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Shapes of Molecular Beam Resonances

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Abstract

A procedure is described for rapid digital computer calculations of the shapes of molecular beam resonances. Resonances are calculated under a wide variety of circumstances. Results are presented which show that variations in the amplitudes of the oscillatory fields change the appearance of the resonance and may even invert it, but the mid-point of the resonance remains at the Bohr frequency. Likewise variations of the fixed field amplitude between oscillatory field regions do not shift the resonance frequency provided the average values of the energy levels equal the uniform values in the oscillatory regions. On the other hand, it is shown that perturbations by neighboring resonances, perturbations by extraneous oscillatory fields, variations of fixed field amplitudes in regions of non-vanishing oscillatory fields, and phase shifts all produce shifts in the resonance frequency whose magnitudes ordinarily depend on the amplitude of the oscillatory field. It is pointed out that there are many ways in which irregularities of the above nature can be achieved accidentally: a change in direction of the oscillatory field, for example, produces an effective phase shift, modulation of the oscillatory field produces extraneous frequencies, etc. General expressions are given for the shift in resonance frequency to be expected with neighboring resonances and with extraneous oscillatory fields.

I. Introduction

Ordinarily in a molecular or atomic beam resonance experiment one measures a resonance curve and then assumes that the mid-point of the resonance is at the Bohr frequency $\nu_0 = (W_q - W_p)/h$. In any precision experiment it is therefore important to know the conditions that can significantly distort the resonance so that the mid-point becomes other than the Bohr frequency.

Unfortunately most of the features of an experiment that distort a resonance also make it difficult or impossible to solve the probability amplitude equations. However, in a recent report, the author[1] has described two procedures for digital computer calculations of the shapes of molecular beam resonances with non-uniform oscillatory fields. One of these applies when only two energy levels and a single oscillatory perturbation is involved. The other involves a much longer calculation but applies with three energy levels and up to nine different perturbations between the energy levels. Unfortunately, the expense of calculations with the latter procedure is sufficiently great that calculations have been made for only a few cases. In the present report a procedure is described which makes possible rapid calculations of problems with three energy levels and several perturbations.

Results of calculations are presented in subsequent sections which show the effects of variations in the oscillatory field amplitudes, perturbations by neighboring resonances, perturbations by oscillatory fields, variations in the fixed field amplitudes, and phase shifts of the oscillatory fields. Various means by which such irregularities can accidentally occur are described.

II. Method of Calculation

Consider a system with three eigenstates, p, q, and r of the Hamiltonian $\mathscr{H}_0$. Let the system be acted upon by the additional time dependent perturbation V and let $\langle p|t \rangle$ represent the transformation function between the eigenvector $|p\rangle$ of the pth eigenstate of $\mathscr{H}_0$ and the general time dependent state vector $|t\rangle$ of the system with $\mathscr{H} = \mathscr{H}_0 + V$. Then,[1]

$$i\hbar \frac{d}{dt}\langle p|t \rangle = \langle p|\mathscr{H}_0|p \rangle\langle p|t \rangle + \langle p|V|p \rangle\langle p|t \rangle +$$
$$+ \langle p|V|q \rangle\langle q|t \rangle + \langle p|V|r \rangle\langle r|t \rangle \qquad (1)_{\text{cyc}}$$

together with the two equations obtained by cyclic permutations of p, q, r as indicated by the subscript cyc behind the equation number. A wide variety of relevant problems can be included if $\mathscr{H}_0$ and V are restricted to forms which provide Hermitian matrix elements such that

$$\langle p|\mathscr{H}_0|p \rangle/\hbar = a_p$$
$$\langle p|V|p \rangle/\hbar = 0$$
$$\langle p|V|q \rangle/\hbar = b_r \exp i(\omega_{br}t + \delta_{br}) + c_r \exp i(\omega_{cr}t + \delta_{cr})$$
$$\langle p|V|r \rangle/\hbar = b_q \exp i(-\omega_{bq}t - \delta_{bq}t) + c_q \exp i(-\omega_{cq}t - \delta_{cq})$$

$$(2)_{\text{cyc}}$$

where a_p, b_p, δ_{bp}, δ_{cp}, etc., are real constants that are not explicit functions of the time, although they may vary along the path of the beam. The quantities ω_{bp}, etc., correspond to the various frequencies of the perturbations and are assumed to be unaltered throughout the transition region.

