Reaction Kinetics Probed by Dynamic Light Scattering*

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The method of quasi-elastic light scattering as applied to the problem of chemical kinetics is reviewed. A theoretical discussion pertaining to the dissipation modes of the fluctuations of chemically reacting species in a simple bimolecular reaction $2A \leftrightarrows A_2$ is presented. Both the normal mode relaxation times and their corresponding intensities have been calculated. A discussion of the optical wave-mixing technique necessary for high resolution scattering spectroscopy in terms of time correlation analysis and/or spectral distribution is also given. The use of more conventional optical interferometer is suggested for study of rate phenomena faster than 10^{-6} sec.

1. INTRODUCTION

One of Professor Salsburg's most recent contributions in chemical physics before his untimely death was his detailed analysis of the dynamic interaction of light with chemical kinetics. His interest in this problem was stimulated by some discussions with the authors during the spring of 1967. Following these discussions, Professor Salsburg and his students at Rice University carried on some extensive theoretical efforts [1–3] which resulted in very thorough theoretical descriptions of the phenomenon of dynamic light scattering from reactive systems. Subsequent to those discussions, the authors also attained experimental verification of this interaction mechanism in their studies of the kinetics of ionic reactions [4] and biopolymer conformations [5].

Although the field of chemical kinetics has been under very thorough study during the past fifteen years [6–8], the investigation of reaction mechanisms by light scattering is nonetheless appealing in two very important aspects. First of all, light scattering as a probe exerts no perturbation on the chemical system. The high sensitivity of the scattering probe can detect spontaneous fluctuations of the species about their chemical equilibrium. Thus linear approximation to reaction governing kinetics equations is valid at all times. Secondly, the mechanism of interaction between light and matter is the microscopic polarizability of the molecules. This

is different from more conventional probes such as optical density of the samples or volume change upon reaction. Thus, this new technique may serve as a complementary tool to other probes in the investigation of chemical kinetics.

In the ensuing discussion, the kinetics of a chemical reaction with no complications due to solvent interaction will be presented. The theoretical procedure is analogous to those previously used by Professor Salsburg's group. A critical examination of the present experimental status in connection with this light scattering problem will also be given. It will then be obvious that in dealing with experimental problems of statistical mechanics, extensive use of the modern computational facilities is rapidly becoming a necessity.

2. THEORY

As mentioned in the introduction, the coupling mechanism between optical radiation and matter in a scattering process is the molecular polarizability tensor $\bar{\bar{\alpha}}$. If an incident plane wave, characterized by

$$\mathbf{E}_{in} = \mathbf{E}_0 e^{i(\mathbf{k}_0 \cdot \mathbf{r} - \omega_0 t)}, \tag{1}$$

where $\mathbf{k}_0$ is the light wave vector and ω_0 is the optical frequency, impinges upon a molecule of polarizability $\bar{\bar{\alpha}}(\mathbf{r}, t)$, then the induced dipole moment takes on the form:

$$\mathbf{p}(\mathbf{r}, t) = \bar{\bar{\alpha}}(\mathbf{r}, t) \cdot \mathbf{E}_{in}. \tag{2}$$

The scattered radiation into any solid angle is the collection of elementary dipole oscillators whose radiation field is along some scattered direction θ subtended by the element of solid angle $d\Omega$:

$$\mathbf{E}_{sc}(\theta, t) \propto \sum_n \ddot{\mathbf{p}}_n(\mathbf{r}, t). \tag{3}$$

