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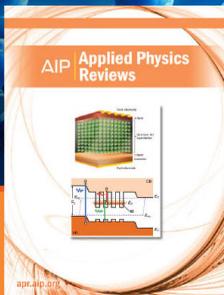
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# Picosecond photoisomerization and rotational reorientation dynamics in solution<sup>a)</sup>

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The *trans*–*cis* isomerization rates for stiff-diphenylbutadiene (S-DPB) in *n*-alkane solvents were measured using single photon counting methods and the rotational reorientation times  $\tau_R$  for S-DPB and *trans* stilbene were obtained by picosecond polarization spectroscopy. In neither case did  $\tau_R$  vs viscosity show Stokes–Einstein–Debye (SED) behavior. The values of  $\tau_R$  were used to calculate the angular velocity correlation frequencies  $\beta$  using the Hubbard relation. The variation of isomerization rate with  $\beta$  was found to be predicted well by the Kramers equation when barrier frequencies of  $154\text{ cm}^{-1}$  for stilbene and  $16\text{ cm}^{-1}$  for S-DPB were used. This Kramers-Hubbard fit finesses questions regarding the validity of the one dimensional Kramers model and focuses attention on the SED equation. The dynamical relationship between the torsional friction, important in isomerization, and rotational friction, which determines the overall angular motion of the molecules, is discussed.

## I. INTRODUCTION

The angular motion of a large molecule immersed in surrounding media is usually partitioned into the overall rotation and the internal rotation describing conformational changes. Both motions are influenced by solvent frictional forces. One theoretical approach to this stochastic dynamical problem has been based on the Fokker–Plank theory in which molecular rotation is described by an angle dependent Langevin equation. The equation of motion for internal rotation is distinguished from that for overall rotation in that it includes forces from a potential barrier. The solution of this internal motion problem gives a barrier crossing rate describing the decay of reactant configurations into the product well. The problem of a Brownian particle escaping over a barrier, first solved by Kramers about five decades ago,<sup>1</sup> has since attained considerable attention in chemical reaction dynamics.<sup>2–22</sup> In Kramers' method the entire friction range is divided into an inertial regime, controlled by energy diffusion, and a diffusive regime, controlled by spatial diffusion. In the energy diffusion region the rate increases with the friction, or collision frequency, whereas when spatial diffusion is controlling the internal motion, the rate decreases as the friction increases. Therefore a peak known as Kramers turnover should exist in the variation of rate with friction. According to Kramers, this peak is the upper limit of the two barrier crossing rates and is always less than the value given by the transition state theory.

In a previous study<sup>2</sup> we reported the Kramers turnover region for the isomerism of stilbene in supercritical fluid ethane at 350 K. The experimental temperature was chosen to be as high as possible above the critical temperature of ethane (305.2 K), within the limits of the experimental apparatus, in order to avoid the density gap between gas and liquid. The result clearly showed a peak rate at 120 atm, corre-

sponding to a shear viscosity of 0.03 cp. However, the result showed an anomaly near the critical pressure, indicating that solvent effects such as spatial correlations are important to the isomerism in this region.

The spatial diffusion regime has also been the subject of extensive experimental studies including measurements of nonradiative decay rates of stilbene and diphenylbutadiene in *n*-alkane solvents.<sup>3,7</sup> The *trans*–*cis* isomerization rates for these aromatic molecules in nonpolar solvents were examined as a function of solvent viscosity. To fit these data to the Kramers model a hydrodynamic description of solute–solvent interaction was assumed in which the shear viscosity, a measurable macroscopic solvent property, is a linear function of the friction. Both stilbene and diphenylbutadiene showed significant deviations from Kramers equation in the high viscosity region. However the deviations were rationalized by introducing a frequency dependent friction which amounts to employing a generalized (non-Markovian) Langevin equation.<sup>13,14</sup> Although this introduction of memory effects has permitted the experiments to be fitted to a Kramers equation, the resulting harmonic potential surface seemed unphysical, leading to a barrier frequency of  $\sim 10\text{ cm}^{-1}$ . Furthermore, the effect of frequency dependent friction is expected to be pronounced only for high barriers, so that the applicability of this theory to these model systems having barriers of a few kcal/mol requires validation.<sup>15</sup>

On the other hand, the viscosity dependent isomerism of diphenylbutadiene<sup>8</sup> and binaphthyl<sup>5</sup> in polar solvents, such as the *n*-alcohol series, were well fit by a Kramers model. For *trans*-stilbene in hydroxylic solvents limiting (Smolukowski) behavior was observed.<sup>4</sup> The photoisomerization of stiff-stilbene in nonpolar solvents also showed a barrier crossing time that was proportional to viscosity.<sup>3</sup> However in that case there is also a reduction in the potential barrier compared with *trans*-stilbene thus rendering the Kramers theory less applicable.

