

Frequency Modulation in the Spectroscopy of an Inhomogeneously Broadened Line*

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The effect of frequency modulation on an inhomogeneously broadened line is studied when the modulation frequency or amplitude is larger than the homogeneous width but less than the inhomogeneous width. It is shown that the deviation from the instantaneous response for the polarization disappears as a result of the averaging effect when the field intensity is weak.

Frequency modulation in microwave spectroscopy was theoretically studied by Karplus.¹ Further theoretical and experimental studies were done mainly for magnetic resonance,² including the case of a strong rf field.³⁻⁵ Recently, frequency modulation was used in the infrared region for Stark spectroscopy by lasers.^{6,7} The same technique was applied for the modulation of the laser beam itself.⁸ In this paper, we discuss the effect of frequency modulation on an inhomogeneously broadened line, which is the case in infrared or optical spectroscopy at low pressure.

The response of an ensemble of molecules which have the same resonant frequency is obtained by solving the equation for the density matrix of the molecules,⁹

$$\frac{d}{dt} \rho = -\frac{i}{\hbar} [H, \rho] - \gamma(\rho - \rho^{eq}), \quad (1)$$

where ρ^{eq} is the equilibrium value of ρ in the absence of the optical field. Restricting to two levels which are near resonance with the optical field and neglecting off-resonant terms, we assume for the Hamiltonian the following form:

$$H = \begin{pmatrix} \hbar[\omega_0 + \omega_m(t)] & -\mu E e^{-i\omega t} \\ -\mu E^* e^{i\omega t} & 0 \end{pmatrix}, \quad (2)$$

where μ is the dipole matrix element, $E e^{-i\omega t} + E^* e^{i\omega t}$ is the optical field and $\omega_0 + \omega_m(t)$ is the resonant frequency of the molecule, in which $\omega_m(t)$ is the modulating part. In case of the Doppler broadening we take $\omega_0 = \epsilon/\hbar + v\omega/c$, where ϵ is the energy difference of the two levels and v is the longitudinal velocity of the molecule along the propagation direction of the optical field. The polarization from all molecules which is responsible for the absorption of the optical field is obtained by integrating the solution of Eq. (1) over ω_0 . When the homogeneous width γ is much narrower than the inhomogeneous width, we can expand the distribution function of the resonant frequency $W(\omega_0)$ around $\omega - \omega_m(t) = \omega_0 - \Delta\omega$. Then the polarization P is in the first order of this expansion,

$$P = n\mu \int [W(\omega - \omega_m(t)) + W'(\omega - \omega_m(t)) \Delta\omega] \rho_{ab} d\omega_0, \quad (3)$$

where n is the density of the molecule and ρ_{ab} is the off-diagonal element of the density matrix, a and b representing the upper and lower levels, respectively. If E is weak, $\mu E/\hbar \ll \gamma$, the solution of Eq. (1) with (2) is¹

$$\rho_{ab} = i \frac{\mu E}{\hbar} (\rho_{bb}^{eq} - \rho_{aa}^{eq}) \exp(-i\omega t) \int_0^\infty \exp[-i(\omega_0 - \omega)t_0 - \gamma t_0 - i \int_{t-t_0}^t \omega_m(t') dt'] dt_0.$$

Rewriting as

$$\int \omega_m(t') dt' = \omega_m(t)t_0 + \int [\omega_m(t') - \omega_m(t)] dt',$$

and repeating the partial integration, ρ_{ab} is rewritten

$$\rho_{ab} = i \frac{\mu E}{\hbar} (\rho_{bb}^{eq} - \rho_{aa}^{eq}) e^{-i\omega t} \left(\frac{1}{i\Delta\omega + \gamma} + \int_0^\infty \frac{i\omega_m'(t-t_0) - [\omega_m(t-t_0) - \omega_m(t)]^2}{(i\Delta\omega + \gamma)^2} \exp\left\{-i\Delta\omega t_0 - \gamma t_0 - i \int_{t-t_0}^t [\omega_m(t') - \omega_m(t)] dt'\right\} dt_0 \right)$$

It is easy to prove by repeating the partial integration again that the integration in Eq. (3) for the second term in the above expression is zero. Since the first term does not converge in the integration, retaining the original form $W(\omega_0)$, the polarization is

$$P = n \frac{\mu^2 E}{\hbar} (\rho_{bb}^{eq} - \rho_{aa}^{eq}) \int \frac{W(\omega_0)}{\Delta\omega - i\gamma} d\omega_0. \quad (4)$$

This is the same form as the solution which is obtained assuming $\omega_m(t)$ is time independent. Therefore, the polarization changes as if all molecules are in the equilibrium state for the instantaneous value of $\omega_m(t)$, although the individual molecule behaves in a completely different way when $\mu E/\hbar > \gamma$. Equation (4) is valid if the spectral width of the individual molecule is much less than the inhomogeneous width.

