order to satisfy the double resonance condition. For this, the frequency of one laser is locked to that of another.

[†] Since this thesis is a theoretical consideration of the collision induced double resonance, actual experiment has not been done in our lab. Reference for this chapter is No. 5 and No. 6.

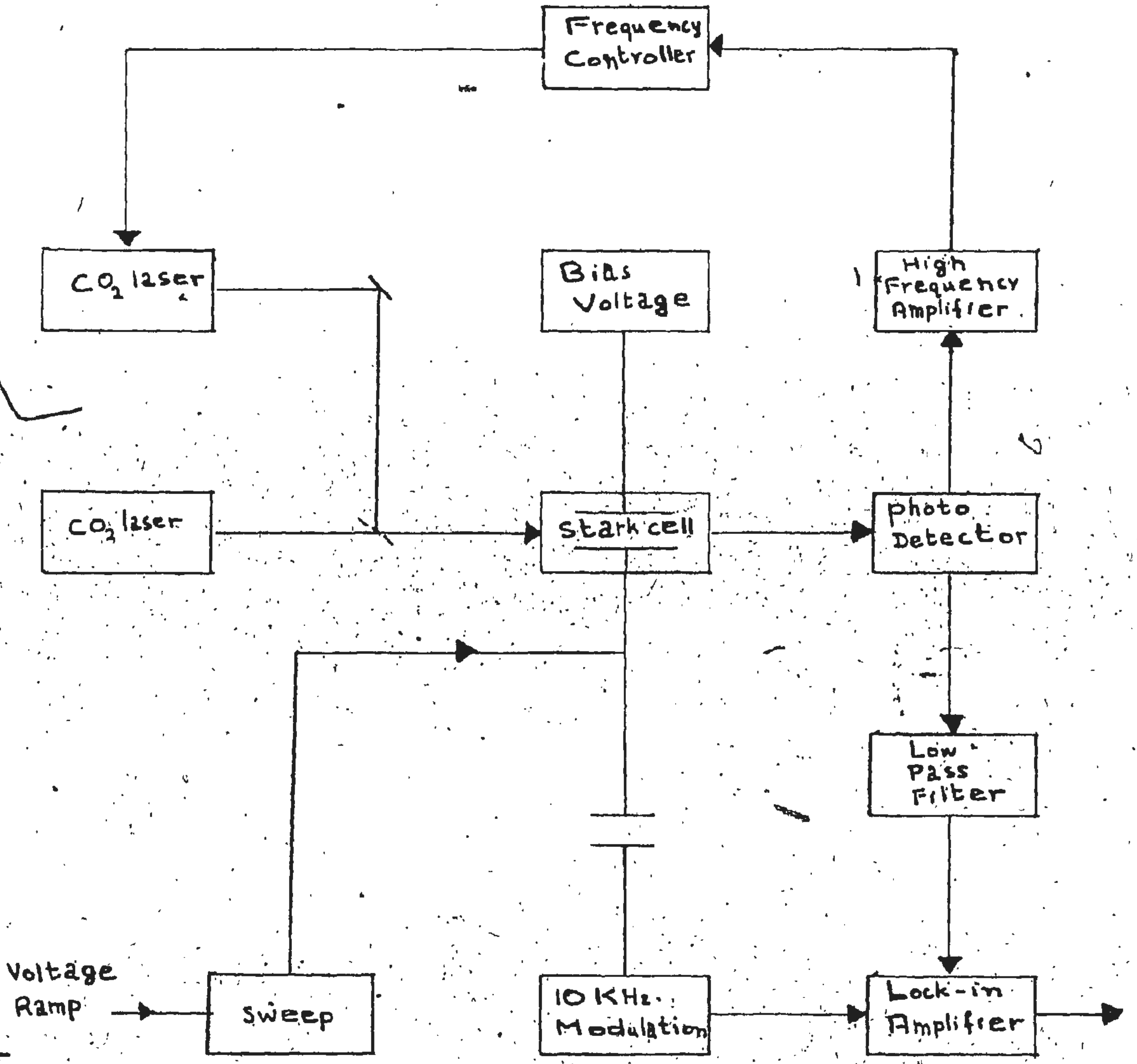


Fig. 3.1. The block diagram of the experimental set-up for the collision induced double resonance.

This is done by the frequency difference $(\Omega_1 - \Omega_2)$ being monitored by a photodetector and compared to a reference frequency. The circuit containing the high frequency amplifier and the frequency controller is the stabilization circuit. This produces an error signal, (the amplitude of which depends upon the amplitude of the high frequency component), which acts upon a piezoelectric, the vibration of which causes an oscillating electric field. This drives the cavity length of one of the lasers and hence controls the frequency of the laser. This causes the frequency difference to remain constant. The low pass filter removes the high frequency components and feeds the signal to the lock-in-amplifier. The lock-in-amplifier increases the signal to noise ratio of the signal fed to it. The first step in a lock-in-amplifier is the modulation. An important aspect of the modulation step is the generation of a reference signal that is of the same frequency as the carrier wave and phase locking them. It need not be exactly in phase with the carrier, but only phase-locked to it, as their relative phases can be adjusted. Lock-in-amplifier has an internally generated reference signal that is used to drive the external modulator. The resulting modulated carrier wave is demodulated by using this internal reference.

The stark field is swept in steps and the double resonance spectrum recorded. The intensity change of the signal is a measure of the energy absorbed in the system.

CHAPTER 4

THE ENERGY ABSORBED IN THE MOLECULAR SYSTEM

This chapter gives the expression for the energy absorbed in the molecular system. We are considering two cases. First, the general case when the velocity changes during the collision; second, the particular case when the velocity is maintained constant during the collision.

(i) General case

We start our discussion with the equation of motion for the velocity dependent density matrix.

Consider the molecular level system shown in Fig. (2.1). The equation of motion^4 for the velocity dependent density matrix is as given below: (See Appendix A).

$$i\,\frac{\partial \rho(v)}{\partial t} = i\Lambda(v) + \left[H, \rho(v)\right] - \frac{i}{\tau}\,\rho(v) + i\int \frac{dv'}{T(v')}\left[\Pi(v,v') - \delta(v-v')\right]\rho(v') \qquad \ldots\ldots\ldots\ldots 4.1$$

Here the diagonal matrix Λ is the pumping term. It is the steady state rates at which molecules enter the optically active levels. The term $\left[H, \rho(v)\right]$ accounts for the dynamical evolution of ρ. The radiative decay constant is given by τ. It is the duration of interraction assumed to be dominated by the molecular transit time across the laser beam. Also it is taken to be equal for all density matrix elements. The last term in eq (4.1) represents the effects of collision on the density matrix. The average time between the collisions is $T(v)$. The velocity after the collision is v'. (Note: there is a slight change in the velocity after the collision). The collision kernel is given by $\Pi(v, v')$ (see Appendix B). It is a matrix operator in the indices of the density matrix.

The phases of the complex off-diagonal elements Π_{ab} cause phase shifts of the molecular oscillators. Also the integration in the collision operator is because of the velocity changes induced by the molecular scattering process.

Since we are considering two level systems, ρ has got four elements, i.e., ρ_{aa}, ρ_{ab}, ρ_{ba} and ρ_{bb}.

From Eq (4.1) we get

$$i\dot{\rho}_{bb} = i\lambda_b + [H,\rho]_{bb} - \frac{i}{\tau}\rho_{bb} + i\int\frac{dv'}{T(v')}\Pi(v,v')\,\rho(v') - i\int\frac{dv'}{T(v')}\delta(v-v')\,\rho(v'), \quad \ldots\ldots 4.2$$

$$[H,\rho]_{bb} = (H\rho-\rho H)_{bb} = H_{ba}\rho_{ab} - \rho_{ba}H_{ab} + H_{bb}\rho_{bb} - \rho_{bb}H_{bb}$$

$$\text{i.e., } [H,\rho]_{bb} = H_{ba}\rho_{ab} - \rho_{ba}H_{ab} \quad \ldots\ldots\ldots 4.3$$

$$H_{ba} = -\mu_{ba}E_x$$

We are taking the radiation to be along the z-axis, with the electric field taken along x-axis.

Substitute for E_x from eq. (2.10). But at the same time we discard the off resonance driving. i.e., we assume that E_1 has effect on a - b alone and E_2 on c - d alone. Then,

$$H_{ba} = -\mu_{ba} E_1 \cos(\Omega_1 t - kz)$$

$$\text{i.e., } H_{ba} = -2\alpha_1 \cos(\Omega_1 t - kz) \quad \cdots\cdots\cdots 4.4$$

where $\alpha_1 = \mu_{ba} E_1 / 2\hbar$

so that $[H, \rho]_{bb} = 2\alpha_1 (\rho_{ba} - \rho_{ab}) \cos(\Omega_1 t - kz) \quad \cdots\cdots 4.5$

The fifth term of eq (4.2) = $-(i/T)\, \rho_{bb}(v)$.

This combines with the third term of (4.2) to give

$$-i\rho_{bb}\left(\frac{1}{T} + \frac{1}{\tau}\right) = -i\gamma \rho_{bb} \quad \cdots\cdots\cdots 4.6$$

where $\gamma = 1/\tau + 1/T$ is the collision broadened linewidth.

Substituting (4.5) and (4.6) in (4.2) we get

$$i\dot{\rho}_{bb} = i(\lambda_b - \gamma \rho_{bb}) + 2\alpha_1 (\rho_{ba} - \rho_{ab}) \cos(\Omega_1 t - kz).$$
$$+ i \int \frac{dv'}{T(v')} \Pi(v, v')\, \rho_{dd}(v') \quad \cdots\cdots\cdots 4.7$$

Collisional transfer to the level b is from the level d and that is why we have $\rho_{dd}(v')$ in the integrand.

Similarly

$$i\dot{\rho}_{ab} = i\lambda_{ab} + [H, \rho]_{ab} - \frac{i}{\tau} \rho_{ab} + i \int \frac{dv'}{T(v')} \Pi(v, v')\, \rho(v')$$
$$- i \int \frac{dv'}{T(v')} \delta(v - v')\, \rho(v') \quad \cdots\cdots\cdots\cdots 4.8$$

$\lambda_{ab} = 0$ since Λ is diagonal.

$$[H,\rho]_{ab} = H_{aa}\rho_{ab} - \rho_{aa}H_{ab} + H_{ab}\rho_{bb} - \rho_{ab}H_{bb}$$

i.e., $$[H,\rho]_{ab} = (H_{aa}-H_{bb})\rho_{ab} + H_{ab}(\rho_{bb}-\rho_{aa})$$

i.e, $$[H,\rho]_{ab} = \omega_{ab}\rho_{ab} - 2\alpha_1(\rho_{bb}-\rho_{aa})\cos(\Omega_1 t-kz)$$

4th term in eq. (4.8) = 0 since there is no collisional transition between a and b. Substituting these in (4.8) we get

$$i\dot{\rho}_{ab} = \omega_{ab}\rho_{ab} - 2\alpha_1(\rho_{bb}-\rho_{aa})\cos(\Omega_1 t-kz) - i\gamma\rho_{ab} \quad \ldots\ldots\ldots\ldots\ldots 4.9$$

By analogy with eq. (4.7) we get

$$i\dot{\rho}_{aa} = i(\lambda_a - \gamma\rho_{bb}) + 2\alpha_1(\rho_{ab}-\rho_{ba})\cos(\Omega_1 t-kz) + i\int\frac{dv'}{T(v')}\Pi(v,v')\rho_{cc}(v') \quad \ldots\ldots\ldots\ldots 4.10$$

Now, to simplify the calculations we remove the rapidly oscillating component of the off-diagonal element by setting

$$\rho_{ab} = \tilde{\rho}_{ab}e^{-i(\Omega_1 t-kz)}$$

where exponential term is the rapidly oscillating component. Differentiating, we get:

$$\dot{\rho}_{ab} = -i\Omega_1\tilde{\rho}_{ab}e^{-i(\Omega_1 t-kz)} + ik\frac{\partial z}{\partial t}\tilde{\rho}_{ab}e^{-i(\Omega_1 t-kz)} + \dot{\tilde{\rho}}_{ab}e^{-i(\Omega_1 t-kz)} \quad \ldots\ldots\ldots\ldots 4.10a$$

Similarly

$$\rho_{bb} = \frac{\lambda_b}{\gamma} - \frac{2i\alpha_1}{\gamma}(\rho_{ba} - \rho_{ab})\cos(\Omega_1 t - kz) + \frac{1}{\gamma}\int \frac{dv'}{T(v')}\Pi(v,v')\cdot\rho_{dd}(v') \quad \ldots 4.16$$

