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Frequency Modulation of a Laser by Fluctuations in a Chemical Reaction

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A variant of zero-angle light scattering is proposed with particular emphasis on the use of this technique for measuring chemical reaction rates. The system analyzed consists of a laser oscillator with a reacting sample placed inside the resonant cavity. Fluctuations about equilibrium of the chemical reaction frequency modulate the oscillator, and the power spectrum of the modulating signal is Lorentzian with width proportional to the reaction rate. The modulation signal is very weak, but should be detectable with modern techniques.

KEY WORDS: Light scattering; chemical reaction; laser modulation.

1. INTRODUCTION

A material sample will always appear inhomogeneous on a microscopic scale because atoms and molecules are discrete. Hence such systems always scatter a small fraction of light passed through them, even if the light frequency is not spectroscopically active. The intensity of this scattering is proportional to the magnitude of the microscopic variations (or fluctuations) and there are small frequency shifts due to the time variation of the fluctuations.(1)

Any microscopic mechanism causing fluctuations gives rise to light scattering and, conversely, measurements of the light scattering give information about such microscopic behavior. In particular, a chemical reaction, even at thermodynamic equilibrium, will generate microscopic fluctuations

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and a measurement of the frequency shifts due to these fluctuations will reveal the reaction rate.[2]

The theory and practice of inelastic light scattering (observing the frequency shifts) has been greatly stimulated by the dramatic improvement in the accuracy of these experiments which followed the development of laser light sources and new detection schemes.(3,4) Stimulated by these developments, Blum and Salsburg(5) and Berne and Frisch(6) presented analyses of inelastic light scattering from chemically reacting systems. Their results are, roughly, that a chemical reaction contributes an additional Lorentzian line to the inelastic scattering spectrum with width approximately proportional to the reaction rate. In general, however, the reaction rate cannot be determined by a simple analysis of an experimental spectrum except in the zero-angle or forward scattering case. The next section explains why the zero-angle case is exceptionally easy to interpret.

Section 3 describes a variant of the zero-angle scattering experiment: The reacting system is placed inside the laser cavity. The fluctuations of the reaction about equilibrium cause the oscillation frequency to fluctuate. The laser output itself is observed. Section 4 determines the power spectrum of the fluctuations of the oscillator frequency in the particular case of a chemical reaction. Section 5 then gives a numerical example of the effect and discusses the detection possibilities.

2. ZERO-ANGLE SCATTERING

There are two distinct mechanisms whereby the frequency of the scattered light is altered. First, the translational motion of the scatterers produces a Doppler shift. This effect operates twice: The molecule moves through the driving field and hence its induced dipole actually oscillates at a Doppler-shifted frequency, and a second shift occurs because the molecule moves with respect to the observer. The fluctuations associated with this type of change have been quantitatively explained in terms of a hydrodynamic model(7) as scattering off soundlike and heatlike fluctuations or diffusionlike fluctuations. This scattering will be present in any fluid.

Second, the molecules may change internally as a function of time. This leads to a time-dependent polarizability and an amplitude modulation of the scattered light. Examples of this which have actually been observed are vibrational–translational relaxation,(8) internal rotational diffusion,(9) and chemical reactions.(10)

In a real fluid, these two mechanisms are not statistically independent. Internal transformations influence and are influenced by the kinetic motions

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[2] An excellent popular exposition of this idea is presented by Perrin.(2)

in the fluid. Hence, in general, the explanation of the spectrum of the scattered light is complicated and this makes it difficult to infer from an experimental spectrum simple properties such as a reaction rate.

A practical separation of the hydrodynamic and internal effects has been achieved in two ways. First, when looking for internal transformations which occur much more rapidly than the hydrodynamic processes, the large-frequency-shift region of the spectrum corresponds to a time scale where there simply are no hydrodynamic events occurring. Hence this region of the spectrum is due entirely to the internal transformations. Yeh and Keeler(10) examined an ionic reaction which occurred much more rapidly than the competing diffusional broadening. Similarly, the broadening due to vibrational–translational relaxation is much greater than the hydrodynamic broadening.(8)

The second route, which is the basis for the following analysis, is to look at zero-angle or forward scattering. This direction is unique because there is no Doppler frequency shift in the forward direction: The frequency shift experienced on moving through the driving field is exactly compensated by the motion with respect to the observer. This holds for any velocity. Hence the frequency shift present at zero angle is due entirely to the internal transformations occurring and is completely independent of the translational motions. This result has been deduced from the hydrodynamic analyses (Blum and Salsburg(5) and Berne and Frisch(6) for the chemical reaction, Berne and Pecora(11) for internal rotation, and Mountain(12) for vibrational–translational relaxation), but would follow from any model whatsoever.