In this paper we address experimentally the validity of using hydrodynamic variables in the Kramers theory. Such

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an assumption was not involved in the original development by Kramers. There were already reports in literature which show the breakdown of the Stokes–Einstein–Debye (SED) equation which relates the rotational reorientation time to the solvent viscosity. Rhodamine 6G<sup>23,24</sup> and DODCI<sup>25</sup> in *n*-alcohol solvents and *p*-terphenyl in *n*-alkane solvents<sup>26</sup> are typical examples. Evidently the hydrodynamic description of rotational motion in the liquid phase often fails just as expected on elementary grounds when the size of the solvent is larger than that of the solute. It is appealing to relate these deviations to the free volume effect<sup>27</sup> arising from the molecular nature of the solution. The *trans*–*cis* isomerization process is a torsional motion around a fixed axis and so the frictional forces that determine it may be simply proportional to those determining the overall rotation. We might therefore expect the free volume to be important in the isomerization reaction. The solvent drag coefficients or rotational correlation frequencies obtained directly from measured rotational relaxation times may therefore provide a route to the velocity correlation frequencies needed to evaluate the Kramers prediction for the isomerization. The purpose of this paper is to test these ideas on the molecules stilbene and stiff-diphenylbutadiene (S-DPB).

Velsko, Waldeck, and Fleming<sup>7(b)</sup> found that the assumption of proportionality between the rotational friction and the effective friction for the isomerism of DODCI did not generate an improved fit of the Kramers equation. They concluded that the isomerism motion in that case feels a different friction than isomerization. As mentioned below, the different frictions are expected to be proportional only when the response to collisions is linear.

First we review briefly the Kramers theory in order to focus more sharply on the purpose of the work. Then experiments on the rotational relaxation times and isomerism of S-DPB and stilbene in *n*-alkanes are described. Finally the consequences of the connections between the angular velocity correlations and the rotational correlation function are discussed in relation to the experiments.

## II. KRAMERS THEORY

*Trans*–*cis* isomerization is basically the escape over a barrier of a solute molecule in a reactant configuration, under the influence of the irregular fluctuating torque exerted by surrounding media. If the isomerization were an internal rotation (twisting), the dynamics would be described by a Langevin equation with one independent variable  $\theta$ , the dihedral angle between two twisting subgroups around a fixed axis,

$$I\ddot{\theta} + \zeta\dot{\theta} + \frac{dV}{d\theta} = f(t), \quad (1)$$

where  $I$  is the moment of inertia,  $\zeta$ , is the angular drag coefficient, and  $f(t)$  is a random fluctuating torque. A delta correlated torque is appropriate when the time scale of the motion of the solvent molecule is much faster than the internal rotational motion.  $V(\theta)$  is the relevant part of the excited state potential surface. Quantum mechanical *ab initio* calculations and spectroscopic studies have confirmed that in the excited singlet state of *trans*-stilbene and all *trans*-diphenyl-

butadiene a barrier exists between the *trans* and twisted configurations. To obtain an analytic solution of Eq. (1) the intramolecular potential is assumed to be piecewise parabolic,

$$V(\theta) = \begin{cases} \frac{1}{4}I\omega_a^2\theta^2 & (\theta < \theta_R) \\ E_b - \frac{1}{4}I\omega_b^2(\theta - \theta_b)^2 & (\theta \geq \theta_R) \end{cases}, \quad (2)$$

where  $\omega_a$  and  $\omega_b$  are the well frequency and barrier frequency, respectively. The  $\theta_R$  is an inflection point, joining two piecewise potentials as shown in Fig. 1. A description of the product well is not necessary<sup>20</sup> in a Kramers model.

Kramers assumed that for sufficiently high barriers compared with  $kT$ , the probability density in the initial well would decay exponentially with rate constant  $k_{nr}$ , so that the solution of the stochastic differential Eq. (1) becomes<sup>1,11</sup>

$$k_{nr} = \frac{\omega_a}{2\pi\omega_b} \frac{\beta}{2} \left\{ \left[ 1 + \left( \frac{2\omega_b}{\beta} \right)^2 \right]^{1/2} - 1 \right\} \exp(-E_b/kT), \quad (3)$$

where  $\beta$  is angular velocity correlation frequency.