From these two equations we get :

$$\rho_{bb} - \rho_{aa} = \frac{\lambda_b - \lambda_a}{\gamma} - \frac{4i\alpha_1}{\gamma}(\rho_{ba} - \rho_{ab})\cos(\Omega_1 t - kz) + \frac{1}{\gamma}\int \frac{dv'}{T(v')}\Pi(v,v')\left\{\rho_{dd}(v') - \rho_{cc}(v')\right\}$$

$$\text{i.e., } \rho_{bb} - \rho_{aa} = \frac{\lambda_b - \lambda_a}{\gamma} - \frac{2i\alpha_1}{\gamma}(\rho_{ba} - \rho_{ab})\left\{e^{i(\Omega_1 t - kz)} + e^{-i(\Omega_1 t - kz)}\right\} + \frac{1}{\gamma}\int \frac{dv'}{T(v')}\Pi(v,v')\, n_{dc}(v')$$

i.e,

$$n_{ba} = \frac{\lambda_b - \lambda_a}{\gamma} + \frac{2i\alpha_1}{\gamma}(\tilde{\rho}_{ab} - \tilde{\rho}_{ba}) + \frac{1}{\gamma}\int \frac{dv'}{T(v')}\Pi(v,v')\, n_{dc}(v') \quad \ldots 4\text{-}17$$

Now substitute (4.14) in (4.17) we get :

$$n_{ba} = \frac{\lambda_b - \lambda_a}{\gamma} + \frac{2i\alpha_1}{\gamma}\left\{\alpha_1 n_{ba}\frac{2i\gamma}{(\Delta_1 + kv)^2 + \gamma^2}\right\} + \frac{1}{\gamma}\int \frac{dv'}{T(v')}\Pi(v,v')\, n_{dc}(v') \quad \text{so that}$$

$$n_{ba} = \frac{(\Delta_1 + kv)^2 + \gamma^2}{(\Delta_1 + kv)^2 + \Gamma_1^2}\left\{\frac{\lambda_b - \lambda_a}{\gamma} + \frac{1}{\gamma}\int \frac{dv'}{T(v')}\Pi(v,v')\, n_{dc}(v')\right\} \quad \ldots\ldots\ldots 4.18$$

where

$$\Gamma_1^2 = \gamma^2 + 4\alpha_1^2$$

$\dot{\tilde{\rho}}_{ab} = 0$ since it is the slowly varying component. Then,

$$i\,\dot{\rho}_{ab} = (\Omega_1 - kv)\,\tilde{\rho}_{ab}\, e^{-i(\Omega_1 t - kz)} \quad \ldots\ldots\ldots 4{\cdot}11$$

since $\dfrac{\partial z}{\partial t} = v$

Substitute eq. (4.11) in eq. (4.9). We get :

$$(\Omega_1 - kv - \omega_{ab} + i\gamma)\,\tilde{\rho}_{ab}\, e^{-i(\Omega_1 t - kz)} = -2\alpha_1 n_{ba} \cos(\Omega_1 t - kz)$$

so that
$$\tilde{\rho}_{ab} = \frac{\alpha_1}{(\Delta_1 + kv) - i\gamma}\left\{ e^{2i(\Omega_1 t - kz)} + 1 \right\} n_{ba}$$

where
$$\Delta_1 = \omega_{ab} - \Omega_1$$

Here the exponential term is the rapidly oscillating component and so this can be neglected under Rotating Wave Approximation (see Appendix C). Hence

$$\tilde{\rho}_{ab} = \frac{\alpha_1}{(\Delta_1 + kv) - i\gamma}\, n_{ba} \quad \ldots\ldots\ldots\ldots\ldots 4{\cdot}12$$

$$\tilde{\rho}_{ba} = \tilde{\rho}_{ab}^{*} = \frac{\alpha_1}{(\Delta_1 + kv) + i\gamma}\, n_{ba} \quad \ldots\ldots\ldots\ldots 4{\cdot}13$$

so that
$$\tilde{\rho}_{ab} - \tilde{\rho}_{ba} = \alpha_1 n_{ba}\, 2i\gamma \Big/ \left\{(\Delta_1 + kv)^2 + \gamma^2\right\} \quad \ldots\ldots 4{\cdot}14$$

$\dot{\rho}_{aa} = 0$, because of the small variation of the diagonal elements compared to the off-diagonal elements.
Hence from eq. (4.10) we have:

$$\rho_{aa} = \frac{\lambda_a}{\gamma} - \frac{2i\alpha_1}{\gamma}(\rho_{ab} - \rho_{ba})\cos(\Omega_1 t - kz) + \frac{1}{\gamma}\int \frac{dv'}{T(v')}\, \Pi(v, v')\cdot \rho_{cc}(v') \quad \ldots\ldots 4{\cdot}15$$

Similarly

$$n_{dc} = \frac{(\Delta_2+kv)^2+\gamma^2}{(\Delta_2+kv)^2+\Gamma_2^2}\left\{\frac{\lambda_d-\lambda_c}{\gamma}+\frac{1}{\gamma}\int\frac{dv'}{T(v')}\Pi(v,v')\, n_{ba}(v')\right\} \ldots 4.19$$

where $\Gamma_2^2 = \gamma^2 + 4\alpha_2^2$

Now substitute (4.17) in (4.14). We get :

$$\tilde{\rho}_{ab}-\tilde{\rho}_{ba} = \frac{2i\alpha_1\gamma}{(\Delta_1+kv)^2+\Gamma_1^2}\left\{\frac{\lambda_b-\lambda_a}{\gamma} + \frac{1}{\gamma}\int\frac{dv'}{T(v')}\Pi(v,v')\, n_{dc}(v')\right\} \ldots 4.20$$

Similarly

$$\tilde{\rho}_{cd}-\tilde{\rho}_{dc} = \frac{2i\alpha_2\gamma}{(\Delta_2+kv)^2+\Gamma_2^2}\left\{\frac{\lambda_d-\lambda_c}{\gamma}+\frac{1}{\gamma}\int\frac{dv'}{T(v')}\Pi(v,v')\, n_{ba}(v')\right\} \ldots\ldots 4.21$$

From eq. (4.15) and eq. (4.16) we get :

$$N_{ba} = \rho_{aa}+\rho_{bb} = \frac{\lambda_a+\lambda_b}{\gamma}+\frac{1}{\gamma}\int\frac{dv'}{T(v')}\Pi(v,v')\, N_{dc}(v') \ldots\ldots 4.22$$

Similarly

$$N_{dc} = \rho_{cc}+\rho_{dd} = \frac{\lambda_c+\lambda_d}{\gamma}+\frac{1}{\gamma}\int\frac{dv'}{T(v')}\Pi(v,v')\, N_{ba}(v') \ldots\ldots 4.23$$

Now solve the simultaneous equations (4.18) and (4.22) we get :

$$2\rho_{aa} = \frac{\lambda_a+\lambda_b}{\gamma}+\frac{1}{\gamma}\int\frac{dv'}{T(v')}\Pi(v,v')\, N_{dc}(v') - \frac{(\Delta_1+kv)^2+\gamma^2}{(\Delta_1+kv)^2+\Gamma_1^2}\left\{\frac{\lambda_b-\lambda_a}{\gamma}+\frac{1}{\gamma}\int\frac{dv'}{T(v')}\Pi(v,v')\, n_{dc}(v')\right\} \ldots\ldots 4.24$$

$$2\rho_{bb} = \frac{\lambda_a+\lambda_b}{\gamma}+\frac{1}{\gamma}\int\frac{dv'}{T(v')}\Pi(v,v')\, N_{dc}(v') + \frac{(\Delta_1+kv)^2+\gamma^2}{(\Delta_1+kv)^2+\Gamma_1^2}\left\{\frac{\lambda_b-\lambda_a}{\gamma}+\frac{1}{\gamma}\int\frac{dv'}{T(v')}\Pi(v,v')\, n_{dc}(v')\right\} \ldots\ldots 4.25$$

Substitute (4.32) in (4.14). We get :

$$\tilde{\rho}_{ab} - \tilde{\rho}_{ba} = \frac{2i\alpha_1\gamma}{(\Delta_1+kv)^2+\Gamma_1^2}\left\{K_{bd}\,\rho_{dd} - K_{ac}\,\rho_{cc} + \frac{\lambda_b-\lambda_a}{\gamma}\right\} \cdots 4.33$$

Similarly

$$\tilde{\rho}_{cd} - \tilde{\rho}_{dc} = \frac{2i\alpha_2\gamma}{(\Delta_2+kv)^2+\Gamma_2^2}\left\{K_{bd}\,\rho_{bb} - K_{ac}\,\rho_{aa} + \frac{\lambda_d-\lambda_c}{\gamma}\right\} \cdots 4.34$$

Now substitute (4.14) in (4.32) and as a first approximation neglect the collisional terms, which are small compared to other terms. We get :

$$n_{ba}(v) = \frac{\lambda_b-\lambda_a}{\gamma}\left(1 - \frac{4\alpha_1^2}{(\Delta_1+kv)^2+\Gamma_1^2}\right) \cdots\cdots 4.35$$

Similarly

$$n_{dc}(v) = \frac{\lambda_d-\lambda_c}{\gamma}\left(1 - \frac{4\alpha_2^2}{(\Delta_2+kv)^2+\Gamma_2^2}\right) \cdots\cdots 4.36$$

Then,

$$n_{dc}(v') = \frac{\lambda_d-\lambda_c}{\gamma}\left(1 - \frac{4\alpha_2^2}{(\Delta_2+kv')^2+\Gamma_2^2}\right) \cdots\cdots 4.37$$

Substitute (4.37) in (4.28). We get :

$$\tilde{\rho}^{(1)}_{ab} - \tilde{\rho}^{(1)}_{ba} = \frac{2i\alpha_1}{(\Delta_1+kv)^2+\Gamma_1^2}\int\left[\frac{dv'}{T(v')}\,\Pi(v,v')\,\frac{\lambda_d-\lambda_c}{\gamma}\left\{1 - \frac{4\alpha_2^2}{(\Delta_2+kv')^2+\Gamma_2^2}\right\}\right]$$

Hence the double resonance part will be :

$$\tilde{\rho}^{(1)}_{ab} - \tilde{\rho}^{(1)}_{ba} = \frac{2i\alpha_1}{(\Delta_1+kv)^2+\Gamma_1^2}\int\left[\frac{dv'}{T(v')}\,\Pi(v,v')\,\frac{\lambda_d-\lambda_c}{\gamma}\left(-\frac{4\alpha_2^2}{(\Delta_2+kv')^2+\Gamma_2^2}\right)\right]$$

Similarly

$$2\rho_{cc} = \frac{\lambda_c+\lambda_d}{\gamma} + \frac{1}{\gamma}\int\frac{dv'}{T(v')}\Pi(v,v')\,N_{ba}(v')$$

$$-\frac{(\Delta_2+kv)^2+\gamma^2}{(\Delta_2+kv)^2+\Gamma_2^2}\left\{\frac{\lambda_d-\lambda_c}{\gamma}+\frac{1}{\gamma}\int\frac{dv'}{T(v')}\Pi(v,v')\,n_{ba}(v')\right\} \quad \ldots\ldots 4.26$$

$$2\rho_{dd} = \frac{\lambda_c+\lambda_d}{\gamma} + \frac{1}{\gamma}\int\frac{dv'}{T(v')}\Pi(v,v')\,N_{ba}(v')$$

$$+\frac{(\Delta_2+kv)^2+\gamma^2}{(\Delta_2+kv)^2+\Gamma_2^2}\left\{\frac{\lambda_d-\lambda_c}{\gamma}+\frac{1}{\gamma}\int\frac{dv'}{T(v')}\Pi(v,v')\,n_{ba}(v')\right\} \ldots 4.27$$

The double resonance part of eq. (4.20) is

$$\tilde\rho_{ab}^{(1)} - \tilde\rho_{ba}^{(1)} = \frac{2i\alpha_1}{(\Delta_1+kv)^2+\Gamma_1^2}\int\frac{dv'}{T(v')}\Pi(v,v')\,n_{dc}(v') \quad \ldots 4.28$$

Substituting for $n_{dc}(v')$ by analogy with eq. (4.19), we get :

$$\tilde\rho_{ab}^{(1)} - \tilde\rho_{ba}^{(1)} = \frac{2i\alpha_1}{(\Delta_1+kv)^2+\Gamma_1^2}\int\frac{dv'}{T(v')}\Pi(v,v')$$

$$+\frac{(\Delta_2+kv')^2+\gamma^2}{(\Delta_2+kv')^2+\Gamma_2^2}\left\{\frac{\lambda_d-\lambda_c}{\gamma}+\frac{r}{\gamma}\int\frac{dv''}{T(v'')}\Pi(v',v'')\,n_{ba}(v')\right\} \quad \ldots 4.29$$

To simplify the calculation, we may introduce the collisionless result for n_{dc}. This is obtained as follows: Take the eq. (4.15). If we consider that the velocity remains the same after the collision, last term of eq. (4.15) becomes equal to $\kappa_{ac}\,\rho_{cc}$ where κ_{ac} is the collision constant. Therefore

$$\rho_{aa} = \frac{\lambda_a}{\gamma} - \frac{2i\alpha_1}{\gamma}\cos(\Omega_1 t - kz)\,(\rho_{ab}-\rho_{ba}) + K_{ac}\,\rho_{cc} \quad \ldots\ldots 4.30$$

$$\rho_{bb} = \frac{\lambda_b}{\gamma} - \frac{2i\alpha_1}{\gamma}\cos(\Omega_1 t - kz)\,(\rho_{ba}-\rho_{ab}) + K_{bd}\,\rho_{dd} \quad \ldots\ldots 4.31$$

