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Theory of The
RADIOFREQUENCY STARK EFFECTS

by

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PREFACE

The material contained in this report, except for minor changes, consists of two sections of the Doctoral thesis of Dr. D.T.F. Marple. The first section, except for the introduction, is from the main body of his thesis and is complete in itself; the second section, Appendix I of his thesis, is a detailed development of the theory.

In the course of his investigation of the radiofrequency spectra of Li^6Cl by the molecular beam electric resonance method, Dr. Marple discovered that the position of the resonance lines at weak fields depended on the magnitude of the rf voltage. This dependence followed a law deduced by Townes and Merritt* for a similar effect discovered by them in microwave absorption experiments. However, it was not clear to us that the same theory should apply to the electric resonance experiments, for which no change in the rotational state occurs, and for which the rf producing the shift in the line positions is identical with the rf producing the transitions. Hence, Dr. Marple undertook the task of developing a theory which would explain both the microwave absorption experiments and the electric resonance experiments. The theory presented in this report not only explains these experiments, but also predicts the two quantum transitions originally observed and explained by Hughes and Grabner**. An article presenting both this theory and verifying experimental results is in preparation.

Thanks are due to Prof. M. Lax and Prof. P. Bergmann for their advice in the development of the theory presented here.

J.W. Trischka

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* C.H. Townes and F.R. Merritt, Phys. Rev., 72, 1266 (1947).

** V. Hughes and L. Grabner, Phys. Rev., 79, 829 (1950).

INTRODUCTION

The theory presented below was developed to account for the radiofrequency field dependence of the line frequencies in the radiofrequency spectrum of $^{6}Li\,Cl$ as observed by the molecular beam electric resonance method.[1] In this experiment, transitions between the hyperfine structure levels of the rotational state $J = 1$, as modified by a static electric field, were induced by a radiofrequency field superimposed on the static field. The hyperfine structure was produced by the chlorine quadrupole interaction and spin-rotation interaction. The qualitative features of spectra at zero or weak static field could be accounted for by the zero and weak field theory of Hughes and Grabner[2], which predicts no dependence of the observed lines on the radiofrequency field.

A systematic study of the shifts in the frequencies of the observed lines with changes in the strength of the radiofrequency field used to produce them was undertaken when discrepancies between the observations at different field strength were found. In all cases, the observed line frequencies, ν, satisfied the relationship:

$$\nu = \nu_0 + a V_{rf}^2$$

where ν_0 is a constant, the frequency of a line in the absence of radiofrequency field, a is a constant, and V_{rf} is the radiofrequency voltage used to produce the line. Thus the frequency-shift, $\Delta\nu$, caused by the radiofrequency field, $E_{rf}(t) = E_{rf} \cos 2\pi\nu t$, was proportional to E_{rf}^2. This frequency shift will be referred to as "radiofrequency Stark effect".

1. H. K. Hughes, Phys. Rev., 72, 614, 1947; J.W. Trischka, Phys. Rev., 74, 718, 1948.
2. V. Hughes and L. Grabner, Phys. Rev., 79, 829, 1950

Townes and Merritt[18] have observed shifts in the frequencies of lines in the microwave spectra of OCS as well as "extra" lines when transitions were produced in the presence of a radiofrequency field. In their experiments, frequencies of the order of 10^4 mc/sec were used to produce transitions between rotational levels. The perturbing field was much more intense than the transition-inducing fields, and frequencies between 20 and 1200 kc/sec were used. They presented theoretical results which explain their observations.

Since the effects observed in the Li^6Cl experiments were similar in form to the quadratic Stark effect due to the interaction of the static field with the molecular electric dipole moment, several experiments were tried to detect changes in the static field produced by application of the radiofrequency field. Such changes could, for example, be produced by rectification of the radiofrequency voltage in the wiring. No evidence for apparatus defects was found. It was, therefore, necessary to modify or re-interpret the theory.

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18. C. H. Townes and F. R. Merritt, Phys. Rev., 72, 1266, 1947.

The numbering of Fig. 1 and Fig. 2 is reversed in the figures.

PREVIOUS CALCULATIONS OF LINE POSITIONS FROM TRANSITION PROBABILITIES

To clarify the contrasts between the new theory developed below, and the theory used in the past, an outline of the older theory as developed by Torrey[19] will be presented.

The complete Hamiltonian is written as

$$H(t) = H_o + H' + V(t) \tag{1}$$

where H_o is the Hamiltonian of the molecule in the absence of any fields, H' is the interaction of the molecule with any steady fields, and $V(t)$ is the interaction between the molecule and a varying field where

$$V(t) = V_o \cos (2\pi \nu t + \delta) \tag{2}$$

The time independent Schrödinger equation is

$$(H_o + H') \Phi_m = E_m \Phi_m \tag{3}$$

The time dependent Schrödinger equation is

$$H(t)\psi = ih \frac{\partial \psi}{\partial t} \tag{4}$$

It is assumed that a solution to (4) may be written as

$$\psi = \sum_m c_m \Phi_m \tag{5}$$

When (5) is inserted into (4) there results the set of equations:

$$ih \frac{\partial c_n}{\partial t} = \sum_m (n | H | m) c_m \tag{6}$$

This set of equations must be solved simultaneously to find expressions for the expansion coefficients, c_n, from which the transition probabilities are calculated. The center of an observed line is expected to occur at the frequency for which the transition probability is a maximum. This frequency may be shown to be

$$\nu = \frac{E_p - E_q}{h} \tag{7}$$

19. H. C. Torrey, Phys. Rev., 59, 293, 1941.

where E_p and E_q are the energies of the states p and q given by (3), if it is assumed that initially $c_p = 1$ and $c_m = o$, $m \neq p$, that $V_o << 2\pi h\nu$, and that all terms in (6) leading to time variation of the c's faster than $\left(\frac{E_p - E_q}{h}\right)t$ may be neglected.

A THEORY FOR THE RADIOFREQUENCY STARK EFFECT

(1) General Method

A theory which predicts the Townes and Merritt result and the results in the present experiment has been obtained by abandoning (3) as a starting point and using in its place the equation which represents the adiabatic approximation namely

$$H(t)\, u_n\,(t) = E_n\,(t) u_n(t) \qquad (8)$$

The solutions of (8) are used as expansion functions to form the true wave function $\psi(t)$ which satisfies (4). Following Schiff and Bohm the expansion is written as

$$\psi = \sum_n a_n u_n(t) \quad \exp\left(-i \int_{t_o}^{t} \frac{E_n(t')dt'}{h}\right) \qquad (9)$$

The function $u_n(t) \quad \exp\left(-i \int_{t_o}^{t} \frac{E_n(t')dt'}{h}\right)$ is a solution to (4) if no transitions are induced by the time dependent part of H between the stationary states existing in its absence, that is, if the adiabatic approximation is valid.

