crystals (which in any case should *not* be similar to that of $(CH_2)_{34}$ since the band origins are different) therefore implies nothing about the presence or absence of regular folding, contrary to previous assertions.[7]

We conclude that an analysis of the vibrational spectrum of $(CH_2)_{34}$ does not permit a determination of whether folding in polyethylene single crystals is tight or not, beyond the statement that it cannot involve the specific tight fold of $(CH_2)_{34}$. Our analysis does suggest that if GG conformations are present in the fold they are (relative to $(CH_2)_{34}$) unstrained.

Longitudinal Acoustic Modes. It has been suggested[8,9] that the LA modes of polyethylene single crystals would be characteristic of their fold length. It was, however, noted that the relationship obtained for the finite paraffins would be valid for polyethylene only if it could be assumed that oscillations in a planar zigzag segment were completely decoupled from oscillations in segments joined to it by folds. In order to determine whether or not such an assumption is valid, we have calculated the LA modes of some linear paraffins (see Table III) for purposes of comparison with the calculation for $(CH_2)_{34}$.

A comparison first of the observed LA modes of $(CH_2)_{34}$ with the relationship found for linear paraffins (*cf.* Figure 4 of ref 8) shows that these frequencies do not fit in with those of the finite molecules. If we assume $n = 15$ for each planar segment of the $(CH_2)_{34}$ molecule, then the observed frequencies of 147, 431, and 496 cm^{-1} are far from their expected values of about 153, 410, and 560 cm^{-1}. This suggests that coupling effects are not negligible. A similar conclusion is reached by comparing the ω_1 modes of the linear paraffins (Table III) and of $(CH_2)_{34}$ (Table II). In all cases the observed frequency for the former is higher than the calculated frequency, while for the latter (using the same force field) the observed frequency is lower than the calculated frequency. This suggests that for cyclic structures such as $(CH_2)_{34}$ the ω_1 LA mode of the planar segments will be consistently lower than the value for a linear chain. If this effect extends to n values appropriate to polyethylene crystals, *viz.*, about 100, then use of the relationship for finite paraffins will tend to overestimate the planar zigzag chain length. This effect is of the order of 6% for $(CH_2)_{34}$, but may be different for longer segments and for different fold geometries (for example, folds in polyethylene single crystals may not consist of GGTGG conformations, but in addition they do not give rise to cyclic structures).

We conclude that caution must be used in applying the relationship for LA frequencies in finite paraffin chains to the determination of the lengths of planar zigzag segments in folded chain polyethylene.[16]

Acknowledgment. We are indebted to R. F. Schaufele for making his Raman data available to us prior to publication. This research was supported by a grant from the National Science Foundation, No. GP-10922.

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Inelastic Light-Scattering Study of Macromolecular Reaction Kinetics. I. The Reactions A $\rightleftharpoons$ B and 2A $\rightleftharpoons$ A_2

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ABSTRACT: This paper considers the effect of chemical reactions on the spectrum of light scattered from macromolecular solutions. A general formalism is developed, taking into account only diffusion and chemical reaction, using the matrix eigenvalue technique of Salsburg and coworkers. This formalism is applied to the reactions A $\rightleftharpoons$ B and 2A $\rightleftharpoons$ A_2, which are shown to yield identical results after appropriate definition of relaxation times and effective equilibrium constants. Particular attention is focused on the case where the diffusion coefficients of reactants and products are different, while their polarizabilities are identical. Numerical calculations, using plausible values of diffusion coefficients and chemical relaxation times for macromolecular solutions, indicate that macromolecular reaction processes should measurably perturb inelastic light-scattering spectra in the audiofrequency region.

Inelastic light scattering, which measures the spectrum of Rayleigh light scattered from solutions illuminated with monochromatic laser light, has emerged as a significant new technique for studying macromolecules in solution. A useful review of this technique, with extensive bibliography, has been written by Chu.[2] Most of the applications to polymers have been concerned with measurement of diffusional motion. However, one of the potentially most significant applications is measurement of the kinetics of fast reactions. This has been the subject of many theoretical[3-11] and a few experimental[12,13a] investigations.

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These investigations have generally emphasized the case in which the inelastic light-scattering spectrum associated with the reaction arises because of polarizability differences between reactants and products. However, particularly for reactions involving macromolecules, the differences in diffusion coefficients of reactants and products are likely to be more important. It is the purpose of this article to develop the theory appropriate for this case, as applied to the simple reactions $A \rightleftharpoons B$ and $2A \rightleftharpoons A_2$.