This situation does not hold when the optical field is larger. If $\omega_m(t)$ is slowly varying, the effect of the optical field intensity can be studied from the perturbation solution of Eq. (1) by treating the time derivatives of $\omega_m(t)$ as a perturbation. The solution in the first-order approximation is¹⁰

$$\rho_{ab} = \frac{\Delta\omega + i\gamma}{\Delta\omega^2 + \gamma_s^2} V (\rho_{bb}^{eq} - \rho_{aa}^{eq}) + \left(\frac{4\Delta\omega\gamma(\Delta\omega + i\gamma)}{(\Delta\omega^2 + \gamma_s^2)^3} - \frac{i\Delta\omega\gamma + \gamma_s^2}{\gamma(\Delta\omega^2 + \gamma_s^2)^2} \right) V (\rho_{bb}^{eq} - \rho_{aa}^{eq}) \frac{d\omega_m}{dt}, \quad (5)$$

where $V = (\mu E/\hbar)e^{-i\omega t}$ and $\gamma_s = (\gamma^2 + 4|V|^2)^{1/2}$. The second-order terms are rather lengthy and are proportional either to $d^2\omega_m/dt^2$ or to $(d\omega_m/dt)^2$. This approach is a good approximation only when the modulation is relatively slow, therefore, the deviation from the equilibrium behavior is small, but it is valid for the arbitrary field intensity. The polarization (3) is then integrated as

$$P = n\mu V (\rho_{bb}^{eq} - \rho_{aa}^{eq}) \int W(\omega_0) \frac{\Delta\omega + i\gamma}{\Delta\omega^2 + \gamma_s^2} d\omega_0 - 2\pi n\mu \times V \frac{d\omega_m}{dt} \frac{|V|^2}{\gamma\gamma_s^3} \left[W(\omega - \omega_m) + i\gamma W'(\omega - \omega_m) \right]. \quad (6)$$

The first term corresponds to Eq. (4) for the arbitrary field intensity. The deviation from the equilibrium behavior grows as V approaches γ . But the relative amount of the deviation is not al-

ways large for large V . The imaginary part of the second term in Eq. (6), which causes the distortion in the absorption coefficient, drops off faster than the equilibrium term for larger V .

For the sinusoidal modulation $\omega_m(t) = \omega_m \cos\Omega t$, the response can be calculated numerically by expanding ρ in the Fourier series of Ω ,

$$\rho = \sum_{k=-\infty}^{\infty} \rho(k) e^{ik\Omega t}. \quad (7)$$

Inserting Eq. (7) into Eq. (1) and after eliminating diagonal components of ρ , we obtain a series of coupled equations for $\rho_{ab}(k)$ and $\rho_{ba}(k)$. These equations can be rewritten in the form which does not depend on the phase of V by introducing new variables $\beta_{ab}(k) = \rho_{ab}(k) V^{-1}$ and $\beta_{ba} = \rho_{ba}(k) V^{*-1}$. The resultant equations for $\beta_{ab}(k)$ and $\beta_{ba}(k)$ are in a 2×2 matrix form,

$$S_k \beta_k = \beta_{k+1} + \beta_{k-1} + (2/\omega_m)(\rho_{aa}^{eq} - \rho_{bb}^{eq}) \delta_{k0}, \quad (8)$$

where $\beta_k = \begin{pmatrix} \beta_{ab}(k) \\ \beta_{ba}(k) \end{pmatrix}$,

$$S_k = \frac{2i}{\omega_m} \begin{pmatrix} ik\Omega + i(\omega_0 - \omega) + \frac{2|V|^2}{ik\Omega + \gamma} + \gamma & -\frac{2|V|^2}{ik\Omega + \gamma} \\ \frac{2|V|^2}{ik\Omega + \gamma} & -ik\Omega + i(\omega_0 - \omega) - \frac{2|V|^2}{ik\Omega + \gamma} - \gamma \end{pmatrix}$$