When  $\beta$  approaches a sufficiently large value, the rate becomes inversely proportional to  $\beta$  (the Smoluchowski approximation):

$$k_{nr} = \frac{\omega_a\omega_b}{2\pi\beta} \exp(-E_b/kT). \quad (4)$$

However, for small  $\beta$  the reaction is controlled by energy diffusion as in the Lindeman–Hinshelwood theory<sup>28</sup> so that the rate increases monotonically with  $\beta$ .

In the foregoing simple analysis the multidimensionality is not incorporated into the rate. The partition functions for transition state and reactant will in general be different and this will alter the rate.<sup>22,29</sup> In the present instance we assume these factors are unity so that the interpretation of  $\omega_a$  obtained by fitting data to Eq. (3) is not straightforward.

This competition between the energy controlled and diffusion controlled processes results in a turnover of the reaction rate. However it is now experimentally suspected that the turnover region can be complicated by density changes.<sup>2,22,30</sup> The turnover region was extensively studied by us, but in this paper we will focus on the moderate friction

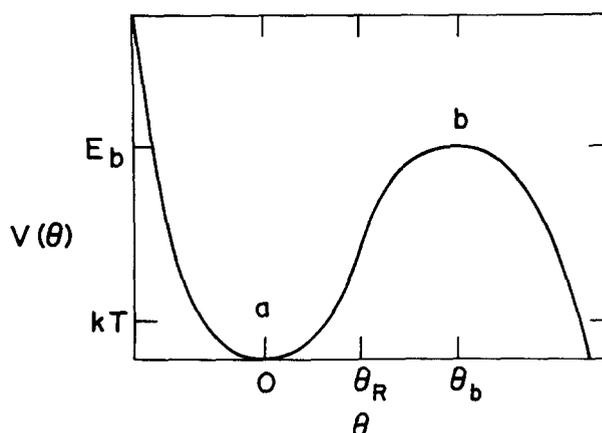
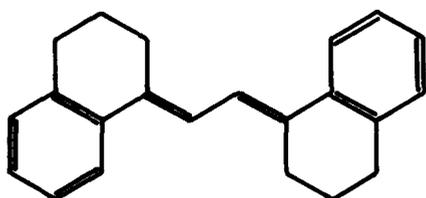


FIG. 1. The schematic potential function diagram of S-DPB in the excited state, relevant to the Kramers model.

regime for which one would naturally use Eq. (3). The question addressed here concerns what value of the angular velocity correlation frequency  $\beta$  should be used when comparing experiment and theory.

### III. EXPERIMENTAL

Two laser systems were used in this experiment. A time correlated single photon counting (TCSPC) system was employed to measure the fluorescence lifetimes of stiff-diphenylbutadiene. The UV excitation pulse at 327 nm was obtained by doubling the DCM dye laser pulse in a lithium iodate crystal. Data were collected at 410 nm with magic angle polarization and processed on an IBM personal computer. The number of counts in the peak channel of the 512 channels was about  $10^4$  and the ratio of the counting rate to the repetition rate was less than 1% for the entire experiment. The instrument function was 180 ps and time scale per channel 3.53 ps. Measurements of the fluorescence anisotropy of the molecule were carried out with the computer controlled rotating analyzer and an instrument function of 130 ps; the deconvolution procedure yielded rotational reorientation times which agreed well with those obtained from picosecond polarization spectroscopy. The rotational reorientation times of *trans*-stilbene were only measured by the polarization method, largely confirming the values published earlier on the basis of the fluorescence anisotropy,<sup>31</sup> the details of which are described elsewhere.<sup>32</sup> The initially prepared first singlet excited state ( $S_1$ ) produced by pumping at 296 nm was probed with a visible pulse at 592 nm in the region of the  $S_1 \rightarrow S_n$  transient absorption. The dye laser pulse width was 6–8 ps. The lifetime and reorientation time measurements were performed at 19 and 22.5–24 °C, respectively.



*E,E*-Ditetrahydronaphthylidene-ethane (stiff-diphenylbutadiene):  $C_{22}H_{22}$  (mp 144–146 °C) was prepared from commercially available  $\alpha$ -tetralone (Aldrich) in four steps. Specifically,  $\alpha$ -tetralone was converted to 1-vinyl-1-tetralol via the method of Normat<sup>33</sup> and in turn treated with concentrated hydrobromic acid to afford the 1,3-rearranged allylic bromide. Reaction of the latter with triphenylphosphine led to the phosphonium bromide which was then subjected to Wittig reaction<sup>34</sup> with  $\alpha$ -tetralone. The purity of S-DPB was checked by the excitation wavelength independence of the fluorescence quantum yield. All *n*-alkane solvents (pentane–hexadecane) were obtained from Aldrich. Some solvents, not labeled as Gold or Spectroscopic grade were purified by distillation. Those 99% pure solvents showed no detectable differences in the lifetime measurements compared with the purified solvents for 327 nm excitation. The radiative decay rate determination required the fluorescence emission spectra of stiff-diphenylbutadiene in hexane and

hexadecane which were recorded by a Perkin Elmer MPF-4 spectrofluorometer. A solution of quinine sulfate in 1N  $H_2SO_4$  was used as a fluorescence intensity standard.