It is interesting to note that experimental investigations to date[12,13a] of fast reaction kinetics by inelastic light scattering have dealt with very fast reactions, characterized by relaxation times of microseconds or faster. However, in order for reactions to be observable by inelastic light scattering, it is required only that the characteristic time for reaction be comparable to or less than that for diffusion. The spectral half-width associated with diffusion is

$$\nu_{1/2} = K^2D/2\pi \text{ sec}^{-1} \tag{1}$$

where D is the diffusion coefficient and

$$K = 4\pi/\lambda \sin (\theta/2) \tag{2}$$

where θ is the scattering angle and λ is the wavelength of light in the medium. With light from the He–Ne laser of wavelength 6328 Å *in vacuo* irradiating an aqueous solution of refractive index 1.334 containing a polymer with diffusion coefficient $D = 1 \times 10^{-7}$ cm^2/sec, the half-width for diffusion, measured at $\theta = 30°$, is 75 sec^{-1}. This may be compared with turnover numbers for enzyme-catalyzed reactions, which are typically in the range $\tau^{-1} = 10^2$–10^4 sec^{-1}, or with reciprocal half-times for diffusion-controlled bimolecular association reactions which would be in the range of 10^4 sec^{-1} for a 10^{-5} M solution of a globular protein. Thus it appears that inelastic light-scattering studies of the kinetics of biologically important macromolecular reactions should be feasible using low audio-frequency techniques.

In section I of this paper, a general formalism for the calculation of inelastic light-scattering spectra will be developed, using the matrix eigenvalue technique of Salsburg and co-workers,[5–6] but considering only diffusion and reaction, and neglecting other transport processes such as viscosity and heat conduction which will contribute negligibly to the scattering from polymer solutions. In section II, the formalism is applied to the unimolecular reaction $A \rightleftharpoons B$. When the diffusion coefficients D_A and D_B of the two species are equal, and the polarizabilities or refractive index increments are unequal, the result obtained by Berne, *et al.*,[3b] is obtained. When $D_A \neq D_B$, but the polarizabilities are equal, more complicated equations are obtained whose consequences are illustrated graphically for some sample cases. In section III, it is shown that the equations pertinent for the bimolecular association reaction $2A \rightleftharpoons A_2$ are identical, after appropriate redefinition of parameters, with those for $A \rightleftharpoons B$.

I. General Formalism

Light scattering arises from refractive index fluctuations. In polymer solutions, the most important of these fluctuations come from concentration fluctuations. If the refractive index increment due to species i is $\epsilon_i = (\partial\epsilon/\partial c_i)$, and the concentration fluctuation in i at point R and time t is $\delta c_i(R, t)$, then the total refractive index fluctuation is

$$\delta\epsilon(R, t) = \sum_i \epsilon_i \delta c_i(R, t) \tag{3}$$

The angular dependence of light scattering is related to the spatial Fourier transform $\delta\epsilon(K, t)$ of the refractive index fluctuation, and the spectrum of light scattered in a given direction is related to the space–time Fourier transform $\delta\tilde{\epsilon}(K, \omega)$. The intensity of light scattered in direction K with angular frequency shifted by ω from that of the irradiating light is, neglecting various constants of proportionality

$$I(K, \omega) = \text{Re}\langle \delta\tilde{\epsilon}(K, \omega)\delta\epsilon(-K, 0)\rangle \tag{4}$$

where Re denotes the real part and the angular brackets denote an ensemble average. Using eq 3, this becomes

$$I(K, \omega) = \text{Re}\sum_i\sum_j \epsilon_i\epsilon_j\langle \delta\tilde{c}_i(K, \omega)\delta c_j(-K, 0)\rangle \tag{5}$$

Fluctuations in concentrations will occur due to diffusion and reaction. The equation governing the space and time dependence of these fluctations is taken to be of the macroscopic form

$$\frac{\partial \delta c_i(R, t)}{\partial t} = D_i\nabla^2\delta c_i(R, t) + \sum_l T_{il}\delta c_l(R, t) \tag{6}$$

It is assumed that fluctuations are so small that reaction terms of the form $\delta c_l \delta c_m$ are negligible. T_{il} is a reaction matrix which contains rate constants and equilibrium concentrations of reactants and products.