There is considerable experimental difficulty at zero angle because most of the emerging light is unscattered, the scattered component being about one part in 10^{11}. This difficulty was circumvented experimentally by Wada *et al.* by using a plane polarized source and looking for zero-angle scattered light polarized perpendicular to the source. Hence a polarizer could reject the unscattered light. An analysis of this type of experiment with respect to measuring chemical reaction rates has been given by Berne and Pecora.(11) These authors have, incidentally, proposed another approach to measuring reaction rates via light scattering.(13)

3. A LASER OSCILLATOR

An analysis has been presented by Harris and McDuff,(14) based upon the semiclassical Lamb(15) analysis, of the effect of a time-varying optical path length within a laser oscillator's resonant cavity. The emphasis was upon the situation where the modulation frequency was close to the mode spacing in the cavity and hence "locking" or stabilization would occur. The present analysis is much simpler. The modulation frequency is much smaller and the coupling effects are not important. Each mode survives as reasonably independent. Actually, the details of the operation of the laser are unimportant.

The experimental configuration envisioned is something like that shown in Fig. 1. The mirrors *M* define the resonant cavity. Optical gain is provided in region *G* by some typical laser mechanism such as a gaseous discharge. The reacting sample is placed in region *F* and the basic effect of the sample is to cause the optical path length in the cavity to fluctuate. Hence the oscillator frequency fluctuates.

The actual system has lumped losses at *M*, gain at *G*, and fluctuations at *F*, but it is much easier to analyze a system in which loss, gain, and fluctuation are distributed. The prototype of such an analysis has been given by Lamb(15) and would only fail to be a good approximation when the spontaneous emission lifetime of the lasing transition becomes smaller than the optical transit time in the cavity. The laser will be described as linear, which is to say, the nonlinearity which limits the amplitude of oscillation will be ignored. Lamb has described the consequences of nonlinear induced emission, but in the presence of an inserted reacting system, high losses will probably cause the power level to be limited by the pumping rate. The description developed in this section is the same as that which follows from applying the linear Lamb analysis to the same problem. The internal fluctuations cause no change in the amplitude of the oscillation and the frequency fluctuates.

Maxwell's equation may be written as

$$\begin{aligned} \nabla \times \mathbf{E} &= -\frac{1}{c}\frac{\partial \mathbf{B}}{\partial t}, \qquad \nabla \cdot \mathbf{E} = -4\pi \mathbf{P} \\ \nabla \times \mathbf{B} &= \frac{1}{c}\frac{\partial \mathbf{E}}{\partial t} + 4\pi\left[\nabla \times \mathbf{M} + \frac{1}{c}\frac{\partial \mathbf{P}}{\partial t}\right], \qquad \nabla \cdot \mathbf{B} = 0 \end{aligned} \tag{1}$$

in Gaussian units.[3] In the coordinate system depicted in Fig. 2, the mirrors (idealized as perfect) are located at $z = 0, L$. Hence $\mathbf{E}(z = 0) = \mathbf{E}(z = L) = 0$ are the boundary conditions. Eliminating **B** gives the field equation

$$\nabla \times (\nabla \times \mathbf{E}) + \frac{1}{c^2}\frac{\partial^2 \mathbf{E}}{\partial t^2} = -\frac{4\pi}{c}\nabla \times \left(\frac{\partial \mathbf{M}}{\partial t}\right) - \frac{4\pi}{c^2}\frac{\partial^2 \mathbf{P}}{\partial t^2} \tag{2}$$

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[3] These units are convenient because molecular polarizabilities are invariably reported in cgs units.