For a macroscopic continuum, this summation goes over to an integral over all space. One can then describe the polarizability tensor as a macroscopic dielectric constant tensor, $\bar{\bar{\epsilon}}(\mathbf{r}, t)$. It is convenient to separate the stationary uniform part of $\bar{\bar{\epsilon}}$ by letting

$$\bar{\bar{\epsilon}}(\mathbf{r}, t) = \epsilon_0 + \delta\bar{\bar{\epsilon}}(\mathbf{r}, t), \tag{4}$$

where now $\delta\bar{\bar{\epsilon}}$ is that portion of the dielectric tensor which exhibits space–time variations. The integral over the first part of Eq. (4) leads to a zero contribution scattering, while the second part leads to the momentum conservation condition that

$$\mathbf{k}_0 = \mathbf{k}_s + \mathbf{K}, \tag{5}$$

where $\mathbf{K}$ is the momentum of K-th spatial Fourier component of $\delta\bar{\epsilon}$, and $\mathbf{k}_s$ is the scattered wave vector. One finds, therefore, scattered light collected at angle θ comes solely from the coherent contributions of the dielectric constant gradient whose spacing is $\Lambda \equiv 1/K$, and that

$$K \cong 2k_0 n \sin \frac{\theta}{2},\qquad\qquad (6)$$

where n is the index of refraction of the medium. Equation (3) now can take the form

$$\mathbf{E}_{sc}(\theta, t) \propto \omega^2 \, \delta\bar{\epsilon}(\mathbf{K}, t) \cdot \mathbf{E}_{in}.\qquad\qquad (7)$$

Since these macroscopic regions of size Λ each contain many molecules, the concept of local thermodynamics with these regions is valid within these regions. One can thus discuss the fluctuations of the local dielectric constant resulting from fluctuations of these local thermodynamic or hydrodynamic variables. These are the material density, the local temperature, or the extent of progress of chemical reactions. In the discussions of Blum and Salsburg, the detailed coupling of the progress variable λ, to density ρ and temperature T is discussed. Their work shows that the rates of chemical reactions are coupled to density fluctuations of the solvent giving rise to the hypersonic analog of ultrasonic relaxation due to chemical reactions. These effects are, of course, exhibited in the Brillouin doublets of the scattered spectrum. They also show that there exists the direct coupling of the polarizabilities of the reacting species to other species dependent variables such as species diffusion. Thus far, the experiments have indicated that the direct coupling mode yields a much higher scattering cross section than the coupling through the solvent. Therefore the remaining theoretical discussion will deal with a particular reaction, the monomer-dimer equilibrium, taking into consideration only diffusion and chemical reaction. Such an equilibrium may be described by

$$2A \underset{k_b}{\overset{k_f}{\underset{\longleftarrow}{\longrightarrow}}} A_2,\qquad\qquad (8)$$

where A is the monomer species and A_2 is the corresponding dimer. k_f and k_b are the rate constants for the reaction.

The essence of this discussion has been presented by Berne, et al. [9, 10], Yeh and Keeler [11], and Weinberg and Kapral [12]. The starting point is the assumption of an isotropic medium. $\delta\bar{\epsilon}(r, t)$ is then a scalar quantity, and one can write

$$\delta\epsilon(\mathbf{r}, t) = \sum_{i=1}^{N} \left(\frac{\partial \epsilon}{\partial n_i}\right) \delta n_i(\mathbf{r}, t) = \mathbf{m} \cdot \delta\mathbf{n}\qquad\qquad (9)$$

and δn_i is the species fluctuation of the i-th component. Here $(\partial \epsilon / \partial n_i) \equiv m_i$, and the vector quantities are $\mathbf{m} = \{m_1, m_2, ..., m_i, ..., m_N\}$ and

$$\delta n_i = \{\delta n_1, \delta n_2, \cdots \delta n_2 \cdots \delta n_N\},$$

where N species are present. In the present case, $N = 2$. Using Fick's law for diffusion of individual species and coupling the reaction linearly, one obtains

$$\frac{\partial}{\partial t} \delta n_i(\mathbf{r}, t) = D_i \nabla^2 \delta n_i(\mathbf{r}, t) - k_f' \delta n_i(\mathbf{r}, t) + k_b \delta n_j(\mathbf{r}, t), \qquad i, j = 1, 2, \quad (10)$$

where D_i is the translational diffusion coefficient of the i-th species, $k_f' = 4k_f(n_A)_0$. Here $(n_A)_0$ is the equilibrium concentration of the monomer species. Taking the spatial Fourier transforms, one obtains

$$\frac{\partial}{\partial t} \delta n_i(\mathbf{K}, t) + \sum_{j=1}^{2} M_{ij} \delta n_j(\mathbf{K}, t) = 0, \qquad i, j = 1, 2, \quad (11)$$

where

$$M_{ij} = \begin{vmatrix} D_A K^2 + k_f' & -k_b \\ -k_f' & D_{A_2} K^2 + k_b \end{vmatrix}. \quad (12)$$

