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NOTES ON INFRARED ABSORPTION EXPERIMENTS IN A METHANE MOLECULAR BEAM

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NOTES ON INFRARED ABSORPTION EXPERIMENTS IN A METHANE MOLECULAR BEAM*

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The problem of calculating the transition probability of methane molecules in a molecular beam interacting with an infrared (3.39 μ) radiation beam is discussed. Contrary to the usual microwave molecular beam experiments, first-order Doppler frequency shifts cannot be neglected. This makes the solution of the wave-equations more difficult. Weak field approximations to the transition probability have been calculated. Single optical beam experiments analogous to the Rabi-type interaction result in a Doppler-broadened absorption line with an estimated half-power width of a few MHz. For separated multiple field experiments analogous to the Ramsey-type interaction, no observable response is predicted, the expected sharp resonance pattern being smeared out by the random Doppler shifts due to the spread of the molecular beam trajectories. Further investigations are required in order to predict the resonance line shapes for strong fields, i.e., saturated absorption.

Key Words: Frequency standard; methane resonance; molecular beam; Ramsey resonance; saturated absorption; stabilized laser; transition probability.

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1. INTRODUCTION

In 1970 H. Hellwig suggested a methane molecular beam absorption experiment for the investigation of the photon recoil effect [1] which might limit the accuracy of the 3.39-μm saturated absorption cell frequency standard of R. Barger and J. Hall. This note summarizes some first attempts to gain more understanding of the interactions between the infrared radiation field and the molecular beam. We shall see that one of the main problems is the first order Doppler shift which is not negligible at these short wavelengths. The situation is very different from that encountered in a microwave molecular beam apparatus (e.g., cesium). We first note some initial data and facts:

a) Dimensions of the interaction region

Optical beam diameter $\ell = 0.1$ cm

Separation for Ramsey interaction $L = 5$ cm

Molecular Beam Dimensions: Width $\sim$ 1 cm
Height $\sim$ 0.1 cm

Divergence of molecular trajectories < 0.1 radian.

A compromise between divergence, which can be reduced by collimation, and useful flux has to be made. Similarly to the absorption cell, selection of trajectories is also possible by saturated absorption. However, we then have more problems in understanding the recoil effect.

b) State selection

The source temperature can be situated between 78K and 300 K; thus the ratio $\frac{h\nu}{kT}$ lies between 56 and 15 and the initial population of the upper energy level of the transition can be neglected.

c) Doppler shift

We have

$$\nu = \nu_o (1 + \beta)$$

where $\beta = \zeta \frac{v}{c}$, v being the velocity of the molecule and $\zeta \ll 1$ the angle

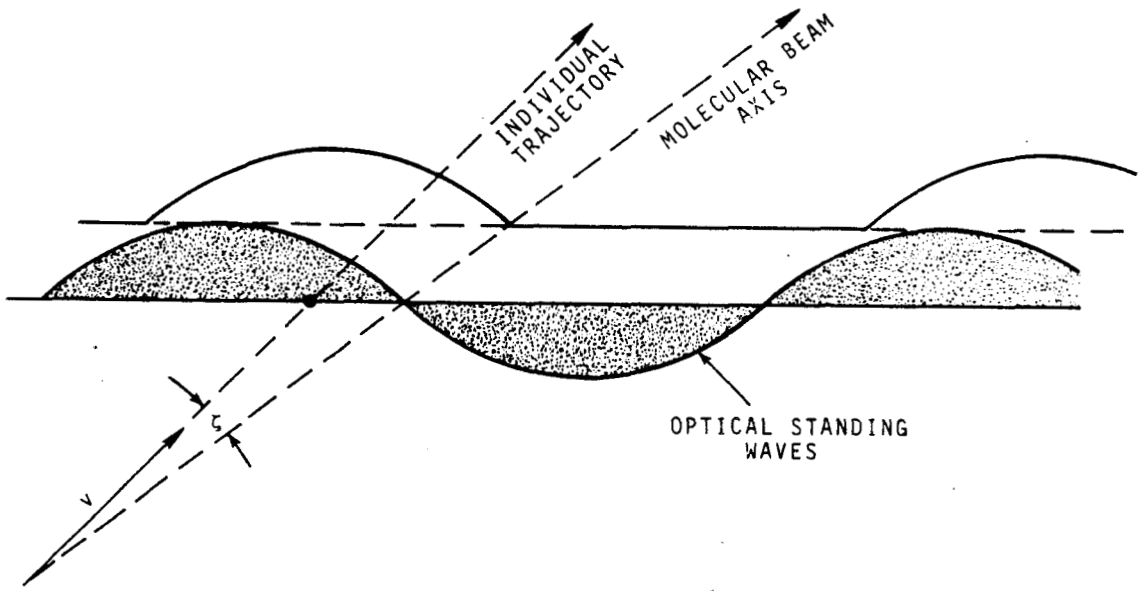

Figure 1. Geometry of molecular beam-optical wave interaction.

between the molecule trajectory and the wavefront in the plane of the trajectory. For methane, we have $v \sim 3 \times 10^4$ cm s^{-1} and thus with $c = 3 \times 10^{10}$ cm s^{-1} $\beta = 10^{-6} \zeta$. An absorption experiment using a traveling wave puts an unfulfillable requirement on the adjustment of the optical and molecular beams with respect to each other, as $\zeta = 10^{-3}$ radian would shift the absorption line by its entire width.