(9) is now inserted into (4). It may be shown[20,21] that the resulting equations for the expansion coefficients a_n in (9) must satisfy

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20. L.I. Schiff, Quantum Mechanics, 1st Ed., New York, McGraw-Hill, 1949, pp. 207-208.

21. D. Bohm, Quantum Theory, 1st. Ed., New York, Prentice-Hall, 1951, pp. 498-99.

$$\dot{a}_k = \sum_n \frac{a_n}{\hbar\omega_{kn}} \exp\left(-i \int_{t_o}^{t} \omega_{k_n}\, dt'\right) \left(\frac{\partial H}{\partial t}\right)_{kn} \quad (10)$$

where $\omega_{kn} = -\omega_{nk} = \dfrac{E_k(t) - E_n(t)}{h}$ (11)

If it is assumed that at $t = t_o$, just as the perturbation is turned on, the molecules are in a definite state m, then for a short time afterwards a good approximation will be

$$\dot{a}_k = \frac{a_m}{\hbar\,\omega_{kn}} \exp\left(-i \int_{t_o}^{t} \omega_{km}\, dt'\right) \left(\frac{\partial H}{\partial t}\right)_{km} \quad (12)$$

Following Schiff (Ref. 20, p. 190) one may expand a_n and $H'(t)$ in series: $a_n = a_n^o + \lambda\, a_n^{(1)} + \lambda^2\, a_n^{(2)}$, and $H(t) = H_o + \lambda H'(t) + \lambda^2 H^{(2)}(t)$. These expansions are substituted into (12); equal powers of λ are equated and when λ is set = 1,

$$\dot{a}_n^o = 0 \qquad a_n^o = C$$

$$\dot{a}_k^{(s+1)} = \sum \frac{a_n}{\hbar\,\omega_{kn}} \exp\left[-i \int_{t_o}^{t} \omega_{kn}(t')\,dt'\right] \left(\frac{\partial H'(t)}{\partial t}\right)_{kn} \quad (13)$$

where $\left(\dfrac{\partial H'(t)}{\partial t}\right)_{kn} = \displaystyle\int \bar{u}_k(t) \frac{\partial H'(t)}{\partial t} u_n(t)\, d\tau$

By use of these equations, better approximations to the true value of each expansion coefficient may be obtained.

These general results will be used to locate the resonance frequencies in the following way: Second order time independent perturbation theory is used to calculate the energy from equation (8).

First order perturbation theory is used to calculate the wave functions. The first order ($s = 0$) approximation expansion coefficients, a_k, are calculated by means of (13). The method of Hughes and Grabner[22] is used to locate the resonances. In this method the frequency at which the denominator of an expansion coefficient vanishes is interpreted as a resonance frequency. Since the denominators are real and the numerators nonvanishing, this procedure predicts resonances at the same frequencies as $|a_k|^2$, which is proportional to the transition probability.

(2) Application to Specific Cases

a) The Townes Merritt Case

In the Townes-Merritt experiments transitions between rotational states are produced by a high frequency field

$$E_H(t) = E_H \cos \omega_H t$$

in the presence of a low frequency field

$$E_L(t) = E_L \cos \omega_L t$$

The relative frequencies and magnitudes of these fields, and the experimental results have been described in the Introduction of the THEORY.

A detailed development of the theoretical results is given in APPENDIX I, part I. In this development it is assumed that E_H is so weak that the shifts produced by it are negligible. The results of the detailed calculation are summarized below.

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22. Hughes and Grabner, op. cit.

Case I ω_L is so small that the field intensity does not vary appreciably over the time of absorption (the intercollision time in the gas). In the case where the Stark effect is quadratic, the frequency shift of an observed line, $\Delta\nu$, varies with the time

$$\Delta\nu = aE_{RF}^{2} \cos^{2} \omega t$$

The coefficient a is the coefficient describing the frequency shift due to Stark effect produced by a steady field of strength, E, for a given transition.

Case II ω_L is so large that the field passes through many cycles of variation in the time of one absorption. The frequency shift, $\Delta\nu$, is independent of the time, and is given by

$$\Delta\nu = \frac{aE_{RF}^{2}}{2} \pm 2n\,\omega_L$$

where n is a positive integer. The relative intensities of lines with different values of n is given by

$$\left\{ J_n \frac{(aE_{RF}^{2})}{4\nu_L} \right\}^2$$

Thus if ω_L is large compared to the frequency shift aE_{RF}^{2}, only resonance with n = 0 will be observed.

b) Electric Resonance Cases

In electric resonance experiments in which J does not change, frequency-shifts are caused by the transition-inducing field. Detailed calculations are given in the APPENDIX, part 2. Only the cases where $E_{DC} \gg E_{RF}$ are considered in detail. The general result is that the frequency shift $\Delta\nu$, is

$$\Delta\nu = \frac{aE_{RF}^{2}}{2}$$

where a is the D.C. Stark coefficient for the transition under consideration. At zero D.C. field, the theory predicts that only half-frequency transitions will be observed. At strong fields, if $E_{DC} \cong E_{RF}$ half-frequency transitions may occur both with $\Delta m_J = \pm 2$, as predicted by the old theory, and also with $\Delta m_J = \pm 1$. The $\Delta m_J = \pm 1$ transitions were not searched for in the present experiments. It is also expected that if $E_{DC} \cong E_{RF}$, resonances will be observed at $2\nu_T$, $3\nu_T$, $4\nu_T$, etc., where ν_T is the ''normal'' transition frequency. These cases are not examined in detail.

(3) Discussion

The main difference between the new and old theories is that the new theory starts from an equation which (in the absence of transitions) is the adiabatic approximation, instead of the time independent Schrödinger equation. If the radiofrequency field produces no transitions between states which in its absence are separated in energy, the adiabatic approximation is valid and $E_m(t)$ may be interpreted as the energy of state m. But if the field induces such transitions, it is not proved that this interpretation is possible. Therefore, it does not appear that the success of the theory in predicting an r.f. Stark effect is directly related to the fact that (8) may represent this approximation. It is not clear what conditions, if any, a proper starting equation should satisfy in the presence of the radiofrequency field. It is also not clear why equation (8) gives a result which may be readily interpreted as a radiofrequency Stark effect.

However, if the expansion coefficients of equations such as (5) or (9) are to be interpreted as transition probabilities, it seems necessary that the starting equations should correctly describe the states of the system before and after the transitions occur. For example, in an electric resonance experiment transitions are detected by changes in the deflection of the beam. States with different deflection are states of different and well defined energy. Since definite energy levels and states may be assigned to the molecule just before and just after it interacts with the radiofrequency field, it seems necessary that the starting equations give the correct energy levels for the molecules in the D.C. field.

Both starting equations (3) and (8) satisfy this condition. Both methods of calculation also assume that the only really correct description of the molecule in the C-field is the time dependent Schrödinger equation and both attempt to calculate the number of molecules that enter the C-field in a different state. For these reasons it is expected that the transition probabilities calculated by both theories have the same meaning. The writer believes that the transition probabilities calculated from the new theory do not contain any result that could not be obtained by a more refined calculation based on (3) as a starting equation. However, his attempts to obtain results interpretable as r.f. Stark effect using (3) as a starting equation have not been successful.