## IV. RESULTS AND DISCUSSION

### A. Photoisomerization dynamics of stiff-DPB

The time constants from the polarization spectroscopy experiments were obtained by deconvolution of the instrument functions using a simple numerical procedure. The previously unreported lifetimes of stiff-DPB in various alkane solvents are shown in Table I. They all satisfactorily fit single exponential decays and gave acceptable values of  $\chi^2$ . The nonradiative decay rate was obtained from the inverse of the measured lifetime  $k_{obs}$  through the following relation:

$$k_{obs} = k_r + k_{nr} = F(\eta) \exp(-E_b/kT) + k_r, \quad (5)$$

where  $k_r$  is radiative rate constant and  $F(\eta)$  is a viscosity dependent frequency factor.  $k_r$  was determined in several solvents from the Strickler and Berg formula<sup>35</sup> and the average value  $6.2 \times 10^{+8} \text{ s}^{-1}$  was used. This value can be compared with the  $k_r$  for *trans*-DPB of  $7.7 \times 10^{+8} \text{ s}^{-1}$ . The isomerization process of diphenylpolyenes usually dominates all other nonradiative pathways and, therefore we will assume that the isomerization rate of stiff-DPB is given by the nonradiative rate, although this has not yet been directly measured.

The excited state potential surface of *trans*-stilbene and diphenylbutadiene has been frequently studied.<sup>7(a),36</sup> The nature of the potential surface of DPB in the excited state is thought to arise from the avoided crossing of a  $B_u$  state with an  $A_g$  state just as in the stilbene case. The frequency factor  $F(\eta)$  depends on viscosity, so the barrier to isomerism can be obtained by an isoviscosity plot which measures the rate in several solvents at the same viscosity but at different temperatures. The result of this experiment is shown in Fig. 2, which yields 3.3 kcal mol<sup>-1</sup> for the barrier. Figure 3 shows the isomerization rate as a function of viscosity for stiff-DPB and for stilbene<sup>3</sup>: in both cases a best fit to Eq. (3) is also shown.

### B. Reorientation time and breakdown of Stokes' law

The decay curve obtained by polarization spectroscopy depends on both the rotational relaxation and fluorescence

TABLE I. Fluorescence lifetimes for stiff-diphenylbutadiene

Solvent	Viscosity <sup>a</sup> (cp)	Lifetime (ps)	$\chi^2$
<i>n</i> -Pentane	0.226	54	1.09
<i>n</i> -Hexane	0.308	70	1.06
<i>n</i> -Heptane	0.413	88	1.29
<i>n</i> -Octane	0.546	109	1.01
<i>n</i> -Nonane	0.713	131	0.97
<i>n</i> -Decane	0.920	155	1.27
<i>n</i> -Undecane	1.176	174	1.02
<i>n</i> -Dodecane	1.488	203	1.13
<i>n</i> -Tridecane	1.865	230	1.00
<i>n</i> -Tetradecane	2.319	261	1.00
<i>n</i> -Pentadecane	2.862	288	1.16
<i>n</i> -Hexadecane	3.505	311	1.21

<sup>a</sup>Viscosity is taken from Ref. 44 at 20.0 °C.

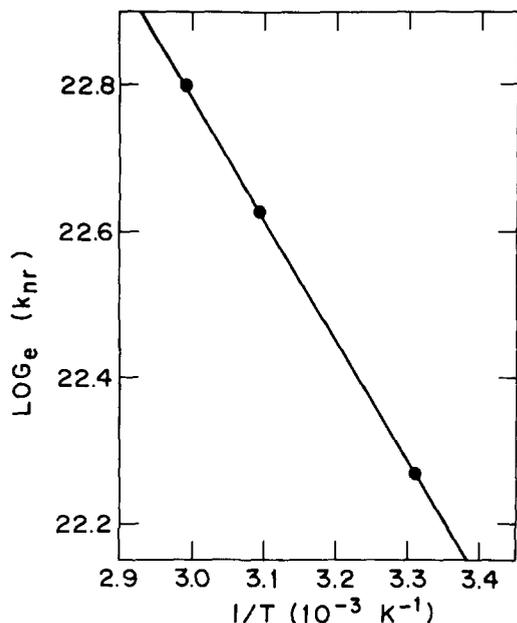


FIG. 2. The isoviscosity plot for the radiationless rate constants of stiff-DPB in normal alkanes, a shear viscosity of 1.57 cp was used.

lifetimes. The rotational reorientation time can be obtained from

$$\tau_p^{-1} = 2[\tau_R^{-1} + \tau_f^{-1}], \quad (6)$$

where  $\tau_R$  is rotational reorientation time,  $\tau_p$  the measured decay time, and  $\tau_f$  the known fluorescence lifetime, tabulated in Table I.