Hence

$$n_{ba} = \frac{\lambda_b-\lambda_a}{\gamma} + K_{bd}\,\rho_{dd} - K_{ac}\,\rho_{cc} + \frac{2i\alpha_1}{\gamma}(\tilde\rho_{ab}-\tilde\rho_{ba}) \quad \ldots 4.32$$

i.e, $$\tilde{\rho}^{(1)}_{ab} - \tilde{\rho}^{(1)}_{ba} = - \frac{8i\alpha_1\alpha_2^2}{(\Delta_1+kv)^2+\Gamma_1^2}\int \frac{\Pi(v,v')}{\gamma T(v')} \frac{\lambda_d(v') - \lambda_c(v')}{(\Delta_2+kv')^2+\Gamma_2^2} dv' \quad \ldots\ldots\ldots 4\cdot38$$

Similarly
$$\tilde{\rho}^{(1)}_{cd} - \tilde{\rho}^{(1)}_{dc} = - \frac{8i\alpha_2\alpha_1^2}{(\Delta_2+kv)^2+\Gamma_2^2}\int \frac{\Pi(v,v')}{\gamma T(v')} \frac{\lambda_b(v') - \lambda_a(v')}{(\Delta_1+kv')^2+\Gamma_1^2} dv' \quad \ldots\ldots 4\cdot39$$

The polarization induced in the molecules by the field E_x (z, t) is :

$$P(z,t) = N\left[\mu_{ab}(\rho_{ab}+\rho_{ba}) + \mu_{cd}(\rho_{cd}+\rho_{dc})\right] \quad \ldots\ldots 4\cdot40$$

Here $N\rho_{ab}$ and $N\rho_{ba}$ are the numbers of molecules per unit volume having μ_{ab} as their expectation value of the dipole moment. Similarly, $N\rho_{cd}$ and $N\rho_{dc}$ have μ_{cd} as the expectation value of their dipole moment. The number N is the total number of molecules per unit volume of the molecular sample.

The energy absorbed per unit volume in the sample = Power absorbed

i.e., $W = V\langle E(z,t)\,\dot{P}(z,t)\rangle^{time}_{velocity}$

where $\langle\ \rangle^{t}_{v}$ denotes the time and velocity average and V is the volume of the gas under the effect of the laser beam. In other words, it is the volume occupied by the laser beam in the Stark cell.

We are finding the velocity average since there are different groups of velocities. We are finding the time average because the excitation of the molecules to the upper vibrational - rotational energy level has time dependence.

From (4·40), $\dot{P}(z,t) = N\left[\mu_{ab}(\dot{\rho}_{ab}+\dot{\rho}_{ba}) + \mu_{cd}(\dot{\rho}_{cd}+\dot{\rho}_{dc})\right]$

From (4·11), $\dot{\rho}_{ab} = i\tilde{\rho}_{ab}e^{-i(\Omega_1 t - kz)}(kv - \Omega_1)$

so that $\dot{\rho}_{ba} = -i\tilde{\rho}_{ba}e^{i(\Omega_1 t - kz)}(kv - \Omega_1)$

Substituting,
$$\dot{P}(z,t) = N\Big[i\mu_{ab}\tilde{\rho}_{ab}(kv-\Omega_1)\left(e^{-i(\Omega_1 t - kz)} - e^{i(\Omega_1 t - kz)}\right) + i\mu_{cd}\tilde{\rho}_{cd}(kv-\Omega_2)\left(e^{-i(\Omega_2 t - kz)} - e^{i(\Omega_2 t - kz)}\right)\Big]$$

Hence

$$E(z,\ t)\ \dot{P}(z,\ t) = \left[E_1 \cos(\Omega_1 t - kz) + E_2 \cos(\Omega_2 t - kz)\right] \cdot$$

$$N\left[i\mu_{ab}\tilde{\rho}_{ab}(kv-\Omega_1)\left(e^{-i(\Omega_1 t - kz)} - e^{i(\Omega_1 t - kz)}\right) + i\mu_{cd}\tilde{\rho}_{cd}(kv-\Omega_2)\left(e^{-i(\Omega_2 t - kz)} - e^{i(\Omega_2 t - kz)}\right)\right] \quad \ldots\ldots 4.42$$

where we have made the following substitutions:

$$\cos(\Omega_1 t - kz) = \tfrac{1}{2}\left\{e^{i(\Omega_1 t - kz)} + e^{-i(\Omega_1 t - kz)}\right\}$$

and $\sin(\Omega_1 t - kz) = \frac{1}{2i}\left\{e^{i(\Omega_1 t - kz)} - e^{-i(\Omega_1 t - kz)}\right\}$

Substitute this in eq. (4.42) and discard the terms multiplied by exponential terms, since they vanish under time averaging. We get the following expression for the power absorbed:

$$W = \frac{VN}{2}\left\{\frac{\mu_{ab}E_1\Omega_1}{i}\left\langle \tilde{\rho}_{ab}^{(1)} - \tilde{\rho}_{ba}^{(1)}\right\rangle_{vel} + \frac{\mu_{cd}E_2\Omega_2}{i}\left\langle \tilde{\rho}_{cd}^{(1)} - \tilde{\rho}_{dc}^{(1)}\right\rangle_{vel}\right\} \quad \ldots\ldots\ldots 4.43$$

The molecular system under consideration obey the Gaussian distribution. In Gaussian distribution, average value of say,

x is $\overline{x} = \sqrt{\frac{\beta}{\pi}} \int_{-\infty}^{\infty} x\ e^{-\beta x^2}\, dx \quad \ldots\ldots\ldots\ldots 4.44$

This follows from statistical mechanics where the average value of any function g(x) is given by

$$\overline{g(x)} = \int_{x_1}^{x_2} g(x)\ f(x)\ dx$$

where f(x) is the distribution function.

For continuous distribution like Gaussian distribution,

$$f(x) = \sqrt{\frac{\beta}{\pi}} \quad e^{-\beta x^2}$$

Substituting this we get eq. (4.44).

Using (4.44) and (4.38), we get :

$$\left\langle \tilde{\rho}^{(1)}_{ab} - \tilde{\rho}^{(1)}_{ba} \right\rangle^{time}_{velocity} = \frac{1}{ku\pi^{1/2}} \int e^{-x^2/k^2u^2} \left\{ \frac{-8i\alpha_1\alpha_2^2}{(\Delta_1+x)^2+\Gamma_1^2} \right.$$

$$\left. \int \frac{\Pi(v,v')}{\gamma T(v')} \frac{\lambda_d(v') - \lambda_c(v')}{(\Delta_2+kv')^2+\Gamma_2^2} dv' \right\} dx \quad \ldots\ldots 4.45$$

where $\frac{1}{ku\pi^{1/2}} e^{-x^2/k^2u^2}$ is the velocity distribution function, $x = kv$ and u is the mean velocity of all the velocity groups involved in the transition. In other words, u is the average of all the velocities in the Maxwellian distribution curve.

By analogy with eq. (4.45), we get :

$$\left\langle \tilde{\rho}^{(1)}_{cd} - \tilde{\rho}^{(1)}_{dc} \right\rangle^{t}_{v} = \frac{1}{ku\pi^{1/2}} \int e^{-x^2/k^2u^2} \left\{ \frac{-8i\alpha_2\alpha_1^2}{(\Delta_2+x)^2+\Gamma_2^2} \right.$$

$$\left. \int \frac{\Pi(v,v')}{\gamma T(v')} \frac{\lambda_b(v') - \lambda_a(v')}{(\Delta_1+kv')^2+\Gamma_1^2} dv' \right\} dx \quad \ldots 4.46$$

Substitute (4.45) and (4.46) in (4.43). We get the expression for the power absorbed as follows:

$$W = \frac{NV}{2} \left[\frac{\mu_{ab}E_1\Omega_1}{i} \frac{1}{ku\pi^{1/2}} \int e^{-x^2/k^2u^2} \left\{ \frac{-8i\alpha_1\alpha_2^2}{(\Delta_1+x)^2+\Gamma_1^2} \right. \right.$$

$$\left. \int \frac{\Pi(v,v')}{\gamma T(v')} \frac{\lambda_d(v') - \lambda_c(v')}{(\Delta_2+kv')^2+\Gamma_2^2} dv' \right\} dx$$

$$+ \frac{\mu_{cd}E_2\Omega_2}{i} \frac{1}{ku\pi^{1/2}} \int e^{-x^2/k^2u^2} \left\{ \frac{-8i\alpha_2\alpha_1^2}{(\Delta_2+x)^2+\Gamma_2^2} \right.$$

$$\left. \left. \int \frac{\Pi(v,v')}{\gamma T(v')} \frac{\lambda_b(v') - \lambda_a(v')}{(\Delta_1+kv')^2+\Gamma_1^2} dv' \right\} dx \right] \quad \ldots\ldots 4.47$$

i.e., $$\bar{W} = \frac{N V}{2} \frac{1}{k u \pi^{1/2}} \frac{-8 i \alpha_1^2 \alpha_2^2}{i} 2\hbar$$

$$\Big[\Omega_1 \int e^{-x^2/k^2u^2} \Big\{ \frac{1}{(\Delta_1+x)^2+\Gamma_1^2} \int \frac{\Pi(\frac{x}{k}, v')}{\gamma T(v')} \frac{\lambda_d(v') - \lambda_c(v')}{(\Delta_2+kv')^2+\Gamma_2^2} dv' \Big\} dx$$

$$+ \Omega_2 \int e^{-x^2/k^2u^2} \Big\{ \frac{1}{(\Delta_2+x)^2+\Gamma_2^2} \int \frac{\Pi(\frac{x}{k}, v')}{\gamma T(v')} \frac{\lambda_b(v') - \lambda_a(v')}{(\Delta_1+kv')^2+\Gamma_1^2} dv' \Big\} dx \Big] \quad \text{...... } 4.47$$

Case (ii): Particular case

Now we try to have more practicable form for the power absorbed by using approximate values of collision kernels all throughout the calculation. This is the case where the velocity is maintained constant during the collision.
In that case eq. (4.7) becomes

$$i \dot{\rho}_{bb} = i(\lambda_b - \gamma \rho_{bb}) + 2\alpha_1 (\rho_{ba} - \rho_{ab}) \cos(\Omega_1 t - kz) + i\gamma K_{bd} \rho_{dd} \quad \text{........ } 4.48$$

Eq. (4.9) remains the same

$$i \dot{\rho}_{ab} = \omega_{ab} \rho_{ab} - 2\alpha_1 (\rho_{bb} - \rho_{aa}) \cos(\Omega_1 t - kz) - i\gamma \rho_{ab} \quad \text{........ } 4.9$$

By analogy with eq. (4.48), we get :

$$i \dot{\rho}_{aa} = i(\lambda_a - \gamma \rho_{aa}) + 2\alpha_1 (\rho_{ab} - \rho_{ba}) \cos(\Omega_1 t - kz) + i\gamma K_{ac} \rho_{cc} \quad \text{........ } 4.49$$

$$\tilde{\rho}_{ab} = \frac{\alpha_1}{(\Delta_1 + kv) - i\gamma} n_{ba} \quad \text{........ } 4.12$$

$$\tilde{\rho}_{ab} - \tilde{\rho}_{ba} = \alpha_1 n_{ba} \frac{2i\gamma}{(\Delta_1+kv)^2+\gamma^2} \quad \ldots\ldots\ldots 4\cdot 14$$

$\dot{\rho}_{aa} = 0$ as we saw before. Hence, from eq.(4.49), we have:

$$\rho_{aa} = \frac{\lambda_a}{\gamma} - \frac{2i\alpha_1}{\gamma}(\rho_{ab}-\rho_{ba})\cos(\Omega_1 t - kz) + K_{ac}\rho_{cc} \quad \cdots 4\cdot 30$$

Similarly

$$\rho_{bb} = \frac{\lambda_b}{\gamma} - \frac{2i\alpha_1}{\gamma}(\rho_{ba}-\rho_{ab})\cos(\Omega_1 t - kz) + K_{bd}\rho_{dd} \quad \cdots 4\cdot 31$$

Then

$$n_{ba} = \rho_{bb} - \rho_{aa} = \frac{\lambda_b-\lambda_a}{\gamma} + \frac{2i\alpha_1}{\gamma}(\tilde{\rho}_{ab}-\tilde{\rho}_{ba}) + K_{bd}\rho_{dd} - K_{ac}\rho_{cc} \quad \cdots\cdots 4\cdot 32$$

Now substitute (4.14) in (4.32). We have :

$$n_{ba} = \frac{(\Delta_1+kv)^2+\gamma^2}{(\Delta_1+kv)^2+\Gamma_1^2}\left\{\frac{\lambda_b-\lambda_a}{\gamma} + K_{bd}\rho_{dd} - K_{ac}\rho_{cc}\right\} \quad \cdot\cdot 4\cdot 50$$