APPENDIX I

Part I. R. F. Stark Effect in the Townes Merritt Case

Townes and Merritt have assumed that no nuclear-molecular interactions are present in the molecule and that it is in a $^1\Sigma$ electronic state. Thus it may be considered as a rotator with dipole moment, μ, and moment of inertia, A, in the presence of high and low frequency fields, E_H and E_L respectively, with angular frequencies ω_H and ω_L.

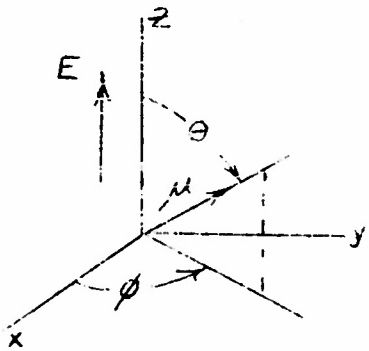
The high frequency, $\frac{\omega H}{2\pi}$, is of the order of 10^4 mc./sec. This is the difference in energy between two rotational states of the molecules. $\frac{\omega_L}{2\pi}$ is of the order of 1 mc./sec. or less in these experiments.

The Hamiltonian for the molecule, based on classical expressions for the energy is

$$(1) \quad H = \frac{h^2}{2A} \vec{J}^2 - \mu \left(\vec{E}_H \cos \omega_H t + \vec{E}_L \cos \omega_L t\right) = H_o + H'(t)$$

where J is the rotational angular momentum.

The energy difference between rotational states is of the order of 100 times as great as the interaction energy of the molecule with any of the fields to be considered, so that a perturbation calculation for the Stark effect is adequate. In the absence of the fields, the unperturbed time-independent Schrödinger equation is[1]



$$\frac{\hbar^2}{2A} \vec{J}^2 \Phi_{J,m} = E_J \Phi_{J,m} \qquad (2a)$$

$$E_J = \frac{\hbar^2}{2A} J(J+1) \qquad (2b)$$

$$\Phi_{J,m} = \frac{1}{\sqrt{2\pi}} e^{im\phi} \left\{ \frac{(2J+1)(J-|m|)!}{2(J+|m|)!} \right\}^{\frac{1}{2}} \times P_J^{|m|}(\cos\theta). \qquad (2c)$$

The electric field will be taken in the Z direction.

In the case of constant field H'(t) in (1) reduces to $H' = -\mu E\cos\theta$. From the properties of the associated Legendre functions it may be shown that

$$\langle J'm' \mid H' \mid Jm \rangle = 0 \text{ if } J' = J \text{ or } J' \neq J \quad m' \neq m$$

Thus there is not first order energy perturbation. The wave function is perturbed, however, and in first order the wave function is

$$\psi_{Jm} = \Phi_{Jm} + \sum_{J',m'}{}' \frac{\langle J'm' \mid H' \mid Jm \rangle \Phi_{J'm'}}{(E_{J'} - E_J)} \qquad (J, m' \neq J m) \tag{3}$$

The sum consists of two terms,

$$\frac{\langle J,m \mid H' \mid J+1, m \rangle}{E_J - E_{J+1}} \Phi_{J+1,m} \quad \text{and}$$

$$\frac{\langle J,m \mid H' \mid J-1, m \rangle}{E_J - E_{J+1}} \Phi_{J-1,m}$$

$$(4) \quad \langle J,m \mid H' \mid J+1,m \rangle = -\mu E \left[\frac{2J+3}{2J+1} \quad \frac{(J+1-m)}{(J+1+m)}\right]^{1/2} \quad \frac{(J+1+m)}{(2J+3)}$$

$$= k_{(1)} E \quad (E_{J+1} - E_J)$$

$$(5) \quad \langle m \mid H' \mid J-1,m \rangle = -\mu E \left[\frac{(2J-1)}{(2J+1)} \quad \frac{(J+m)}{(J-m)}\right]^{1/2} \quad \frac{(J-m)}{(2J-1)}$$

$$= k_{(-1)} E \quad (E_{J-1} - E_J)$$

The second order perturbation energy may be calculated most directly using Schiff's[2] result, and the properties of the associated Legendre functions[3]. The perturbation energy is:

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1. G. Herzberg, Spectra of Diatomic Molecules, 2nd Ed. New York Van Nostrand, pp. 69 - 73.

2. L.I. Schiff, Quantum Mechanics, 1st. Ed., New York, McGraw-Hill, 1949, equ. 25.12, p. 151.

3. G. Herzberg, op. cit., p. 72-73.

$$W'' = \sum \frac{\langle J', m \mid H' \mid J, m \rangle^2}{E_J' - E_J} \tag{6}$$

which gives the well known result

$$W'' = \frac{-2\mu^2 A E^2}{h^2} \left\{ \frac{J(J+1) - 3m^2}{2J(J+1)(2J-1)(2J+3)} \right\} \tag{7}$$

$$= b(J,m) E^2 \tag{7a}$$

These energy and wave function expressions may now be used to write down the first order wave functions and 2nd order energies of the "adiabatic approximation" Schrödinger equation. E_H and E_L are considered to be in the same direction.

$$\left\{ \frac{h^2}{2A} \vec{J}^2 - \mu \cos\theta \, (E_H \cos\omega_H t + E_L \cos\omega_L t) \right. \quad u_{J,m}(t)$$

$$= E_{J,m}(t) \, u_{J,m}(t). \tag{8}$$

The time dependence does not influence the values of the matrix elements, so that

$$E_{J,m}(t) = E_J + b_{J,m} (E_H \cos\omega_H t + E_L \cos\omega_L t)^2 \tag{9}$$

$$u_{J,m}(t) = \Phi_{J,m} + (E_H \cos\omega_H t + E_L \cos\omega_L t)$$

$$(k_{(+1)} \Phi_{J+1} + k_{(-1)} \Phi_{(J-1)}) \tag{10}$$

The expansion coefficients in the series expansion of the wave functions (10) which form the solution of the time dependent Schrödinger equation are now to be calculated using (13) of the THEORY, which in the first order perturbation gives

$$\dot{a}^{(1)}_{J'm'} = \frac{1}{\hbar \omega_{J'm' J m}} \exp\left[-i \int_{t_0}^{t} \omega_{J'm' J m}(t') dt' \right] \left\langle J'm' \left| \frac{\partial H'(t)}{\partial t} \right| J m \right\rangle \tag{11}$$

with the present notation. It has been assumed that when the molecule enters the region of the field it is in the definite state (J,m). In terms of the energies this is

$$a^{(1)}_{J'm'} = \frac{1}{E_{J'm'}(t)-E_{Jm}(t)} \exp\left[-\frac{i}{\hbar}\int_{t_0}^{t}\left(E_{J'm'}(t')-E_{Jm}(t')\right)dt'\right] \langle J'm'|\frac{\partial H'(t)}{\partial t}|Jm\rangle. \tag{12}$$