The advantages of the rapid single perturbation procedure can be achieved with several levels by replacing the actual problem by one which simulates it by a number of iterative steps such that in each step only a single perturbation is present while successive steps may have different perturbations between different energy levels so that the average over several adjacent steps is equivalent to the actual problem being simulated. Then if for a step of duration Δ beginning at time t the perturbation is b_r between levels p and q while all the other perturbations vanish in that step, the probability amplitudes after that step become[1,2]

$$\langle p|t+\Delta\rangle_R = F'_+ \langle p|t\rangle_R + G'_+ \langle q|t\rangle_R + H'_+ \langle p|t\rangle_I + I'_+ \langle q|t\rangle_I$$

$$\langle p|t+\Delta\rangle_I = -H'_+ \langle p|t\rangle_R - I'_+ \langle q|t\rangle_R + F'_+ \langle p|t\rangle_I + G'_+ \langle q|t\rangle_I$$

$$\langle q|t+\Delta\rangle_R = G'_- \langle p|t\rangle_R + F'_- \langle q|t\rangle_R + H'_- \langle p|t\rangle_I + I'_- \langle q|t\rangle_I \quad (3)$$

$$\langle q|t+\Delta\rangle_I = -H'_- \langle p|t\rangle_R - I'_- \langle q|t\rangle_R + F'_- \langle p|t\rangle_I + G'_- \langle q|t\rangle_I$$

$$\langle r|t+\Delta\rangle_R = \cos (a_r\Delta)\langle r|t\rangle_R + \sin (a_r\Delta)\langle r|t\rangle_I$$
$$\langle r|t+\Delta\rangle_I = -\sin (a_r\Delta)\langle r|t\rangle_R + \cos (a_r\Delta)\langle r|t\rangle_I$$

where the subscripts R and I indicate real and imaginary components and where

$$F_\pm = \cos\,[(\pm\omega - a_p - a_q)\Delta/2]\,\cos A\Delta/2 +$$
$$\pm (\omega + a_p - a_q)\sin [(\pm\omega - a_p - a_q)\Delta/2]\,[\sin A\Delta/2]/A$$
$$G_\pm = 2b_r \sin [\pm\omega(t+\Delta/2) - (a_p + a_q)\Delta/2 \pm \delta]\,[\sin A\Delta/2]/A$$
$$H_\pm = -\sin [(\pm\omega - a_p - a_q)\Delta/2]\cos A\Delta/2 + \qquad (4)$$
$$\pm (\omega + a_p - a_q)\cos [(\pm\omega - a_p - a_q)\Delta/2]\,[\sin A\Delta/2]/A$$
$$I_\pm = 2b_r \cos [\pm\omega(t+\Delta/2) - (a_p + a_q)\Delta/2 \pm \delta][\sin A\Delta/2]/A$$

with

$$A = [(a_q - a_p - \omega)^2 + (2b_r)^2]^{\frac{1}{2}}. \qquad (5)$$

In each successive step only a single perturbation is present so that in each step relations similar to the first four of Eq. (3) give the transformation functions of the two levels affected by the perturbation while the last two equations apply to the unperturbed level.

By successive applications of Eq. (3) the final probability amplitudes can be obtained in terms of the initial amplitudes $\langle p|0 \rangle$, etc. This iterative procedure has been programmed for the Harvard Univac I digital computer. In the program the fifteen quantities a_p, b_p, c_p, δ_{bp}, δ_{cp}, etc., may vary along the beam path in an arbitrary fashion provided only that their values can be satisfactorily inferred by linear interpolation between values tabulated at twenty arbitrarily chosen points along the beam. For each resonance frequency the transition probability can be calculated at as many different velocities as desired and these can be averaged with arbitrarily chosen weights to provide an average over any desired probability distribution.

It should be noted that when the above procedure is applied, for example, to the separated oscillatory field method the effective length of the short oscillatory field regions is the sum of the lengths of only those iterative steps in which the particular perturbation of concern occurs in the simulating problem. In any case in which there is reason to doubt the validity of the simulation, a few critical points can be calculated both by the present fast method and the previously described[1] slow but direct method; a comparison of the results indicates the applicability of the simulating problem. In all cases so far for which the same problem has been calculated by both the rapid and the slow method, the agreement has been excellent.