Figure 4 shows the rotational correlation times of stiff-DPB and *trans*-stilbene in *n*-alkane solvents as a function of viscosity at 24 and 22.5 °C, respectively. These plots clearly demonstrate the breakdown of the Stokes–Einstein–Debye relation, because the rotational correlation time is not proportional to viscosity and it does not linearly extrapolate to zero at zero viscosity. We will briefly summarize the hydrodynamic description of rotational motion in a liquid and discuss its applicability to these observations.

According to Stokes' law a particle moving in a continuous fluid feels a friction which is a monotonic function of

viscosity. Einstein and Debye extended this idea to the rotational motion of the molecule and so the rotational orientation time is often given approximately by the formula known as SED equation:

$$\tau_R = (V_h/kT)\eta, \quad (7)$$

where  $V_h$  is the hydrodynamic volume of the molecule. This relationship has customarily been adjusted by relaxing the following assumptions which are usually invoked in its derivation: (a) The shape of molecule: The SED equation assumes the rotating molecule is a sticky sphere and  $V_h$  is  $4\pi a^3/3$ , where  $a$  is the radius of the molecule. Many molecules, such as diphenylpolyenes, are better approximated as ellipsoidal rather than spherical. When the molecule can be treated as a prolate or oblate ellipsoid, the correction for the hydrodynamic volume is given by the Perrin formula<sup>37</sup> which contains the axial ratio of the rotor. (b) Changing boundary conditions: The SED equation is based on a stick boundary condition. In other words, the velocity of the solvent molecules is zero on the "surface" of the solute. It is experimentally known that this is probably valid only when there is a strong solvent–solute interaction such as hydrogen bonding. Otherwise the slip boundary condition is more appropriate. There is no rotational friction on the surface for slip boundary conditions and the rotational correlation time of the perfect smooth hard sphere does not depend on viscosity. Of course, for real molecules the rotational friction is never zero on the surface and the solute molecule can displace the solvent molecules upon rotation. In addition, it has been reported that there are some cases of partial slip or subslip boundary conditions.<sup>38</sup> (c) Free volume effect: The rotational relaxation is a result of collisional events between the solute and the solvent. The discontinuous nature of the solution phase rationalizes the concept of there being, at any instant, free space between the solute and solvent molecules, which lessens the friction, or angular momentum transfer, which may occur only on "contact." Qualitatively, the solute molecule can be considered to have a larger probability of being found in a freely rotating state. The leveling off observed in the viscosity dependence of rotational relaxation in condensed media has been explained by this free volume