In this case the exponent is

$$-\frac{i}{\hbar}\int_{t_0}^{t}\left[E_{J'}-E_J+(b_{J'm'}-b_{Jm})(E_H^2\cos^2\omega_H t'+2E_HE_L\cos\omega_H t'\cos\omega_L t'+E_L^2\cos^2\omega_L t')\right]dt' \tag{13}$$

When the integration is carried out the exponent becomes

$$-\frac{i}{\hbar}\Big\{(E_{J'}-E_J)(t-t_0)+(b_{J'm'}-b_{Jm})\Big[E_H^2\left(\frac{t-t_0}{2}+\frac{\sin 2\omega_H t-\sin 2\omega_H t_0}{4\omega_H}\right) \tag{14}$$

$$+2E_HE_L\left(\frac{\sin(\omega_H\pm\omega_L)t}{2(\omega_H\pm\omega_L)}-\sin(\omega_L\pm\omega_H)t_0\right)+E_L^2\left(\frac{t-t_0}{2}+\frac{\sin 2\omega_L t-\sin 2\omega_L t_0}{4\omega_L}\right)\Big]\Big\}$$

Before manipulating the exponent further the term

$$\left[E_{J'}-E_J+(b_{J'm'}-b_{Jm})(E_H^2\cos\omega_H t+2E_HE_L\cos\omega_H t\cos\omega_L t+E_L^2\cos\omega_L t)\right]^{-1}$$

will be examined. Expanding in a power series it is found to be

$$\frac{1}{(E_{J'}-E_J)}\left\{1-T(t)+\frac{2}{2!}T(t)^2-\frac{3}{3!}T(t)^3-\cdots\right\} \tag{15}$$

where

$$T(t)=\frac{(b_{J'm'}-b_{Jm})}{(E_{J'}-E_J)}(E_H^2\cos^2\omega_H t+2E_HE_L\cos\omega_H t\cos\omega_L t+E_L^2\cos^2\omega_L t)$$

It will be seen that T(t) is of the order of 10^{-2} at most since the Stark energy difference is of the order of 100 mc./sec. at most, while $(E_J' - E_J)$ is $\sim 10^4$ mc./sec. Thus to an excellent approximation (15) is simply

$$\frac{1}{(E_J' - E_J)} \tag{15a}$$

The matrix elements of $\frac{\partial H'}{\partial t}$ are readily evaluated since

$$\frac{\partial H'(t)}{\partial t} = -\mu \cos\theta \left(\omega_H E_H \sin\omega_H t + \omega_L E_L \sin\omega_L t\right) \tag{16}$$

When the series wave functions given by (3) are used, the terms will be seen to have the following orders of magnitudes and time dependences.

$$\langle J+1, m | \frac{\partial H'(t)}{\partial t} | J, m \rangle \sim \mu \omega_H \overset{(1)}{E_H} \sin\omega_H t + \mu \overset{(10^{-4})}{E_L} \omega_L \sin\omega_L t$$
$$+ \frac{\mu^2 \omega_H E_H^2}{E_{J+1} - E_J} \overset{(10^{-4})}{\sin\omega_H} \cos\omega_H t + \frac{\mu^2 \omega_L E_L^2}{E_{J+1} - E_J} \overset{(10^{-8})}{\sin\omega_L} t \cos\omega_L t$$
$$+ \frac{\mu^2 \omega_L \omega_H E_L E_H}{E_{J+1} - E_J} \overset{(10^{-6})}{\sin\omega_H} t \cos\omega_L t \tag{17}$$

In the Townes-Merritt experiments $\frac{\omega_H}{\omega_L} \cong 10{,}000$ and the energy ratio, $\frac{\mu^2 E_H^2 \text{ or } E_L^2}{(E_J' - E_J)}$, is always of the order of 10^{-2} or less.

The relative orders of magnitudes of the terms are indicated in (17) by the numbers just beneath each term. It is seen that the most important term is the matrix element

$$\langle J+1, m | \frac{\partial H'}{\partial t} | J, m \rangle \sim \mu \omega_H E_H \sin\omega_H t \tag{18}$$

The coefficients, a, will now be evaluated for two different cases.

CASE I: The time between collisions is much less than the time of one cycle of the low frequency radiation:

$\omega_L (t - t_o) << 1$ (Thus $\frac{\omega_L}{2\pi} \cong$ 10 kc./sec. or less)

In this case E(t) varies only slightly during the time available for one absorption process, and use may be made of the approximations

$$\sin \omega_L (t - t_o) \cong \omega_L (t - t_o)$$

$$\cos \omega_L (t + t_o) \cong \cos 2 \omega_L t_o$$

so that

$$E_L^2 \left[\frac{t - t_o}{2} + \frac{(\sin 2 \omega_L t - \sin 2 \omega_L t_o)}{4 \omega_L} \right] \cong E_L^2 (t - t_o) \cos^2 \omega_L t_o$$

and the exponent, equ (14) is

$$-\frac{i}{\hbar}\Big\{\Big[(E_{J'} - E_J) + (b_{J'm'} - b_{Jm})\Big(\frac{E_H^2}{2} + E_L^2 \cos^2 \omega_L t_o\Big)\Big](t - t_o)$$
$$+ (b_{J'm'} - b_{Jm})\Big\{\Big[E_H^2 \frac{(\sin 2\omega_H t - \sin 2\omega_H t_o)}{4\omega_H}$$
$$+ 2E_H E_L \frac{\sin(\omega_H \pm \omega_L)t}{2(\omega_H \pm \omega_L)t} - \frac{\sin(\omega_H \pm \omega_L)t}{2(\omega_H \pm \omega_L)}\Big]\Big\}. \qquad (19)$$

The exponent may now be expanded. We use

$$\exp[ix \sin t] = \sum_{-\infty}^{+\infty} J_n(x) \exp[int] \text{ (Jeffries)}^4 \qquad (20)$$

The parts depending on t_o need not be expanded, and are collected together to form $B(t_o)$. Thus the exponential term is

$$B(t_o) \exp\Big\{-\frac{i}{\hbar}\Big[E_{J'} - E_J + (b_{J'm'} - b_{Jm})\Big(\frac{E_H^2}{2} + E_L^2 \cos^2 \omega_L t_o\Big)\Big]t\Big\}$$
$$\sum_{-\infty}^{\infty} J_n\Big\{\frac{(b_{J'm'} - b_{Jm})}{4\hbar\omega_H} E_H^2\Big\} \exp[2in\omega_H t] \sum_{-\infty}^{\infty} J_p\Big\{\frac{(b_{J'm'} - b_{Jm})}{2\hbar(\omega_H - \omega_L)}\Big\} \exp[2ip(\omega_H - \omega_L)t]$$

(cont'd next page)