III. Variations in Amplitudes of Oscillatory Perturbations

The above procedure has been used to calculate the effect of unequal amplitudes of the oscillatory fields in the separated oscillatory field resonance method. Fig. 1 shows the resonance to be expected when the first oscillatory field is three times the optimum value while the second is at the optimum value. The shape of the resonance is greatly altered by these oscillatory field amplitudes, in fact, the resonance is converted from a transition maximum to a transition minimum. However, despite this marked change in character, this inequality of oscillatory field amplitudes does not produce a shift in the resonance frequency; the Bohr frequency is still at the point of symmetry of the curve even though it is a minimum instead of a maximum.

Effects obtainable with equal but non-optimum values of the two oscillatory fields have been discussed by the author in earlier articles.[1-4] With excessively weak fields the resonance is weaker but also of a

narrower half width.[2] With excessive oscillatory perturbations $2b$ the resonance width is not importantly changed but two extraneous velocity independent resonances are produced at the frequencies $\nu_0 \pm 2bl/(\pi L)$ where l is the length of each of the two oscillatory field regions and L is the distance between them. The effects of gradual application and removal of the oscillatory fields have also been discussed previously.[1]
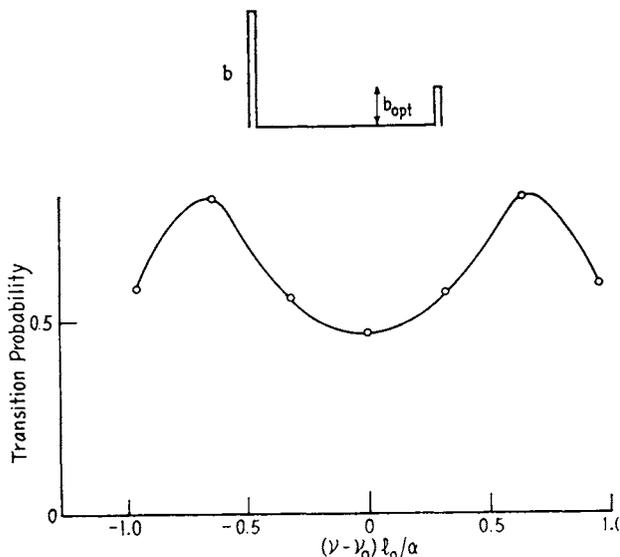

Fig. 1. Resonance shape for separated oscillatory fields with the first oscillatory field three times optimum and the second at optimum value. The amplitude of the perturbation as a function of the distance along the beam is shown in the upper illustration. The transition probability is plotted as a function of frequency in the lower curve.

IV. Variations in Magnitude of the Fixed Field

Variations of the magnitude of the fixed field between (but not in) the oscillatory field regions do not ordinarily distort a molecular beam resonance provided that the average Bohr frequency equals the value of the Bohr frequency in the oscillatory field regions.

However, if the preceding conditions are not attained or if the magnitude of the fixed field varies within the oscillatory field regions, the resonance may be seriously distorted. Fig. 2 shows the distortion when the static field varies in the oscillatory field region. The separated oscillatory field resonance is plotted for two different oscillatory field amplitudes. It is to be noted that the apparent resonance position

shifts as a function of the oscillatory field amplitude. The physical reason for this power shift is that the effective field is averaged over slightly different regions with different oscillatory power.
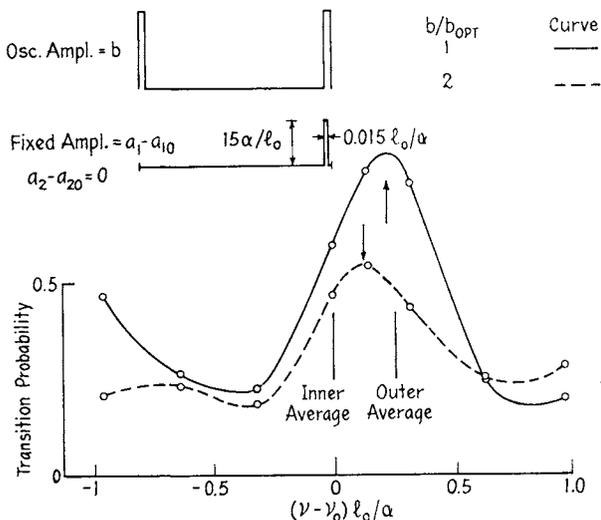

Fig. 2. Distortion of resonance by variation of the fixed field magnitude within the oscillatory field region. The nature of the assumed variation along the length of the beam is shown at the top of the figure and the resonance curve at the bottom. The "inner average" is the average Bohr frequency excluding the oscillatory field region whereas the "outer average" includes this as well.