Spatial Fourier transformation of eq 6 yields

$$\frac{\mathrm{d}\delta c_i(K, t)}{\mathrm{d}t} = -K^2D_i\delta c_i(K, t) + \sum_l T_{il}\delta c_l(K, t) \tag{7}$$

which may be written in matrix form

$$\mathrm{d}\delta c(K, t)/\mathrm{d}t = M\cdot\delta c(K, t) \tag{8}$$

δc is the concentration fluctuation vector ($\delta c_1, \delta c_2, \ldots, \delta c_r$), while the elements of the matrix M are

$$M_{ij} = -K^2D_i\delta_{ij} + T_{ij} \tag{9}$$

where δ_{ij} is the Kronecker delta.

Equation 8 has the formal solution

$$\delta c(K, t) = e^{Mt}\delta c(K, 0) \tag{10}$$

According to Sylvester's theorem,[13b] the matrix operator $\exp(Mt)$ can be expanded as

$$\exp(Mt) = \sum_m \exp(\mu_m t)\,\frac{\mathbf{F}_m(M)}{F_m(\mu_m)} \tag{11}$$

where the eigenvalues of M are μ_m, and

$$\mathbf{F}_m(M) = \prod_{n\neq m} (M - \mu_n I) \tag{12a}$$

$$F_m(\mu_m) = \prod_{n\neq m} (\mu_m - \mu_n) \tag{12b}$$

I is the unit matrix.

Substituting these results into eq 10, and taking the time Fourier transform

$$\delta\tilde{c}(K, \omega) = \int_0^\infty e^{-i\omega t}\delta c(K, t)$$

we find

$$\delta\tilde{c}(K, \omega) = -\sum_m \frac{1}{\mu_m - i\omega}\,\frac{\mathbf{F}_m(M)}{F_m(\mu_m)}\delta c(K, 0) \tag{13}$$

Inserting this result in eq 5, taking the real part, and converting back to component notation, we obtain

$$I(K, \omega) = -\sum_m \frac{B_m \mu_m}{\omega^2 + \mu_m{}^2} \tag{14}$$

where

$$B_m = \sum_i \sum_j \sum_k \epsilon_i \epsilon_k \left[\frac{\mathbf{F}_m(M)}{F_m(\mu_m)}\right]_{ij} \langle \delta c_j(K, 0) \delta c_k(-K, 0) \rangle \tag{15}$$

Equation 14 expresses the inelastic light-scattering spectrum as a sum of Lorentzian curves with half-widths at half-heights of $-\mu_m$ (the eigenvalues are negative, since the concentration fluctuations in eq 8 are decreasing exponential functions of time) and intensities B_m. Using the results of Kirkwood and Goldberg,[14] the concentration fluctuations can be expressed in terms of the equilibrium concentrations (by mass) $\bar{c}_j$ and the relative fluctuations ξ_{jk}

$$\langle \delta c_j(K, 0) \delta c_k(-K, 0) \rangle = \bar{c}_j \bar{c}_k \xi_{jk} \tag{16}$$

If the chemical potential per gram of the jth species, with molecular weight M_j, is written

$$\tilde{\mu}_j = \tilde{\mu}_j{}^0(T, P) + (RT/M_j) \ln \gamma_j \bar{c}_j \tag{17}$$

and the logarithm of the activity coefficient γ_j is taken as linear in the concentrations

$$\ln \gamma_j = \sum_k A_{jk} \bar{c}_k + O(\bar{c}_j \bar{c}_k) \tag{18}$$

then Kirkwood and Goldberg show that

$$\xi_{jk} = M_j \delta_{jk} / \bar{c}_j - M_j A_{kj} \tag{19}$$

These results lead to the following expression for the intensity of the mth Lorentzian

$$B_m = \sum_i \sum_j \epsilon_i \epsilon_j \left[\frac{\mathbf{F}_m(M)}{F_m(\mu_m)}\right]_{ij} M_j \bar{c}_j - \sum_i \sum_j \sum_k \epsilon_i \epsilon_k \times \left[\frac{\mathbf{F}_m(M)}{F_m(\mu_m)}\right]_{ij} M_j \bar{c}_j \bar{c}_k A_{kj} \tag{20}$$

In all subsequent calculations we shall assume ideal solution behavior, for which $A_{kj} = 0$.