4. H. Jeffries and B.S. Jeffries, Methods of Mathematical Physics 2nd Ed., Cambridge Univ. Press, 1950, p. 589.

$$\times \sum_{-\infty}^{+\infty}{}' J_q\left\{\frac{(b_{J'm'}-b_{Jm})E_H E_L}{2\hbar(\omega_H+\omega_L)}\right\} \exp\left[2iq(\omega_H+\omega_L)t\right] \tag{21}$$

$E_H^2\,(b_{J'm'} - b_{J\,m})$ is in these experiments of the order of 10^{-4} times the energy $h\nu$. Hence, the arguments of all the Bessel functions are very small and the only important terms are $J_0(x)$, which = 1 for small arguments--all the others are of the order of 10^{-4} or less. Thus to a good approximation the exponential, (20), is

$$B(t_0)\exp\left\{-\frac{i}{\hbar}\left[E_{J'}-E_J+(b_{J'm'}-b_{Jm})\left(\frac{E_H^2}{2}+E_L^2\cos^2\omega_L t_0\right)\right]\right\} \tag{22}$$

The leading terms - expressions (15a), (18), and (21) are inserted into (12). The time dependence of the leading term is:

$$a_{J\pm1,m} \propto \int_{t_0}^{t} \frac{\omega_H E_H \sin\omega_H t}{(E_{J\pm1}-E_J)} \exp\left[-\frac{i}{\hbar}\left\{E_{J\pm1}-E_J+(b_{J\pm1m}-b_{Jm})\left(\frac{E_H^2}{2}+E_L^2\cos^2\omega_L t_0\right)\right\}t\right]dt. \tag{23}$$

$$\propto \left[\frac{\left\{\begin{matrix}\sin\\ \cos\end{matrix}\,\omega_H t+\text{terms}\right\}\exp\left[-\frac{i}{\hbar}\left\{E_{J\pm1}-E_J+(b_{J\pm1,m}-b_{Jm})\left(\frac{E_H^2}{2}+E_L^2\cos^2\omega_L t_0\right)\right\}t\right]}{\omega_H^2-\frac{1}{\hbar^2}\left\{E_{J\pm1}-E_J+(b_{J\pm1,m}-b_{Jm})\left(\frac{E_H^2}{2}+E_L^2\cos^2\omega_L t_0\right)\right\}^2}\right]_{t_0}^{t}$$

Since the numerator does not vanish and the denominator of (23) is "resonant", transitions are expected to occur at the frequency for which the denominator vanishes -- these are

$$\omega_H = \pm \frac{1}{\hbar}\left\{E_{J\pm1} - E_J + (b_{J\pm1,m} - b_{Jm})\left(\frac{E_H^2}{2} + E_L^2 \cos^2 \omega_L t_0\right)\right\} \tag{24}$$

The field E_H is considered to be so weak that perturbations in the energy from this cause may be neglected -- thus

$$\omega_H = \pm \frac{1}{\hbar}\left\{E_{J\pm1} - E_J + (b_{J\pm1,m} - b_{Jm})(E_L^2 \cos^2 \omega_L t_0)\right\}$$

or

$$\nu_H = \frac{E_{J\pm1} - E_J}{h} + \frac{(b_{J\pm1,m} - b_{Jm})}{h} E_L^2 \cos^2 \omega_L t_0 \tag{25}$$

$a = \dfrac{(b_{J+1,m} - b_{Jm})}{h}$ is the same coefficient that determines the size of the Stark effect in the D.C. case. The time of entrance into the field is t_0 -- thus the shift in the transition frequency due to the radio frequency perturbing field is

$$\Delta\nu = a E_L^2 \cos^2 \omega_L t_0 \tag{26}$$

the result stated in the text of the thesis, and obtained by Townes and Merritt.

CASE II: <u>The time between collisions is the same order of magnitude or greater than the period of the low frequency field.</u>

In this case the approximation $\omega_L (t-t_o) \ll 1$ is not valid. The terms in ω_L are therefore treated in the same way as ω_H. When (20) is used to expand the sine terms in the exponent (14) and the terms containing t_o are collected to form $C(t_o)$, the exponential term in (12) becomes

$$C(t_o)\exp\left[-\frac{i}{\hbar}\left\{E_{J'}-E_J+(b_{J'm'}-b_{Jm})\left(\frac{E_H^2}{2}+\frac{E_L^2}{2}\right)\right\}t\right]$$
$$\sum_{-\infty}^{\infty} J_n\left\{\frac{(b_{J'm'}-b_{Jm})}{4\hbar\omega_L}E_L^2\right\}\exp\left[2in\omega_L t\right]\sum_{-\infty}^{\infty} J_p\left\{\frac{(b_{J'm'}-b_{Jm})}{4\hbar\omega_L}E_H^2\right\} \quad (27)$$
$$\exp\left[2ip\omega_H t\right]\sum_q^{\infty}(\text{SEE } 21)\sum_r(\text{SEE } 21)$$

As before, the sums over p,q, and r may be replaced by 1 because the arguments of the Bessel functions are very small. However, this is not true for the sum over n, as $\frac{b(_{J'm} - b_{J\,m})\ E_L^2}{4\ h\ \omega_L}$ may be of the order of 1 cr larger thus (27) is

$$\exp\left[-\frac{i}{\hbar}\left\{E_{J'}-E_J+(b_{J\pm1,m}-b_{Jm})\left(\frac{E_H^2+E_L^2}{2}\right)\right\}t\right]\sum_{-\infty}^{\infty} J_n\left\{\frac{(b_{J'm'}-b_{Jm})}{4\hbar\omega_L}E_L^2\right\}\exp\left[2in\omega_L t\right]$$

(15a), (18) and (21) are still the larger terms in the expressions for other parts of $a_{J'm'}$, so that

$$a_{J\pm1,m} \propto \int_{T_0}^{t}\frac{\omega_H E_n \sin\omega_H t}{(E_{J\pm1,m}-E_J)}\exp\left[-\frac{i}{\hbar}\left\{E_{J\pm1,m}-E_J\ (b_{J\pm1,m}-b_{Jm})\left(\frac{E_H^2+E_L^2}{2}\right)\right\}t\right] \quad (28a)$$
$$\sum_{-\infty}^{\infty} J_n\left(\frac{b_{J\pm1,m}-b_{Jm}}{4\hbar\omega_L}E_L^2\right)\exp\left[2in\omega_L t\right]dt$$

$$a_{J\pm1,m} \propto \left\{\begin{matrix}\sin\\ \cos\end{matrix}\ \omega_H t + \text{TERMS}\right\}\left\{\sum_{-\infty}^{\infty}\left\{\frac{(b_{J\pm1,m}-b_{Jm})}{4\hbar\omega_L}E_L^2\right\}\right\}\times$$
$$\frac{\exp\left[-\frac{i}{\hbar}\left\{E_{J\pm1}-E_J\ (b_{J\pm1,m}-b_{Jm})\left(\frac{E_H^2+E_L^2}{2}\right)\right\}t+2in\omega_L t\right]t_0}{\omega_H^2-\left[\frac{i}{\hbar}\left\{E_{J\pm1}-E_J+(b_{J\pm1,m}-b_{Jm})\left(\frac{E_H^2+E_L^2}{2}\right)\right\}+2n\omega_L\right]^2} \quad (28b)$$