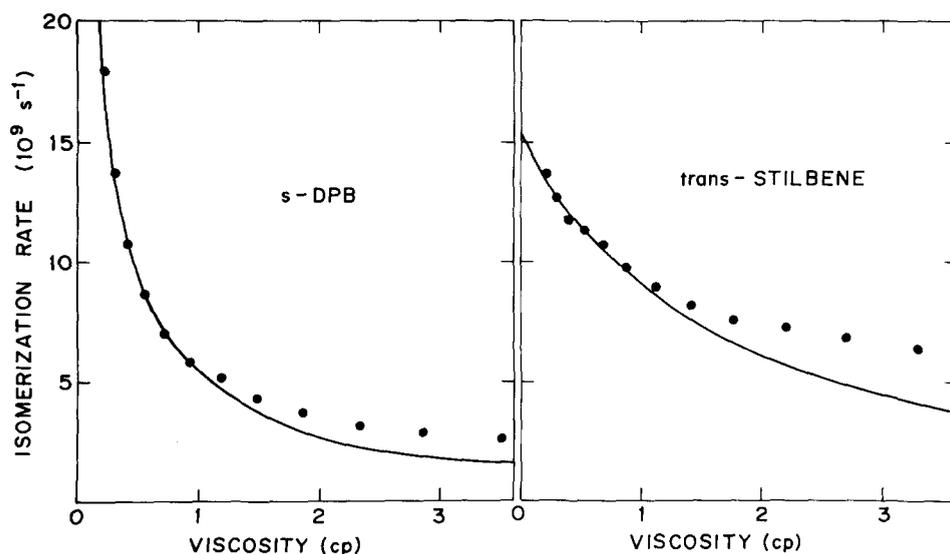


FIG. 3. The Kramers fit of the photoisomerization rate of diphenyl-polyenes vs viscosity. (i) The parameters for S-DPB are:  $I = 1.17 \times 10^{-44} \text{ m}^2 \text{ kg}$ ,  $d = 4.3 \text{ \AA}$ , and  $r = 1.8 \text{ \AA}$ . The calculated curve is optimized to the low viscosity region with  $\omega_a = 5.0 \times 10^{13} \text{ s}^{-1}$  and  $\omega_b = 3.0 \times 10^{12} \text{ s}^{-1}$ . (ii) The hydrodynamic parameters for *trans*-stilbene are taken from Ref. 3, with  $\omega_a = 3.5 \times 10^{13} \text{ s}^{-1}$  and  $\omega_b = 2.9 \times 10^{13} \text{ s}^{-1}$ .

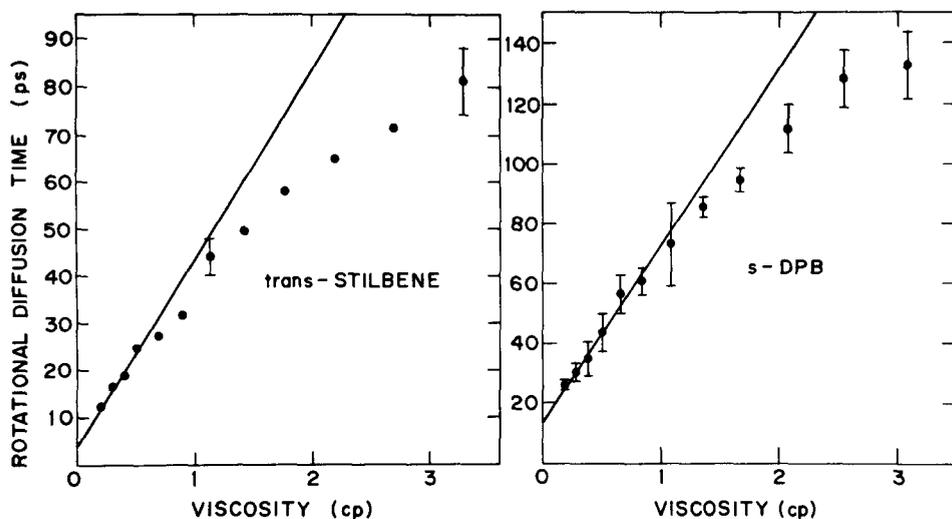


FIG. 4. The rotational diffusion times of diphenylpolyenes in *n*-alkane solvents as a function of viscosity. The solid lines are the least square fits of the six data points (pentane–decane) for S-DPB and the four data points (pentane–octane) for *trans*-stilbene corresponding to the most linear regime.

effect. The idea of introducing the molecular nature of the solution into the hydrodynamic theory was initiated by Gierer and Wirtz<sup>39</sup> and modified and improved by Dote *et al.*<sup>27</sup> According to the free space model the correction factor is given as a function of the hydrodynamic volume of solvent and solute. The uncertainty involved in the evaluation of the correction factor may be large.<sup>26,27</sup> (d) Free rotor correlation time: When a molecule rotates without suffering a collision, classical time correlation function formalism gives a characteristic decay time estimated by the free rotor correlation time

$$\tau^0 = \left(\frac{I_R}{kT}\right)^{1/2}, \quad (8)$$

where  $I_R$  is the moment of inertia about the axis under consideration. The hydrodynamic description of rotational reorientation on the other hand gives zero intercept at zero viscosity. But experimentally the zero viscosity intercept appears to have some value. This intercept,  $\tau_R^0$ , has been suggested to equal  $\tau^0$ .<sup>40,41</sup>

Based on these four factors the modified SED equation is of the form

$$\tau_R = (V_h/kT)\eta(fC) + \tau_R^0, \quad (9)$$

where  $f$  is a variable parameter depending on molecular shape,  $C$  is a dimensionless parameter which accounts for boundary conditions associated with the free volume effect.<sup>27</sup> Figure 4 illustrates that  $\tau_R$  is linearly proportional to the solvent shear viscosity in the low viscosity region for the cases studied here. But at higher viscosities than *n*-octane (stilbene) and *n*-decane (S-DPB) the rotational reorientation time starts to deviate significantly from linearity. The deviations become important when the solvent molecules are longer than the solutes, so that the hydrodynamic description is not expected to be valid and the SED equation can be expected to break down. This failure of the SED equation has now been observed in many experiments.<sup>23–26,38</sup> We suggest that the deviation results from the breakdown of Stokes' law, that is, the effective friction is not a linear function of shear viscosity when the solvent becomes larger than the solute.