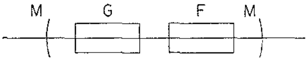

Fig. 1. The mirrors *M* define the resonant frequencies of the cavity. Inside the cavity is both a region of gain *G* (population inversion) and a region of fluctuation *F* (chemical reaction).

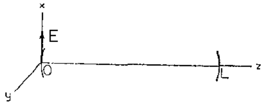

Fig. 2. The cavity corresponds to $0 < z < L$ and the electric field is parallel with the x axis.

for **E**. The magnetization **M** and polarization **P** are the sources of the field. **M**, which arises through the motion of the molecules, is smaller than **P** by a factor of v/c (v is a molecular velocity) and will be dropped. **P** will be written $\mathbf{P}_0 + \mathbf{P}'$, with $\mathbf{P}_0$ a fixed part of no real interest: $\mathbf{P}_0 = \eta\mathbf{E}$, with the susceptibility η a constant. $\mathbf{P}'$ is the fluctuating part and will be examined in detail in Section 4. The active gain of the medium and the loss have been assumed to balance each other (the steady state) and are thus not represented in Eq. (2). Thus

$$\nabla \times (\nabla \times \mathbf{E}) + \frac{1 + 4\pi\eta}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} = -\frac{4\pi}{c^2} \frac{\partial^2 \mathbf{P}'}{\partial t^2} \tag{3}$$

The factor $1 + 4\pi\eta$ will be written n^2; n is the effective index of refraction.

An analysis of the eigenfrequencies and field patterns for practical cavities has been given by Fox and Li.(16) For simplicity, a cavity of square cross section $l \times l \times L$ with a field uniform over the cross section and varying as $\sin kz$ in the z-direction (the length of the cavity) will be assumed. If only one such normal mode of the cavity is excited, $\mathbf{E}(\mathbf{r}, t) = \hat{\mathbf{i}}E(t) \sin kz$; $E(t)$ is the amplitude of the oscillation.

Equation (3) governs the time evolution of $E(t)$ and may be rewritten

$$\left[k^2 E(t) + \left(\frac{n}{c}\right)^2 E''(t)\right] \sin kz = -\frac{4\pi^2}{c^2} \frac{\partial^2 P_x'}{\partial t^2} \tag{4}$$

Performing $\int_0^l \int_0^l dx\, dy \int_0^L dz \sin kz$ gives

$$k^2 E(t) + \left(\frac{n}{c}\right)^2 E''(t) = -\frac{4\pi^2}{c^2} \frac{\partial^2}{\partial t^2} \frac{2}{Ll^2} \int_0^l \int_0^l dx\, dy \int_0^L dz \sin kz P_x'(z, t) \tag{5}$$

Let the N reaction centers in the system be labeled $i = 1,..., N$. Each reaction center is characterized by a polarizability $\alpha_i = \alpha_i(t)$. α_i varies in time as the raction occurs. The induced dipole moment is $\mathbf{d}_i = \alpha_i(t)\mathbf{E}(z, t)$ and **P** is just the induced dipole moment per unit volume. (α is being taken as the rotationally averaged polarizability tensor and optical activity(17) is not considered.)

The polarization arising from the reaction centers is thus

$$\sum_{i=1}^{N} \alpha_i(t)\, \delta(\mathbf{r} - \mathbf{r}_i(t))\, \mathbf{E}(\mathbf{r}_i, t)$$

with $\delta(\mathbf{r} - \mathbf{r}_i)$ the Dirac delta-function. If $\bar{\alpha}$ is the average (equilibrium) value of $\alpha(t)$,

$$\mathbf{P}'(\mathbf{r}, t) = \sum_{i=1}^{N} (\alpha_i - \bar{\alpha})\, \delta(\mathbf{r} - \mathbf{r}_i)\, \mathbf{E}(\mathbf{r}_i, t) = \mathbf{E}(\mathbf{r}, t) \sum_{i=1}^{N} (\alpha_i - \bar{\alpha})\, \delta(\mathbf{r} - \mathbf{r}_i) \tag{6}$$

and

$$\frac{\partial^2 \mathbf{P}'}{\partial t^2} = \frac{\partial^2 \mathbf{E}}{\partial t^2} \sum_{i=1}^{N} (\alpha_i - \bar{\alpha})\, \delta(\mathbf{r} - \mathbf{r}_i) \tag{7}$$

because α_i changes much more slowly than $\mathbf{E}$. With this result, Eq. (5) becomes

$$k^2 E(t) + \left[\frac{n^2}{c^2} + \frac{4\pi^2}{c^2} \frac{2}{Ll^2} \times \int_0^l \int_0^l dx\, dy \int_0^L dz \sin^2 kz \sum_{i=1}^{N} (a_i - \bar{\alpha})\, \delta(\mathbf{r} - \mathbf{r}_i)\right] E''(t) = 0 \tag{8}$$