As before, this expression for a_{J+1} is resonant, so that a transition is expected to occur when the denominator vanishes. This occurs when

$$\omega_H = \pm\left[\frac{1}{\hbar}\left\{E_{J\pm1} - E_J + (b_{J\pm1,m} - b_{Jm})\left(\frac{E_H^2 + E_L^2}{2}\right)\right\} + 2n\,\omega_L\right]$$

or

$$\nu_L = \pm\left[\frac{E_{J+1} - E_J}{h} + \frac{(b_{J\pm1,m} - b_{Jm})}{h}\left(\frac{E_H^2 + E_L^2}{2}\right) + 2n\nu_L\right] \qquad (29)$$

As before, the field E_H is so small that it does not significantly shift the lines, so that the final result for the shift in observed lines is

(30) $\Delta\nu_H = \dfrac{a\,(E_L^2)}{2} \pm 2n\,\nu_L$, where n is an integer, as stated in the text of the thesis and by Townes and Merritt.

The relative intensities of lines corresponding to different values of n are expected to be proportional to the relative magnitudes of the transition probabilities. Since these are proportional[5] to $|a_{J\pm1,m}|^2$ if all other factors are left unchanged, the relative intensities will be proportional to the relative sizes of

$$J_m^2\left\{\frac{(b_{J\pm1} - b_{Jm})E_L^2}{4\pi\omega_L}\right\} = J_m^2\left(\frac{a\,E_L^2}{4\nu_L}\right) \qquad (31)$$

for different n values, as stated in the thesis text, and by Townes and Merritt.

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5. L. I. Schiff, op. cit., p. 192.

Part II. R.F. Stark Effect in Electric Resonance Experiments.

In an electric resonance experiment, molecules from the A field pass into the C field moving with thermal velocities. During the time they are in the field, of the order of 10^{-4} sec., transitions may be induced by the radiofrequency field E_{RF} with angular frequency, ω, between the energy levels perturbed by the homogeneous field E_c. Two cases will be treated. In the first case, the molecule will be assumed to have an electric quadrupole interaction, and the DC and RF fields will be assumed to be so weak that the weak field approximation may be used to treat all the effects due to fields. In the second case the DC field will be assumed to be so strong that the Stark effect may be treated ignoring the quadrupole interaction. In both cases, the frequency $\frac{\omega}{2\pi}$ is considered to be so great that E_{RF} undergoes several oscillations in the time that the molecule is in the field.

CASE I: The Hamiltonian is

$$H = \frac{h^2}{2A} \vec{J}^2 + HQ - \vec{\mu}\cdot(\vec{E}_{DC} + \vec{E}_{RF} \cos \omega t) \tag{32}$$

The energy levels for the weak field case are given by Hughes and Grabner[6]. The result for the d.c. field case may be generally expressed as

$$W = E_J + E_Q (F_1) + d(F_1, m_{F1}) E^2 \tag{33}$$

The coefficients, d, are proportional to the coefficients given by Hughes and Grabner for the Stark effect at weak fields.

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6. Hughes and Grabner, Phys. Rev., 79, 829, 1950.

Since the time dependence does not affect the values of matrix elements

(34) $$W(I,J,F,m_F,t) = E_J + E_Q(F_1) + \alpha(F_1,m_{F_1})\,(E_{DC}+E_{RF}\cos\omega t)^2$$

The last term is small compared to the second. The wave functions in the absence of any fields are[7]

$$\psi(J,I,F,m_F) = \sum_{m_I m_J} C^{m_J m_I}_{F,m_F}\,\Phi(J,m_J)\,\Phi(I,m_I)$$

The presence of a field mixes into this wavefunction states of different J, so that the wave function in the present field, so far as its time dependence and mixture of rotational states are concerned will be

$$u(J,I,F,m_F,t) = \overset{A}{\psi(J,I,F,m_F)} + \overset{B}{g(E_{DC})\,\Phi_{J\pm1,m}} + \overset{C}{k(E_{RF})\,\Phi_{J\pm1,m}\cos\omega t} \qquad (36)$$

where $g(E_{DC})$ and $k(E_{RF})$ are $\ll$ 1 at these weak fields. The analysis will proceed in a manner analogous to the Townes and Merritt <u>case II</u>, since $\omega \sim 10^6$ and $(t-t_0) \sim 10^{-4}$ so that $\omega(t-t_0) \sim 10^{+2}$. The transitions to be considered do not involve changes in the rotational states. Thus $E_{J'} - E_J = 0$, and this term will, for simplicity, be dropped out of the energy-difference expressions. Thus the exponent in (12) is:

$$-i/\hbar \int_{t_0}^{t} \left\{ E_Q(F_1') - E_Q(F_1) + \left(\alpha(F_1,m_{F_1}) - \alpha'(F_1,m_{F_1})\right)\left(E_{DC} + E_{RF}\cos\omega t\right)^2 \right\} dt \qquad (37)$$

= (over)

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7. E.V. Condon and G. H. Shortley, <u>Theory of Atomic Spectra</u>, pp. 73-78.

$$= -\frac{i}{\hbar}\Big[\big(E_Q(F') - E_Q(F)\big)t + \big(d(F', m_F) - d(F, m_F)\big)$$

$$\Big\{E_{DC}^2 + \frac{2E_{DC}E_{RF}}{\omega}\sin\omega t + E_{RF}^2\Big(\frac{t}{2} + \frac{\sin 2\omega t}{4\omega}\Big)\Big\}\Big]_{t_0}^{t} \qquad (38)$$

$$= D(t_0)\exp\Big[-\frac{i}{\hbar}G(t)\Big]$$

where G(t) is the value of (38) with the upper limit inserted.

The orders of magnitude and time-dependence of $\left\langle\left|\frac{\partial H'}{\partial t}\right|\right\rangle$ will now be explained.

(39) $$\frac{\partial H'}{\partial t} = \underbrace{-\mu E_{RF_z}\cos\theta\,\omega\sin\omega t}_{(a)} \underbrace{-\mu E_{RF_{xy}}\sin\theta\begin{Bmatrix}\cos\Phi\\ \text{or}\\ \sin\Phi\end{Bmatrix}\omega\sin\omega t}_{(b)}$$

Terms (a) will induce transitions without change in m_{F_1}, and only its contribution will be considered as all the observed transitions are of this type. The present discussion is not concerned with the changes in F that may occur. With $\mu'(J,I,F,m_F,t)$ (expression (36)) as the initial state and $\mu(J,I,F',m_F,t)$ as the final state, the largest contributions from (39) are:

type1: from terms (A) and (B) as initial and final states respectively:

$$\left\langle\left|\frac{\partial H'}{\partial t}\right|\right\rangle \sim \sin\omega t \qquad (40a)$$

type2: from terms (A) and (C) in the initial and final states respectively:

$$\left\langle\left|\frac{\partial H'}{\partial t}\right|\right\rangle \sim \sin\omega t \quad \cos\omega t \qquad (40b)$$

Note that the type (1) terms vanish if $E_{DC} = 0$.