If the magnitude of the fixed field in a single oscillatory field experiment varies importantly the resonance pattern may be tremendously distorted; one or more extraneous transition maxima can easily be produced in this manner as discussed previously.[2]

V. Distortion by Neighboring Resonances

In systems involving more than two energy levels, the same oscillatory field which produces the desired transition between energy levels p and q may also provide perturbations between level p and another level r, or between s and q. One consequence of this is the production of multiple quantum transitions.[2,5,6] Another consequence, however, is that the presence of this undesired additional perturbation will shift the apparent position of the $p-q$ resonance.

The problem of the simultaneous presence of the three oscillatory perturbations in each of the two oscillatory field regions of the separated

oscillatory field method has not been solved in general. However, a theoretical expression can be obtained for the very closely related problem of a molecule which first for a time τ passes through a region where there is the desired perturbation between levels p and q, then for a time T_1 the molecule is in a region of length l_1 in which the p–r and s–q perturbations are excited, then for a time T_2 in a region of length l_2 with no oscillatory perturbations, then for a time T_3 in a region of length l_3 with the p–r and s–q perturbations excited, and finally for a time τ in a region in which only the desired p–q perturbation is excited If $T_1 = T_3 = \tau$ this problem is clearly closely related to the above general problem except that the effects of the extra perturbations are overestimated by a factor of the order of 2 since the extraneous oscillatory perturbations are more effective when they occur between the two p–q transition regions rather than within these two regions.

This problem can be solved in a fashion similar to that of earlier papers[7,8] on the effects of extraneous oscillatory fields provided one assumes for simplicity that the duration τ (but not $b\tau$) of the desired perturbation is small and that the magnitudes b_{pr} and b_{qs} of the undesired perturbations are small compared to the magnitudes of the differences $\omega_{0pr} - \omega_0$ and $\omega_{0sq} - \omega_0$ where ω_0 is the Bohr angular frequency $(W_q - W_p)/\hbar$ of the desired transition between levels p and q, while ω_{0pr} is the Bohr angular frequency between levels p and r and ω_{0sq} is between levels s and q. With these assumptions it can be shown that the experimental resonance angular frequency ω_e will be shifted by an amount

$$\delta\omega = \omega_e - \omega_0 = \frac{1}{2}\sum_r{}'' \{\omega_{0pr} - \omega_0\}\{[1 + (2b_{pr})^2/(\omega_{0pr} - \omega_0)^2]^{\frac{1}{2}} - 1\}\beta +$$

$$\tag{6}$$

$$+ \frac{1}{2}\sum_s{}'' \{\omega_{0sq} - \omega_0\}\{[1 + (2b_{sq})^2/(\omega_{0sq} - \omega_0)^2]^{\frac{1}{2}} - 1\}\beta$$

where

$$\beta = (l_1 + l_3)/(l_1 + l_2 + l_3) \tag{7}$$

and where Σ'' indicates that the summation does not include $r = p$ or q.

If, as in the actual case, all perturbations are simultaneously present for times τ in regions of length l on each side of a perturbation free region of length L, the shift should be similar to the above except that

the undesired perturbation will be somewhat less effective. It would appear to be reasonable to assume that Eq. (6) should apply in this case as well with β however being determined approximately by

$$\beta = \tfrac{1}{2}(2l)/L = l/L \tag{8}$$

When

$$|\,\omega_{0pr} - \omega_0\,||\gg|\,2b_{pr}\,|,$$

Eq. (6) and (8) become

$$\delta\omega = \tfrac{1}{4}(l/L)\left[\sum_r{}'' (2b_{pr})^2/(\omega_{0pr} - \omega_0) + \sum_s{}'' (2b_{sq})^2/(\omega_{0sq} - \omega_0)\right] \tag{9}$$