The linear portions of the  $\tau_R$  vs  $\eta$  curves gave slopes of

39 ps/cp for stilbene and 59 ps/cp for S-DPB. The intercepts are 4 and 13 ps for stilbene and S-DPB. These values are 3 to 4 times larger than  $(I_R/kT)^{1/2}$ .

### C. Comparison with Kramers model

When the hydrodynamic interaction between two twisting groups is ignored, the angular velocity correlation frequency in Kramers equation is usually regarded as a reduced friction coefficient given by

$$\beta = \zeta_r/I, \quad (10)$$

where  $\zeta_r$  is the friction coefficient for the rotation of the twisting group about the relevant axis and  $I$  is its moment of inertia. And the hydrodynamics relates the friction constant to the solvent shear viscosity,

$$\zeta_r = 4\pi\eta dr^2, \quad (11)$$

where the slip boundary condition was applied.<sup>13</sup>

Figure 3 shows the photoisomerization rate of stilbene and stiff-DPB in the series of *n*-alkane solvents as a function of viscosity. The solid lines are best fit to Eqs. (3), (10), and (11) using the parameters noted in the figure captions. The calculated barrier crossing rate deviates significantly from the experimental data in the high viscosity region. Such data were previously suggested to illustrate the breakdown of the *Kramers theory* for stilbene<sup>3</sup> and diphenylbutadiene.<sup>7</sup> However, it seems reasonable to test the applicability of Stokes' law. This was carried out as discussed in the previous section through measurements of the rotational correlation times of the molecule in the same solvents, as shown in Fig. 4. From this information it is evident that the torsional friction coefficient in Kramers equation cannot be obtained from the macroscopic solvent viscosity through Eq. (11). The (reduced) friction constant or angular velocity correlation frequency can be directly related to the rotational reorientation time by the Hubbard relation<sup>42</sup>

$$\beta = \frac{6kT}{I} \cdot \tau_R. \quad (12)$$

This relation is exact for a rigid body undergoing collision induced angular velocity fluctuations with correlation frequency  $\beta$  while tumbling end-over-end with correlation time

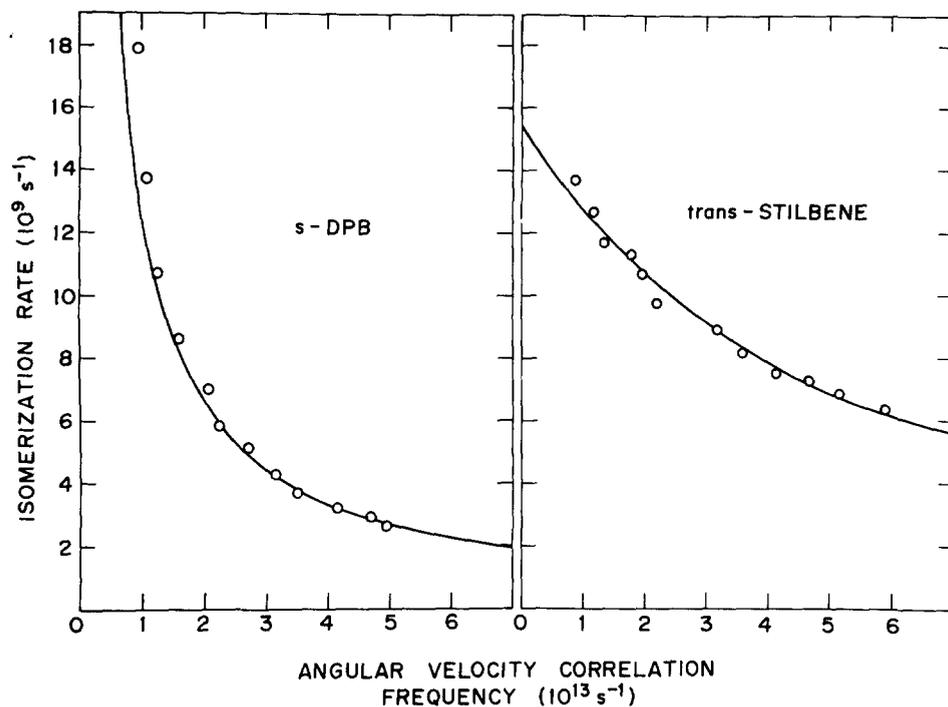


FIG. 5. The Kramers-Hubbard fit of the isomerization rate of diphenyl-polyenes vs angular velocity correlation frequency  $\beta_n$  calculated from Eq. (12).