Furthermore,

$$\int_0^l \int_0^l dx\, dy \int_0^L dz \sin^2 kz \sum_{i=1}^{N} (\alpha_i - \bar{\alpha})\, \delta(\mathbf{r} - \mathbf{r}_i) = \sum_{i=1}^{N} (\alpha_i - \bar{\alpha}) \sin^2 kz_i \tag{9}$$

The average value of $\sin^2 kz_i$ is 1/2.[4] The actual value varies in time since the reaction centers are moving. This is one of the contributions to the finite linewidth of the unperturbed laser. On the assumption that the unperturbed linewidth is narrow, these fluctuations can be ignored. With this assumption,

$$k^2 E(t) + \left[\frac{n^2}{c^2} + \frac{4\pi^2}{c^2 L l^2} \sum_{i=1}^{N} (\alpha_i - \bar{\alpha})\right] E''(t) = 0 \tag{10}$$

This is of the form $E''(t) + \omega(t)^2 E(t) = 0$ with

$$\omega(t)^2 = \frac{k^2 c^2}{n^2} \left[1 + \frac{4\pi^2}{n^2 L l^2} \sum_{i=1}^{N} (\alpha_i - \bar{\alpha})\right]^{-1} \tag{11}$$

$\omega(t)$ will change with a rate comparable to the reaction rate and hence much

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[4] The sum $\sum(\alpha_i - \bar{\alpha}) \sin k_1 z_i \sin k_2 z_i$ with $k_1 \neq k_2$ is very much smaller than the sum in Eq. (9). Hence the coupling between different modes is negligible.

slower than ω itself. For all practical purposes, this is just a frequency modulation of the laser output.

$\omega(t)$ fluctuates around $\omega_0 = kc/n$. Since the fluctuations are small,

$$\frac{\Delta\omega}{\omega_0} = \frac{\omega - \omega_0}{\omega_0} = -\frac{2\pi^2}{n^2 L l^2} \sum_{i=1}^{N} (\alpha_i - \bar{\alpha}) \tag{12}$$

The actual frequency of the laser is a simple linear function of the extent of the reaction and fluctuates as the extent of reaction fluctuates.

4. CHARACTERIZATION OF THE FLUCTUATION

Each reaction center has two states with polarizabilities α_1, α_2. At equilibrium, the state changes due to fluctuations. The changes may be viewed as instantaneous, i.e., they occur on a very rapid time scale compared to the time scale of the macroscopic reaction. The changes are completely random, i.e., the system possesses no memory. Different reaction sites will be completely uncorrelated if, as is the usual case, the reactive degrees of freedom are greatly outnumbered by the unreactive degrees of freedom (a heat bath).

Let k_{12} be the probability per unit time of the transformation $\alpha_1 \to \alpha_2$, and k_{21} that for the reverse. $\alpha(t) = \alpha_1$ or α_2 and changes with rates k_{12}, k_{21}. For a unimolecular reaction

$$A \underset{k_r}{\overset{k_f}{\rightleftarrows}} B$$

the number of reaction centers is the sum of the numbers of A and B molecules. $k_{12} = k_f$; $k_{21} = k_r$.