The shift can be reduced or compensated by using a standing wave produced by a Fabry-Perot cavity. We then have an interaction

with two equal and opposite running waves. We thus expect no shift but only a Doppler broadening due to the divergence of the beam, assuming that we have indeed a pure standing wave. Actual resonators will not be entirely perfect and this may limit the accuracy of the experiment.

2. ABSORPTION IN SINGLE STANDING WAVE OPTICAL BEAM

The following treatment is based on Ramsey's calculations of the transition probability of a two-level system perturbed by a periodic field [2, Section V. 3] . The form of the perturbation is different, however, because we have to deal with two simultaneously applied oscillating fields of equal amplitude but slightly different frequencies. This case has not been treated in the earlier literature on microwave molecular beam spectroscopy because there it was usually either possible to neglect first order Doppler shifts [3] - [6], or if simultaneous perturbations by two frequencies were considered, one was assumed to be very much weaker than the other. We therefore could not see how the older work could be used. If we look at the geometry as shown in figure 2, we have a perturbation by each of the two running waves, which has to degenerate into the classical case of Rabi for $\zeta = 0$, i.e. for a molecular trajectory exactly parallel to the plane in which the nodes of the field pattern lie.

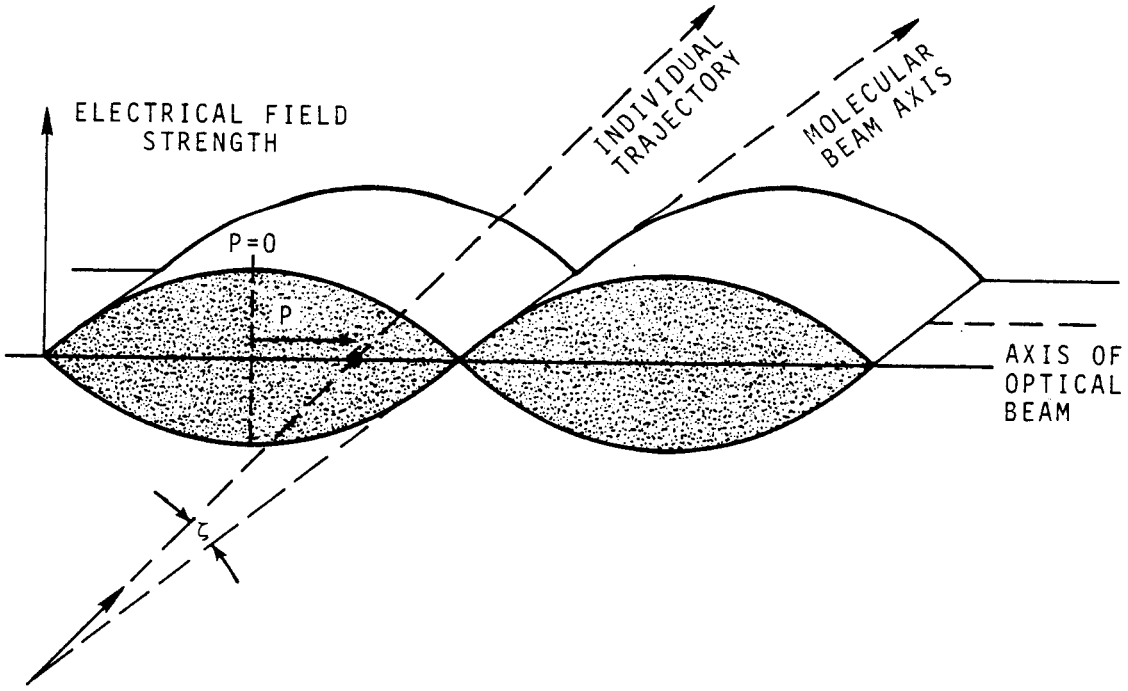

Figure 2. Phase p of individual trajectory.

For the two-level system we have the wave function [2], [7]

$$\psi(t) = C_p \psi_p + C_q \psi_q$$

as a solution of the wave equation

$$i\hbar \frac{\partial \psi}{\partial t} = (H_o + V)\psi .$$

Since we have two equal amplitude waves running in opposite directions, the perturbation takes the following form

$$V_{pq} = \frac{\hbar b}{2}\left(e^{i(\omega + \omega_D)t} + e^{i(\omega - \omega_D)t}\right)$$

$$V_{qp} = \frac{\hbar b}{2}\left(e^{-i(\omega + \omega_D)t} + e^{-i(\omega - \omega_D)t}\right)$$

which, by adding an initial phase angle p (see fig. 2), can also be written as:

$$V_{pq} = h b e^{i\omega t} \cos(\omega_D t + p)$$

$$V_{qp} = h b e^{-i\omega t} \cos(\omega_D t + p)$$

where ω_D is the Doppler shift (angular frequency)

$$\omega_D = \omega_o \beta = \omega_o \zeta \frac{v}{c} \quad .$$

With the assumed dimensions and velocity it is easy to see that $\omega_D t_o$ varies between the limits:

$$0 \leq \omega_D t_o \leq 40$$

where $t_o = \frac{\ell}{v}$. The wave equations to be solved take the following form; after transformation as in [2]:

$$i \frac{d}{dt} C_p(t) = \omega_p C_p(t) + b e^{i\omega t} \cos(\omega_D t + p) C_q(t) \qquad (1a)$$

$$i \frac{d}{dt} C_q(t) = b e^{-i\omega t} \cos(\omega_D t + p) C_p(t) + \omega_q C_q(t) \qquad (1b)$$

where

$$\hbar \omega_p = W_p$$

$$\hbar \omega_q = W_q$$

are the energies of the two levels p and q, so that

$$W_q - W_p = \hbar \omega_o \quad .$$

The above equations are to be solved with the initial conditions

$$C_p(0) = 1 \qquad C_q(0) = 0 \ . \tag{2}$$

It is easily verified that for $\omega_D = 0$ the case treated by Ramsey is obtained and the solution in closed form is obtained for the transition probability

$$P_{p,q} = |C_q^2| \ .$$

Unfortunately, a closed form solution in our case has not been found.

We have obtained the following approximate solutions using the approach of Appendix A.

The solution depends on the phase angle p, $0 \leq p \leq 2\pi$ of the field where the molecule enters the field region (see fig. 2) and is to be averaged over $(0, 2\pi)$.

For very small values of $b\,t_0$ the solution is: (without higher order terms)

$$\langle |C_q^2(t_0)| \rangle_p = \frac{b^2 t_0^2}{2} \left[\left(\frac{\sin \frac{\lambda + \omega_D}{2} t_0}{(\lambda + \omega_D) t_0} \right)^2 + \left(\frac{\sin \frac{\lambda - \omega_D}{2} t_0}{(\lambda - \omega_D) t_0} \right)^2 \right] \tag{3}$$

with $\lambda = (\omega_0 - \omega)$ and $t_0 = \frac{\ell}{v}$. This solution is valid for one typical trajectory incidence angle and is to be averaged over the possible values of $\omega_D = \frac{\omega_0 v}{C} \zeta$, which again is not possible in closed form but easily done on a computer.

It is nevertheless possible to discuss this result:
We have a superposition of terms of the $\left(\frac{\sin x}{x} \right)^2$ type. Finite ω_D yields the following picture for a single trajectory:

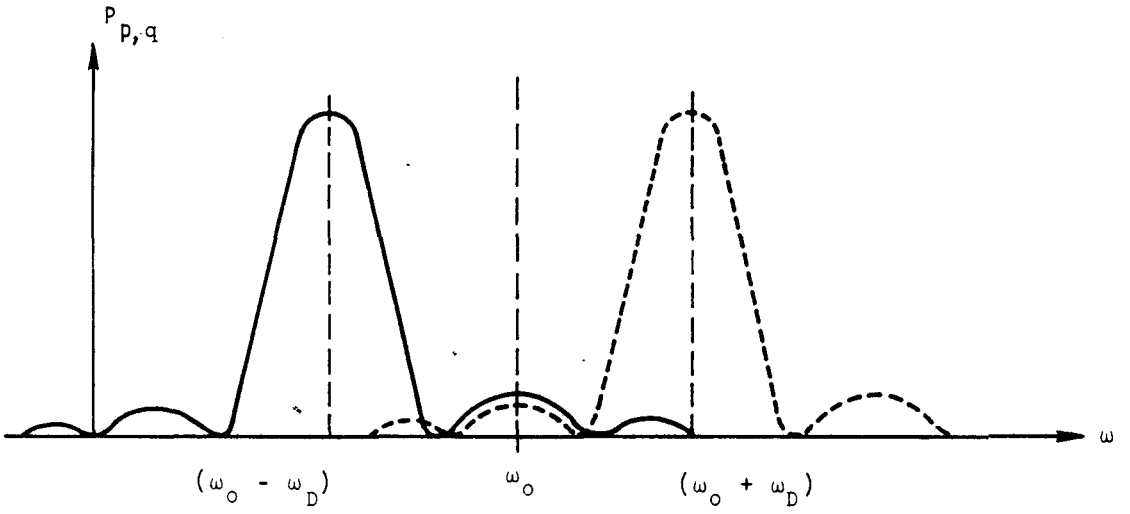

Figure 3. Approximate transition probability for individual trajectory with Doppler shift ω_0.

A finite spread in ζ and ω_D respectively smears out the lateral wiggles and we obtain a simple Doppler-broadened central peak at ω_0 with a half width of about $2\ \omega_{D_{max}}$ (rough estimate) i.e., for

$$t_0 = \frac{\ell}{v} = \frac{0.1}{3 \times 10^4} = 3.3 \times 10^{-6}\ s$$

$$\omega_{D_{max}} = \frac{40}{3.3} \times 10^6 = 1.2 \times 10^7\ s^{-1}$$

$$2\nu_D = 3.8\ \text{MHz} \quad \text{with} \quad 2\pi\nu_D = \omega_D$$

as an estimate for the observed linewidth. This is very broad indeed, so that we obtain a line-Q of only about

$$2 \times 10^7 \qquad (\nu_0 = 8.8 \times 10^{13}\ \text{Hz}) \quad .$$

As a conclusion, saturated absorption has to be attempted also in the case of the molecular beam experiment. The possibility of a Ramsey separated field excitation scheme has been discussed too. For the moment, an attempt to solve the wave equation appears to be a rather formidable task in the case of separated fields. To compute the

discussion of the single beam ("Rabi"-type) case, the following results may be obtained:

a) Expressions valid for larger values of $b t_0$ have been obtained, they are asymptotic for $b t_0 \to \infty$, but