The validity of the shifts predicted by Eqs. (6) and (8) has been confirmed by the use of the Univac procedure described in Section II to calculate the shift of the resonance frequency by a neighboring resonance. The Univac calculations can also be extended to conditions for which Eq. (6) is not valid. In the course of these calculations it was found that when the results were averaged over only 5 velocities they varied rather randomly and were very sensitive to the exact velocity distribution. It soon became apparent that this was a genuine effect with a limited discrete velocity distribution and with two or more resonances overlapping within the broad pedestal which characterizes the separated oscillatory field method. This velocity sensitivity arises from the fact that with a single velocity the desired resonance occurs in a region where there are still large sharp subsidiary resonances from the undesired resonance since it is only the velocity distribution which averages these out in the separated oscillatory field method. Furthermore, with large perturbation amplitudes sharp interference effects in the magnitude of the shifts should occur even though they do not occur in Eq. (6) which is based on the assumption $|b_{pr}| \ll |\omega_{0pr} - \omega_0)|$. Since these effects are large, an average over only 5 velocities is inadequate and an average over even 20 velocities provides only moderate accuracy. Similar fluctuations should occur in experiments with severely limited velocity distributions. Novick[9] has reported to the author that he has found such phenomena in his resonance experiments with approximately a single velocity.

The results of the calculations are shown in Fig. 3. In addition to the points calculated by the general Univac program the shifts to be expected by Eqs. (6) and (8) are shown as the full curve. There is general agreement as to the magnitude of the effect, but for the reasons discussed in the preceding paragraph, the accuracy of the calculation

is not high since the results were averaged only over twenty discrete velocities.

It should be noted that a perturbation at a given frequency above ν_0 produces a shift equal and opposite to that of an equal perturbation the same frequency below ν_0.   Often neighboring perturbations occur in such mutually compensating pairs. However, before assuming that the compensation is complete, one must confirm that no asymmetry is accidentally produced by slight inequalities of the perturbations or by inequalities in the populations of the molecular states in the beam.
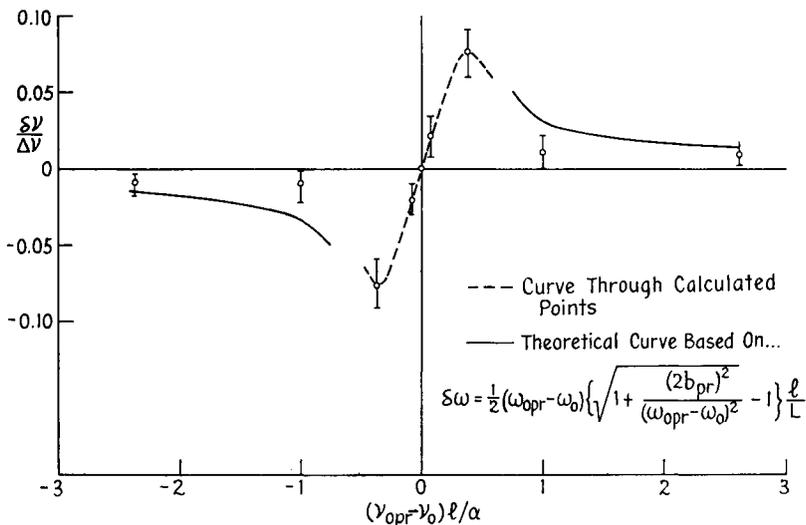

Fig. 3. Shift of resonance frequency by presence of a neighboring resonance. The indicated points are those calculated by the digital computer. The indicated uncertainty arises for the reasons discussed in Section V. The full curve corresponds to Eqs. (6) and (8).

From Eq. (9) it is apparent that if neighboring resonances are a source of major trouble, the shift from this source can be diminished by increasing the length l of the oscillatory field regions; for maximum transition probability $2b_{pr}$ is proportional to $1/l$ so $\delta\omega$ in Eq. (9) is proportional to $1/l$. This can be done up to the limit of the apparatus becoming a single oscillatory field experiment. It should be noted that this increase will accentuate other resonance distortions, such as the one discussed in the preceding section.

VI. Perturbations at Two or More Frequencies

In earlier papers[7,8] the effects of one or more extraneous oscillatory fields have been discussed. However, the earlier discussions were not

directly applicable to perturbations in the oscillatory field regions of the separated oscillatory field method since it was assumed that the extraneous oscillatory fields occurred only in the entire intermediate region. However, the theoretical problem is essentially the same as that for neighboring resonances as discussed in the preceding section.