For a bimolecular reaction

$$A + B \underset{k_1}{\overset{k_2}{\rightleftarrows}} C$$

with fewer A molecules present than B molecules, the total number of centers is the number of A's plus the number of C's, and $k_{12} = k_2[B]$; $k_{21} = k_1$.[5]

The time autocorrelation function

$$\phi(\tau) = \langle[\alpha(\tau) - \bar{\alpha}][\alpha(0) - \bar{\alpha}]\rangle_{\mathrm{AV}} \tag{13}$$

will be calculated. This is useful because it is the Fourier transform of the power spectrum⁽¹⁸⁾ of the fluctuations in $\alpha(t) - \bar{\alpha}$. If $p_{ij}(t)$ is the probability

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[5] $[B]$ may be safely taken as the equilibrium concentration.

that $\alpha(0) = \alpha_j$ and $\alpha(t) = \alpha_i$, $i, j = 1, 2$, then the average indicated in Eq. (13) may be expressed explicitly as

$$\begin{aligned}\phi(\tau) = p_{11}(t)(\alpha_1 - \bar{\alpha})^2 + p_{12}(t)(\alpha_1 - \bar{\alpha})(\alpha_2 - \bar{\alpha}) \\ + p_{21}(t)(\alpha_2 - \bar{\alpha})(\alpha_1 - \bar{\alpha}) + p_{22}(\alpha_2 - \bar{\alpha})^2\end{aligned} \tag{14}$$

To determine $p_{ij}(t)$, consider $p_1(t)$, the probability of $\alpha(t) = \alpha_1$. The kinetic equation governing $p_1(t)$ is

$$dp_1(t)/dt = -k_{12}p_1(t) + k_{21}[1 - p_1(t)] \tag{15}$$

whence

$$p_1(t) = p_1(0)e^{-2kt} + (k_{12}/2k)(1 - e^{-2kt}); \qquad 2k = k_{12} + k_{21} \tag{16}$$

As $t \to \infty$, $p_1(t) \to p_1^{\mathrm{eq}} = k_{12}/2k$, its equilibrium value.

$$\bar{\alpha} = \alpha_1 p_1^{\mathrm{eq}} + \alpha_2(1 - p_1^{\mathrm{eq}}) = (\alpha_1 k_{12} + \alpha_2 k_{21})/(k_{21} + k_{21}) \tag{17}$$

Furthermore,

$$\begin{aligned} p_{11}(t) &= p_1(t)|_{p_1(0)=1}\, p_1^{\mathrm{eq}}, \qquad & p_{12}(t) &= p_1(t)|_{p_1(0)=0}\,(1 - p_1^{\mathrm{eq}}) \\ p_{21}(t) &= [1 - p_1(t)|_{p_1(0)=1}]\, p_1^{\mathrm{eq}}, \qquad & p_{22}(t) &= [1 - p_1(t)|_{p_1(0)=0}](1 - p_1^{\mathrm{eq}}) \end{aligned} \tag{18}$$

With these results,

$$\phi(\tau) = [k_{12}k_{21}/(k_{12} + k_{21})^2](\alpha_2 - \alpha_1)^2\, e^{-2k\tau} \tag{19}$$

$\phi(0)$ measures the magnitude of the fluctuations about equilibrium. $k_{12}k_{21}/(k_{12} + k_{21})^2$ has a maximum value 1/4 when $k_{12} = k_{21}$. Thus the magnitude of the reaction fluctuations is a maximum when the equilibrium state corresponds to an equal number of reactant and product centers. For reactions going strongly one way ($k_{12} \gg k_{21}$, say), there will be little fluctuation.

Returning to Eq. (12),

$$\Phi(\tau) = \left\langle \frac{\Delta\omega(\tau)}{\omega_0} \cdot \frac{\Delta\omega(0)}{\omega_0} \right\rangle_{\mathrm{AV}} = \frac{4\pi^4}{n^4L^2l^4} \sum_{i,j=1}^{N} \langle[\alpha_i(\tau) - \bar{\alpha}][\alpha_j(0) - \bar{\alpha}]\rangle_{\mathrm{AV}} \tag{20}$$

Since different reaction centers are uncorrelated and all the reaction centers are alike,

$$\Phi(\tau) = \frac{4\pi^4}{n^4L^2l^4} N\phi(\tau) = \frac{4\pi^4}{n^4L^2l^4} N \frac{k_{12}k_{21}}{(k_{12} + k_{21})^2} (\alpha_2 - \alpha_1)^2\, e^{-2kt} \tag{21}$$

The Fourier transform of $\Phi(\tau)$ is a Lorentzian$^{(18)}$ spectrum with "width" $2k$. Hence if the laser's frequency is detected, this signal will have a Lorentzian power spectrum (about ω_0) with "width" $2k$, the reaction rate.