Similarly

$$n_{dc} = \frac{(\Delta_2+kv)^2+\gamma^2}{(\Delta_2+kv)^2+\Gamma_2^2}\left\{\frac{\lambda_d-\lambda_c}{\gamma} + K_{bd}\rho_{bb} - K_{ac}\rho_{cc}\right\} \quad \cdot\cdot 4\cdot 51$$

Now substititе (4.32) in (4.14). We get :

$$\tilde{\rho}_{ab} - \tilde{\rho}_{ba} = \frac{2i\alpha_1\gamma}{(\Delta_1+kv)^2+\Gamma_1^2}\left\{K_{bd}\rho_{dd} - K_{ac}\rho_{cc} + \frac{\lambda_b-\lambda_a}{\gamma}\right\} \quad \cdots\cdot 4\cdot 33$$

Similarly

$$\tilde{\rho}_{cd} - \tilde{\rho}_{dc} = \frac{2i\alpha_2\gamma}{(\Delta_2+kv)^2+\Gamma_2^2}\left\{K_{bd}\rho_{bb} - K_{ac}\rho_{aa} + \frac{\lambda_d-\lambda_c}{\gamma}\right\} \quad \cdots\cdot 4\cdot 34$$

Adding (4.30) and (4.31), we get :

$$\rho_{aa} + \rho_{bb} = \frac{\lambda_a + \lambda_b}{\gamma} + K_{ac}\rho_{cc} + K_{bd}\rho_{dd} \quad \cdots\cdots \quad 4.52$$

Similarly

$$\rho_{cc} + \rho_{dd} = \frac{\lambda_c + \lambda_d}{\gamma} + K_{ac}\rho_{aa} + K_{bd}\rho_{bb} \quad \cdots \quad 4.53$$

Solving (4.51) and (4.53), we get :

$$2\rho_{dd} = \frac{\lambda_c}{\gamma}\left[1 - \frac{(\Delta_2+kv)^2+\gamma^2}{(\Delta_2+kv)^2+\Gamma_2^2}\right] + \frac{\lambda_d}{\gamma}\left[1 + \frac{(\Delta_2+kv)^2+\gamma^2}{(\Delta_2+kv)^2+\Gamma_2^2}\right]$$

$$+ K_{ca}\rho_{aa}\left[1 - \frac{(\Delta_2+kv)^2+\gamma^2}{(\Delta_2+kv)^2+\Gamma_2^2}\right] + K_{bd}\rho_{bb}\left[1 + \frac{(\Delta_2+kv)^2+\gamma^2}{(\Delta_2+kv)^2+\Gamma_2^2}\right]$$

i.e,

$$\rho_{dd} = \frac{1}{2}\left\{1 - \frac{(\Delta_2+kv)^2+\gamma^2}{(\Delta_2+kv)^2+\Gamma_2^2}\right\}\left(\frac{\lambda_c}{\gamma} + K_{ca}\rho_{aa}\right)$$

$$+ {}^1\!/_2\left\{1 + \frac{(\Delta_2+kv)^2+\gamma^2}{(\Delta_2+kv)^2+\Gamma_2^2}\right\}\left(\frac{\lambda_d}{\gamma} + K_{bd}\rho_{bb}\right) \quad \cdots\cdots \quad 4.54$$

$$\rho_{cc} = \frac{1}{2}\left\{1 + \frac{(\Delta_2+kv)^2+\gamma^2}{(\Delta_2+kv)^2+\Gamma_2^2}\right\}\left(\frac{\lambda_c}{\gamma} + K_{ac}\rho_{aa}\right)$$

$$+ \frac{1}{2}\left\{1 - \frac{(\Delta_2+kv)^2+\gamma^2}{(\Delta_2+kv)^2+\Gamma_2^2}\right\}\left(\frac{\lambda_d}{\gamma} + K_{bd}\rho_{bb}\right) \quad \cdots \quad 4.55$$

Hence double resonance part of (4.33) is

$$\tilde{\rho}_{ab}^{(1)} - \tilde{\rho}_{ba}^{(1)} = \frac{2i\alpha_1\gamma}{(\Delta_1+kv)^2+\gamma^2}\left\{K_{bd}\rho_{dd} - K_{ac}\rho_{cc}\right\}$$

i.e.,

$$\tilde{\rho}_{ab}^{(1)} - \tilde{\rho}_{ba}^{(1)} = \frac{2i\alpha_1\gamma}{(\Delta_1+kv)^2+\Gamma_1^2}\left[2(K_{bd}+K_{ac})\frac{\alpha_2^2}{(\Delta_2+kv)^2+\Gamma_2^2}\right.$$

$$\left.\left(\frac{\lambda_c-\lambda_d}{\gamma} + K_{ac}\rho_{aa} - K_{bd}\rho_{bb}\right) + K_{bd}^2\rho_{bb} - K_{ac}^2\rho_{aa}\right] \quad \cdots\cdots\cdots \quad 4.56$$

Again for simplicity we discard the collisional terms. (For correct expressions of ρ_{ii}, see Appendix D). This is because contribution due to pumping is far more than that due to the collision. So from (4.53) we get :

$$\rho_{cc} + \rho_{dd} = \frac{\lambda_c + \lambda_d}{\gamma} \quad \ldots\ldots\ldots 4.53a$$

Refer to eq. (4.36). Solving eq. (4.36) and (4.53a), we get :

$$\rho_{dd} = \frac{\lambda_d}{\gamma} - \frac{\lambda_d - \lambda_c}{\gamma}\,\frac{2\alpha_2^2}{(\Delta_2 + kv)^2 + \Gamma_2^2} \quad \ldots\, 4.57$$

$$\rho_{cc} = \frac{\lambda_c}{\gamma} + \frac{\lambda_d - \lambda_c}{\gamma}\,\frac{2\alpha_2^2}{(\Delta_2 + kv)^2 + \Gamma_2^2} \quad \ldots\, 4.58$$

Substitute (4.57) and (4.58) in (4.33). We get :

$$\tilde{\rho}_{ab} - \tilde{\rho}_{ba} = -\frac{2i\alpha_1\gamma}{(\Delta_1 + kv)^2 + \Gamma_1^2}\left(K_{bd}\,\rho_{dd} - K_{ac}\,\rho_{cc} + \frac{\lambda_b - \lambda_a}{\gamma}\right)$$

i.e., $$\tilde{\rho}_{ab} - \tilde{\rho}_{ba} = -\frac{4i\alpha_1\alpha_2^2\,(K_{ac} + K_{bd})\,(\lambda_d - \lambda_c)}{\{(\Delta_1 + kv)^2 + \Gamma_1^2\}\{(\Delta_2 + kv)^2 + \Gamma_2^2\}}$$

$$+ \frac{2i\alpha_1\gamma}{(\Delta_1 + kv)^2 + \Gamma_1^2}\left[\frac{\lambda_b - \lambda_a}{\gamma} + K_{bd}\,\frac{\lambda_d + \lambda_c}{2\gamma} - K_{ac}\,\frac{\lambda_d + \lambda_c}{2\gamma}\right]$$

$$+ \frac{i\alpha_1\,(\lambda_d - \lambda_c)\,(K_{bd} + K_{ac})}{(\Delta + kv)^2 + \Gamma_1^2} \quad \ldots\, 4.59$$

Also,

$$\tilde{\rho}_{cd} - \tilde{\rho}_{dc} = \frac{2i\alpha_2\gamma}{(\Delta_2 + kv)^2 + \Gamma_2^2}\left(K_{bd}\,\rho_{bb} - K_{ac}\,\rho_{aa} + \frac{\lambda_d - \lambda_c}{\gamma}\right)$$

$$\ldots\, 4.59a$$

i.e., $$\tilde{\rho}_{cd} - \bar{\rho}_{dc} = \frac{-4i\alpha_2\alpha_1^2(K_{ac}+K_{bd})(\lambda_b-\lambda_a)}{\{(\Delta_1+kv)^2+\Gamma_1^2\}\{(\Delta_2+kv)^2+\Gamma_2^2\}}$$

$$+\frac{2i\bar{\alpha}_2\gamma}{(\Delta_2+kv)^2+\Gamma_2^2}\left[\frac{\lambda_d-\lambda_c}{\gamma}+K_{bd}\frac{\lambda_a+\lambda_b}{2\gamma}-K_{ac}\frac{\lambda_a+\lambda_b}{2\gamma}\right]$$

$$+\frac{i\alpha_2(\lambda_b-\lambda_a)(K_{bd}+K_{ac})}{(\Delta_2+kv)^2+\Gamma_2^2} \quad \ldots\ldots\ldots 4.60$$

From (4.59a) and (4.60) we have:

$$\frac{\lambda_c-\lambda_d}{\gamma}+K_{ac}\rho_{aa}-K_{bd}\rho_{bb} = \frac{2\alpha_1^2}{\gamma}\frac{(K_{ac}+K_{bd})(\lambda_b-\lambda_a)}{(\Delta_1+kv)^2+\Gamma_1^2}$$

$$+\frac{\lambda_c-\lambda_d}{\gamma}+(K_{ac}-K_{bd})\frac{\lambda_a+\lambda_b}{2\gamma}+\frac{1}{2\gamma}(\lambda_a-\lambda_b)(K_{ac}+K_{bd}) \quad \cdots 4.61$$

If we refer to eq. 4.56, we can see that $(\tilde{\rho}^{(1)}_{ab}-\tilde{\rho}^{(1)}_{ba})$ is in terms of ρ_{aa} and ρ_{bb}. Let us replace this by means of measurable quantities. The second term in 4,56 is replaced by R.H.S. of 4.61. Also, expressions for ρ_{aa} and ρ_{bb} as in 4.57a and 4.58a are substituted in 4.56. We have:

$$\tilde{\rho}^{(1)}_{ab}-\tilde{\rho}^{(1)}_{ba} = \frac{2i\alpha_1\gamma}{(\Delta_1+kv)^2+\Gamma_1^2}\left[2(K_{ac}+K_{bd})\frac{\alpha_2^2}{(\Delta_2+kv)^2+\Gamma_2^2}\right.$$

$$\left\{\frac{2\alpha_1^2}{\gamma}\frac{(K_{ac}+K_{bd})(\lambda_b-\lambda_a)}{(\Delta_1+kv)^2+\Gamma_1^2}+\frac{\lambda_c-\lambda_d}{\gamma}+(K_{ac}-K_{bd})\frac{\lambda_a+\lambda_b}{2\gamma}\right.$$

$$\left.\left.+\frac{1}{2\gamma}(\lambda_a-\lambda_b)(K_{ac}+K_{bd})\right\}+K_{bd}^2\rho_{bb}-K_{ac}^2\rho_{aa}\right] \quad \cdots 4.62$$

By analogy with (4.57) and (4.58), we have:

$$\rho_{Bb} = \frac{\lambda_b}{\gamma}-\frac{\lambda_b-\lambda_a}{\gamma}\frac{2\alpha_1^2}{(\Delta_1+kv)^2+\Gamma_1^2} \quad \cdots\cdots 4.57a$$

$$\rho_{aa} = \frac{\lambda_a}{\gamma} + \frac{\lambda_b - \lambda_a}{\gamma} \frac{2\alpha_1^2}{(\Delta_1 + kv)^2 + \Gamma_1^2} \quad \cdots\cdots 4.58a$$

Substitute these in (4.62). We get :

$$\begin{aligned}\tilde{\rho}_{ab}^{(1)} - \tilde{\rho}_{ba}^{(1)} = \frac{2i\alpha_1}{(\Delta_1+kv)^2+\Gamma_1^2} \Bigg[& \frac{4\alpha_1^2\alpha_2^2 (K_{ac}+K_{bd})^2 (\lambda_b-\lambda_a)}{\{(\Delta_1+kv)^2+\Gamma_1^2\}\{(\Delta_2+kv)^2+\Gamma_2^2\}} \\ & + \frac{2\alpha_2^2 (K_{ac}+K_{bd})(\lambda_c-\lambda_d)}{(\Delta_2+kv)^2+\Gamma_2^2} + \frac{\alpha_2^2 (K_{ac}^2-K_{bd}^2)(\lambda_a+\lambda_b)}{(\Delta_2+kv)^2+\Gamma_2^2} \\ & + \frac{\alpha_2^2 (K_{ac}+K_{bd})^2 (\lambda_a-\lambda_b)}{(\Delta_2+kv)^2+\Gamma_2^2} + K_{bd}^2 \lambda_b - K_{ac}^2 \lambda_a \\ & - \frac{2\alpha_1^2 (K_{ac}^2+K_{bd}^2)(\lambda_b-\lambda_a)}{(\Delta_1+kv)^2+\Gamma_1^2} \Bigg] \quad \cdots\cdots 4.63\end{aligned}$$