1) they are singular at the resonance $\lambda = 0$

2) they contain elliptic integrals.

b) At resonance $\lambda = 0$, the following expressions have been obtained:

$$\langle | C_q^2(t_0) | \rangle_p \Big|_{\lambda = 0} = \frac{1}{2} \left(1 + J_0 \left(\frac{2b}{\omega_D} (1 - \cos \omega_D t_0) \right) J_0 \left(\frac{2b}{\omega_D} \sin \omega_D t_0 \right) - 2 J_0 \left(\frac{4b}{\omega_D} \sin \frac{\omega_D t_0}{2} \right) \right) \tag{4}$$

$J_0(x)$ being the Bessel-Function. This is again to be averaged over the range of ω_D.

c) For a particle with zero Doppler shift we have

$$\langle | C_q^2(t_0) | \rangle_p \Big|_{\omega_D = 0,\ \lambda = 0} = \frac{1}{2} \left[1 - J_0(2bt_0) \right] \tag{5}$$

The last expression allows, in principle, to estimate the required power for saturated absorption.

3. DISCUSSION OF MULTIPLE OPTICAL BEAM EXCITATION

At this stage, we can only discuss the weak-field approximations. The result shown in the preceding section (fig. 3) is equivalent to the superposition of the two independent solutions of the Schrödinger-Equation, with one single, Doppler-shifted perturbation applied each time. In other words, and this can easily be verified in [2], we have

the sum of two shifted Rabi-type resonances, the shifts being $+\omega_D$ and $-\omega_D$, respectively.

It therefore seems reasonable to assume, without proof, that the same should be true for Ramsey-type resonances produced by two or more separated fields.

We shall see, however, that for this weak-field assumption, the average result, i.e., averaged over the spread of incidence angles ζ (see fig. 2) vanishes. In an experiment, we can predict that only the Doppler-broadened ($\Delta\nu \sim 3$ MHz) Rabi-Pedestal will be observed. The question if Ramsey-type "interference fringes" could be observed by going into saturation remains still open.

In a first crude experiment performed in January 1970, H. Hellwig and P. Kartaschoff have observed a weak saturation peak with single beam excitation, but we were not able even to estimate the linewidth The weakness of the signal and the bad signal to noise ratio was believed to be due to lack of excitation power and mechanical laser instabilities.

For sake of completeness, we shall give below the results of calculations of probability transition for the multiple field (2 and 3 field) cases, with single frequency perturbation.

A. Two-field case (Ramsey)

This is Ramsey's result (2). The perturbation applied is:

$$V_{pq} = \hbar b\, e^{i\omega t} \qquad V_{qp} = \hbar b\, e^{-i\omega t} \tag{6}$$

and the solution is:

$$P_{p,q} = \langle |C_q|^2 \rangle \tag{7}$$

$$= 4 \sin^2\theta \sin^2 \frac{a\tau}{2} \left[\cos\frac{\lambda T}{2} \cos\frac{a\tau}{2} - \cos\theta \sin\frac{\lambda T}{2} \sin\frac{a\tau}{2} \right]^2$$

where:

$$\cos\theta = \frac{\omega_0 - \omega}{a} \qquad \sin\theta = -\frac{2b}{a}$$

$$a = [(\omega_0 - \omega)^2 + 4b^2]^{1/2} \qquad \tau = \frac{\ell}{v}$$

$$\lambda = \omega_0 - \omega \qquad T = \frac{L}{v} \quad .$$

For weak fields, i.e., $b\tau \ll 1$ and near resonance i.e., $\lambda \ll b$ this reduces to:

$$P_{p,q} \approx 4b^2\tau^2\left(\frac{1}{2} + \frac{1}{2}\cos\lambda T\right) \tag{8}$$

for one single frequency perturbation of amplitude b and angular frequency ω.

If we now assume that the interaction with the two running waves is analogous to the case treated in Section 2, we obtain for a given angle of incidence ζ, i.e., for a given angular frequency Doppler shift, ω_D, the following results:

$$P_{\omega_D} = \frac{1}{2}\left[P_{pq}(\lambda T + \omega_D T) + P_{pq}(\lambda T - \omega_D T)\right] . \tag{9}$$

This probability has to be averaged over all possible angles ζ, i.e., values of $\omega_D T$, corresponding to the divergence of the trajectories in the molecular beam. The simplest, but crude example, is to assume a sharp collimation so that there is an uniform flux between two sharp cutoff angles $\pm\ \zeta'$. We then have:

$$\langle P \rangle_{\zeta'} = \frac{1}{\omega'_D T} \int_0^{\omega'_D T} P_{\omega_D}(\lambda T, \omega_D T) d\,\omega_D T. \qquad (10)$$

From the beam geometry, we estimate the limit value

$$\omega'_D = \zeta' \frac{\omega_{0v}}{c} \approx 40 .$$

If we do the integration for a close multiple of 2π, e.g.,

$$\omega'_D T = 12\pi$$

the integral vanishes exactly except for a constant term, and since $\omega'_D T$ is at least of that order of magnitude, slightly different values of $\omega'_D T$ will produce only a very small term varying with λ. This means that due to the spread in angles of incidence, the Ramsey resonance ("fringe pattern") is smeared out, and we cannot expect to observe anything, at least for the assumed case of weak excitation.