The magnitude of the frequency fluctuations is given by

$$\Phi(0)^{1/2} = \frac{2\pi}{n^2} \frac{(k_{12}k_{21})^{1/2}}{k_{12} + k_{21}} \mid \alpha_2 - \alpha_1 \mid \frac{N^{1/2}}{V} \tag{22}$$

where there are N reaction centers and V is the volume of the laser. Thus

$$\Delta\omega \sim \mid \alpha_2 - \alpha_1 \mid (\rho/V)^{1/2}\, \omega_0 \tag{23}$$

The magnitude of the frequency fluctuations increases with polarizability change, concentration ρ, and base frequency ω_0 and decrease with increasing laser volume.

A more complete characterization of the fluctuations is required to predict the power spectrum of the laser oscillator itself. The assumption that the fluctuations $\Delta\omega(t)$ are a Gaussian random process$^{(19)}$ is very reasonable in view of the fact that thermodynamic fluctuations are in general Gaussian.$^{(20)}$ This means that $\Delta\omega(t)$ may be represented by

$$\frac{\Delta\omega(t)}{\omega_0} = \sum_{n=1}^{\infty} \left(a_n \cos\frac{2\pi nt}{T} + b_n \sin\frac{2\pi nt}{T}\right) \tag{24}$$

with the a_n and n_n independent Gaussian random variables, and T a time much longer than the duration of an experiment ($T \to \infty$). Equation (21) requires

$$\langle a_n^2 \rangle = \langle b_n^2 \rangle = \sigma_n^2 = 2kT\Phi(0)/(n^2\pi^2 + k^2T^2) \tag{25}$$

The oscillator signal may be represented as $E(t) = A\cos[\omega_0 t + \phi(t)]$ if $\dot{\phi}(t) = \Delta\omega(t)$ and the time autocorrelation function for $E(t)$ may be written

$$\begin{aligned} \varphi(\tau) &= \langle E(t)\, E(t+\tau) \rangle \\ &= \tfrac{1}{2}A^2 \langle \cos[\omega_0\tau + \phi(t+\tau) - \phi(t)] \rangle \\ &= \tfrac{1}{2}A^2 \operatorname{Re} e^{i\omega_0\tau} \langle e^{i\phi(t+\tau) - i\phi(t)} \rangle \end{aligned} \tag{26}$$

with neglect of terms oscillating with frequency $\sim 2\omega_0$.

Integrating Eq. (24) gives the phase change

$$\begin{aligned} \phi(t+\tau) - \phi(t) = \frac{\omega_0 T}{2\pi} \sum_{n=1}^{\infty} \Bigg\{ &\frac{a_n}{n} \left[\sin\frac{2\pi n(t+\tau)}{T} - \sin\frac{2\pi nt}{T}\right] \\ &+ \frac{b_n}{n} \left[\cos\frac{2\pi nt}{T} - \cos\frac{2\pi n(t+\tau)}{T}\right] \Bigg\} \end{aligned} \tag{27}$$

whence

$$
\begin{aligned}
\varphi(\tau) &= \frac{1}{2} A^2 \operatorname{Re}[\exp(i\omega_0\tau)] \\
&\quad \times \left\langle \prod_{n=1}^{\infty} \exp \left\{ \frac{i\omega_0 T}{2\pi n} a_n \left[\sin \frac{2\pi n(t+\tau)}{T} - \sin \frac{2\pi n t}{T} \right] \right\} \times \cdots \right\rangle \\
&= \frac{1}{2} A^2 \operatorname{Re}[\exp(i\omega_0\tau)] \prod_{n=1}^{\infty} \exp \left\{ - \left(\frac{{\omega_0}^2 T^2}{2\pi^2} \frac{{\sigma_n}^2}{n^2} \sin \frac{n\pi\tau}{T} \right) \right\} \\
&\xrightarrow[T\to\infty]{} \frac{1}{2} A^2 \cos \omega_0\tau \exp \left[- \frac{1}{4} \Phi(0) \frac{{\omega_0}^2}{k^2} (2k\tau + e^{-2k\tau} - 1) \right]
\end{aligned}
\tag{28}
$$