Similarly

$$\begin{aligned}\tilde{\rho}_{cd}^{(1)} - \tilde{\rho}_{dc}^{(1)} = \frac{2i\alpha_2}{(\Delta_2+kv)^2+\Gamma_2^2} \Bigg[& \frac{4\alpha_1^2\alpha_2^2 (K_{ac}+K_{bd})^2 (\lambda_d-\lambda_c)}{\{(\Delta_1+kv)^2+\Gamma_1^2\}\{(\Delta_2+kv)^2+\Gamma_2^2\}} \\ & + \frac{2\alpha_1^2 (K_{ac}+K_{bd})(\lambda_a-\lambda_b)}{(\Delta_1+kv)^2+\Gamma_1^2} + \frac{\alpha_1^2 (K_{ac}^2-K_{bd}^2)(\lambda_c+\lambda_d)}{(\Delta+kv)^2+\Gamma_1^2} \\ & + \frac{\alpha_1^2 (K_{ac}+K_{bd})^2 (\lambda_c-\lambda_d)}{(\Delta_1+kv)^2+\Gamma_1^2} + K_{bd}^2 \lambda_d - K_{ac}^2 \lambda_c \\ & - \frac{2\alpha_2^2 (K_{ac}^2+K_{bd}^2)(\lambda_d-\lambda_c)}{(\Delta_2+kv)^2+\Gamma_2^2} \Bigg] \quad \cdots\cdots 4.64\end{aligned}$$

Double resonance part of $\tilde{\rho}^{(1)}_{ab} - \tilde{\rho}^{(1)}_{ba}$ is :

$$\tilde{\rho}^{(1)}_{ab} - \tilde{\rho}^{(1)}_{ba} = \frac{2i\alpha_1}{(\Delta_1+kv)^2+\Gamma_1^2}\left[\frac{2\alpha_2^2(K_{ac}+K_{bd})(\lambda_c-\lambda_d)}{(\Delta_2+kv)^2+\Gamma_2^2} + \frac{\alpha_2^2(K_{ac}^2-K_{bd}^2)(\lambda_a+\lambda_b)}{(\Delta_2+kv)^2+\Gamma_2^2} + \frac{\alpha_2^2(K_{ac}+K_{bd})^2(\lambda_a-\lambda_b)}{(\Delta_2+kv)^2+\Gamma_2^2} - \frac{2\alpha_1^2(K_{ac}^2+K_{bd}^2)(\lambda_b-\lambda_a)}{(\Delta_1+kv)^2+\Gamma_1^2}\right] \quad \ldots\ 4.63a$$

Similarly

$$\tilde{\rho}^{(1)}_{cd} - \tilde{\rho}^{(1)}_{dc} = \frac{2i\alpha_2}{(\Delta_2+kv)^2+\Gamma_2^2}\left[\frac{2\alpha_1^2(K_{ac}+K_{bd})(\lambda_a-\lambda_b)}{(\Delta_1+kv)^2+\Gamma_1^2} + \frac{\alpha_1^2(K_{ac}^2-K_{bd}^2)(\lambda_c+\lambda_d)}{(\Delta_1+kv)^2+\Gamma_1^2} + \frac{\alpha_1^2(K_{ac}+K_{bd})^2(\lambda_c-\lambda_d)}{(\Delta_1+kv)^2+\Gamma_1^2} - \frac{2\alpha_2^2(K_{ac}^2+K_{bd}^2)(\lambda_d-\lambda_c)}{(\Delta_2+kv)^2+\Gamma_2^2}\right] \quad \ldots\ldots\ 4.64a$$

Now we find the velocity average as shown below:

$$\left\langle \frac{1}{[(\Delta_1+kv)^2+\Gamma_1^2][(\Delta_2+kv)^2+\Gamma_2^2]} \right\rangle_{vel} = \frac{1}{ku\pi^{1/2}} \int_{-\infty}^{\infty} \frac{e^{-x^2/k^2u^2}\, dx}{[(\Delta_1+x)^2+\Gamma_1^2][(\Delta_2+x)^2+\Gamma_2^2]}$$

$$= \frac{1}{ku\pi^{1/2}}\, e^{-\Delta_1^2/k^2u^2}\, \frac{\pi(\Gamma_1+\Gamma_2)}{\Gamma_1\Gamma_2[(\Delta_1-\Delta_2)^2+(\Gamma_1+\Gamma_2)^2]} \quad \ldots\ldots\ldots\ 4.65$$

Similarly $$\left\langle \frac{1}{[(\Delta_1+kv)^2+\Gamma_1^2]\,[(\Delta_1+kv)^2+\Gamma_1^2]} \right\rangle_{vel} = \frac{1}{ku\pi^{1/2}}\, e^{-\Delta_1^2/k^2u^2}\, \frac{\pi}{2\Gamma_1^3} \quad \cdots\; 4.66$$

Also, $$\left\langle \frac{1}{[(\Delta_2+kv)^2+\Gamma_2^2]\,[(\Delta_2+kv)^2+\Gamma_2^2]} \right\rangle_{vel} = \frac{1}{ku\pi^{1/2}}\, e^{-\Delta_2^2/k^2u^2}\, \frac{\pi}{2\Gamma_2^3} \quad \cdots\; 4.67$$

Substitute (4.63a) and (4.64a) in (4.43) and substitute (4.65), (4.66) and (4.67) in the result and equation, We get for the power absorbed the following expression:

$$\begin{aligned} W = {} & \frac{2VN\alpha_1^2\hbar\Omega_1\pi^{1/2}}{ku}\, e^{-\Delta_1^2/k^2u^2} \Bigg[\frac{(\Gamma_1+\Gamma_2)\alpha_2^2}{\Gamma_1\Gamma_2[(\Delta_1-\Delta_2)^2+(\Gamma_1+\Gamma_2)^2]} \\ & \Big\{ 2(K_{ac}+K_{bd})(\lambda_c-\lambda_d)+(K_{ac}^2-K_{bd}^2)(\lambda_a+\lambda_b) \\ & + (K_{ac}+K_{bd})^2(\lambda_a-\lambda_b)\Big\} \\ & - \frac{\alpha_1^2}{\Gamma_1^3}(K_{ac}^2+K_{bd}^2)(\lambda_b-\lambda_a)\Bigg] \\ & + \frac{2VN\alpha_2^2\hbar\Omega_2\pi^{1/2}}{ku}\, e^{-\Delta_1^2/k^2u^2} \Bigg[\frac{(\Gamma_1+\Gamma_2)\alpha_1^2}{\Gamma_1\Gamma_2[(\Delta_1-\Delta_2)^2+(\Gamma_1+\Gamma_2)^2]} \\ & \Big\{ 2(K_{ac}+K_{bd})(\lambda_a-\lambda_b)+(K_{ac}^2-K_{bd}^2)(\lambda_c+\lambda_d) \\ & + (K_{ac}+K_{bd})^2(\lambda_c-\lambda_d)\Big\} \\ & - \frac{\alpha_2^2}{\Gamma_2^3}(K_{ac}^2+K_{bd}^2)(\lambda_d-\lambda_c)\Bigg] \quad \cdots\; 4.68 \end{aligned}$$

This is the power absorbed in the molecular system due to the collision induced double resonance.

We can see that the power absorbed has got the linear as well as the quadratic dependence on the collisional constants. If we neglect the quadratic dependance assuming that the collisional constants are very small, we get the same expression as obtained by Shoemaker et.al.(see reference 5). In case the collisional constants are large, this expression is to be preferred over the Shoemaker expression.

The significance of the quadratic terms is illustrated in the next chapter using the example of the molecule methyl fluoride. Experimental observation shows that the collisional constant for methyl fluoride, is only 0.15, a small quantity. Even in that case, the quadratic contribution is shown to be 13.1% of the total, which is not negligible by any means. Hence the importance of the expression obtained.

CHAPTER 5

DISCUSSION OF THE RESULT

The Eq. (4.68) gives the expression for the power absorbed in the molecular system due to the collision-induced double resonance, W. This expression leads to the intensity change of the laser beam as follows. Power absorbed per unit area of cross section of the laser beam gives the intensity change of the laser beam. This is given by

$$\Delta I \cong \frac{|W|}{A} \quad \ldots\ldots 5.1$$

Where A is the area of cross section of the laser beam.

Substituting Eq. (4.68) in Eq. (5.1) we get

$$\begin{aligned}
\Delta I = {} & \frac{2NL\alpha_1^2 \hbar \Omega_1 \pi^{1/2}}{ku} e^{-\Delta_1^2/k^2u^2} \\
& \Bigg[\frac{(\Gamma_1+\Gamma_2)\alpha_2^2}{\Gamma_1\Gamma_2\left[(\Delta_1-\Delta_2)^2+(\Gamma_1+\Gamma_2)^2\right]} \Big\{ 2(K_{ac}+K_{bd})(\lambda_d-\lambda_c) \\
& + (K_{bd}^2-K_{ac}^2)(\lambda_a+\lambda_b) + (K_{ac}+K_{bd})^2(\lambda_b-\lambda_a) \Big\} \\
& + \frac{\alpha_1^2}{\Gamma_1^3}(K_{ac}^2+K_{bd}^2)(\lambda_b-\lambda_a) \Bigg] \\
& + \frac{2NL\alpha_2^2 \hbar \Omega_2 \pi^{1/2}}{ku} e^{-\Delta_1^2/k^2u^2} \\
& \Bigg[\frac{(\Gamma_1+\Gamma_2)\alpha_1^2}{\Gamma_1\Gamma_2\left[(\Delta_1-\Delta_2)^2+(\Gamma_1+\Gamma_2)^2\right]} \Big\{ 2(K_{ac}+K_{bd})(\lambda_b-\lambda_a) \\
& + (K_{bd}^2-K_{ac}^2)(\lambda_c+\lambda_d) + (K_{ac}+K_{bd})^2(\lambda_d-\lambda_c) \Big\} \\
& + \frac{\alpha_2^2}{\Gamma_2^3}(K_{ac}^2+K_{bd}^2)(\lambda_d-\lambda_c) \Bigg] \quad \ldots\ldots 5.2
\end{aligned}$$

where $L = \frac{V}{A}$, the sample path length.

Let us now elaborate on all the terms appearing in the Eq. (5.2). The number of molecules/cm^3 is denoted by N. Pathlength of the gas sample is denoted by L. The term α_1 is :

$$\alpha_1 = \frac{\mu_{ab} E_1}{2\hbar} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 5.3$$

where μ_{ab} is the expectation value of the dipole moment for the transition a←b. That is, it is the matrix element of the dipole moment μ between the states |a> and |b>. If we take the laser field along the z direction, then the electric field will be along one of the perpendicular directions, say x-axis. In that case, the dipole moment appearing in the Hamiltonian will be μ_x, i.e., the x component of μ.

Hence

$$\mu_{ab} = \langle a|\mu_x|b\rangle \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 5.4$$

Similarly $\mu_{cd} = \langle c|\mu_x|d\rangle$ 5.4a

The electric field associated with the laser causing transition a←b is E_1. This may be determined from the power of the laser beam by the equation :

$$w = \frac{c}{8\pi} |E|^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 5.5$$

where E is the field strength of the laser beam and w the power density, i.e., the power per unit area of cross section of the laser beam. The frequency of the laser field 1 is denoted by Ω_1 and that of 2 by Ω_2. The term u is the mean of the velocities of the velocity group before and after the collision. The frequency corresponding to the doppler shift of the levels a and b is represented by Δ_1.

i.e., $$\Delta_1 = \omega_{ab} - \Omega_1 \quad \text{.............} \quad 5.6$$

where ω_{ab} is the transition frequency between a and b.

Similarly $\Delta_2 = \omega_{cd} - \Omega_2$ 5.6a

The broadening of the line both due to the collision and the field is given by Γ_1. We have the following equation:

$$\Gamma_1^2 = \gamma^2 + 4\alpha_1^2 \quad \text{......} \quad 5.7$$

where $$\gamma = \frac{1}{\tau} + \frac{1}{T} \quad \text{..........} \quad 5.8$$

Here γ is the collision broadened linewidth. The radiative decay constant is denoted by $1/\tau$ and as said before, τ is dominated by the molecular transit time across the laser beam.

$$\tau \simeq \frac{D}{u} \quad \text{..} \quad 5.9$$

where D is the diameter of the laser beam and u the mean velocity of the molecular velocity group in question. From the Maxwell-Boltzmann distribution law for molecular velocities, the mean square and mean velocities of the molecular group are given by :

$$\overline{u^2} = \frac{3kT_1}{m} \quad \ldots\ldots\ldots\ldots \quad 5.10$$

$$u = \left(8\overline{u^2}/3\pi\right)^{1/2} \quad \ldots\ldots \quad 5.11$$

where T_1 is the absolute temperature and m the molecular weight of the molecule in grams. The term $1/T$ is the collisional decay constant; T is also called the relaxation time. (see reference 16). It is the time between the collisions.

$$T = \frac{4\eta}{5p} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 5.12$$

where η is the viscosity of the gas given by

$$\eta = \frac{5}{16\sigma^2}\left(\frac{mkT}{\pi}\right)^{1/2} \quad \ldots\ldots \quad 5.13$$

where σ is the molecular diameter and m the molecular weight. Also p is the pressure of the molecular system.

The contribution of the field to the line broadening is given by $4\alpha_1^2$.

We also have:

$$\Gamma_2^2 = \gamma^2 + 4\alpha_1^2 \quad \ldots\ldots\ldots \quad 5.7a$$

The term κ_{ac} is the collisional constant between the levels a and c. Also κ_{bd} is the collisional constant between the levels b and d. The injection density is given by λ. It is the number of molecules pumped per unit time into the specific level, divided by the total number of molecules N_0 of the system. In other words, it is the probability for N_0 molecules to be injected to the specific level. It is also called the pumping rate.

