Frequency Modulation in Microwave Spectroscopy

ROBERT KARPLUS*
Mallinckrodt Chemical Laboratory, Harvard University, Cambridge, Massachusetts
(Received December 24, 1947)

The absorption coefficient of a gas is related to the density matrix of that gas. The density matrix is obtained formally from its equation of motion, which takes into account a possible time-dependence of the resonant frequency of the molecule and of the frequency of the exciting radiation. The shape of the absorption line is calculated explicitly in a variety of cases. For low frequency modulation, it reduces to Lorentz's expression with a time-dependent frequency difference. For high frequency sinusoidal modulation, resolved sidebands to the resonant frequency are obtained. Finally, for square wave modulation, the line shape is again given by Lorentz's expression with a varying frequency difference, except that damped oscillations are superimposed on the expected square wave time-dependence. In this case, the deviations from the Lorentz expression are no greater than about ten percent for the zero frequency and fundamental frequency components, if the modulation frequency is less than one-half of the half-width of the absorption line.

I. GENERAL TREATMENT

MODIFICATIONS of the theory of collision-broadened lines of Van Vleck and Weisskopf[1] have been discussed in the paper preceding this.[2] There the theory has been extended to include the effects of the induced transitions on the Boltzmann distribution. In this paper, effects of a time-dependent radiation frequency or resonance frequency will be discussed. Since almost all microwave spectroscopes described in the literature use some such modulation,[3] it seemed worth while to examine the conditions under which easily interpretable results might be obtained. The notation of reference (2) will be adopted. The radiation will be considered sufficiently weak so as not to affect the Boltzmann distribution appreciably, and frequency modulation effects will be of the order of the line width, which in turn is much smaller than the resonant frequency.

The argument in *I* leading to Eq. (14) can now be repeated, provided the Hamiltonian is modified so as to include frequency modulation of both molecule and radiation:

$$\mathbf{H}(t)=\mathbf{H}_0(t)-\mathbf{p}\cdot F\cos\left[\int_0^t \omega(t')dt'\right]$$
$$=\bar{\mathbf{H}}_0+[\mathbf{H}_0(t)-\bar{\mathbf{H}}_0]+\mathbf{V}\cos\left[\int_0^t \omega(t')dt'\right]. \quad (1)$$

$\bar{\mathbf{H}}_0$ is written for some value of the operator $\mathbf{H}_0(t)$. The matrix elements will be calculated in the representation based on the eigenfunctions of $\bar{\mathbf{H}}_0$. Equation (14) of *I* then becomes

$$\left[\frac{\partial}{\partial t}+i\omega_{mn}(t)+1/\tau\right]D_{mn}(t)=-\frac{\partial}{\partial t}[\rho_0(t)]_{mn}, \quad (2)$$

where

$$\hbar\omega_{mn}(t)=[\mathbf{H}_0(t)]_{mm}-[\mathbf{H}_0(t)]_{nn}$$

and the terms in which $\mathbf{D}$ is multiplied by the magnitude of the field have been neglected. After multiplication by

$$\exp\left[i\int_0^t \omega_{mn}(t')dt'+t/\tau\right],$$

Eq. (2) above may be integrated to give

$$D_{mn}(t)=-[\rho_0(t)]_{mn}+\int_0^t dt'[\rho_0(t')]_{mn}[i\omega_{mn}(t)+1/\tau]\times\exp\left[i\int_t^{t'}\omega_{mn}(t'')dt''-(t-t')/\tau\right], \quad (3)$$

the right side of this equation has been integrated

* United States Rubber Company predoctoral fellow.
[1] J. H. Van Vleck and V. F. Weisskopf, Rev. Mod. Phys. 17, 227 (1945).
[2] Robert Karplus and Julian Schwinger (henceforth referred to as I), Phys. Rev. 73, 1020 (1948).
[3] See, for example, (a) W. E. Good, Phys. Rev. 70, 213; (b) C. H. Townes, Phys. Rev. 70, 665 (1946); (c) R. H. Hughes and E. B. Wilson, Jr., Phys. Rev. 71, 562 (1947); (d) B. P. Dailey, Phys. Rev. 72, 84 (1947); (e) R. J. Watts and Dudley Williams, Phys. Rev. 72, 1122 (1947); (f) W. D. Herschberger (to be published).

by parts, and it is assumed that a long time has elapsed, $t \gg \tau$.