II. The Reaction $A \rightleftharpoons B$ (k_f Forward, k_b Backward)

As a first example of the above formalism, we consider the reversible unimolecular interconversion of A to B, with forward and backward rate constants k_f and k_b. Considering only the change in c_A due to reaction, we have

$$(\partial c_A / \partial t)_{rxn} = -k_f c_A + k_b c_B$$

Writing $c_A = \bar{c}_A + \delta c_A$, $c_B = \bar{c}_B + \delta c_B$, and noting that the equilibrium equation is

$$K_e' = k_f / k_b = \bar{c}_B / \bar{c}_A \tag{21}$$

we then have

$$(\partial \delta c_A / \partial t)_{rxn} = -k_f c_A + k_b \delta c_B \tag{22a}$$

and similarly

$$(\partial \delta c_B / \partial t)_{rxn} = k_f \delta c_A - k_b \delta c_B \tag{22b}$$

Thus the matrix M is

$$M = \begin{bmatrix} -K^2 D_A - k_f & k_b \\ k_f & -K^2 D_B - k_b \end{bmatrix} \tag{23}$$

and solution of the eigenvalue equation $|M - \mu I| = 0$ yields, after some rearrangement

$$\mu_\pm = (1/2)\left\{-K^2(D_A + D_B) - \tau^{-1} \pm \tau^{-1} \times \left[1 + 2\left(\frac{K_e' - 1}{K_e' + 1}\right)\frac{K^2 \Delta}{\tau^{-1}} + \left(\frac{K^2 \Delta}{\tau^{-1}}\right)^2\right]^{1/2}\right\} \tag{24}$$

where we have defined $\Delta = D_A - D_B$ and the relaxation time $\tau = (k_f + k_b)^{-1}$. We subsequently let $\mu_1 = \mu_-$, $\mu_2 = \mu_+$.

Case I. $D_A = D_B$. Let us first consider the case where both the diffusion coefficients of A and B are equal to D, which has been previously treated in the literature.[3b] Then $\Delta = 0$, and

$$\mu_1 = -(\tau^{-1} + K^2 D) \tag{25a}$$

$$\mu_2 = -K^2 D \tag{25b}$$

Furthermore, letting $\epsilon_2 = \zeta \epsilon_1$, noting that $M_2 = M_1$, and using eq 12, 20, 21, and 25, we find

$$B_1 = \epsilon_1{}^2 M_1 c_1 \frac{K_e'(1 - \zeta)^2}{1 + K_e'} \tag{26a}$$

$$B_2 = \epsilon_1{}^2 M_1 c_1 \frac{(1 + \zeta K_e')^2}{1 + K_e'} \tag{26b}$$

It is evident from these equations that if $\epsilon_1 = \epsilon_2$, $\zeta = 1$ and only a single Lorentzian will contribute to the spectrum, with half-width $K^2 D$. On the other hand, if $\zeta \neq 1$, the spectrum will be the sum of two Lorentzians, both centered at zero frequency. On decreasing the scattering angle, $K^2 D \rightarrow 0$ so that, when $\tau^{-1} \gg K^2 D$, essentially all of the breadth of the observed spectrum will be due to the isomerization reaction.

Case II. $\epsilon_A = \epsilon_B$. We now consider the other extreme case, which appears more likely for macromolecular reactions, in which the refractive index increment remains constant and equal to $\partial \epsilon / \partial c$ but the diffusion coefficient changes during the reaction. The matrix eigenvalues are then given by the full eq 24, while the associated intensities are

$$B_1 = -\frac{M_1 c_1 (\partial \epsilon / \partial c)^2}{\mu_1 - \mu_2}[K^2(D_A + K_e' D_B) + \mu_2(1 + K_e')] \tag{27a}$$

$$B_2 = -\frac{M_1 c_1 (\partial \epsilon / \partial c)^2}{\mu_2 - \mu_1}[K^2(D_A + K_e' D_B) + \mu_1(1 + K_e')] \tag{27b}$$

Figures 1–3 show plots of the half-width at half-height as a function of K^2, calculated from eq 14, 24, and 27 for various values of D_A, D_B, and τ^{-1}.