The solution to this set of equations is of the form

$$\delta n_i(\mathbf{K}, t) = \delta n_i(\mathbf{K}, 0) e^{-\lambda t}, \quad (13)$$

where the λ's are to be defined by the eigenvalue problem

$$| \bar{M} - \lambda \bar{I} | \cdot \delta n(\mathbf{K}, 0) = 0. \quad (14)$$

Using $D \equiv \frac{1}{2}(D_A + D_{A_2}) K^2$, and $\Delta \equiv \frac{1}{2}(D_A - D_{A_2}) K^2$, the resultant eigenvalues are

$$\lambda_1 \cong D,$$
$$\lambda_2 \cong D + \tau_R^{-1}, \quad (15)$$

where

$$\tau_R^{-1} = k_b + 4k_f n_{A_0}, \quad (16)$$

and $D_A \approx D_{A_2}$.

The general solution to the eigenvector matrices were first obtained by Blum [13]. Since $\bar{M}$ is not a symmetrical matrix, both the left and right eigenmatrices are necessary.

One finds here that the right and left eigenmatrices are, respectively,

$$A = N^{1/2} \begin{bmatrix} 1 & -1 \\ K & 1 \end{bmatrix} \quad \text{and} \quad \mathscr{A} = N^{1/2} \begin{bmatrix} 1 & -K \\ 1 & 1 \end{bmatrix}, \tag{17}$$

where $N = (1 + K)^{-1}$ and $K = k_f'/k_b$.
The scattered intensity is

$$I_{sc}(\mathbf{K}, t) \propto \langle \delta\epsilon^*(\mathbf{K}, 0)\, \delta\epsilon(\mathbf{K}, t) \rangle, \tag{18}$$

where an ensemble average is denoted by the brackets, $\langle \cdots \rangle$. It is therefore necessary to use both left and right eigenfunctions to form this product. Specifically,

$$\delta n_i(\mathbf{K}, t) = \sum_l c_l a_{il} e^{-\lambda_l t},$$

$$\delta n_j^*(\mathbf{K}, t) = \sum_m d_m \alpha_{jm} e^{-\lambda_m t}, \tag{19}$$

where a_{il} and α_{jm} are elements of $\bar{A}$ and $\bar{\mathscr{A}}$, respectively, and c_l, d_m are determined from initial conditions of the specific problem.

Evaluating c_l and d_m by

$$c_l = \sum_i a_{il}\, \delta n_i(\mathbf{K}, 0) \tag{20}$$

and

$$d_m = \sum_j \delta n_j(\mathbf{K}, 0)\, \alpha_{jm}, $$

one can finally put Eq. (17) into the form

$$I_{sc}(\mathbf{K}, t) = \sum_{l=1}^{2} I_l(\mathbf{K}, t), \tag{21}$$

where

$$I_l(\mathbf{K}, t) = (\mathbf{m} \cdot \mathbf{A}_l)(\mathscr{A}_l \cdot \bar{G} \cdot \mathbf{m})\, e^{-\lambda_l t}, \tag{22}$$

and

$$G = \begin{bmatrix} g_{11} & g_{12} \\ g_{21} & g_{22} \end{bmatrix}, \tag{23}$$

where

$$g_{ij} = \langle \delta n_i(-\mathbf{K}, 0)\, \delta n_j(\mathbf{K}, 0) \rangle. \tag{24}$$

For the particular monomer-dimer equilibrium, one finds that

$$I_1 = Ng(m_A + Km_{A_2})[m_A + m_{A_2}] e^{-DK^2t},$$

$$I_2 = Ng(m_{A_2} - m_A)[m_{A_2} - Km_A] e^{-(DK^2 + \tau_R^{-1})t},$$

$$(25)$$

where

$$g_{AA_2} = g_{A_2A} = 0$$

and

$$g_{AA} = g_{A_2A_2} = g \quad \text{are assumed.}$$

The results here indicate that if $m_{A_2} = m_A$, i.e., if the polarizabilities of the two species are the same, then the reaction sensitive component is no longer detectable.