As is shown in I, the matrix $\varrho_0(t)$ may be approximated by

$$[\rho_0(t')]_{mn} = \rho_m{}^0\delta_{mn} + (\rho_m{}^0 - \rho_n{}^0)V_{mn} \times \cos\left[\int_0^{t'} \omega(t'')dt''\right]/\hbar\bar{\omega}_{mn} + (\rho_m{}^0 - \rho_n{}^0)(H_0(t') - \bar{H}_0)_{mn}/\hbar\bar{\omega}_{mn}, \quad (4)$$

where $\hbar\bar{\omega}_{mn} = (\bar{H}_0)_{mn} - (\bar{H}_0)_{nn}$, and ρ^0 is the equilibrium density matrix associated with the Hamiltonian $\bar{\mathbf{H}}_0$,

$$\varrho^0 = \exp[-\bar{\mathbf{H}}_0/kT]/Sp\{\exp[-\bar{\mathbf{H}}_0/kT]\}.$$

Now it has to be assumed that $[H_0(t) - \bar{H}_0]_{mn}$ contains no terms that oscillate at a frequency close to ω_{mn} and are comparable to V_{mn} in magnitude. This means that an alternating electric field, which may be used to introduce a time dependence into $\mathbf{H}_0(t)$ *via* the Stark effect, has no appreciable Fourier components near the resonance frequency of the molecule. If only resonant contributions to the density matrix are considered, therefore, the last term in Eq. (4) as well as the non-resonant term in the cosine may be neglected, so that the equivalent of *I*, Eq. (21), is

$$\bar{\rho}_{mn}(t) = [\rho_0(t)]_{mn} + D_{mn}(t) = \rho_m{}^0\delta_{mn} + (i/2\hbar)(\rho_m{}^0 - \rho_n{}^0)V_{mn} \times \exp\left[-i\int_0^t \omega(t')dt'\right] \times \int_0^t [(\omega_{mn}(t') - i/\tau)/\bar{\omega}_{mn}] \times \exp\left[i\int_t^{t'} [\omega_{mn}(t'') - \omega(t'')]dt'' - (t-t')/\tau\right]dt'. \quad (5)$$

All other off-diagonal elements of $\varrho(t)$ except $\rho_{nm}(t)$ will make negligible contributions to absorption at the frequency ω if the resonances are widely spaced and non-degenerate. Hence the average dipole moment responsible for this absorption is

$$p(t) = Sp\{\mathbf{p}\bar{\varrho}(t)\} = 2Re\{p_{nm}\bar{\rho}_{mn}(t)\} = Re\left\{(1/\hbar)p_{nm}p_{mn}\cdot F\exp\left[-i\int_0^t \omega(t')dt'\right] \times (\rho_n{}^0 - \rho_m{}^0)f(\omega_{mn},\omega;t)\right\}, \quad (6)$$

where the function $f(\omega_{mn},\omega;t)$ has been written for the integral

$$f(\omega_{mn}, \omega; t) = \int_0^\infty idT \times \exp\left[-i\int_{t-T}^t [\omega_{mn}(t'') - \omega(t'')]dt'' - T/\tau\right], \quad (7)$$

which is obtained from the integral in Eq. (5) by setting $T = t - t'$ and by approximating $(\omega_{mn}(t') - i/\tau)/\bar{\omega}_{mn}$ by unity, again with $t \gg \tau$.

Since the transitions occur independently of each other in the absence of saturation, Eq. (6) may readily be extended to include degenerate or approximately degenerate resonances:

$$p(t) = Re\left\{(1/\hbar)\sum_{\kappa,\lambda}|p_{mn}{}^{\kappa\lambda}|^2F\exp\left[-i\int_0^t \omega(t')dt'\right] \times (\rho_{n\lambda}{}^0 - \rho_{m\kappa}{}^0)f(\omega_{mn}{}^{\kappa\lambda},\omega;t)\right\}; \quad (8)$$

here all p's refer to the component of the dipole moment along the field F and κ and λ are degeneracy indices. Finally, the absorption coefficient is

$$\alpha(t) = 4\pi(\omega/\hbar c)\sum_{\kappa,\lambda}|p_{mn}{}^{\kappa\lambda}|^2(\rho_{n\lambda}{}^0 - \rho_{m\kappa}{}^0) \times Im f(\omega_{mn}{}^{\kappa\lambda},\omega;t). \quad (9)$$

Transitions induced by the modulating fields may somewhat alter the populations of the initial and final states, but they will not affect the function $f(\omega_{mn}{}^{\kappa\lambda},\omega;t)$, which alone determines the shape of the absorption line. Since all essential information is obtained from the study of a simple transition, the degeneracy indices will hereafter be omitted.