$\tau_R$ . If the collisions determining the friction have a linear response on the motion along the reaction coordinate in the isomerism process then by choosing  $I$  as  $I_R$ , the angular velocity correlation frequency will be that for the isomerism motion up to a constant value:

$$\beta = \frac{6pkT\tau_R}{I_R} \equiv p\beta_n, \quad (13)$$

where we have introduced a constant of proportionality ( $p$ ) to accommodate the possible differences in the effectiveness of collision in the isomerization and overall rotation process. Equation (12) is obtained from Fokker-Plank theory and was extensively tested by molecular dynamics simulations.<sup>43</sup> It is expected to be an exact proportionality in the regime where the angular momentum correlations decay very rapidly compared with orientational correlations. Figure 5 shows the variation of the isomerization rates of stiff-DPB and stilbene with angular velocity correlation frequency. The plots in Fig. 5 were obtained by the following procedure: The value of  $\tau_R$  for a particular solvent  $C_nH_{2n+2}$  was used to calculate a quantity proportional to the angular velocity correlation frequency  $\beta$  for that solvent through Eq. (12). The observed isomerization rate for that solvent was plotted vs  $\beta_n$  in Fig. 5. The solid lines in Fig. 5 are the best fit of Kramers equation (3) to these data points. The variables in the fit are  $\omega_a$  and  $\omega_b/p$ . Values of  $I_R = 6.67 \times 10^{-44}$  m<sup>2</sup> kg for S-DPB and  $3.4 \times 10^{-44}$  m<sup>2</sup> kg for *trans*-stilbene were used. The optimum fit for stilbene yielded  $\omega_a/2\pi c_0 = 196$  cm<sup>-1</sup> and  $\omega_b/2\pi c_0 = 176p$  cm<sup>-1</sup> and for S-DPB,  $\omega_a/2\pi c_0 = 424$  cm<sup>-1</sup> and  $\omega_b/2\pi c_0 = 16p$  cm<sup>-1</sup>. The quantity  $\omega_a$  cannot be regarded as a molecular frequency for reasons given above. In both cases the Kramers-Hubbard fit to the data is excellent.

The Hubbard relation, as we have employed it, implies that the rate of overall tumbling of the molecule is propor-

tional to the decay time of the correlations of the angular momentum in the isomerization coordinate. The rotational diffusion in the case of stilbene corresponds to motion about the axes perpendicular to the longest axis of the molecule. The validity of the assumed proportionality seems to rest on whether or not the isomerization motion is really linearly dependent on the solvent friction or whether the nature of the solvent interaction is modified by motion in the isomerization coordinate. For example, the isomerization may introduce spatial correlations into the solvent. However, in the absence of such nonlinear effects the Hubbard relation is expected to be valid in the present context. Apparently, in the case of the molecule DODCI these conditions do not apply<sup>7(b)</sup> so there remain interesting questions to address.

## V. CONCLUSIONS

The measured rotational diffusion times of *trans*-stilbene and stiff-diphenylbutadiene in hydrocarbon solvents deviate markedly from the Stokes-Einstein-Debye prediction of linearity with viscosity. The breakdown occurs when the solvent starts to exceed the length of the solutes. We have used the rotational diffusion times to obtain the angular velocity correlation frequencies appropriate for the isomerism motion and used these in the one dimensional Kramers equation to predict the isomerization rates in each of the solvents. The Kramers equation provides an excellent description of the data when the derived correlation frequencies are used rather than the viscosities. This Kramers-Hubbard fit procedure is expected to be valid if the response to the collisional forces is linear for both the rotational diffusion and the angular momentum fluctuations associated with motion along the reaction coordinate.

The barrier frequencies are only determined up to a constant value in the Kramers-Hubbard fit. The values ob-

tained for stilbene are much more physically acceptable than the previous low values<sup>3</sup> if the constant  $p$  is chosen around unity. For S-DPB the low value of  $\omega_b$  represents an extremely flat barrier, so perhaps in this case  $p$  is considerably larger than unity.

The present study does not diminish the importance of frequency dependent friction<sup>13</sup> in the isomerization process. Rather the emphasis is transferred from the Kramers equation to the Stokes–Einstein–Debye relation: We are suggesting that the Kramers equation can work well if the appropriate angular velocity correlation frequencies are used.

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