B. Three-field case

There was some hope in early discussions that the application of three successive separated oscillating fields might lead to an observable resonance pattern. It was assumed that a majority of molecules would be excited under a preferred set of phase relations. Unfortunately, the Doppler shift was neglected then and these early assumptions are wrong, at least for the present case of weak field excitations.

The 3-field excitation geometry is assumed as follows:

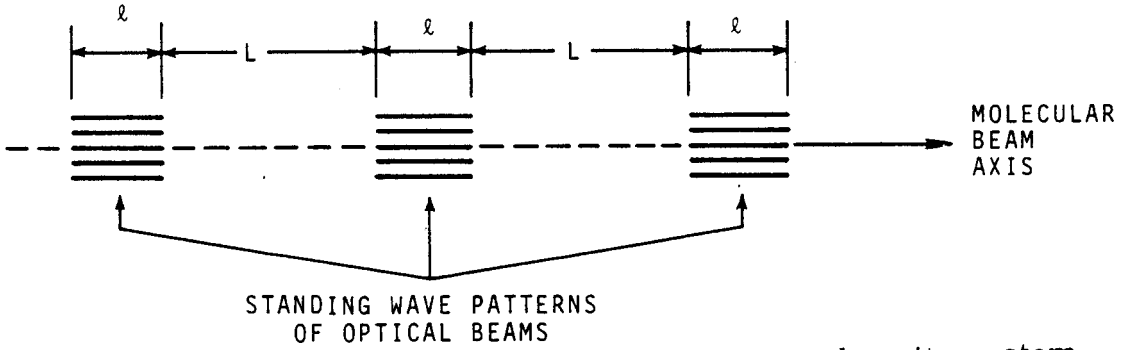

Figure 4. Schematic of three-field separated cavity system.

and the calculations of the transition probability is done using the same notation and method as in Ramsey [2]. The calculation is lengthy but not difficult, an outline is given in Appendix B. We obtain the following result

$$
\begin{aligned}
{}^3P_{p,q} &= \langle |C_q(3\tau + 2T)|^2 \rangle \qquad (11)\\
&= 4\sin^2\theta \sin^2\frac{a\tau}{2}\Big[\cos\theta \sin a\tau \sin \lambda T \\
&\quad + (\cos^2\theta \sin^2\frac{a\tau}{2} - \cos^2\frac{a\tau}{2}) \cos\lambda T \\
&\quad + \sin^2\frac{a\tau}{2} \sin^2\theta - \frac{1}{2}\Big]^2 \quad .
\end{aligned}
$$

Near resonance and with weak perturbation as before, this reduces to

$$
{}^3P_{p,q} \approx b^2\tau^2(3 + 4\cos\lambda T + 2\cos 2\lambda T) \quad . \qquad (12)
$$

This is again periodic in λT and the averaging over ζ or ω_D respectively leads to the same smearing out of the resonance pattern as in the 2-field case.

At exact resonance $\lambda = 0$ we find for all three cases* the common behavior

$$
P_{p,q} = n^2 b\tau \qquad b\tau \ll 1
$$

where n is the number of interacting field regions.

* i. e., single-field (Rabi), 2-field, and 3-field cases.

We would like to thank H. Hellwig and G. Kramer for their valuable contributions through interesting discussions.

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Appendix A

It does not appear possible to solve the wave equations (1), (2) in closed form for arbitrary values of (ω, ω_D, b), but some interesting results can be obtained.

For convenience, we introduce some changes of variable and dimensionless parameters. We take V to be the axial velocity of the atom, and take ℓ to be the width of the optical beam. Let

$$s = t \frac{V}{\ell} \quad ,$$

so that $s = 0$ when the atom enters the perturbing field, and $s = 1$ when it emerges. Let also:

$$E = \frac{\ell}{2V} (\omega_p - \omega_q - \omega) = \frac{\lambda t_0}{2}$$

a dimensionless measured of how near the field angular frequency ω is to the atomic resonance;

$$F = \frac{b \ell}{V} \quad ,$$

a field strength parameter;

$$G = \frac{\omega_D \ell}{V} = k \ell \frac{v_\perp}{V} = k \ell \theta \ ,$$

a Doppler parameter, where k is the optical wave number, and $v_\perp$ is the particle velocity parallel to the optical beam. Then putting

$$C_p(t) = e^{i\omega t} e^{\frac{1}{2} i(\omega_p + \omega_q - \omega) t} \quad d(s)$$

$$C_q(t) = e^{\frac{1}{2} i(\omega_p + \omega_q - \omega)t} c(s) ,$$

we have the equations:

$$\dot{d} = i E d + i F \cos (Gs + p)c$$
$$\dot{c} = -i E c + i F \cos (Gs + p)d$$

subject to initial data

$$d(0) = 1$$
$$c(0) = 0 .$$

We wish to find the transition probability

$$|c^2(1)| = |C_q^2(\frac{\ell}{V})| .$$

Clearly the functions (c, d) are regular functions of the parameters E and F.