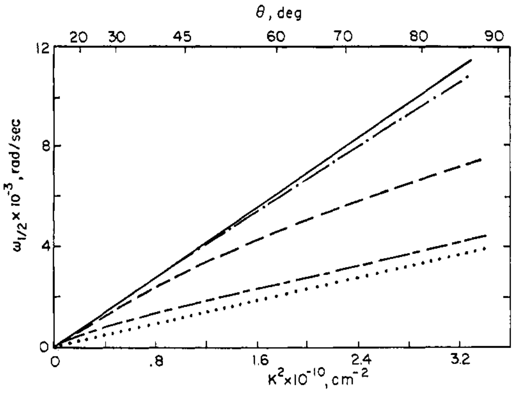

Figure 1. Spectral half-width at half-height, $\omega_{1/2}$, as a function of $K^2 = (16\pi^2/\lambda^2) \sin^2 (\theta/2)$ for solutions undergoing reactions $A \rightleftharpoons B$ or $2A \rightleftharpoons A_2$. $K_e' = 1$, $D_1 = 6 \times 10^{-7}$ cm²/sec, $D_2 = 1 \times 10^{-7}$ cm²/sec. Values of reciprocal relaxation time τ^{-1}, sec^{-1}: · · · · ·, $<10^2$; – – –, 10^3; — — —, 10^4; — · —, 10^5; ———, 10^6.

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[14] J. G. Kirkwood and R. J. Goldberg, *J. Chem. Phys.*, 18, 54 (1950).

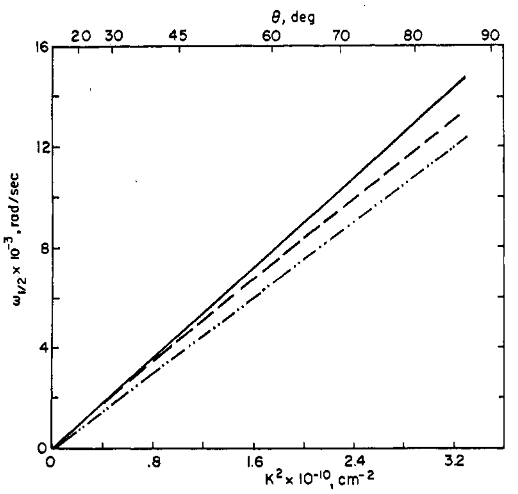

Figure 2. Same as Figure 1, with $D_1 = 6 \times 10^{-7}$ cm^2/sec, $D_2 = 3 \times 10^{-7}$ cm^2/sec. Values of τ^{-1}, sec^{-1}: — · · —, 1; — — —, 10^4; ———, 10^6.

It is possible to simplify these expressions in the limit $\tau^{-1} \gg K^2\Delta$, by expanding the square root in eq 24 and keeping only the leading terms. The result is

$$\mu_1 = \tau^{-1} \tag{28a}$$

$$\mu_2 = -K^2[(D_A + K_e'D_B)/(1 + K_e')] \tag{28b}$$

$$B_1 = M_1c_1(\partial\epsilon/\partial c)^2[K_e'/(1 + K_e')](K^2\Delta/\tau^{-1})^2 \tag{29a}$$

$$B_2 = M_1c_1(\partial\epsilon/\partial c)^2(1 + K_e') \tag{29b}$$

Thus in this limit the half-widths of the Lorentzians are similar to those pertaining to case I, with D replaced by an average diffusion coefficient weighted according to the equilibrium proportions of the two components. However, in contrast to case I, the intensity B_1 associated with the chemical reaction mode decreases rapidly, as K^4, with decreasing scattering angle. Thus in this case nothing is gained by working at low scattering angles in attempting to analyze the contribution made by reaction to the spectrum.

III. The Reaction $2A \rightleftharpoons A_2$ (k_f Forward, k_b Backward)

It is of considerable interest to note that the dimerization reaction $2A \rightleftharpoons A_2$ shows exactly the same behavior as the unimolecular isomerization reaction discussed above, if the constants K_e' and τ^{-1} are suitably redefined. If n_1 and n_2 are the molar concentrations of monomer and dimer, the time rate of change of n_1 is

$$(\partial n_1/\partial t)_{\text{rxn}} = -2k_fn_1^2 + 2k_bn_2$$

Letting $n_1 = \bar{n}_1 + \delta n_1$, $n_2 = \bar{n}_2 + \delta n_2$, and noting that $K_e = k_f/k_b = \bar{n}_2/\bar{n}_1^2$, this becomes

$$(\partial\delta n_1/\partial t)_{\text{rxn}} = -4k_f\bar{n}_1\delta n_1 + 2k_b\delta n_2 \tag{30a}$$

similarly

$$(\partial\delta n_2/\partial t)_{\text{rxn}} = 2k_f\bar{n}_1\delta n_1 - k_b\delta n_2 \tag{30b}$$