The remainder of the paper will be devoted to the evaluation of $Im f(\omega_{mn},\omega;t)$ in various special cases. Periodic modulation alone is of interest in microwave spectroscopy, because only in this case is a quasi-steady state reached eventually. The frequency difference appearing in the function $f(\omega_{mn},\omega;t)$ may then be expressed

$$\omega_{mn}(t)-\omega(t)=\omega' g(\nu t)+\bar{\omega},^{**} \quad (10)$$

with

$$g(x+2\pi)=g(x)\sim\text{unity} \quad (11)$$

and

$$\int_0^{2\pi} g(x)dx=0,$$

so that

$$f(\omega_{mn},\omega;t)=i\int_0^{\infty} dT$$

$$\times\exp\left[-i\omega'\int_{t-T}^{t} g(\nu t')dt'-(i\bar{\omega}+1/\tau)T\right]. \quad (12)$$

It may be noticed that most of the integral comes from values of $T\lesssim\tau$ because of the exponential decrease of the integrand. It should further be pointed out that ω' will be the same for all members of a group of coincident absorption lines if the exciting radiation is frequency modulated, but that ω' will, in general, vary from component to component if the resonance frequency is modulated.

II. SLOW MODULATION

If ν is small compared to $1/\tau$, the function $g(\nu t)$ will change only slightly in a time interval of the order of $1/\tau$. The exponent of the integrand may therefore be replaced by

$$-[i\omega' g(\nu t)+\bar{\omega}+1/\tau]T = -i[\omega_{mn}(t)-\omega(t)]T-T/\tau. \quad (13)$$

Hence

$$Imf(\omega_{mn},\omega;t)=Im\frac{i}{i[\omega_{mn}(t)-\omega(t)]+1/\tau} = \frac{1/\tau}{[\omega_{mn}(t)-\omega(t)]^2+1/\tau^2}. \quad (14)$$

Physically, the line has the same shape as in the absence of modulation; the absorption peak is merely shifted in a straightforward manner, according to the modulation.

This kind of modulation has found most use in microwave set-ups. A low frequency saw-tooth modulation, for instance, is almost universally employed to display the absorption coefficient as a function of frequency (3); the problem of low frequency sinusoidal modulation has recently been discussed by Herschberger (3f); square wave modulation of the resonance frequency by an external electric field has been used to aid detection of absorption lines as well as to study their Stark effect (3d).

** Observe that ν is an angular frequency.

III. WEAK MODULATION††

If the amplitude of the modulation is small compared to the modulation frequency, $\omega'\ll\nu$, the exponential can be expanded to give $(x=\nu t')$

$$f(\omega_{mn},\omega;t)=\int_0^{\infty} idT\left[1-i(\omega'/\nu)\int_{\nu(t-T)}^{\nu t} g(x)dx\right] \times\exp[-(i\bar{\omega}+1/\tau)T], \quad (15)$$

so that

$$Imf(\omega_{mn},\omega;t)=\frac{1/\tau}{\bar{\omega}^2+1/\tau^2}+(\omega'/\nu)Im\int_0^{\infty} dT \times\exp[-(i\bar{\omega}+1/\tau)T]\int_{\nu(t-T)}^{\nu t} g(x)dx. \quad (16)$$

Because it is periodic, $g(x)$ can be expanded in a Fourier series

$$g(x)=\sum_{k=1}^{\infty}[g_{ck}\cos kx+g_{sk}\sin kx]. \quad (17)$$

By carrying out the indicated operations, the shape for any modulation can be obtained (cf. Appendix A). A typical result is that for simple harmonic time dependence, $g(x)=\cos x$. Then

$$Imf(\omega_{mn},\omega;t) = \frac{1/\tau}{\bar{\omega}^2+1/\tau^2}+\frac{\tau^3\bar{\omega}\omega'}{[(\bar{\omega}^2-\nu^2)\tau^2-1]^2+4\bar{\omega}^2\tau^2} \times\left[\nu\tau\frac{[\bar{\omega}^2-\nu^2]\tau^2-3}{\bar{\omega}^2\tau^2+1}\sin\nu t-2\cos\nu t\right]. \quad (18)$$

At low modulation frequency, $\nu\ll1/\tau$, this is seen to represent an effective differentiation of the absorption line shape obtained in II above. At high modulation frequency, the time de-

†† The experimental use of such modulation was suggested by Dr. W. D. Hershberger.

pendent term decreases as (ω'/ν) near the line center $\bar{\omega}=0$.