In the separated oscillatory field case, let ω_e be the experimental resonance transition frequency between the two levels p and q. Let the level p be perturbed to the state r at the frequency ω_i by the matrix element

$$_iV_{pr} = \hbar_i b_{pr} e^{i(\omega_i t + i\varphi_r)} \tag{10a}$$

while q is perturbed by

$$_iV_{sq} = \hbar_i b_{sq} e^{i(\omega_i t + \varphi_s)} \tag{10b}$$

Assume that these perturbations occur only in the two separated oscillatory field regions. Then the discussion of the preceding section may easily be combined with that of the earlier paper to show that the shift in angular frequency is

$$\delta\omega = \omega_e - \omega_0 = \sum_i \{\omega_0 - \omega_i\}\{[1 + (2_i b_{pq})^2/(\omega_0 - \omega_i)^2] - 1\}\beta +$$

$$\tag{11}$$

$$+ \frac{1}{2}\sum_i\sum_r{}'' \{\omega_{0pr} - \omega_i\}\{[1 + (2_i b_{pr})^2/(\omega_{0pr} - \omega_i)^2] - 1\}\beta +$$

$$+ \frac{1}{2}\sum_i\sum_s{}'' \{\omega_{0sq} - \omega_i\}\{[1 + (2_i b_{sq})^2/(\omega_{0sq} - \omega_i)^2] - 1\}\beta$$

The value of β is given in Eq. (8) and the region of validity of this formula is similar to that discussed for Eq. (6).

It is apparent from a comparison of Eqs. (11) and (6) that the effects of additional oscillatory fields and of additional resonances are closely similar. Thus with two energy levels and a single additional oscillatory field, the resonance will be shifted by just twice the amount shown in Fig. 3. Experimental studies of such shifts have been reported previously.[4]

It should be noted that there are many different ways in which an oscillatory field of a different frequency can occur. As first pointed out by Bloch and Siegert[10] the use of an oscillatory instead of a rotating field produces a perturbation at frequency $-\omega_0$. Alternatively if the

fixed field varies its direction in space the result appears as an oscillatory perturbation to the moving molecule. Likewise if the direction of the oscillatory field rotates in space it will appear as a different frequency to the molecule. Furthermore, the basic oscillatory current supplied may easily contain large components at different frequencies. Another important source of extraneous frequencies is that the oscillating field is ordinarily modulated either to detect or to display the resonance. The side band frequencies from the modulation can distort the resonance somewhat; although this distortion is often symmetrical about the resonance frequency it will not be so if one side band is more effective than its symmetrical opposite.

VII. Phase Shifts

Some of the principal sources of asymmetries and frequency shifts in resonance experiments are relative phase shifts of the oscillatory field in different regions. Although the present discussion primarily concerns the separated oscillatory field method, it should be noted that phase shift troubles are ordinarily worse with the single oscillatory field method since there is a much larger region throughout which the phases must be known.

It should be emphasized that there are many different sources of effective phase shifts. The simplest is an erroneous relative phase adjustment of the two oscillatory fields. Theoretical expressions have been published[11] for quantitative calculations of the effect of such simple phase shifts. If any running waves exist in portions of the apparatus through which the beam passes there will be a continuously varying phase shift. Likewise, in a resonant microwave cavity resistive losses can produce phase shifts. Rotation of the direction of the oscillatory field, as in the Millman effect[12] at the ends of the oscillatory fields, produces a phase shift of the rotating component of the field that is effective in producing the transitions.