The same method may be applied to the denominator of (12) that was used before to obtain (15a) from (14), since the energy level perturbation from the field is small. Thus the denominator is approximately

(41) $$E_Q(F', m_F) - E_Q(F, m_F)$$

Combining (41), (40(a) or 40(b)) and (38)

$$a_{F_1' m_{F_1}'} \propto \int_{t_0}^{t} \frac{D(t_0)\exp\left[-\frac{i}{\hbar}G(t)\right]\left\{\begin{matrix}\sin\omega t\cos\omega t\\ \sin\omega t\end{matrix}\right\}dt}{E_Q(F_1' m_{F_1}') - E_Q(F_1 m_{F_1})}$$

The expansion (20) is again used for the sine functions in the exponential. In the present experiment

$$\frac{E_{DC}E_{RF}}{\omega}\quad (d(F'_1 m_{F_1}) - d(F_1, m_{F_1})), \text{ or } \frac{E_{RF}(d'-d)}{4\omega}$$

are always $\ll$ 1 since the transition frequency is always $\gg$ the energy level splitting due to fields. Therefore, the only term that need be considered is $J_0 \cong 1$. Thus

$$a_{F_1' m_{F_1}'} \propto \int_{t_0}^{t} D(t_0)\exp\Big[-\frac{i}{\hbar}\Big\{E_Q(F_1') - E_Q(F_1) + \big(d(F_1' m_{F_1}') - d(F_1 m_{F_1})\big)\big(E_{DC}^2 + \frac{E_{RF}^2}{2}\big)\Big\}t\Big]\left\{\begin{matrix}\sin\omega t\\ \cos\omega t\sin\omega t\end{matrix}\right\}dt$$

using the type (1) time dependence, the result is

$$a_{F_1' m_{F_1}'} \propto \frac{D(t_0)\exp\Big[-\frac{i}{\hbar}\Big\{E_Q(F_1') - E_Q(F_1) + \big(d(F_1' m_{F_1}') - d(F_1 m_{F_1})\big)\big(E_{DC}^2 + \frac{E_{RF}^2}{2}\big)\Big\}t\Big]_{t_0}^{t}}{E_Q(F_1') \mp E_Q(F_1) - \omega^2 - \frac{1}{\hbar}\big(E_Q(F_1') - E_Q(F_1) + (d(\,') - d(\,))\big(E_{DC}^2 + \frac{E_{RF}^2}{2}\big)\big]^2)}$$

The " resonant" denominator vanishes when

$$\omega = \pm\frac{1}{\hbar}\Big[E_Q(F_1') - E_Q(F_1) + \big(d(F_1' m_{F_1}') - d(F_1 m_{F_1})\big)\big(E_{DC}^2 + \frac{E_{RF}^2}{2}\big)\Big]$$

or

$$(42)\qquad \nu = \pm\quad \frac{E_Q(F_1') - E_Q(F_1)}{h} + \frac{\big(d(F_1' m_{F_1}') - d(F_1 m_{F_1})\big)}{h}\big(E_{DC}^2 + \frac{E_{RF}^2}{2}\big)$$

Thus, where the DC "Stark coefficient", $a = \dfrac{(d(F', m_{F'}) - d(F, m_F))}{h}$

the shift in a line due to the radiofrequency fields is

$$(43)\qquad \Delta\nu = a\left\{\frac{E_{RF}}{2}\right\}^2$$

as is stated in the thesis text. The type (2) time dependence yields the term

$$a_{F_1', m_{F_1'}} \propto \frac{(\text{NUMERATOR FINITE AT RESONANCE } (\neq 0))}{2\left[(2\omega)^2 - \left[\frac{1}{\hbar}(E_Q(F_1') - E_Q(F_1)) + (\mathcal{A}(\,') - \mathcal{A}(\,))\left(E_{DC}^2 + \frac{E_{RF}^2}{2}\right)\right]^2\right]}$$

which gives resonance at

$$\nu = \frac{1}{2}\left\{ \frac{E_Q(F_1') - E_Q(F_1)}{h} + \frac{(\mathcal{A}(F_1', m_{F_1'}) - \mathcal{A}(F_1, m_{F_1}))}{h}\left(E_{DC}^2 + \frac{E_{RF}^2}{2}\right)\right\}$$

These are half frequency-resonances. The shift in the doubled half frequency resonances is seen to be the same as the full frequency case, as stated in the thesis. Since $\left\langle \left| \frac{\partial H'}{\partial t} \right| \right\rangle$ with type (1) dependence is zero when $E_{DC} = 0$, no full frequency resonances will be observed at zero field.

CASE II: The Quadrupole energy is not included. This is expected to be a good approximation in the case where the energy level splitting is much greater than the splitting due to the quadrupole interaction. The Hamiltonian is

$$(44) \qquad H = \frac{h^2}{2A} \vec{J}^2 - \vec{\mu}\,(\vec{E}_{DC} + \vec{E}_{RF} \cos \omega t)$$

E_{RF} has components parallel and perpendicular to E_{DC}, which defines the z direction. The parallel par. have matrix elements k_{+1} or k_{-1} (see (4) and (5)). The matrix elements of $\langle J', m \,|\, \vec{\mu}\cdot\vec{E}_y \,|\, J, m \rangle$ vanish except for $\langle J \pm 1, m \pm 1 \,|\, \vec{\mu}\cdot\vec{E}_y \,|\, J, m \rangle$.

$\ell_{\pm 1}$ is defines as

$$\ell_{\pm 1} = \frac{\langle J \pm 1, m \pm 1 \,|\, \vec{\mu}\cdot\vec{E}_{RF_y} \,|\, J, m \rangle}{E_{RF_y}\,(E_{J\pm 1} - E_J)} \qquad (45)$$

$C_{J,m}$ is defined as

$$C_{J,m} = \sum_{J,m}{}' \left(\ell_{+1} + \ell_{-1} \right) \tag{46}$$

The energy, in the adiabatic approximation, by the same methods that led to (9) is

$$W = E_J + b_{Jm} \left(E_{DC} + E_{RF_z} \cos\omega t \right)^2 + C_{Jm} E_{RF_y}^2 \cos^2\omega t .$$