Now let us calculate the value of ΔI using the Eq. (5,2) in relevance to the experiment described in reference No. 5. After that, the contributions due to the linear terms and the quadratic terms are seperately calculated and relative contributions determined. Various terms appearing in Eq. (5.2) are calculated as follows:

Number density of the molecule, N

This follows from the equation relating the pressure, volume and absolute temperature of the molecular gas.

$$\frac{P_0V_0}{T_0} = \frac{P_1V_1}{T_1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ 5.14$$

where P, V, T are pressure, volume and absolute temperature of the molecular gas respectively.

Let us take one mole of the gas. Normal mole volume = $22.4\text{X}10^3\text{cm}^3$.

P_0 = 76cm of Hg; $V_0 = 22.4\text{X}10^3$ cm^3; $T_0 = 273^\circ$A; P_1 = 3 m Torr = $3\text{X}10^{-4}$ cm of Hg; $T_1 = 300^\circ$A.

Substituting these in the Eq. (5.14), we get V_1

This volume contains $6.022\text{X}10^{23}$ molecules (Avogadro number).

Number of molecules per unit volume, $N = 6.022\text{X}10^{23}/V$

$$\text{i.e., } N = \underline{9.658\text{X}10^{13}} \text{ molecules} \quad \ldots\ldots\ldots\ldots\ 5.15$$

The Sample Pathlength, L

$$L = \underline{\underline{10\ \text{cm}}} \quad \ldots\ldots\ldots\ldots \quad 5.16$$

Calculation of α_1 and α_2

This is done using the equations (5.3), (5.4) and (5.5). The states $|J, K, M\rangle$ involved in the transition $a \leftarrow b$ are :

$$|a\rangle = |5, 3, M\rangle \quad \text{and} \quad |b\rangle = |4, 3, M \pm 1\rangle$$

For simiplicity let us consider the levels $|a\rangle = |5, 3, 1\rangle$ and $|b\rangle = |4, 3, 0\rangle$. Therefore,

$$\mu_{ab} = \langle 5, 3, 1 | \mu \sin\theta \cos\phi | 4, 3, 0 \rangle$$

Using the reference No. 2, this turns out to be

$$\mu_{ab} = \mu \frac{(16 \times 5 \times 6)^{1/2}}{5\,(9 \times 11)^{1/2}} = \mu \frac{\{(J^2 - K^2)(J+M-1)(J+M)\}^{1/2}}{J[(2J-1)(2J+1)]^{1/2}}$$

$$\text{i.e.,}\ \mu_{ab} = 0.440\,\mu$$

The sample used is Methyl Fluoride ($^{13}CH_3F$) for which $\mu = 1.85 \times 10^{-18}$ esu cm. Now we calculate the laser field intensity using Eq. (5.5).

Power density in each beam $= 1.2$ Watt$/\text{cm}^2 = 1.2 \times 10^7$ ergs/sec cm^2

$$\text{So that}\ E_1 = \left(\frac{8\pi \times 1.2 \times 10^7}{3 \times 10^{10}}\right)^{1/2} \text{esu cgs}/\text{cm}$$

$$= 1.002 \times 10^{-1}\ \text{esu cgs}/\text{cm}$$

Substituting these, we get :

$$\alpha_1 = \underline{3.941 \times 10^7}\ \text{sec}^{-1} \quad \ldots\ldots\ldots \quad 5.17$$

$$\mu_{cd} \simeq \mu_{ab}\ \text{and so}\ \alpha_2 = \underline{3.941 \times 10^7\ \text{sec}^{-1}} \quad \ldots\ldots \quad 5.18$$

Calculation of Ω_1 and Ω_2

The laser 1 corresponds to 1035.474 cm^{-1}

Hence $\Omega_1 = 1.941 \times 10^{14}$ rad/sec...................... 5.19

Since $\Omega_1 - \Omega_2 = 30$ Mc/sec, $\Omega_2 = 1.941 \times 10^{14}$ rad/Sec..... 5.20

Calcualtion of the mean velocity of the molecular velocity group

Using Eq. (5.10), we get :

$$\overline{u^2} = \frac{3 \times 1.381 \times 10^{-16} \times 300}{35 \times 1.66 \times 10^{-24}}$$

$$\text{i.e., } \overline{u^2} = 2.136 \times 10^{9} \ cm^2/sec^2$$

Using Eq. (5.11), we get

$u = 4.26 \times 10^4$ cm/sec 5.21

Calculation of Δ_1 and Δ_2

$$\Delta_1 = \omega_{ab} - \Omega_1 = \omega_{ab} \, v/c \simeq \Omega_1 \, v/c = ku$$

Hence, $\Delta_1 = 2.76 \times 10^{8}\ sec^{-1}$ 5.22

Collisions cause a velocity change of 85 cm/sec. Hence for the transition $c \leftarrow d$, velocity involved = (u+85) cm/sec $\simeq$ u cm/sec

That is,

$\Delta_2 = 2.76 \times 10^{8}\ sec^{-1}$ 5.23

Calculation of Γ_1 and Γ_2

Γ_1 is calculated using the Eqs. (5.7), (5.8) and (5.3).

Diameter of the laser beam, D = 1 cm.

Using (5.9), τ = 1 cm/u = $2.348\text{X}10^{-5}$ sec

Molecular diameter of CH_3F, $\sigma \simeq 3.8\text{X}10^{-8}$ cm

Using Eq. (5.13) and substituting for m and σ,

$$\eta = 189\times10^{-6} \text{ gm/cm sec}$$

p = 3 m Torr = 3.968 gm/cm sec^2

Substituting for p and η in Eq. (5.12),

$T = 3.8\text{X}10^{-5}$ sec

Substituting for τ and T in Eq. (5.8),

$\gamma = 6.89\text{X}10^{4}\ \text{sec}^{-1}$

Substituting for γ and α_1 in Eq. (5.7),

$\Gamma_1 = \underline{7.88\times10^{7}}\ \text{sec}^{-1}$ 5.24

Similarly $\Gamma_2 = \underline{7.88\times10^{7}}\ \text{sec}^{-1}$ 5.25

Calculation of $(\lambda_b - \lambda_a)$ and $(\lambda_d - \lambda_c)$

The structure of the Methyl Fluoride is as follows:

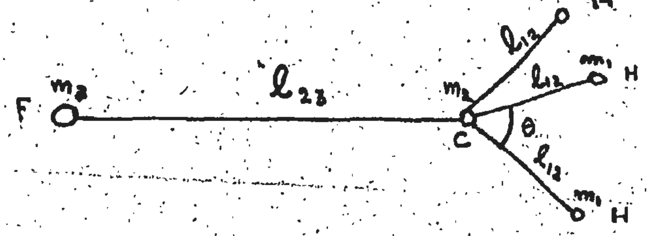


Fig 5.1

The transition observed is between two vibrational levels of the ν_3 stretching. This is the C-F stretching mode. The level b stands for the state $|4, 3\rangle$ (where 4 = J and K = 3) of the vibrational level v = 0. The level a stands for the state $|5, 3\rangle$ of the vibrational level v = 1.

Energy corresponding to the vibrational level (v = 0) = 517.737 cm^{-1}

Energy corresponding to (v = 1) = 1553.211 cm^{-1}

No. of molecules in the level (v = 0),

$$N_1 = N_0 \exp\{-G(v)\ hc/kT\}$$

where N_0 is the total number of molecules and G(v) the energy (in cm^{-1}) of the vibrational level v

$$N_1 = 0.8337\ N_0$$

Similarly $N_2 = 0.0006252\ N_0$

where N_2 is the number of molecules in the vibrational state v = 1.

Now we try to find how many molecules of N_1 are in the rotational level $|4, 3\rangle$ and how many molecules of N_2 are in the rotational level $|5, 3\rangle$.

The rotational energy of the symmetric top, $E_r = \{h/8\pi^2 I_B C\}\{J(J+1)\}$ $+ \quad (h/8\pi^2 I_A C \ - h/8\pi^2 I_B C)K^2$

i.e., $E_r = BJ(J+1) + (A - B)K^2$ 5.26

where I_B is the Moment of Inertia of the molecule perpendicular to the symmetry axis (here it is the C-F axis) and I_A the MI along the symmeyry axis. These are given in terms of the atomic masses, bond lengths and bond angle as follows: (refer to Fig. 5.1)

$$I_A = 2 m_1 l_{12}^2 \ (1 - \cos\theta) \quad \ldots\ldots\ldots \quad 5.27$$

$$I_B = m_1 l_{12}^2 \ (1 - \cos\theta) + \frac{m_1 (m_2 + m_3)\, l_{12}^2}{3 m_1 + m_2 + m_3} \ (1 + 2\cos\theta)$$

$$+ \frac{m_2\, l_{23}}{3 m_1 + m_2 + m_3} \left[(3 m_1 + m_2)\, l_{23} + 6 m_1 l_{12} \left(\frac{1 + 2\cos\theta}{3} \right)^{1/2} \right] \quad \ldots\ldots \quad 5.28$$

For Methyl Fluoride,

$l_{12} = 1.11$ A $= 1.11 \times 10^{-8}$ cm

$l_{23} = 1.39$ A $= 1.39 \times 10^{-8}$ cm

$\theta = 110^\circ$

Substituting these values in Eqs. (5.27) and (5.28),

$I_A = 5.49 \times 10^{-40}$ gm cm^2

$I_B = 45.62 \times 10^{-40}$ gm cm^2

From these, we get :

$A = 5.1$ cm^{-1}

$B = 0.61$ cm^{-1}

No. of molecules in the rotational level ($J = 4$, $K = 3$) of the ground vibrational state is given by :

$$N_{J=4} = N_b^0 = (0.8337\, N_o) \frac{Bhc}{kT} (2J+1)$$

$$\exp\left[-\left\{ BJ(J+1) + (A-B)K^2 \right\} hc/kT \right]$$

Substituting for B and J,

$$N_b^0 = 0.017\,N_0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 5.29$$

Here the superscript 0 denotes the equilibrium value.

Similarly, No. of molecules in the rotational level (J = 5, K = 3) of the vibrational level v = 1 is

$$N_a^0 = 1.52 \times 10^{-5}\,N_0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 5.30$$

Efficiency of pumping,

$$\phi = 1 - \frac{N_b - N_a}{N_b^0 - N_a^0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 5.31$$

where N_b and N_a are the molecular populations under pumping (i.e., molecular populations pumped per second to the levels b and a) and N_b^0 and N_a^0 are the equilibrium molecular populations in the levels b and a respectively. Let us assume a pumping efficeincy of 90%, which may be attained by adjusting the pressure and the pumping power. Substituting this in Eq. (5.31),

$$N_b - N_a = 0.1\,(N_b^0 - N_a^0)$$

$$\text{i.e., } N_b - N_a \simeq 0.1\,N_b^0$$

Substituting for N_b^0 using Eq. (5.29),

$$N_b - N_a = 1.7 \times 10^{-3}\,N_0 \quad . \text{ Hence}$$

$$\lambda_b - \lambda_a = \frac{N_b - N_a}{N_0} = \underline{1.7 \times 10^{-3}}\ \text{sec}^{-1} \quad \ldots\ldots\ldots\ldots \quad 5.32$$

Levels c and d being very near to the levels a and b respectively, $(\lambda_d - \lambda_c)$ will be almost the same as $(\lambda_b - \lambda_a)$.

i.e., $\lambda_d - \lambda_c = \underline{1.7 \times 10^{-3}\ \text{Sec}^{-1}}$ 5.33

Substituting all the above values in eq. 5.2, we get:

$$\Delta I = \underline{1.323 \times 10^{-2}}\ \text{ergs/sec cm}^2$$

Quadratic contribution is separately calculated and it is found to be:

$$(\Delta I)_{Quad} = 0.173 \times 10^{-2}\ \text{ergs/sec cm}^2$$

Hence, the percentage quadratic contribution is :

$$(\Delta I)_{Quad} / (\Delta I)_{total} = 13.1\%$$

This means that the quadratic contribution is not negligible.

It is noteworthy that the signal absorption depends upon the value of J, since the population and hence the pumping rate depend upon J.

Note that we got only approximate value of signal absorption, since we assumed the efficiency of pumping.

It is to be remembered that we used the collision constants K_{ac} and K_{bd}, which are only approximations for the collision kernel.

N.B. Some of the values used in this chapter have been calculated with the help of the references 12 and 13.

APPENDIX A

EQUATION OF MOTION OF VELOCITY DEPENDENT DENSITY MATRIX

The model of the active medium in a laser is taken to be an ensemble of two-level atoms which move like classical point particles. The two level atom can be represented by a 2 x 2 density matrix $\rho(v, z, t)$. When the atom undergoes a collision at time t and position z, its density matrix is changed to $\rho'(v', z, t)$. Let the angle between the velocity and the field axis be ϕ and the impact parameter b. The density matrix of the ensemble of atoms after a given collision event characterized by (ϕ, b) is $\rho'(v', z, t)$. This can be expressed as a linear transformation of $\rho(v, z, t)$. The velocity after the collision depends upon the velocity before the collision, the angle ϕ and the impact parameter b.