The matrices U_k which connect β_k and β_{k+1} by $\beta_{k+1} = U_k \beta_k$ satisfy the equations

$$U_{k-1} = (S_k - U_k)^{-1}, \quad k \neq 0. \quad (9)$$

Therefore the evaluation of β_k can be done in a similar way to evaluating a fractional series. First set $U_N = 0$ for sufficiently large N , then all U_k for $0 \leq k \leq N$ are successively calculated from (9). The term β is obtained from Eq. (8) for $k=1$ by using U_0 and the relations $\beta_{ab}(k) = \beta_{ba}^*(-k)$ and $\beta_{ba}(k) = \beta_{ab}^*(-k)$. Finally β_k are calculated back from $\beta_k = U_{k-1} \beta_{k-1}$. Assuming that ω_m is less than the inhomogeneous width, we can expand the distribution function as $W(\omega_0) = W(\omega) + W'(\omega)(\omega_0 - \omega)$. The imaginary part of P/V , which is proportional to the absorption coefficient, is then written using the solution of Eq. (8) in the Fourier series of Ω as

$$\text{Im}(P/V) = n\mu \int W(\omega_0) \text{Im}\beta_{ab}(0) d\omega_0 - \frac{1}{2} \pi n\mu \times (\rho_{bb}^{eq} - \rho_{aa}^{eq}) \left\{ W(\omega) \sum_{k=1}^{\infty} M_0(k) \sin[k\Omega t + \phi_0(k)] \right\}$$

$$+ \omega_m W'(\omega) \sum_{k=1}^{\infty} M_1(k) \sin[k\Omega t + \phi_1(k)] \},$$

where $M_i(k)$ and $\phi_i(k)$ are the magnitude and the argument of the complex number

$$\frac{2}{\pi(\rho_{bb}^{eq} - \rho_{aa}^{eq})} \int \frac{(\omega_0 - \omega)^i}{\omega_m^i} [\beta_{ab}(k) - \beta_{ba}(k)] d\omega_0,$$

where i is zero or one. A similar expression can be obtained for the real part of P/V . We define $M_0(0)$ as half the value of the above expression. The $M_0(k)$ represents the relative magnitude of the harmonic components in the absorption coefficient, in which the constant part of the absorption coefficient is normalized to one, when $W = \text{const}$ and $|V| \rightarrow 0$. Since $\beta_{ab}(k) - \beta_{ba}(k)$ is an odd function of $\omega_0 - \omega$ for odd k and an even function for even k , $M_i(k)$ is nonzero only when ik is even. Figure 1 shows an example of the variation of $M_1(k)$ and $M_0(k)$ with the optical field intensity. They are calculated for the parameters $\Omega/\omega_m = 0.1$ and $\gamma/\omega_m = 0.025$.

For the inhomogeneously broadened line the absorbed power increases linearly with E even in the saturated region, although the absorption coefficient decreases. Therefore, the higher intensity can improve the S/N ratio of the spectrum in the case when the noise of the spectrometer is determined by some source other than the intrinsic noise of the optical field. The above discussions show that the polarization P behaves in the normal way if $d\omega_m/dt < \gamma^2$ or $|V| < \gamma$. This restriction is weaker than for the homogeneously broadened line, but for strong E the modulation speed must be slow. The distortion of P does not necessarily mean the distortion of the observed line shape in the spectrum. If ω_m is much less than the inhomogeneous width, the absorption coefficient always has the form

$$A(t) W(\omega) + B(t) W'(\omega),$$

where A and B are periodic functions of the modulation frequency. For sinusoidal modulation, the