This corresponds to a line centered at $\omega = \omega_0$ with shape factor

$$
\begin{aligned}
F(\omega - \omega_0) &= \frac{1}{\pi} \int_0^{\infty} \cos[(\omega - \omega_0)\,\tau] \\
&\quad \times \exp \left\{ - \frac{1}{4} \Phi(0) \frac{{\omega_0}^2}{k^2} (2k\tau + e^{-2k\tau} - 1) \right\} d\tau
\end{aligned}
\tag{29}
$$

The zeroth and second moments are

$$
\int_{-\infty}^{\infty} F(\omega)\, d\omega = 1 \qquad \text{and} \qquad \int_{-\infty}^{\infty} F(\omega)\, \omega^2\, d\omega = {\omega_0}^2 \Phi(0) = |\Delta\omega|^2 \tag{30}
$$

and higher moments do not converge since

$$
F(\omega) \underset{\omega\to\infty}{\sim} 2k\, |\Delta\omega|^2 / \pi\omega^4
$$

5. NUMERICAL EXAMPLE

The effect is very small and there may not be enough signal to detect it. As a numerical example, consider a cavity 1 mm × 1 mm × 50 cm with a 0.1 M concentration of reaction centers. Then $Ll^2 = 0.5$ cm^3; $N = 3 \times 10^{19}$. The polarizabilities of simple organic and inorganic molecules are listed in Landolt-Börnstein$^{(21)}$ along with the bond polarizabilities of Denbigh.$^{(22)}$ Typical bond polarizabilities are of the order of 2×10^{-24} cm^3. Suppose $|\alpha_1 - \alpha_2| \sim 10^{-24}$ cm^3. A wide range of k_{12}, k_{21} values are known. If the optimum situation $k_{12} = k_{21}$ is chosen,

$$
\Phi(0) \sim 1.2 \times 10^{-26} \qquad \text{and} \qquad \Delta\omega/\omega_0 \sim 1.1 \times 10^{-13}
$$

At a wavelength of 6000 Å, this corresponds to $\Delta\omega \sim 2\pi \times 50$ Hz.

A modulation with a typical frequency swing of $\sim$50 Hz in an optical frequency of 5×10^{14} is an exceedingly small modulation. There is no intensity problem, of course, since the laser output itself is being analyzed. The direct frequency-demodulation schemes usually envisioned for optical frequencies(23) will probably not be practical because of the low modulation level. This modulation could be detected, however, by a heterodyne frequency conversion to a much lower radio frequency, at which point, standard electronic detection should succeed. This requires a second laser and creates the requirement that it be stable (i.e., have a narrow linewidth; drift could be compensated in the radio equipment) and hence only frequency shifts larger than the natural linewidths would be detectable in practice.[6] This is very difficult experimentally, however.(25)

A direct determination of the lineshape of the oscillator signal itself is much easier than a determination of the frequency fluctuations. The second moment of the lineshape [Eq. (30)] is always $|\Delta\omega|^2$, but the lineshape [Eq. (29)] is not simple. It is very close to Gaussian with second moment $|\Delta\omega|^2$ when $\Delta\omega \gg 2k$ but becomes more or less Lorentzian with $\omega_{1/2} = |\Delta\omega|^2/2k$ with a very long tail in the opposite limiting case. A very wide range of $\Delta\omega/2k$ ratios actually occurs because of the large range of possible values for k.

In summary, the insertion of a chemical reaction into a laser cavity will create a small frequency modulation. The magnitude of the modulation signal is proportional to the number of reactants and the change in polarizability in the reaction. The frequency spectrum of the modulating signal is Lorentzian and the advantage of this type of measurement over more conventional light-scattering experiments is that the "width" of the Lorentzian spectrum is simply related to the reaction rate. Other internal transformations such as rotational diffusion and vibrational relaxation modulate the oscillator in the same way. Two detection schemes are proposed. Frequency demodulation is technically difficult, but seems possible under favorable conditions and the results are easy to interpret. A direct power spectrum analysis is technically easier, but the resulting lineshape is more difficult to interpret.

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