IV. SINUSOIDAL MODULATION

If the modulation is simply harmonic, $g(\nu t) = \cos\nu t$, the exponential in the integrand may be expanded in the Fourier series

$$\exp[-i\beta\sin x]=\sum_{l=-\infty}^{\infty} J_l(\beta)\exp[-ilx],^5 \quad (19)$$

so that

$$f(\omega_{mn},\omega;t)=\int_0^\infty idT\exp\left[-i\omega'\int_{t-T}^{t}\cos\nu t'dt'-i\bar{\omega}T-T/\tau\right], \quad (20)$$

$$f(\omega_{mn},\omega;t)=\int_0^\infty idT\exp[-i(\omega'/\nu)\sin\nu t]\exp[-i(\omega'/\nu)\sin(\nu T-\nu t)]\exp[-(i\bar{\omega}+1/\tau)T]$$

$$=i\sum_{l=-\infty}^{\infty}J_l(\omega'/\nu)\exp[-il\nu t]\int_0^\infty dT\sum_{s=-\infty}^{\infty}J_s(\omega'/\nu)\exp[-is(\nu T-\nu t)-(i\bar{\omega}+1/\tau)T]$$

$$=\sum_{s=-\infty}^{\infty}\sum_{l=-\infty}^{\infty}J_s(\omega'/\nu)J_l(\omega'/\nu)\exp[i(s-l)\nu t]\frac{(s\nu+\bar{\omega})+i/\tau}{(s\nu+\bar{\omega})^2+1/\tau^2}. \quad (21)$$

$$Imf(\omega_{mn},\omega;t)=(1/\tau)\sum_{s,\,k=-\infty}^{\infty}J_s(\omega'/\nu)J_{s+k}(\omega'/\nu)\frac{\cos k\nu t-(s\nu+\bar{\omega})\tau\sin k\nu t}{(s\nu+\bar{\omega})^2+1/\tau^2}. \quad (22)$$

This expression is convenient only for relatively high modulation frequencies $(\nu\sim 1/\tau)$, since otherwise it converges slowly.

The average value of the shape factor is relatively simple $(k=0)$:

$$\langle Imf(\omega_{mn},\omega;t)\rangle_{\text{Av}}=\sum_{s=-\infty}^{\infty}[J_s(\omega'/\nu)]^2\frac{1/\tau}{(s\nu+\bar{\omega})^2+1/\tau^2}. \quad (23)$$

This predicts a series of absorption lines separated by a frequency ν and resolved if $\nu\sim 1/\tau$; their intensity varies as $[J_s(\omega'/\nu)]^2$. This phenomenon has been observed and accounted for.[6,7]

Also of interest is that component of the line shape that oscillates at the modulation frequency. It is (see Appendix B)

$$\sum_{s=-\infty}^{\infty}\frac{1/\tau}{(s\nu+\bar{\omega})^2+1/\tau^2}a_s\cos(\nu t+\varphi_s). \quad (24)$$

The coefficients a_s depend to some extent on the frequency $\bar{\omega}$. This results in removing the central line $(s=0)$ and in distorting the side-band lines.

Similar results will be obtained for the higher harmonics.

V. SQUARE WAVE MODULATION

As already pointed out, square wave modulation has been applied particularly successfully. This has been made possible by the fact that a low frequency square wave modulation of the molecular resonance together with a still slower saw-tooth sweep of the exciting frequency permits the simultaneous observation of two absorption lines, corresponding to the two values of the resonance frequency in the two half-cycles. If these two resonance frequencies are sufficiently different, a Lorentz shape will be obtained at each one. The detection of weak lines can be facilitated by using a filter circuit tuned to the square wave frequency or to any of its harmonics, because all Fourier components of the absorption coefficient reproduce the true line shape. Furthermore, the Stark effect pattern of a degenerate transition as well as the unperturbed line are obtained if the modulation is brought about by a square wave electric field based on zero voltage (3d); measurement of the splitting and square

[5] E. T. Whittaker and C. N. Watson, *Modern Analysis* (Cambridge University Press, Teddington, England, 1927), p. 358.
[6] C. H. Townes and F. R. Merritt, Phys. Rev. **72**, 1266 (1947).
[7] D. Blochinzew, Phys. Zeit. USSR, **4**, 501 (1933).

wave amplitude then give the Stark effect coefficient directly.††

Square wave modulation will be obtained if

$$g(x)=+\tfrac{1}{2},\quad 0<x-2r\pi<\pi,$$
$$g(x)=-\tfrac{1}{2},\quad \pi<x-2r\pi<2\pi. \tag{25}$$

It is convenient to rename the frequencies

$$\bar{\omega}+\tfrac{1}{2}\omega'=\omega_1,\quad \bar{\omega}-\tfrac{1}{2}\omega'=\omega_2.$$