The effects of both constant and varying phase shifts have been calculated under a wide variety of circumstances. Some of the results are shown in Fig. 4. At the top of the figure is an extreme example with a large amplitude at a different phase. The results show that there is no displacement of the resonance for a phase shift of 0° or 180° but that there is a large shift for a 90° phase shift. The middle of the figure corresponds to a long wavelength running wave. The bottom portion corresponds to smaller amplitudes of running waves. For symmetry of the amplitudes about the center of the apparatus ($\lambda = \mu$ in the figure) the effects cancel. For $\lambda \neq \mu$ a shift occurs which is much less for a short wavelength running wave than a long one. The
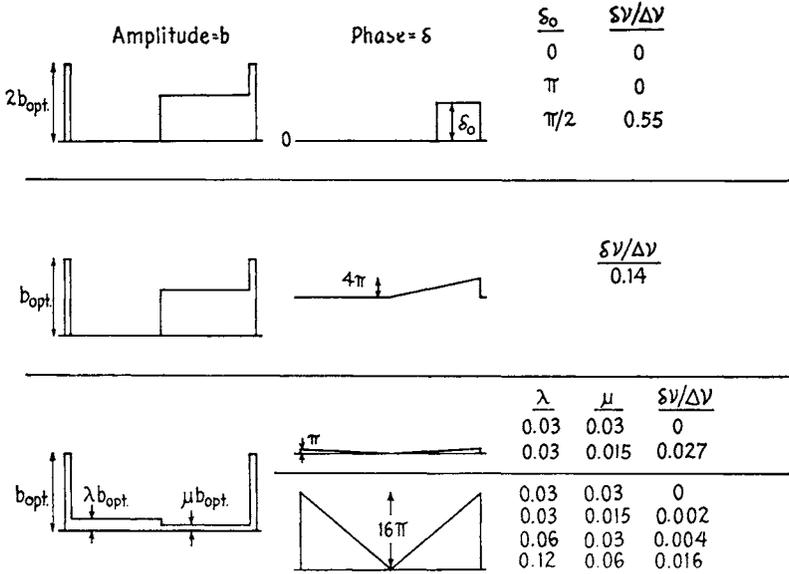
Fig. 4. Effects of phase shifts. The amplitudes of the perturbations and the phase shifts as functions of the distance along the beam are shown in the different cases on the left portion of the figure. The magnitudes of the phase shifts are listed in the tables on the right. $\delta\nu/\Delta\nu$ is the ratio of the shift in resonance frequency to the full half width of the resonance.
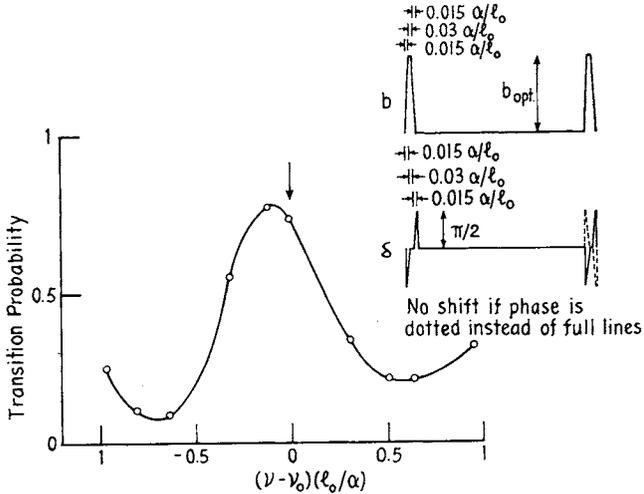

Fig. 5. Effects of phase shifts due to rotation of the direction of oscillatory field at ends of oscillatory field regions. The natures of the assumed amplitudes and phase shifts are indicated schematically at the top of the figure.

condition with $\lambda = 0.03$ and $\mu = 0.015$ for which $\delta\nu/\Delta\nu = 0.002$ is one that might have occurred in the early models of the National Company Atomichron.

In Fig. 5 the shape of the resonance is calculated for a case in which a large rotation of the direction of the oscillatory field occurs on entering and leaving the oscillatory field regions, as in the Millman effect. It can be seen that an appreciable shift occurs. The assumed case is an extreme one; the magnitudes of the frequency shifts are ordinarily much smaller than those assumed.

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REFERENCES

[1] N. F. Ramsey, *Phys. Rev.* (to be published).
[2] N. F. Ramsey, "Molecular Beams," Oxford University Press, 1955.
[3] N. F. Ramsey, *Phys. Rev.* **78**, 695 (1950).
[4] H. Lewis, A. Pery, W. Quinn and N. F. Ramsey, *Phys. Rev.* **107**, 446 (1957).
[5] P. Kusch, *Phys. Rev.* **93**, 1022 (1954).
[6] H. Salwen, *Phys. Rev.* **99**, 1274 (1955).
[7] N. F. Ramsey, *Phys. Rev.* **100**, 1191 (1955).
[8] J. Winter, *C.R. Acad. Sci., Paris.* **241**, 600 (1955).
[9] R. Novick, Private communication and report at Brookhaven Molecular Beam Conference (1957).
[10] F. Bloch and A. Siegert, *Phys. Rev.* **57**, 522 (1940).
[11] N. F. Ramsey and H. B. Silsbee, *Phys. Rev.* **84**, 506 (1951).
[12] S. Millman, *Phys. Rev.* **55**, 628 (1939).