The experimental problems associated with this technique of studying reaction kinetics reside with being able to provide for sensitive enough instrumentations to detect this weak reactive component accurately in the presence of a stronger diffusion component. The following section on experimental techniques will try to emphasize methods of data acquisition and analysis for these complex spectra.

Even though considerable extensions of the theoretical problem have been made to include charge fluctuations of ionic species [14] and depolarized scattering spectrum due to reacting anisotropic molecules [15, 16], no experiments have been performed along these directions. Some of the difficulties anticipated for these latter problems include the smallness of the intensity contribution to charge fluctuations and the necessity of an apriori knowledge of rotational diffusion constants in depolarized scattering. These two effects will not be further explored here.

3. EXPERIMENTAL TECHNIQUES

The photoelectric detector is a square law detector for the scattered parameter $\mathbf{E}_{sc}(t)$. That is, the detected current, $i_{det}(t)$, can be given by:

$$i_{det}(t) = \langle \mathbf{E}_{sc}^*(t) \mathbf{E}_{sc}(t) \rangle. \tag{26}$$

In order to find the appropriate field correlation function given by Eq. (17), one must calculate correlation functions of the instantaneous photocurrent. The current correlation function is then given by

$$I(\tau) \equiv \langle i^*(t) i(t + \tau) \rangle = \langle \mathbf{E}_{sc}(t) \mathbf{E}_{sc}^*(t) \mathbf{E}_{sc}^*(t + \tau) \mathbf{E}_{sc}(t + \tau) \rangle. \tag{27}$$

This product, however, is already a second-order field correlation function, and is not in general that function discussed in the above section. The first assumption necessary for the reduction of the expression in Eq. (26) to simpler form is that the fluctuation variables are stationary Gaussian random variables. For small fluctuations of chemical species about the equilibrium, this can be considered valid. One can then apply the ergodic hypothesis and reduce Eq. (26) to terms of less formidable form:

$$I(\tau) = \langle \mathbf{E}_{sc}(0) \, \mathbf{E}_{sc}^{*}(0) \rangle \langle \mathbf{E}_{sc}^{*}(\tau) \, \mathbf{E}_{sc}(\tau) \rangle$$

$$+ \langle \mathbf{E}_{sc}(0) \, \mathbf{E}_{sc}^{*}(\tau) \rangle \langle \mathbf{E}_{sc}^{*}(0) \, \mathbf{E}_{sc}(\tau) \rangle$$

$$+ \langle \mathbf{E}_{sc}(0) \, \mathbf{E}_{sc}(\tau) \rangle \langle \mathbf{E}_{sc}^{*}(0) \, \mathbf{E}_{sc}^{*}(\tau) \rangle. \tag{28}$$

The last term is a fast osccilation term of zero mean. The first two terms can be written as

$$I(\tau) = |\, R(0)|^2 + |\, R(\tau)|^2, \tag{29}$$

where $R(0) = \langle \mathbf{E}_{sc}^{*}(0) \, \mathbf{E}_{sc}(0) \rangle$ and $R(\tau) = \langle \mathbf{E}_{sc}^{*}(0) \, \mathbf{E}_{sc}(\tau) \rangle$. It is the $R(\tau)$ term which is directly related to the field correlation function of Eq. (17).

A most obvious procedure to extract the experimental information is to bias the detectors thus eliminating $|\, R(0)|^2$, and then to perform the a.c. correlation function analysis. The desired result $R(\tau)$ is obtained by calculating $(I(\tau))^{1/2}$. This technique has been successfully used in the study of the diffusion of single species of macromolecules [17], and the binary mixture diffusion near critical points [18]. At present, this is the technique used by the authors in their studies of the kinetics of biological macromolecules [19, 20]. The most severe complication confronting this procedure is the periodic oscillations of any component of the system. An oscillation of period T will be felt throughout all times in the calculation of the correlation function. Even minor oscillations may be as intense as the scattered intensity at a few time constants away from $\tau = 0$, and thus may cause much uncertainty in data analysis. Great care must be taken to minimize the magnitude of these persistent oscillations.