As is shown in Appendix C, the function determining the line shape then has the following time dependence:

$$f(\omega_{mn},\omega;t)=\frac{\omega_1+i/\tau}{\omega_1^2+1/\tau^2}\{1-A_1\exp[-(i\omega_1+1/\tau)(t-2\pi r/\nu)]\},\quad 0<\nu t-2\pi r<\pi, \tag{26a}$$

$$f(\omega_{mn},\omega;t)=\frac{\omega_2+i/\tau}{\omega_{12}+1/\tau^2}\{1-A_2\exp[-(i\omega_2+1/\tau)(t-(2r+1)\pi/\nu)]\},\quad \pi<\nu t-2r\pi<2\pi, \tag{26b}$$

where A_1 and A_2 are complex functions of ω_1, ω_2, ν, and τ. These equations show that the square wave shape that would be predicted from the treatment of slow modulation has superimposed damped oscillations. The damping decreases with an increase in modulation frequency. In the case of slow modulation, of course, the fundamental frequency component reproduces the true shape of the line.

It is of interest to calculate at what modulation frequency the line shape becomes distorted by the modulation. As long as the frequency ν is still smaller than the line width ($\nu\tau\lesssim\frac{1}{2}$), the coefficients A_1 and A_2 are practically unity. Experimentally, also, the line is usually swept from near resonance ($\omega_1\sim 1/\tau$) to non-resonance, ($\omega_2\gg 1/\tau$), so that terms with ω_2 in the denominator may be neglected. The average value of $Imf(\omega_{mn},\omega;t)$ and the fundamental frequency component of this function are then, to about 1 percent accuracy,

$$\langle Imf(\omega_{mn},\omega;t)\rangle_{\text{Av}}=\frac{1}{2}\frac{1/\tau}{\omega_1^2+1/\tau^2+(\nu/\pi\tau)(1-\omega_1^2\tau^2)}, \tag{27a}$$

and

$$\langle Imf(\omega_{mn},\omega;t)\rangle_{\text{fund}}=(2/\pi)\frac{1/\tau}{\omega_1^2+1/\tau^2+(1/8)\nu^2(3-\omega_1^2\tau^2)}. \tag{27b}$$

Inspection of these equations shows that the distortion is largest at the line center. Quantitatively, the peak intensity is changed as follows:

$$\langle\alpha_{\nu\sim 1/\tau}\rangle_{\text{Av}}/\langle\alpha_{\nu\ll 1/\tau}\rangle_{\text{Av}}\cong 1-\nu\tau/\pi, \tag{28a}$$

and

$$\langle\alpha_{\nu\sim 1/\tau}\rangle_{\text{fund}}/\langle\alpha_{\nu\ll 1/\tau}\rangle_{\text{fund}}\cong 1-(3/8)\nu^2\tau^2. \tag{28b}$$

Thus the corrections are indeed small up to $\nu\tau\sim\frac{1}{2}$. Another interesting parameter is the half-width $\Delta\omega$ of the absorption line. This may also be estimated from Eq. (27) and (28):

$$\langle\Delta\omega_{\nu\sim 1/\tau}\rangle_{\text{Av}}/\langle\Delta\omega_{\nu\ll 1/\tau}\rangle_{\text{Av}}\cong 1+\nu\tau/\pi, \tag{29a}$$

and

$$\langle\Delta\omega_{\nu\sim 1/\tau}\rangle_{\text{fund}}/\langle\Delta\omega_{\nu\ll 1/\tau}\rangle_{\text{fund}}\cong 1+(1/4)\nu^2\tau^2. \tag{29b}$$

The effects here are of the same order of magnitude as the effects on the peak intensity. It may be noticed that the fundamental frequency component is affected much less than the average value.

VI. CONCLUSION

A general equation has been derived for the shape of a collision-broadened absorption line. When the transition frequency and the exciting frequency depend on time, only their difference enters into the final result. Hence, modulation of the exciting radiation and modulation of the molecular resonances are equivalent.

The author wishes to express his appreciation to Professor Julian Schwinger and to Professor J. H. Van Vleck for many clarifying discussions.

†† This observation prompted the author last March to suggest the replacement of the sinusoidal modulation used by Hughes and Wilson (Phys. Rev. 71, 562 (1947)) by square wave modulation (B. P. Dailey, Phys. Rev. 72, 84 (1947)) to permit better interpretation of experimental results.