Hence $v' = v'(v, \phi, b)$ .... (A1)

The collision changes the density matrix of the two levels. After the collision, the density matrix must be a linear combination of the elements of the matrix before collision.

i.e., $\rho' = \mathbb{T}(v, \phi, b)\rho$ .... (A2)

This arises from the fact that any microscopic collision model will lead to the integration of Schrodinger's equation and give linear connections between wavefunctions before and after the collision.

From (A1) and (A2) we get :

$$\rho'(\phi, b, v', z, t) = \delta(v' - v'(v, \phi, b))\, \Pi(v, \phi, b)\, \rho(v, z, t) \quad \ldots\ldots A3$$

Velocity distribution in the ensemble after the collision is contributed by all velocities in the ensemble before the collision.

$$\rho'(\phi, b, v', z, t) = \int_{-\infty}^{\infty} \delta(v' - v'(v, \phi, b))\, \Pi(v, \phi, b)\, \rho(v, z, t)\, dv \quad \ldots\ldots A4$$

Now we average the density matrix $\rho'(\phi, b, v', z, t)$ over the collisions and get :

$$\rho'(v', z, t) = \iint P(\phi, b)\, d\phi\, db\, \rho'(\phi, b, v', z, t)$$

where $\rho(\phi, b)$ is the weight with which the collision with parameter (ϕ, b) occurs.

Introducing (A4) this becomes :

$$\rho'(v', z, t) = \int_{-\infty}^{\infty} \Pi(v', v)\, \rho(v, z, t)\, dv \quad \ldots\ldots A5$$

where

$$\Pi(v', v) = \iint P(\phi, b)\, \delta(v' - v'(v, \phi, b))\, \Pi(v, \phi, b)\, d\phi\, db \quad \ldots\ldots A6$$

Note that $\Pi(v', v)$ is an integral kernel and an operator on the matrix indices of ρ.

Now we concentrate on the time development of the density matrix between the collisions. The electromagnetic field in the sample causes the transitions between the two atomic levels through the dipole interaction

$$\hbar V(z, t) = -\wp E(t)\, U(z) \cos \nu t \quad \ldots\ldots A7$$

where $E(t)$ is an amplitude function changing slowly compared to $\cos \nu t$, with ν being the frequency of the e - m field and $U(z)$ is the spatial mode of the cavity in which the gas is situated.

Consider an atom undergoing a collision at z_0, t_0. After this, the time development of its density matrix is given by

$$\frac{\partial}{\partial t}\rho = -i[H_0, \rho] - \frac{1}{2}(\Gamma\rho + \rho\Gamma) + i\frac{\wp}{\hbar}E(t)\,U(z_0 + v\overline{t-t_0})\,[\sigma, \rho]\cos\nu t \quad \cdots A8$$

where

$$H_0 = \begin{pmatrix} W_a & 0 \\ 0 & W_b \end{pmatrix} \quad \cdots\cdots A9 \qquad ; \quad \Gamma = \begin{pmatrix} \gamma_a & 0 \\ 0 & \gamma_b \end{pmatrix} \quad \cdots\cdots A10$$

$$\sigma = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \cdots\cdots\cdots\cdots A11$$

Introduce the main time dependence exp(ivt) in the off diagonal elements of the density matrix. That is,

$$\rho_{ab} = \rho_1 e^{-i\nu t} \quad \cdots\cdots\cdots\cdots A12$$

We also neglect the rapidly varying terms proportional to exp(±2ivt). Then from (A8) we get :

$$\dot{\rho}_{aa}(v,z,t) = -\gamma_a\rho_{aa}(v,z,t) - \frac{i}{2}[\wp E(t)|\hbar]\,[\rho_1(v,z,t) - \rho_1^*(v,z,t)]\,U(z_0 + v\overline{t-t_0})$$

$$\rho_{bb}(v,z,t) = -\gamma_b\rho_{bb}(v,z,t) + \frac{1}{2}i[\wp E(t)|\hbar]\,[\rho_1(v,z,t) - \rho_1^*(v,z,t)]\,U(z_0 + v\overline{t-t_0})$$

$$\dot{\rho}_1(v,z,t) = -\gamma_{ab}\rho_1(v,z,t) + i(\nu - \omega)\rho_1(v,z,t) - \frac{1}{2}i[\wp E(t)/\hbar]\,[\rho_{aa}(v,z,t) - \rho_{bb}(v,z,t)]\,U(z_0 + v\overline{t-t_0})$$

$$\cdots\cdots\cdots A13$$

where $\gamma_{ab} = 1/2(\gamma_a + \gamma_b)$ and $\omega = \omega_a - \omega_b$

Instead of using the operator $\Pi(\phi, b, v)$ we can use the linear transformation of ρ as shown below:

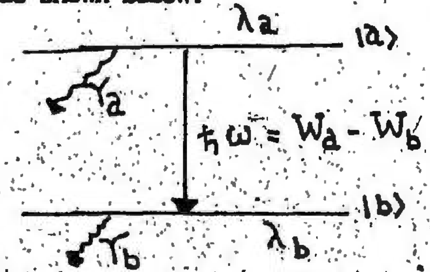
Consider the molecular system entering the collision region. The initial state of the molecule is :

$$|\bar{\Psi}\rangle = \alpha|a\rangle + \beta|b\rangle \quad \ldots\ldots\ldots \quad A14$$

Immediately after the collision characterized by (ϕ, b), the state becomes

$$|\Psi'\rangle = \alpha'|a\rangle + \beta'|b\rangle \quad \ldots\ldots\ldots \quad A15$$

The system is as shown below:



The initial velocity of the molecule is v and the velocity after the collision is v'. Collisions do not cause transition between the levels $|a\rangle$ and $|b\rangle$ so that the molecule is found in the state $|a\rangle$ with the same probability both before and after the collision. Same situation applies for the state $|b\rangle$.

i.e., $|\alpha'|^2 = |\alpha|^2$; $|\beta'|^2 = |\beta|^2$

from which its follows that :

$$\alpha' = \alpha \exp[i\eta_a(\phi, b, v)]$$

$$\text{and} \quad \beta' = \beta \exp[i\eta_b(\phi, b, v)]$$

The relative phase change is

$$\eta(\phi, b, v) = \eta_a(\phi, b, v) - \eta_b(\phi, b, v)$$

The pure state density matrix before the collision is

$$\rho = \begin{pmatrix} \alpha^* \alpha & \alpha^* \beta \\ \alpha \beta^* & \beta^* \beta \end{pmatrix} \quad \ldots\ldots\ldots \quad A16$$

After the collision it becomes

$$\rho' = \begin{pmatrix} \alpha^* \alpha & e^{-i\eta} \alpha^* \beta \\ e^{i\eta} \alpha \beta & \beta^* \beta \end{pmatrix} = U \rho U^\dagger \quad \ldots \quad A17$$

where U is the unitary matrix given by

$$U(\phi, b, v) = \begin{pmatrix} \exp[-\frac{i}{2}\eta(\phi, b, v)] & 0 \\ 0 & \exp[\frac{i}{2}\eta(\phi, b, v)] \end{pmatrix} \quad \ldots\ldots \quad A18$$

Here the linear transformation of ρ defined by (A17) is identical with the operator $\Pi(\phi, b, v)$.

APPENDIX B

THE PROPERTIES OF THE KERNEL

The function called 'kernel' appears in the integral equation of the second kind.

The functional relation

$$\phi(x) - \lambda \int_a^b K(x,t)\, \phi(t)\, dt = f(x) \quad \ldots\ldots B1$$

where K(x, t) and f(x) are given functions, is known as the integral equation of the second kind for the unknown $\phi(x)$. The function K(x, t) is called the kernel or the nucleus of the integral equation and λ is a parameter. The interval (a, b) may be finite or infinite.

The integral equation

$$\phi(x) - \lambda \int_a^b K(x,t)\, \phi(t)\, dt = 0 \quad \ldots\ldots B2$$

is called the homogeneous equation corresponding to (B1).

The integral equation

$$\psi(x) - \lambda \int_a^b K(t,x)\, \psi(t)\, dt = f(x) \quad \ldots\ldots B3$$

is called the transposed integral equation corresponding to (B1).

If we assume that (1) f(x) is continuous, (2) K(x, y) is piecewise continuous or has at most a denumerably infinite number of finite discontinuities for either x or y constant, that is, $|K(x, y)| < M$ where M is a constant, (3) the integrals $\iint K^2(s,t)\, ds\, dt$, $\int f^2(t)\, dt$ exist and (4) the integrals $\int K^2(x,t)\, dt$ and $\int K^2(t,x)\, dt$ are bounded, the following statements can be made concerning the solutions of (B1) and (B3) for a fixed value of λ:

1. The number of linearly independent solutions $\phi^{(1)}(x)$, $\phi^{(2)}(x)$, ... $\phi^{(\nu)}(x)$ of (B2) is equal to the number of linearly independent solutions of (B3). The number ν is called the defect of the kernel $K(x, t)$ corresponding to the value of λ. The general solution of (B2) is $\sum_{i=1}^{\nu} C_i \phi^{(i)}(x)$ where the C_i are arbitrary constants.
2. If $\nu = 0$ and if $f(x)$ is continuous, (B1) and (B3) have one solution. There then exists a kernel $L(x, t)$ known as the resolvent kernel such that the solution is given by :

$$\phi(x) = f(x) + \int_a^b L(x, t) f(t)\,dt$$

$$\psi(x) = f(x) + \int_a^b L(t, x) f(t)\,dt$$

3. If $\nu>0$ and if $\int_a^b \psi^i(t) f(t)\,dt = 0, \quad i = 1, 2, \ldots \nu$ then (B1) has a unique solution. The general solution of (B1) is obtained by adding the general solution of (B2) to a particular solution of (B1).

Symmetric kernels

If $K(x, y) = K(y, x)$ then the kernel is symmetric. Under the assumption made previously, the homogeneous integral equation (B2) with a symmetric kernel will have nontrivial solutions only when λ has any one of a discrete number of values, λ_n, known as eigenvalues, which are all real. The corresponding solutions $\phi_n(x)$ are eigenfunctions belonging to the kernel $K(x, y)$.

The kernel $K(x, y)$ may be represented by the series

$$K(x,y) = \sum_{n=1}^{\infty} \sum_{\alpha=1}^{n} \frac{\phi_n^{(\alpha)}(x)\,\phi_n^{(\alpha)}(y)}{\lambda_n} \quad \ldots \text{B4}$$

which converges uniformly in x and y if $K(x, y)$ has only a finite number of characteristic values and satisfies a Lipschitz condition: $|K(x, t) - K(y, t)| < M|x-y|$ where M is independent of x and y.

Nonsymmetric kernels

If the kernel of (B2) is not symmetric, the solutions do not form an orthogonal system and the equation may not have solutions; thus there may exist kernels which do not have eigenvalues. Every kernel $K(x, y)$ may be made to correspond to two orthogonal sets of functions which are defined with the aid of two symmetric kernels that are positive definite. This is shown below :

$$K_1(x,y) = \lambda \int_a^b K(x,t)\, K(y,t)\, dt$$

$$K_2(x,y) = \lambda \int_a^b K(t,x)\, K(t,y)\, dt$$

which have equal eigenvalues $\mu_n = \lambda_n^2$.

In order to solve (B1), the methods of successive approximation, Neumann series or approximations by separable kernels may be employed. If we replace the integral by a finite sum, the problem reduces to the solution of a system of linear equations. In an effective procedure employing a quadrature formula of Gaussian type, one approximates the integral by a sum in which the integrand is evaluated at the zeros of an approximate set of orthogonal polynomials. The type of polynomial is determined by the range of integration and choice of suitable weight function. Assigning to the variable x the values of zeros of Legendre polynomial, we obtain a system of equations for the unknown function $\phi(t)$. Then returning to (B1) and using Gaussian quadrature formula we may evaluate $\phi(x)$ for any desired value of x.

APPENDIX C

ROTATING WAVE APPROXIMATION

This term comes from the representation of sine function by two counter rotating vectors of frequency ω. When we are considering the time development of the two level molecular system, we get two ascillating frequencies $(\omega_{ab} - \omega)$ and $(\omega_{ab} + \omega)$ where ω_{ab} is the transition frequency and ω the frequency of the applied field. The first term is the low frequency resonance term. The second term is the high frequency antiresonance term. Over any physically significant time, the antiresonance term averages to zero and so we consider only the resonance term.

Consider a spin 1/2 particle interracting with a classical radiation field. This can be done by quantizing the radiation field and taking into account the reaction of the spin on the field. Let us consider a small sample of the material containing spin 1/2 particles located at a position in a cavity in which the magnetic field has a component only in the x-direction for a paticular mode. The energy of this mode of the field is

$$\hat{H}_{field} = \hbar \omega a a^{\dagger} \quad \text{(C1)}$$

where ω is the frequency of the mode and

$$a = \frac{1}{\sqrt{2\hbar\omega}}(\omega q + ip) \quad \text{(C2)}$$

For an electron of spin angular momentum $\hbar/2$, the magnetic moment is $\vec{\mu} = -\frac{\gamma\hbar}{2}\vec{\sigma}$ where γ is the gyromagnetic ratio.