Converting these equations to a mass concentration basis, $c_i = n_iM_i$, and noting that $M_2 = 2M_1$, we find

$$(\partial\delta c_1/\partial t)_{\text{rxn}} = (-4k_f\bar{c}_1/M_1)\delta c_1 + k_b\delta c_2 \tag{31a}$$

$$(\partial\delta c_2/\partial t)_{\text{rxn}} = (4k_f\bar{c}_1/M_1)\delta c_1 - k_b\delta c_2 \tag{31b}$$

Since in a chemical relaxation experiment of the Eigen[15] type, $\delta c_2 = -\delta c_1$, the relaxation time according to eq 31 is

$$\tau^{-1} = 4k_f\bar{c}_1/M_1 + k_b \tag{32}$$

It is thus easily seen that the matrix eigenvalues for the dimerization reactions are given by eq 24, if we let $D_A = D_1$, $D_B = D_2$, define τ^{-1} by eq 32, and let

$$K_e' = 4\bar{c}_1k_f/M_1k_b \tag{33}$$

The intensity factors, according to eq 20, are, using the definitions given above

$$B_1 = -\frac{M_1\bar{c}_1\epsilon_1^2}{\mu_1 - \mu_2}[K^2(D_1 + \zeta^2K_e'D_2) + \mu_2(1 + \zeta^2K_e') + k_bK_e'(1 - \zeta)^2] \tag{34a}$$

$$B_2 = -\frac{M_1\bar{c}_1\epsilon_1^2}{\mu_2 - \mu_1}[K^2(D_1 + \zeta^2K_e'D_2) + \mu_1(1 + \zeta^2K_e') + k_bK_e'(1 - \zeta)^2] \tag{34b}$$

It is easily verified that these equations become identical with eq 26 if $D_1 = D_2$, or with eq 27 if $\zeta = 1$.

IV. Discussion

From Figures 1–3 it appears that inelastic light scattering represents a feasible approach to measuring the kinetics of rapid macromolecular isomerization and dimerization reactions involving appreciable changes in diffusion coefficients. In fact, changes in D of 30% or more are to be expected for many such processes. The unimolecular interconversion between the slow and fast sedimenting forms of T2 bacteriophage involves a 40% change in D,[16] and the dimerization of two spherical proteins to form a dumbbell-shaped dimer will cause a decrease of 25% in D.[17] Helix–random coil transitions in high molecular weight polypeptides or polynucleotides should occasion even greater changes in hydrodynamic radius,[18] and hence in diffusion coefficient.[19]

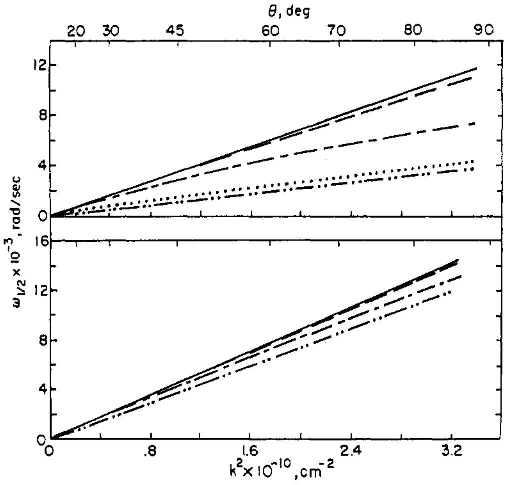

Figure 3. Same as Figure 1. Upper figure, $D_1 = 6 \times 10^{-8}$ cm^2/sec, $D_2 = 1 \times 10^{-8}$ cm^2/sec; lower figure, $D_1 = 6 \times 10^{-8}$ cm^2/sec, $D_2 = 3 \times 10^{-8}$ cm^2/sec. Values of τ^{-1}, sec^{-1}: — · · —, 1; · · · · ·, 10^2; — — —, 10^3; — — —, 10^4; ———, 10^6.

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On the other hand, the refractive index increments of DNA preparations under a variety of conditions do not vary by more than ±5%,[20] and similar results would be expected for proteins. Therefore, the intensity B_1 associated with the chemical reaction, according to eq 26a, would be quite small under most circumstances, and the deviation from pure diffusion behavior consequently difficult to detect.