An alternative procedure is to perform a spectral analysis of $|\, R(\tau)|^2$:

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} |\, R(\tau)|^2 \, e^{i\omega t} \, d\tau. \tag{30}$$

Here, however, $I(\omega)$ is related to the $|\, R(\tau)|^2$ function, and for a complicated $R(\tau)$ field correlation function as those of the previous section, a cross term enters to further complicate experimental situations. In spectral analysis, one therefore normally resorts to a different scattering configuration. Here, a part of the

unscattered light is then mixed with the scattered light. The detected photocurrent is then given by

$$i_{\text{det}} = \langle \mathbf{E}_{L0}^{*}(t)\, \mathbf{E}_{sc}(t) \rangle, \tag{31}$$

where $\mathbf{E}_{L0}(t)$ is considered an optical reference local oscillator of constant amplitude and fixed frequency. Then one obtains

$$I'(\tau) = \text{d.c.} + I_{L0}(\tau)\, R(\tau). \tag{32}$$

Under the assumption that $I_{L0}(\tau)$ is a constant, the new $I'(\tau)$ is a direct measure of the field correlation function. $I'(\omega)$ can then be formed to obtain the true transform of $R(\tau)$. This technique has found wide applicability in light scattering problems [21, 22]. Recently, conformation transition kinetics in (dAT) polymer has been observed by this method [5].

The main drawback of this technique is the stability of $I_{L0}(\tau)$. For some of the more high power ion lasers, line voltage instabilities arising from the three-phase power lines is usually sufficient to modulate signal function $R(\tau)$ so as to be detrimental to results within those low frequency ranges of interest.

For relaxation processes which occur between small molecules where the rate information is fast and the intensity of scattering is small, the optical correlation techniques become inefficient. In those situations, $\tau_R < 10^{-6}$ sec, the most appropriate technique is the Fabry–Perot interferometer of high resolution. Here the spectral analysis takes place prior to detection by means of multiple reflection interferometry. The photocurrent simply registers d.c. pulses corresponding to single photoelectron emissions. Less than one photoelectron per sec may be detected when the emission pulses are selected with appropriate pulse shaping and noise discrimination levels. The Fabry–Perot interferometer length may be swept by piezoelectric crystal and the resultant signal subjected to digital summation procedures. An alternative sweeping procedure is by pressure variation of a gas in the Fabry–Perot interferometer cavity. Weak scattering systems, such as ionic solutions undergoing hydration equilibria [4], have been observed using this technique.

Principal drawbacks to this procedure at the present lies with the nonexistence of high powered, single frequency, stable, cw laser. This is certainly not an intrinsic limitation on the technique described here.

CONCLUSION

The versatility of this method of dynamic light scattering for the investigation of reaction kinetics cannot be overemphasized. The sensitivity of this technique to

hydrodynamic conformation changes, particularly within the range where chemical reactions take place adds a further handle for the detection of intermediate complexes whose formation may have thus far eluded investigators. This is particularly true with respect to the research in macromolecular kinetics.

The experimental difficulties encountered have also been placed in proper perspective. There is no intrinsic limitation except when the reacting species exhibit no change in molecular polarizabilities. Such possibilities are clearly small. The experimental problems of signal-to-noise, arising from either a small differential polarizability or microphonic oscillations, should and will be eliminated in further development of this technique.

Since diffusive effects are always present in the study of reaction kinetics by light scattering, it is imperative to have available accurate and sophisticated techniques for data analysis for complex spectra. Present curve fitting routines can perform adequately, fits to multiples of exponential curves or Lorentzian curves in the presence of low noise [23]. More precision and even faster data analysis methods for these experimental statistical mechanics problems are highly desirable.

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