Hence $\mathcal{H}_{in} = \int_{\text{Sample}} \gamma \frac{\hbar}{2} \vec{\sigma} \cdot \vec{H} \, d\tau$

i.e, $\mathcal{H}_{in} = \gamma H_0 \frac{\hbar}{2} \sigma_z + \gamma \frac{\hbar}{2} \int_{\text{sample}} \sigma_x H_x \, d\tau \quad \ldots . \; C3$

where H_0 is the value of the d - c field in the z direction and H_x is the rf field at the sample. (C3) can be written as :

$$\mathcal{H}_{in} = \frac{\omega_0 \hbar}{2} \sigma_z + \hbar K (a + a^{\dagger}) \sigma_x \quad \ldots . \; C4$$

which follows from the equations

$$\nabla \cdot \vec{A} = 0$$

$$\text{and} \quad \vec{A}(\underline{r}, t) = \sum_{\ell} \sum_{\sigma=1}^{2} \sqrt{\frac{\hbar}{2\omega_\ell \epsilon_0 \tau}} \; \hat{e}_{\ell\sigma} \left\{ a_{\ell\sigma} \exp[i(k_\ell \cdot \underline{r} - \omega_\ell t)] + a^{\dagger}_{\ell\sigma} \exp[-i(k_\ell \cdot \underline{r} - \omega_\ell t)] \right\}$$

Here we also use the assumption that σ_x occupes a small volume of the cavity. Also all the quantities multiplying σ_x in (C3) and not appearing emplicitly in (C4) are grouped into a coupling constant K.

Add (C1) and (C4) . We get:

$$\mathcal{H} = \hbar \omega a^{\dagger} a + \frac{\hbar \omega_0}{2} \sigma_z + \hbar K (a + a^{\dagger})(\sigma_+ + \sigma_-) \quad \ldots \; C5$$

This hamiltonian may be simplified by the following considerations. Where K = 0, i.e., when there is no rf field, the Heisenberg operators have a time dependence given by

$$a(t) = a(0) e^{-i\omega t} \; ; \quad \sigma_+(t) = \sigma_+(0) e^{i\omega_0 t}$$

$$a^{\dagger}(t) = a^{\dagger}(0) e^{i\omega t} \; ; \quad \sigma_-(t) = \sigma_-(0) e^{-i\omega_0 t}$$

so that near resonance ($\omega \simeq \omega_0$) the interraction terms $a\sigma_+$ and $a^+\sigma_-$ in (C5) are practically dc terms whereas the terms $a\sigma_-$ and $a^+\sigma_+$ vary rapidly at frequencies $\pm(\omega + \omega_0)$. To a good degree of approximation for times of interest, the high frequency terms average to zero and so (C5) can be written as ;

$$\mathcal{H} = \hbar\omega a^+a + \frac{\hbar\omega_0}{2} + \hbar K(a^+\sigma_- + a\sigma_+)$$

This is the rotating wave approximation. This is equivalent to decomposing the linearly polarized rf cavity field into two opposite circularly polarized waves and keeping only the one rotating in the same sense as the spin precession. Hence the name rotating wave approximation.

APPENDIX D

EXPRESSIONS FOR ρ_{aa}, ρ_{bb}, ρ_{cc} AND ρ_{dd} WHEN COLLISIONAL TERMS ARE TAKEN INTO ACCOUNT

By analogy with eq(4.54) we get ;

$$\rho_{aa} = \frac{1}{2}\left\{1 + \frac{(\Delta_1+kv)^2+\gamma^2}{(\Delta_1+kv)^2+\Gamma_1^2}\right\}\frac{\lambda_a}{\gamma} + \frac{1}{2}\left\{1 + \frac{(\Delta_1+kv)^2+\gamma^2}{(\Delta_1+kv)^2+\Gamma_1^2}\right\}K_{ac}\rho_{cc}$$

$$+ \frac{1}{2}\left\{1 - \frac{(\Delta_1+kv)^2+\gamma^2}{(\Delta_1+kv)^2+\Gamma_1^2}\right\}\frac{\lambda_b}{\gamma} + \frac{1}{2}\left\{1 - \frac{(\Delta_1+kv)^2+\gamma^2}{(\Delta_1+kv)^2+\Gamma_1^2}\right\}K_{bd}\rho_{dd}$$

$$\rho_{bb} = \frac{1}{2}\left\{1 - \frac{(\Delta_1+kv)^2+\gamma^2}{(\Delta_1+kv)^2+\Gamma_1^2}\right\}\frac{\lambda_a}{\gamma} + \frac{1}{2}\left\{1 - \frac{(\Delta_1+kv)^2+\gamma^2}{(\Delta_1+kv)^2+\Gamma_1^2}\right\}K_{ac}\rho_{cc}$$

$$+ \frac{1}{2}\left\{1 + \frac{(\Delta_1+kv)^2+\gamma^2}{(\Delta_1+kv)^2+\Gamma_1^2}\right\}\frac{\lambda_b}{\gamma} + \frac{1}{2}\left\{1 + \frac{(\Delta_1+kv)^2+\gamma^2}{(\Delta_1+kv)^2+\Gamma_1^2}\right\}K_{bd}\rho_{dd}$$

$$\rho_{cc} = \frac{1}{2}\left\{1 + \frac{(\Delta_2+kv)^2+\gamma^2}{(\Delta_2+kv)^2+\Gamma_2^2}\right\}\frac{\lambda_c}{\gamma} + \frac{1}{2}\left\{1 + \frac{(\Delta_2+kv)^2+\gamma^2}{(\Delta_2+kv)^2+\Gamma_2^2}\right\}K_{ac}\rho_{aa}$$

$$+ \frac{1}{2}\left\{1 - \frac{(\Delta_2+kv)^2+\gamma^2}{(\Delta_2+kv)^2+\Gamma_2^2}\right\}\frac{\lambda_d}{\gamma} + \frac{1}{2}\left\{1 - \frac{(\Delta_2+kv)^2+\gamma^2}{(\Delta_2+kv)^2+\Gamma_2^2}\right\}K_{bd}\rho_{bb}$$

$$\rho_{dd} = \frac{1}{2}\left\{1 - \frac{(\Delta_2+kv)^2+\gamma^2}{(\Delta_2+kv)^2+\Gamma_2^2}\right\}\frac{\lambda_c}{\gamma} + \frac{1}{2}\left\{1 - \frac{(\Delta_2+kv)^2+\gamma^2}{(\Delta_2+kv)^2+\Gamma_2^2}\right\}K_{ac}\rho_{aa}$$

$$+ \frac{1}{2}\left\{1 + \frac{(\Delta_2+kv)^2+\gamma^2}{(\Delta_2+kv)^2+\Gamma_2^2}\right\}\frac{\lambda_d}{\gamma} + \frac{1}{2}\left\{1 + \frac{(\Delta_2+kv)^2+\gamma^2}{(\Delta_2+kv)^2+\Gamma_2^2}\right\}K_{bd}\rho_{bb}$$

Substitute

$$A = \frac{1}{2}\left\{1 + \frac{(\Delta_1 + kv)^2 + \gamma^2}{(\Delta_1 + kv)^2 + \Gamma_1^2}\right\}$$

$$B = \frac{1}{2}\left\{1 - \frac{(\Delta_1 + kv)^2 + \gamma^2}{(\Delta_1 + kv)^2 + \Gamma_1^2}\right\}$$

$$C = \frac{1}{2}\left\{1 + \frac{(\Delta_2 + kv)^2 + \gamma^2}{(\Delta_2 + kv)^2 + \Gamma_2^2}\right\}$$

$$D = \frac{1}{2}\left\{1 - \frac{(\Delta_2 + kv)^2 + \gamma^2}{(\Delta_2 + kv)^2 + \Gamma_2^2}\right\}$$

So that,

$$\rho_{aa} = A\frac{\lambda_a}{\gamma} + A K_{ac}\rho_{cc} + B\frac{\lambda_b}{\gamma} + B K_{bd}\rho_{dd}$$

$$\rho_{bb} = B\frac{\lambda_a}{\gamma} + B K_{ac}\rho_{cc} + A\frac{\lambda_b}{\gamma} + A K_{bd}\rho_{dd}$$

$$\rho_{cc} = C\frac{\lambda_c}{\gamma} + C K_{ac}\rho_{aa} + D\frac{\lambda_d}{\gamma} + D K_{bd}\rho_{bb}$$

$$\rho_{dd} = D\frac{\lambda_c}{\gamma} + D K_{ac}\rho_{aa} + C\frac{\lambda_d}{\gamma} + C K_{bd}\rho_{bb}$$

These are rewritten as

$$\rho_{aa} - A K_{ac} - B K_{bd} \rho_{dd} = A \lambda_a' + B \lambda_b' \quad \cdots D1$$

$$\rho_{bb} - B K_{ac} \rho_{cc} - A K_{bd} \rho_{dd} = B \lambda_a' + A \lambda_b' \quad \cdots D2$$

$$-C K_{ac} \rho_{aa} - D K_{bd} \rho_{bb} + \rho_{cc} = C \lambda_c' + D \lambda_d' \quad \cdots D3$$

$$-D K_{ac} \rho_{aa} - C K_{bd} \rho_{bb} + \rho_{dd} = D \lambda_c' + C \lambda_d' \quad \cdots D4$$

where $\lambda_a' = \lambda_a/\gamma$ etc.

These four equations can be solved by the matrix method. We get the following:

$$\Delta = 1 - AC\,(K_{ac}^2 + K_{bd}^2) - 2BD\,K_{ac} K_{bd} + (A^2 - B^2)(C^2 - D^2)\,K_{ac}^2 K_{bd}^2$$

$$\begin{aligned}\Delta_1 = {} & \lambda_a' \{ A - (A^2 - B^2)\, C K_{bd}^2 \} + \lambda_b' \{ B + (A^2 - B^2)\, D K_{ac} K_{bd} \} \\ & + \lambda_c' \{ AC K_{ac} + BD K_{bd} - A^2 C^2 K_{ac} K_{bd}^2 \\ & \qquad + (BC^2 - AD^2 - BD^2) K_{ac} K_{bd} \} \\ & + \lambda_d' \{ AD K_{ac} + BC K_{bd} - A^2 CD K_{ac} K_{bd}^2 - ACD K_{ac} K_{bd}\end{aligned}$$

$$\begin{aligned}\Delta_2 = {} & \lambda_a' \{ B + (A^2 + B^2)\, D K_{ac} K_{bd} \} \\ & + \lambda_b' \{ A - (A^2 - B^2)\, C K_{ac}^2 + 2ABD\, K_{ac} K_{bd} \} \\ & + \lambda_c' \{ BC K_{ac} + AD K_{bd} \} + \lambda_d' \{ BD K_{ac} + AC K_{bd}^2 \\ & \qquad + (A^2 D^2 - A^2 C^2 - B^2 D^2 + B^2 C^2) K_{ac}^2 K_{bd} \}\end{aligned}$$

$$\Delta_3 = \lambda_a^1 \left\{ AC\,K_{ac} + BD\,K_{bd} - A^2 (C^2 - D^2) K_{ac} K_{bd}^2 \right\}$$

$$+ \lambda_b^1 \left\{ AD\,K_{bd} + BC\,K_{ac} - AB\,(C^2 - D^2) K_{ac} K_{bd}^2 \right\}$$

$$+ \lambda_c^1 \left\{ C - A\,(C^2 - D^2) K_{bd}^2 \right\}$$

$$+ \lambda_d^1 \left\{ D + B\,(C^2 - D^2)\,K_{ac} K_{bd} \right\}$$

$$\Delta_4 = \lambda_a^1 \left\{ AD\,K_{ac} + BC\,K_{bd} + B\,(C^2 - D^2) K_{ac} K_{bd} \right.$$

$$\left. + AB\,(C^2 - D^2) K_{ac}^2 K_{bd} \right\}$$

$$+ \lambda_b^1 \left\{ AC\,K_{bd} - BD\,K_{ac} + A(C^2 - D^2) K_{ac} K_{bd} \right.$$

$$\left. - B^2 (C^2 - D^2)\,K_{ac}^2 K_{bd} \right\}$$

$$+ \lambda_c^1 \left\{ D + B\,(C^2 - D^2) K_{ac} K_{bd} \right\}$$

$$+ \lambda_d^1 \left\{ C - A\,(C^2 - D^2)\,K_{ac}^2 \right\}$$

Hence

$$\rho_{aa} = \frac{\Delta_1}{\Delta}$$

$$\rho_{bb} = \frac{\Delta_2}{\Delta}$$

$$\rho_{cc} = \frac{\Delta_3}{\Delta}$$

$$\rho_{44} = \frac{\Delta_4}{\Delta}$$

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N. B. In the above list, the numbers 7, 10, 11, 14, 15 and 16 are used only as general references.