It can be shown that

$$\int \Theta_{\ell+1,m+1} \sin\theta \, \Theta_{\ell,m} \, d\tau = \int \Theta_{\ell+1,m+1} \cos\theta \, \Theta_{\ell,m} \, d\tau .$$

that $C_{JM} = b_{Jm}$ (see 7a) thus

$$W_{J,m} = E_J + b_{Jm} \left\{ E_{DC}^2 + 2 E_{DC} E_{RF_z} \cos\omega t + \left(E_{RF_z}^2 + E_{RF_y}^2 \right) \cos^2\omega t \right\}$$

$$= E_J + b_{Jm} E_{DC}^2 + B(E_{RF}) \cos 2\omega t + K(E_{RF}, E_{DC}) \cos\omega t . \tag{47}$$

The exponent in (12) is thus

$$-\frac{i}{\hbar} \int_{t_0}^{t} \Big\{ (b_{Jm'} - b_{Jm}) E_{DC}^2 + \left(B'(E_{RF}) - B(E_{RF}) \right) \cos^2\omega t + \left(K'(E_{DC}, E_{RF}) - K(E_{DC}, E_{RF}) \right) \cos\omega t \Big\} dt .$$

which on integration gives

$$-\frac{i}{\hbar} \left[(b_{Jm'} - b_{Jm}) E_{DC}^2 (t - t_0) + (B' - B) \left(\frac{t}{2} + \frac{\sin 2\omega t}{4\omega} \right) + \frac{(K' - K)}{\omega} \sin\omega t \right]_{t_0}^{t}$$

so that the exponential term is

$$M(t_0) \exp \left[-\frac{i}{\hbar} \left((b_{Jm'} - b_{Jm}) E_{DC}^2 t + (B' - B) \left(\frac{t}{2} + \frac{\sin 2\omega t}{4\omega} \right) + \frac{(K' - K)}{\omega} \sin\omega t \right) \right] \tag{48}$$

The transitions to be considered do not involve changes in E_J. Since $E_{DC} \gg E_{RF}$, a good approximation for the denominator in (12) will be (compare 15a)

$$(b_{Jm'} - b_{Jm}) E_{DC}^2 \tag{49}$$

The first order wave function is

$$u_{J,m}(t) = \Phi_J + k_{\pm 1} \Phi_{J\pm 1, m} (E_{DC} + E_{RF_z} \cos\omega t) + l_{\pm 1} \Phi_{J\pm 1, m\pm 1} (E_{RF_y} \cos\omega t) \tag{50}$$

The time dependence of $\langle J',m' \left| \frac{\partial H'}{\partial t} \right| J,m \rangle$ will be investigated.

$$\frac{\partial H'}{\partial t} = -\mu E_{RF_z} \cos\theta\, \omega \sin\omega t - \mu E_{RF_y} \sin\theta \sin\phi\, \omega \sin\omega t.$$

The initial state will be taken as J,m. The biggest term giving a $\Delta m = \pm 1$ transition involves (A) in the initial (b) in the operator and (B) in the final state, and has $\omega \sin\omega t$ time dependence, (type 1). It will be seen that the other terms are much smaller than this one if

$$E_{DC} \gg E_{RF}$$

If $E_{DC} \gtrsim E_{RF}$ terms with type 2 time dependence,

$\cos\omega t \sin\omega t$, ($\langle (C) \mid (b) \mid (A) \rangle$ or $\langle (D) \mid (a) \mid (A) \rangle$).

will be of the same order of magnitude as the type 1 terms.

Under the same conditions, terms such as

$$\langle (D) \mid (b) \mid (A) \rangle$$

involving $m = \pm 2$ and having type 2 time dependence will be important. Combining terms (51), (49) and type 1 or type 2 matrix elements of $\frac{\partial H'}{\partial t}$ the expansion coefficient (12) has the time dependence

$$a_{J,m'} \propto \int_{t_0}^{t} \frac{M(t_0)}{(b_{J,m'} - b_{J,m}) E_{DC}^2} \exp\left[-\frac{i}{\hbar}\left\{(b_{J,m'} - b_{J,m}) E_{DC}^2 t + (B' - B)\left(\frac{t}{2} + \frac{\sin 2\omega t}{4\omega}\right) + \frac{k' - k}{\omega} \sin \omega t\right\}\right] \begin{Bmatrix} \sin \omega t \\ \sin \omega t \cos \omega t \end{Bmatrix} dt \tag{51}$$

The exponential may be expanded using (20). Only the case where J_0 is the most important term will be considered. Thus $\frac{(B'-B)}{4\omega}$ or $\frac{(k'-k)}{\omega} \ll 1$. This condition is satisfied well so long as $E_{DC} \gg E_{RF}$.

The approximate expansion of (51) gives

$$a_{J,m\pm 1} \propto \int_{0}^{t} \frac{M(t_0)}{(b_{J,m\pm 1} - b_{J,m}) E_{DC}^2} \exp\left[-\frac{i}{\hbar}\left\{(b_{J,m\pm 1} - b_{J,m}) E_{DC}^2 t + (B' - B)\frac{t}{2}\right\}\right] \begin{Bmatrix} \sin \omega t \\ \sin \omega t \cos \omega t \end{Bmatrix} dt \tag{52}$$

As in the previous cases, the integration leads to "resonance" denominators, the type 1 time dependence gives

$$\nu = \frac{1}{h}\left[(b_{J,m+1} - b_{J,m}) E_{DC}^2 + \frac{(B' - B)}{2}\right] \tag{53}$$

so that the frequency shift due to the radio frequency terms, (B' - B) are

$$\Delta\nu = \frac{1}{2h}\left(b_{J,m\pm1} - b_{J,m}\right)\left(E_{RF_z}^2 + E_{RF_y}^2\right)$$
$$= \frac{1}{2h}\left(b_{J,m\pm1} - b_{J,m}\right)E_{RF}^2 \qquad (54)$$

As before, the type 2 time dependence yields the half-frequency resonances. The shift of frequency in the doubled half frequency is the same as (54). It will be noted that the expansion coefficient, a, is large only when $\left\langle\left|\frac{\partial H'}{\partial t}\right|\right\rangle$ is large. Thus $\Delta m = \pm 1$ or $\Delta m = \pm 2$ half frequency resonances occur only when $E_{RF} \gtrsim E_{DC}$. If $E_{DC} \lesssim E_{RF}$, Bessel functions of higher order than J_o must be included in the expansion of (51). If these terms are included other time dependences of the bracketed expression (52) will appear, such as sin $2\omega t$, sin $2\omega t$ cos $2\omega t$, etc. Evaluation of the integrals to give $a_{m \pm 1}$ in these cases shows that the other types of resonances will arise besides those already considered. These resonances are of the general type

$$\nu = \frac{1}{h}\left[\left(b_{J,\,m\pm1} - b_{J,m}\right)E^2_{DC} + \frac{B' - B}{2}\right] \pm h\nu$$

$$\text{or} \quad m\nu = \frac{1}{h}\left[\left(b_{J,\,m\pm1} - b_{J,m}\right)E^2_{DC} + \frac{B' - B}{2}\right].$$

and may lead to "multiple" or "fractional" frequency resonances of various types. Some of these possibilities are mentioned in the text.

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