APPENDIX

A. Weak Modulation

Following Eq. (17),

$$\int_{\nu(t-T)}^{\nu t} g(x)dx=\sum_{n=1}^{\infty}(1/n)\{g_{cn}[\sin n\nu t+\sin n\nu(T-t)]+g_{sn}[-\cos n\nu t+\cos n\nu(T-t)]\}$$

$$=\sum_{n=1}^{\infty}(1/n)\{\sin n\nu t[g_{cn}-g_n\cos n\nu T-g_{sn}\sin n\nu T]$$
$$+\cos n\nu t[-g_{sn}+g_{cn}\sin n\nu T+g_{sn}\cos n\nu T]\}. \quad \text{(A1)}$$

Using the fact that

$$\int_0^\infty dt\,\sin n\nu t\exp[-(i\bar{\omega}+1/\tau)t]=n\nu/[n^2\nu^2+(i\bar{\omega}+1/\tau)^2],$$
$$\int_0^\infty dt\,\cos n\nu t\exp[-(i\bar{\omega}+1/\tau)t]=(i\bar{\omega}+1/\tau)/[n^2\nu^2+(i\bar{\omega}+1/\tau)^2], \quad \text{(A2)}$$

gives

$$Im\int_0^\infty dT\exp[-(i\bar{\omega}+1/\tau)T]\int_{\nu(t-T)}^{\nu t}g(x)dx$$

$$=\sum_{n=1}^{\infty}(\tau/n)\left\{\sin n\nu t\left[-\frac{\bar{\omega}\tau}{\bar{\omega}^2\tau^2+1}g_{cn}+\frac{[\bar{\omega}\tau(\bar{\omega}^2-n^2\nu^2)\tau^2+1]g_{cn}-2n\nu\bar{\omega}\tau^2g_{sn}}{[(\bar{\omega}^2-n^2\nu^2)\tau^2-1]^2+4\bar{\omega}^2\tau^2}\right]\right.$$
$$\left.+\cos n\nu t\left[\frac{\bar{\omega}\tau}{\bar{\omega}^2\tau^2+1}g_{sn}-\frac{\bar{\omega}\tau[(\bar{\omega}^2-n^2\nu^2)\tau^2+1]g_{sn}-2n\nu\bar{\omega}\tau^2g_{cn}}{[(\bar{\omega}^2-n^2\nu^2)\tau^2-1]^2+4\bar{\omega}^2\tau^2}\right]\right\}$$

$$=\frac{\bar{\omega}\nu\tau^3}{\bar{\omega}^2\tau^2+1}\sum_{n=1}^{\infty}\left\{\frac{n\nu\tau[(\bar{\omega}^2-n^2\nu^2)\tau^2-3]g_{cn}-2(\bar{\omega}^2\tau^2+1)g_{sn}}{[\bar{\omega}^2-n^2\nu^2)\tau^2-1]^2+4\bar{\omega}^2\tau^2}\sin n\nu t\right.$$
$$\left.-\frac{n\nu\tau[(\bar{\omega}^2-n^2\nu^2)\tau^2-3]g_{sn}-2(\bar{\omega}^2\tau^2+1)g_{cn}}{[(\bar{\omega}^2-n^2\nu^2)\tau^2-1]^2+4\bar{\omega}\tau^2}\cos n\nu t\right\}. \quad \text{(A3)}$$

B. Sinusoidal Modulation

The imaginary part of the fundamental frequency term of the shape-determining function is, from Eq. (21),

$$(1/\tau)\sum_{s=-\infty}^{\infty}\frac{J_s(\omega'/\nu)[J_{s+1}(\omega'/\nu)+J_{s-1}(\omega'/\nu)]\cos\nu t-J_s(\omega'/\nu)[J_{s+1}(\omega'/\nu)-J_{s-1}(\omega'/\nu)]\tau(s\nu+\bar{\omega})\sin\nu t}{(s\nu+\bar{\omega})^2+1/\tau^2}$$

$$=(1/\tau)\sum_{s=-\infty}^{\infty}\frac{a_s\cos(\nu t+\varphi_s)}{(s\nu+\bar{\omega})^2+1/\tau^2}, \quad \text{(B1)}$$

where

$$\varphi_s=\tan^{-1}\left[\tau(s\nu+\bar{\omega})\frac{J_{s+1}(\omega'/\nu)-J_{s-1}(\omega'/\nu)}{J_{s+1}(\omega'/\nu)+J_{s-1}(\omega'/\nu)}\right]\quad -\pi/2<\varphi_s<\pi/2, \quad \text{(B2)}$$

$$a_s=J_s(\omega'/\nu)\{[J_{s+1}(\omega'/\nu)+J_{s-1}(\omega'/\nu)]^2+\tau^2(s\nu+\bar{\omega})^2[J_{s+1}(\omega'/\nu)-J_{s-1}(\omega'/\nu)]^2\}^{\frac{1}{2}}. \quad \text{(B3)}$$