When $D_1 = 6 \times 10^{-7}$ cm^2/sec, $D_2 = 3 \times 10^{-7}$ cm^2/sec, and the scattering angle is 90°, it may be seen from Figure 2 that the half-width at half-height in frequency units $(\omega_{1/2}/2\pi)$ varies from 2.09 kHz at $\tau^{-1} = 1$ sec^{-1}, to 2.27 kHz at $\tau^{-1} = 10^4$ sec^{-1}. Thus it is required to detect a frequency shift of 180 Hz to distinguish the rapidly reacting mixture from the slowly reacting one. This shift of 8.6% is easily measurable with current apparatus. When $D_1 = 6 \times 10^{-8}$ cm^2/sec and $D_2 = 3 \times 10^{-8}$ cm^2/sec, the comparable half-widths are 209 Hz for $\tau^{-1} = 1$ sec^{-1}, and 247 Hz for $\tau^{-1} = 10^4$ sec^{-1}. This shift of 38 Hz, or 18%, should also be measurable with adequate precision.

In these calculations we have neglected nonideality effects by setting the coefficients $A_{kj} = 0$. Nonzero values of these coefficients will produce two effects. First, the diffusion coefficients will be functions of the concentrations of the macromolecular and small molecular components of the solution. Therefore, the diffusion coefficients D_A and D_B appearing in the expression for μ, eq 24, should be those determined under the same conditions of ionic strength, temperature, pH, and concentration as those under which the light-scattering measurements on the reacting mixtures are performed. Second, the A_{kj}'s enter into the intensities of the various Lorentzian components, eq 20. The relative intensities of these components will thus be different from the ideal case, but the differences can be minimized by working at low macromolecular concentrations.

From the fact that the half-widths and intensities are identical functions of the diffusion coefficients, chemical relaxation times, and suitably defined equilibrium constants for both the isomerization and dimerization reactions, it may be conjectured that the inelastic light-scattering spectrum of a reacting solution depends only on the number of species and the number of reactions among them. This conjecture will be examined in future work.

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Rayleigh Line-Width Measurements of Diffusion Constants of Polydisperse Random-Coil Macromolecules

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ABSTRACT: Measurements of the concentration dependence of the apparent diffusion constant of the polydisperse polystyrene NBS-706 in 2-butanone at 25.0° have been made by Rayleigh line-width spectroscopy over the concentration range 0.0007–0.0046 g cm^{-3}. Extrapolation of these data yields a value of 3.88×10^{-7} cm^2 sec $^{-1}$ for D_c, the apparent diffusion constant at zero concentration for this polymer. Rayleigh line-width measurements of the concentration dependence of two polystyrenes with narrow molecular weight distributions were made in order to establish the relation between the zero concentration diffusion constant D_0 and molecular weight over a limited range. The data for the narrow-distribution polymers allowed determination of D_w, the diffusion coefficient of the species having molecular weight equal to the weight-average molecular weight of NBS-706. The experimental value of D_c/D_w is in good agreement with predictions based on the theory of Pecora for the spectrum of the Rayleigh line in light scattered from solutions of polydisperse random-coil macromolecules. Experiments are also reported which show that very small amounts of dust in solutions can lead to serious error in diffusion constants determined by Rayleigh line-width spectroscopy.

Since its inception in 1964, the technique of Rayleigh line-width spectroscopy has found increasing application to determination of diffusion constants of both synthetic and naturally occurring macromolecules in dilute solution. Several significant advantages of this method have become apparent.[1] Only a small amount of solution is required. A direct measurement of the diffusion constant at a given concentration is obtained from a solution in macroscopic equilibrium; the need for tedious corrections or extrapolations to eliminate effects due to macroscopic concentration gradients is eliminated. Line-width measurements are rapid compared to conventional methods, and the speed of measurement is independent of the diffusion constant; determinations of diffusion constants of slowly diffusing species for which conventional measurements are difficult or impractical may thus be made with acceptable precision. Because of these many advantages, the Rayleigh line-width technique seems likely to gain increasing use in routine measurements of translational diffusion of high-molecular-weight substances in solution.

One complication frequently encountered in such measurements, however, is the effect of sample polydispersity on the shape and width of the Rayleigh line. The effects of polydispersity on the Rayleigh line spectrum have been treated theoretically by Pecora and Tagami[2,3] for both random-coil and rigid-rod macromolecules, and detailed numerical calcu-

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