Weak field approximation

The solutions can be expanded in power series in the field strength parameter F:

$$d(s) = \sum_{k=0}^{\infty} F^{2k} d_k(s)$$

$$c(s) = \sum_{k=0}^{\infty} F^{2k+1} c_k(s)$$

where

$$d_0(s) = e^{iEs}$$

and the recursion equations are

$$c_k(s) = i\int_0^s dx e^{-iE(s-x)} \cos(Gx + p) d_k(x)$$

$$d_{k+1}(s) = i\int_0^s dx e^{iE(s-x)} \cos(Gx + p) c_k(x) \quad .$$

The weakest field-dependent term is

$$c_0(s) = \frac{1}{2}\left\{ \frac{e^{i[(E+G)s + p]} - e^{-i(Es - p)}}{2E + G} \right.$$

$$\left. - \frac{e^{i[(E-G)s - p]} - e^{-i(Es + p)}}{2E - G} \right\} .$$

Averaging $|F c_0(1)|^2$ over the phase p leads to the result shown in equation (3) in the text.

Expansions near resonance

The solutions can be expanded in power of E to describe the solution in a neighborhood at the resonance $E = 0$. For this, we put

$$d = \sum_{k=0}^{\infty} E^k d_k$$

$$c = \sum_{k=0}^{\infty} E^k c_k$$

and define

$$d_k(s) = \frac{1}{2}(\psi_k + \phi_k)$$

$$c_k(s) = \frac{1}{2}(\psi_k - \phi_k) \quad .$$

These new functions satisfy the system

$$\dot{\psi}_k - iF\cos(Gs + p)\,\psi_k = i\,\phi_{k-1}$$

$$\dot{\phi}_k + iF\cos(Gs + p)\,\phi_k = i\,\psi_{k-1} \quad .$$

For $k = 0$, the initial data are satisfied by the solutions

$$\psi_0(s) = e^{i\frac{F}{G}\left[\sin(Gs + p) - \sin p\right]}$$

$$\phi_0(s) = e^{-i\frac{F}{G}\left[\sin(Gs + p) - \sin p\right]} \quad .$$

The higher order functions could be obtained, with some pain, from the recursions $k \geq 1$

$$\psi_k(s) = i\,e^{i\frac{F}{G}\sin(Gs + p)} \cdot \int_0^s dx\,\phi_{k-1}(x) e^{-i\frac{F}{G}\sin(Gx + p)}$$

$$\phi_k(s) = i\,e^{-i\frac{F}{G}\sin(Gs + p)} \cdot \int_0^s dx\,\psi_{k-1}(x) e^{i\frac{F}{G}\sin(Gx + p)} \quad .$$

Note that $\phi_k(s) = (-)^k\,\tilde{\psi}_k(s)$.

Restricting ourselves to the resonance solution, $E = 0$

$$d_o = \cos\left[\frac{F}{G}(\sin(Gs + p) - \sin p)\right]$$

$$c_o = \sin\left[\frac{F}{G}(\sin(Gs + p) - \sin p)\right] .$$

To this approximation

$$|C_q^2(\tfrac{\ell}{V})| = |c_o^2(1)|$$

$$= \sin^2\left[F^*(\sin(G + p) - \sin p)\right]$$

where

$$F^* \equiv \frac{F}{G} = \frac{b}{\omega_D} .$$

To average this result over the phase p, we note that we can write

$$|C_q^2(\tfrac{\ell}{V})| = \frac{1}{2}\{1 - \cos\left[2F^* \sin p(\cos G - 1)\right]\cos\left[2F^* \cos p \sin G\right]$$

$$+ \sin\left[2F^* \sin p(\cos G - 1)\right]\sin\left[2F^* \cos p \sin G\right]\} .$$

The third term in the bracket can be dropped, since it is anti-symmetric about $p = 0$. Using the expansions

$$\begin{bmatrix}\cos(x \sin p)\\ \cos(x \cos p)\end{bmatrix} = \sum_{k=0}^{\infty} \epsilon_k J_{2k}(x) \cos 2k_p \begin{bmatrix}1\\ (-)^k\end{bmatrix} ,$$

where $\epsilon_0 = 1$, $\epsilon_k = 2\ (k \geq 1)$, and noting that

$$\frac{1}{2\pi}\int_0^{2\pi} dp \cos 2k_p \cos 2\ell_p = s_{k\ell} \qquad (k, \ell) \geq 0$$

we have, averaging over p.

$$\langle C_q^2 (\tfrac{\ell}{V}) \rangle_p = \tfrac{1}{2} \{ 1 + J_0(A) J_0(B) - 2 \sum_{k=-\infty}^{\infty} (-)^k J_{2k}(A) J_{2k}(B) \}$$

where $A = 2F^* (\cos G - 1)$, $B = 2F^* \sin G$. By Graf's Addition Theorem

$$\sum_{k=-\infty}^{\infty} (-)^k J_{2k}(A) J_{2k}(B) = \sum_{l=-\infty}^{\infty} J_l(A) J_l(B) \cos \tfrac{l\pi}{2}$$

$$= J_0\left(\sqrt{A^2 + B^2} \right) .$$

Thus,

$$\langle C_q^2 (\tfrac{\ell}{V}) \rangle_p = \tfrac{1}{2} \{ 1 + J_0(2F^* (\cos G - 1)) J_0(2F^* \sin G) - 2 J_0(4F^* \sin \tfrac{G}{2}) \}$$

which leads to equation (4).