Note that

$$a_0 = 2J_0(\omega'/\nu)J_1(\omega'/\nu)\tau\bar{\omega} = 0 \text{ if } \bar{\omega} = 0.$$

C. Square Wave Modulation

$$f(\omega_{mn}, \omega; t) = \int_0^\infty idT \exp\left[-i\int_{t-T}^{t} (\omega_{mn}-\omega)dt' - T/\tau\right], \tag{C1}$$

where

$$\left.\begin{aligned} \omega_{mn}-\omega &= \omega_1 \quad 0<\nu t-2r\pi<\pi \\ \omega_{mn}-\omega &= \omega_2 \quad \pi<\nu t-2r\pi<2\pi \end{aligned}\right\} r=0, \pm 1, \pm 2, \cdots. \tag{C2}$$

To simplify the manipulations, it is convenient to use

$$\varphi = \int_{t-T}^{t} (\omega_{mn}-\omega)dt'; \tag{C3}$$

$$\nu t_k \begin{cases} = \nu t - 2r\pi + (k-1)\pi \text{ and } t_0 = 0 \quad (0<\nu t-2r\pi<\pi) \\ = \nu t - 2r\pi + (k-1)\pi - \pi, \quad t_0 = 0 \quad (\pi<\nu t - 2r\pi<2\pi); \end{cases} \tag{C4}$$

and

$$A_k = \int_{t_k}^{t_{k+1}} dT \exp[-i\varphi - T/\tau]. \tag{C5}$$

Comparing (C.5) and (C.1), one can see that

$$f(\omega_{mn}, \omega; t) = i\sum_{k=0}^{\infty} A_k. \tag{C6}$$

The calculation of the A_k will now be divided into four cases ($s=0, 1, 2, \cdots$):

I

$$\left.\begin{aligned} &0<\nu t-2r\pi<\pi \\ &0<\nu(t-T)-2(r-s)\pi<\pi \end{aligned}\right\} t_{2s}<T<t_{2s+1}, \tag{C7}$$

$$\varphi^{\mathrm{I}} = (\omega_1+\omega_2)(s\pi/\nu) + \omega_1(T-2s\pi/\nu), \tag{C8}$$

$$A_0^{\mathrm{I}} = (i\omega_1+1/\tau)^{-1}\{1-\exp[-(i\omega_1+1/\tau)(t-2r\pi/\nu)]\}, \tag{C9}$$

$$A_{2s}^{\mathrm{I}} = (i\omega_1+1/\tau)^{-1}\exp[-(i(\omega_1+\omega_2)+2/\tau)s\pi/\nu]\exp[-(i\omega_1+1/\tau)(t-2r\pi/\nu)] \times\{\exp[(i\omega_1+1/\tau)\pi/\nu]-1\}. \tag{C10}$$

II

$$\left.\begin{aligned} &0<\nu t-2r\pi<\pi \\ &-\pi<\nu(t-T)-2(r-s)\pi<0 \end{aligned}\right\} t_{2s+1}<T<t_{2s+2}, \tag{C11}$$

$$\varphi^{\mathrm{II}} = (\omega_1+\omega_2)(s\pi/\nu) + (\omega_1-\omega_2)(t-2r\pi/\nu) + \omega_2(T-2s\pi/\nu), \tag{C12}$$

$$A_{2s+1}^{\mathrm{II}} = (i\omega_2+1/\tau)^{-1}\exp[-(i(\omega_1+\omega_2)+2/\tau)s\pi/\nu]\exp[-(i\omega_1+1/\tau)(t-2r\pi/\nu)] \times\{1-\exp[-(i\omega_2+1/\tau)\pi/\nu]\}. \tag{C13}$$

III

$$\left.\begin{aligned} &\pi<\nu t-2r\pi<2\pi \\ &\pi<\nu(t-T)-2(r-s)\pi<2\pi \end{aligned}\right\} t_{2s}<T<t_{2s+1}, \tag{C14}$$

$$\varphi^{\mathrm{III}}=(\omega_1+\omega_2)(s\pi/\nu)+\omega_2(T-2s\pi/\nu), \tag{C15}$$

$$A_0{}^{\mathrm{III}}=(i\omega_2+1/\tau)^{-1}\{1-\exp[-(i\omega_2+1/\tau)(t-(2r+1)\pi/\nu)], \tag{C16}$$

$$A_{2s}{}^{\mathrm{III}}=(i\omega_2+1/\tau)^{-1}\exp[-(i(\omega_1+\omega_2)+2/\tau)s\pi/\nu]\exp[-(i\omega_2+1/\tau)(t-(2r+1)\pi/\nu)] \times\{\exp[(i\omega_2+1/\tau)\pi/\nu]-1\}. \tag{C17}$$