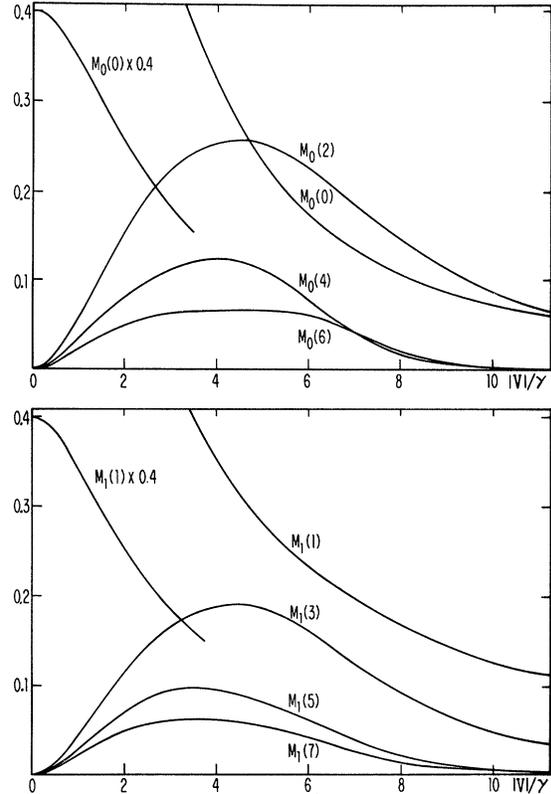


FIG. 1. Relative intensities of the harmonic components of the absorption coefficient. Note that the $M_0(k)$ are zero for odd k and that the $M_1(k)$ are zero for even k . The even harmonics (upper figure) are proportional to $W(\omega)$ and the odd harmonics (lower figure) are proportional to $W'(\omega)$. Other parameters are $\Omega/\omega_m = 0.1$ and $\gamma/\omega_m = 0.025$.

first term A has only the even harmonics. Therefore, if the phase-sensitive detector is perfectly symmetric, this term has no effect on the output of the spectrometer.

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¹⁰See Appendix for derivation.

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Coherent and Incoherent X-Ray Scattering by Bound Electrons. I. Helium Isoelectronic Sequence*

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Atomic form factors and incoherent scattering functions for the helium isoelectronic sequence through $Z=10$ have been calculated with correlated ground-state wave functions. The wave functions are 120-term configuration-interaction expansions which give total ground-state energies differing from the most accurate available values by 0.02% for He I and 0.0007% for Ne IX. Comparison with published accurate calculations for helium indicates that the scattering factors, both coherent and incoherent, for the other members of the isoelectronic sequence, should be correct to at least three, and probably four, significant figures.

I. INTRODUCTION

The dependence on wave function of the cross sections for coherent and incoherent scattering of a photon by an N -electron atom or atomic ion is contained in the form factor, or atomic scattering factor,

$$F(K) = \sum_{j=1}^N \langle \psi_0 | e^{i\vec{K} \cdot \vec{r}_j} | \psi_0 \rangle, \quad (1)$$

and the incoherent scattering function

$$S(K) = N^{-1} \left(\sum_{j,k=1}^N \langle \psi_0 | \exp[i\vec{K} \cdot (\vec{r}_j - \vec{r}_k)] | \psi_0 \rangle - |F(K)|^2 \right), \quad (2)$$

respectively. In Eqs. (1) and (2), the momentum transfer is denoted by $\hbar \vec{K}$, ψ_0 is the ground-state wave function, and \vec{r}_j is the radius vector from the nucleus to the j th electron. The momentum transfer is given by $K = 4\pi(\sin \frac{1}{2}\theta)/\lambda$, where λ is the wavelength of the incident photon, and θ the angle between incident and scattered photon directions. The coherent-scattering cross section is

$$d\sigma_c = I_c |F(K)|^2 d\Omega, \quad (3)$$

where I_c is the Thomson cross section. The total incoherent-scattering cross section is

$$d\sigma_i = I_i NS(K) d\Omega, \quad (4)$$

where I_i is the Klein-Nishina cross section, which for small values of K may be replaced by the Thomson cross section.

There are now available quite accurate correlated ground-state wave functions for many low- Z atoms and it is no longer necessary to use approximations such as the Hartree-Fock or Thomas-Fermi methods in these cases. This paper describes the results of calculation of form factors and incoherent scattering functions for helium and two-electron atomic ions through $Z=10$.

II. WAVE FUNCTIONS

The two-electron ground-state wave functions used in the present work are 120-term configuration-interaction expansions

$$\psi_{1S} = \sum_{n_1=1}^8 \sum_{n_2=1}^{n_1-1} \sum_{l=0}^{n_2-1} c(n_1, n_2, l) \Phi_{1S}(n_1, n_2, l), \quad (5)$$

in which each configuration Φ_{1S} is the linear combination of Slater determinants

$$\begin{aligned} \Phi_{1S} = & \sum_m C(l l 0; m, -m) \\ & \times [| \varphi_{n_1 l m}(\vec{r}_1) \alpha \varphi_{n_2 l -m}(\vec{r}_2) \beta | \\ & + | \varphi_{n_2 l -m}(\vec{r}_1) \alpha \varphi_{n_1 l m}(\vec{r}_2) \beta |], \quad (6) \end{aligned}$$