For a particle with no Doppler shift, $\omega_D = 0$:

$$\langle C_q^2 (\tfrac{\ell}{V}) \rangle_p \Big|_{\omega_D = 0} = \tfrac{1}{2} \{ 1 - J_0(\tfrac{2b\ell}{V}) \}$$

as given in equation (5).

To derive even the linear dependence of $|C_q^2|$ on E appears to be a very difficult problem. Solutions for large F (saturating fields) can be obtained. These are singular at E = 0, but if the E-series could be determined to linear terms, its form for large F could be matched to the large-F solutions to give a uniform solution for saturating fields.

The solutions for large F will not be discussed in this report.

Appendix B

The problem is to solve the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = (H_0 + V)\psi$$

where

$$\psi(t) = C_p(t)\psi_p + C_q(t)\psi_q$$

using the Rayleigh-Schrödinger Perturbation Method [7]. The initial conditions are more general than in Section 2, i.e., we assume the values

$$C_p(t_1), \quad C_q(t_1)$$

and look for the solutions at $t = T$.

The perturbation is:

$$V_{pq} = \hbar b e^{i\omega t}, \quad V_{qp} = \hbar b e^{-i\omega t}.$$

The general solution has been given by Ramsey [2] as follows; we just introduce the abbreviations

$$\omega_p = \omega_p/\hbar \qquad \omega_q = \omega_q/\hbar$$

and assume these values to be constant throughout the interaction space. (This simplifies somewhat the computations and it is valid for this case since we can assume the Zeemann and Stark Shifts to be negligible.) The solutions are:

$$C_p(t_1 + T) = \left\{ \left[i\cos\theta \sin\frac{aT}{2} + \cos\frac{aT}{2} \right] C_p(t_1) \right.$$

$$\left. + \left[i\sin\theta \sin\frac{aT}{2} e^{i\omega t_1} \right] C_q(t_1) \right\}$$

$$\times e^{i\,T/2\,(\omega - \omega_p - \omega_q)}$$

$$C_q(t_1 + T) = \left\{ \left[i\sin\theta \sin\frac{aT}{2} e^{-i\omega t_1} \right] C_p(t_1) \right.$$

$$\left. + \left[-i\cos\theta \sin\frac{aT}{2} + \cos\frac{aT}{2} \right] C_q(t_1) \right\}$$

$$\times e^{-i\frac{T}{2}(\omega + \omega_p + \omega_q)}$$

where $\sin\theta$, $\cos\theta$, a, are the same as defined in Section 3A. The computation for three successive separated oscillating fields follows closely that of Ramsey [2, pp. 127-128]; we used the same notation in order to allow an easy comparison. Before proceeding further, let us note the special case of b = 0, which is used for the regions between the oscillating fields:

$$^{o}C_p(t_1 + T) = C_p(t_1)e^{-\omega_p T}$$

$$^{o}C_q(t_1 + T) = C_q(t_1)e^{-i\omega_q T}$$

To avoid further complication, we restrict ourselves to the case of equal b in all three field regions of length ℓ, separated by regions of length L, where b = 0 (see fig. 4).

The molecule enters the first region at $t_1 = 0$ and leaves it at $T = \tau$. During that time τ, b is constant (not exactly true, but simpler). Furthermore, $C_p(0) = 1$, $C_q(0) = 0$. We then have, after the first

field region:

$$C_p(\tau) = \left(i\cos\theta \sin\frac{a\tau}{2} + \cos\frac{a\tau}{2} \right) \times e^{i\frac{\tau}{2}(\omega - \omega_p - \omega_q)}$$

$$C_q(\tau) = \left(i\sin\theta \sin\frac{a\tau}{2} \right) \times e^{-i\frac{\tau}{2}(\omega + \omega_p + \omega_q)} .$$

These results are the initial conditions for the next step: b = 0 for time T. We obtain

$$C_p(\tau + T) = \left(i\cos\theta \sin\frac{a\tau}{2} + \cos\frac{a\tau}{2} \right) \times e^{+i\left[\frac{\tau}{2}(\omega - \omega_p - \omega_q) - \omega_p T\right]}$$

$$C_q(\tau + T) = \left(i\sin\theta \sin\frac{a\tau}{2} \right) \times e^{-i\left[\frac{\tau}{2}(\omega + \omega_p + \omega_q) + \omega_q T\right]} .$$

In the second field region, another perturbation b is applied for time τ, with the above $C_p(\tau + T)$, $C_q(\tau + T)$ as initial conditions. We therefore apply the general solutions by setting therein: $t_1 = \tau + T$ and $T = \tau$ and obtain:

$$C_p(2\tau + T) = \left\{ \left[i\sin\theta \sin\frac{a\tau}{2} + \cos\frac{a\tau}{2} \right] C_p(\tau + T) + \left[i\sin\theta \sin\frac{a\tau}{2} e^{i\omega(\tau + T)} \right] C_q(\tau + T) \right\} \times e^{+i\frac{\tau}{2}(\omega - \omega_p - \omega_q)}$$

$$C_q(2\tau + T) = \{ [\, i \sin\theta \sin \frac{a\tau}{2}\, e^{-i\omega(\tau + T)}] C_p(\tau + T)$$