IV

$$\left.\begin{array}{l}\pi<\nu t-2r\pi<2\pi\\ 0<\nu(t-T)-2(r-s)\pi<2\pi\end{array}\right\}t_{2s+1}<T<t_{2s+2}, \tag{C18}$$

$$\varphi^{\mathrm{IV}}=(\omega_1+\omega_2)(s\pi/\nu)-(\omega_1-\omega_2)(t-(2r+1)\pi/\nu)+\omega_1(T-2s\pi/\nu), \tag{C19}$$

$$A_{2s+1}{}^{\mathrm{IV}}=(i\omega_1+1/\tau)^{-1}\exp[-(i(\omega_1+\omega_2)+2/\tau)s\pi/\nu]\exp[-(i\omega_2+1/\tau)(t-(2r+1)\pi/\nu)] \times\{1-\exp[-(i\omega_1+1/\tau)\pi/\nu]\}. \tag{C20}$$

These results may now be substituted into Eq. (C6). The sums are geometric series that are easily evaluated. Inspection of (C10), (C13), (C16), and (C20) shows that

$$f(\omega_{mn},\omega;t)=i\sum_{s=1}^{\infty}(A_{2s}{}^{\mathrm{I}}+A_{2s+1}{}^{\mathrm{II}})\qquad(0<\nu t-2r\pi<\pi), \tag{C21}$$

$$f(\omega_{mn},\omega;t)=i\sum_{s=0}^{\infty}(A_{2s}{}^{\mathrm{III}}+A_{2s+1}{}^{\mathrm{IV}})\qquad(\pi<\nu t-2r\pi<2\pi). \tag{C22}$$

The result can be written most conveniently with the aid of two constants:

$$A_1=\frac{1-\exp[-(i\omega_2+1/\tau)\pi/\nu]}{1-\exp[-(i(\omega_1+\omega_2)+2/\tau)\pi/\nu]}\left\{1-\frac{i\omega_1+1/\tau}{i\omega_2+1/\tau}\exp[-(i(\omega_1+\omega_2)+2/\tau)\pi/\nu]\right\}, \tag{C23}$$

$$A_2=\frac{1-\exp[-(i\omega_1+1/\tau)\pi/\nu]}{1-\exp[-(i(\omega_1+\omega_2)+2/\tau)\pi/\nu]}\left\{1-\frac{i\omega_2+1/\tau}{i\omega_1+1/\tau}\exp[-(i(\omega_1+\omega_2)+2/\tau)\pi/\nu]\right\}. \tag{C24}$$

It is

$$f(\omega_{mn},\omega;t)=(\omega_1-i/\tau)^{-1}\{1-A_1\exp[-(i\omega_1+1/\tau)(t-2r\pi/\nu)]\}\qquad(0<\nu t-2r\pi<\pi), \tag{C25}$$

$$f(\omega_{mn},\omega;t)=(\omega_2-i/\tau)^{-1}\{1-A_2\exp[-(i\omega_2+1/\tau)(t-(2r+1)\pi/\nu)]\}\qquad(\pi<\nu t-2r\pi<2\pi). \tag{C26}$$

It may be observed that the deviation of A_1 and A_2 from unity depends on the exponential $\exp[-\pi/\nu\tau]$. If $\nu\tau\gtrsim\frac{1}{2}$, as considered in the body of the paper, $\exp[-\pi/\nu\tau]\gtrsim\exp[-6]\sim2\times10^{-3}$, certainly a negligible quantity as far as comparison with experiment is concerned.

With the assumption, moreover, that $\omega_2\gg1/\tau$, the function $f(\omega_{mn},\omega;t)$ becomes effectively zero during one-half of the cycle. Hence

$$\begin{aligned}\langle f(\omega_{mn},\omega;t)\rangle_{\mathrm{Av}}&=(\omega_1-i/\tau)^{-1}\left\{1/2-A_1(\nu/2\pi)\int_0^{\pi/\nu}dt\exp[-(i\omega_1+1/\tau)t]\right\}\\&=\{i/2(i\omega_1+1/\tau)\}\{1+\nu/\pi(i\omega_1+1/\tau)\}\\&=i/2(i\omega_1+1/\tau+\nu/\pi).\end{aligned} \tag{C27}$$

Taking the imaginary part then leads to Eq. (27a). Equation (27b) is derived in a similar way.