$$+ [\, - i \cos\theta \sin \frac{a\tau}{2} + \cos \frac{a\tau}{2}\,] C_q(\tau + T) \}$$

$$\times e^{-i \frac{\tau}{2} (\omega + \omega_p + \omega_q)} .$$

Up to this point, the results are copied out of reference [2]. To go beyond, we apply again b = 0 for time T and obtain:

$$C_p(2\tau + 2T) = C_p(2\tau + T)\, e^{-i\omega_p T}$$

$$C_q(2\tau + 2T) = C_q(2\tau + T)\, e^{-i\omega_q T} .$$

Finally we need only:

$$C_q(3\tau + 2T) = \{ [\, i \sin\theta \sin \frac{a\tau}{2}\, e^{-i\omega(2\tau + 2T}] C_p(2\tau + 2T)$$

$$+ [\, - i \cos\theta \sin \frac{a\tau}{2} + \cos \frac{a\tau}{2}\,] C_q(2\tau + 2T) \}$$

$$\times e^{- \frac{\tau}{2} (\omega + \omega_p + \omega_q)}$$

in order to obtain:

$$^3P_{p,q} = \langle\, |\, C_q(3\tau + 2T)\, |^2 \rangle$$

where the $\langle\ \rangle$ just denote that this is an expectation value. There is no need for a further averaging over initial phases of entry into the first field, since Ramsey's solution is independent of the initial phase. (This is no longer true for the case treated in Appendix A.)

For the detailed computation we introduce the following substitutions:

$$\alpha = i \sin\theta \sin\frac{a\tau}{2}$$

$$\beta = i \cos\theta \sin\frac{a\tau}{2}$$

$$\gamma = \cos\frac{a\tau}{2} .$$

Then:

$$C_p(2\tau + T) = \{ (\beta + \gamma)^2 e^{i[\frac{\tau}{2}(\omega - \omega_p - \omega_q) - \omega_p T]}$$

$$+ \alpha^2 e^{-i[\frac{\tau}{2}(\omega + \omega_p + \omega_q) + \omega_q T - \omega(\tau + T)]} \}$$

$$\times e^{i\frac{\tau}{2}(\omega - \omega_p - \omega_q)}$$

$$C_q(2\tau + T) = \{ \alpha(\beta + \gamma) e^{i[\frac{\tau}{2}(\omega - \omega_p - \omega_q) - \omega_p T - \omega(\tau + T)]}$$

$$+ (\gamma - \beta)\alpha e^{-i[\frac{\tau}{2}(\omega + \omega_p + \omega_q) + \omega_q T]} \}$$

$$\times e^{-i\frac{\tau}{2}(\omega + \omega_p + \omega_q)} .$$

We want to obtain

$$C_q(3\tau + 2T) = \{ \alpha e^{-i\omega(2\tau + 2T)} C_p(2\tau + 2T)$$

$$+ (\gamma - \beta) C_q(2\tau + 2T) \}$$

$$\times e^{-i\frac{\tau}{2}(\omega + \omega_p + \omega_q)} .$$

This expression can be written in the following form:

$$C_q(3\tau + 2T) = A_1 e^{i\xi_1} + A_2 e^{i\xi_2} + A_3 e^{i\xi_3} + A_4 e^{i\xi_4}$$

where

$$A_1 = \alpha(\beta + \gamma)^2$$
$$A_2 = \alpha^3$$
$$A_3 = \alpha(\gamma^2 - \beta^2)$$
$$A_4 = \alpha(\gamma - \beta)^2 .$$

And by introducing $\lambda = \omega_q - \omega_p - \omega$, $\omega_q - \omega_p = \omega_0 \therefore \lambda = \omega_0 - \omega$ we have

$$\xi_1 = -\frac{1}{2}(2T + 3\tau)(\omega + \omega_p + \omega_q) + \lambda T$$

$$\xi_2 = \xi_3 = -\frac{1}{2}(2T + 3\tau)(\omega + \omega_p + \omega_q) = -\mu$$

$$\xi_4 = -\frac{1}{2}(2T + 3\tau)(\omega + \omega_p\, \omega_q) - \lambda T$$

and thus:

$$C_q(3\tau + 2T) = (A_1 e^{i\lambda T} + A_2 + A_3 + A_4 e^{-i\lambda T}) e^{-i\mu}.$$

Of this last expression we need only the terms in the parenthesis, since the factor $e^{-i\mu}$ drops out in calculating the modulus of this complex quantity, and we obtain, by using

$$\sin \lambda T = \frac{1}{2i}(e^{i\lambda T} + e^{-i\lambda T})$$
$$\cos \lambda T = \frac{1}{2}(e^{i\lambda T} + e^{-i\lambda T})$$

the final solution:

$$
\begin{aligned}
{}^{3}P_{p,q} = 4 \sin^2\theta \sin^2\frac{a\tau}{2} \{ & \cos\theta \sin a\tau \sin\lambda T \\
& + (\cos^2\theta \sin^2\frac{a\tau}{2} - \cos^2\frac{a\tau}{2}) \cos\lambda T \\
& + \sin^2\frac{a\tau}{2} \sin^2\theta - \frac{1}{2} \}^2
\end{aligned}
$$

having re-substituted for α, β, and γ .