

Histons: New Quasi-particles and Time-Resolved Fluorescence Shift of Polar Disordered Media

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Received October 27, 1997; accepted December 19, 1997

With statistical thermodynamics methods, it is shown that the evolution of a "polar luminescence probe + polar disordered medium" system after pulse excitation is described by an equation for damped vibrations. From this it follows that in the solvation shell of the excited solute probe, not only synchronous librations but also cooperative jump reorientations of solvent molecules take place, and their damping motion is caused by localized dielectric friction. This collective molecular dynamics is examined as the motion of a quasi-particle called a *histon*. The *histon* moment of inertia and mass are determined. The concept of *l*- and *j*-*histons* are also introduced. In terms of this model the full correlation functions for nonequilibrium solvent dynamics are derived. The behavior of steady-state and time-resolved spectra is examined and it is found that the limiting short-wavelength position of the steady-state spectrum at a low temperature and that for time-dependent fluorescence at $t \rightarrow 0$ are not identical. The *histon* model has been used for interpretation of the emission band *collapse* that is observed in long-time evolution experiments. Some other problems of spectral broadening are also discussed. As predicted, sharp expansion of the fluorescence band takes place on an ultrafast time scale due to *dephasing of l-histons*.

KEY WORDS: New quasi-particles; histons; dephasing of histons; correlation functions; solvation dynamics; time-resolved fluorescence; polar disordered media.

INTRODUCTION

Photoinduced orientational solvent relaxation has been a topic of great interest for experimental as well as theoretical works over the past few decades⁽¹⁻²⁴⁾ (for references on many other works see Refs. 1 and 13). Using glass-forming solvents, like alcohols, one can smoothly change the viscosity by cooling a solution and thus monitor the effects of orientational relaxation on the Stokes shift of fluorescence or phosphorescence spectra. Picosecond and nanosecond molecular dynamics in polar liquids are studied with fluorescence probes.^(1-4,6,7,14,15,17-19) In the case of glass at temperatures near the phase tran-

sition and lower, millisecond dynamics have been investigated with phosphorescence probes.^(5,16) It has been found that at low temperatures the photoinduced reorientation of solvent molecules is much faster than the longitudinal relaxation time of pure solvents, by several orders of magnitude. This early and most interesting result of investigations in this field is discussed in Refs. 4 and 7.

The principal new results over the last decade are presented in Refs. 5-15, 17-19, and 21. Van der Zwan and Hynes⁽⁸⁾ introduced a model which includes solvent inertia and solvent polarization relaxation. They suggested that non-Debye behavior in time-dependent fluorescence (TDF) shifts might be observable. In this theoretical work it was shown that the TDF shift will oscillate in time when the underdamped limit for collective solvent motion is realized. Pavlovich *et al.*^(6,19) re-

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corded non-Debye TDF shifts for cooling alcohol solutions of phthalimides on a nanosecond and, earlier,⁽⁵⁾ a millisecond scale for phosphorescence probes. They observed⁽⁶⁾ that with increasing delay times, the usual red TDF shift changes to blue and some elements of slow oscillations take place.

Molecular dynamics simulations of dipolar solvation have shed light on the ultrafast processes of the solvent response.^(11–13) Theoretical consideration in this work was based on the linear response and liquid structure theory. Maroncelli⁽¹¹⁾ showed that the solvation dynamics depends significantly on the solute charge and has a two-part character. One part consists of a fast Gaussian initial relaxation and attendant oscillations which are attributed to librational modes. The second dynamic component occurs on a much slower time scale and accounts for the remainder of the relaxation. Maroncelli assigned the fast part of the solvent response to low-amplitude inertial dynamics of solvent molecules in the first solvation shell, while the slow tail arises from diffusive reorientation. Employing the fluorescence up-conversion technique, the ultrafast molecular dynamics predicted by Maroncelli is investigated by Fleming and co-workers in Refs. 14 and 15.

Bingemann and Ernsting⁽²¹⁾ studied spectra of transient absorption and stimulated emission of a styryl dye with a resolution of 100 fs. The evolution of the $S_1 \rightarrow S_0$ transition energy distribution was obtained for methanol and acetonitrile at several temperatures. In both solvents an ultrafast component was observed. For methanol an oscillatory evolution was observed, mainly in the asymmetry of the fluorescence spectrum. They supposed that the oscillations may indicate underdamped coherent solvent motion. It is interesting that this effect was observed only at temperatures $>40^\circ\text{C}$.

A direct method of spectral registration is used by Pavlovich *et al.*⁽¹⁷⁾ for investigation of TDF shifts on the nanosecond scale with 0.5-ns pulse excitation. The evolution has been studied with a resolution of 1.5 ns at a delay time greater than the fluorescence lifetime by a factor of 5–6 or more. They examined the shape change of instantaneous spectra and observed a compression (collapse) of the band with an increase in delay time of between 2.5 and 100 ns for various phthalimide derivatives and 2-acetylanthracene in alcohols. A collapse of the TDF spectrum was observed for liquid and glass solutions. Surprisingly, the half-width of the instantaneous spectrum at the minimum delay time (2.5 ns) slightly exceeded that of the stationary spectrum measured under the same experimental conditions. The collapse was accompanied by contour symmetrization. Starting at 150–200 ns a tendency toward band expansion was observed.

For example, the half-width at delay times of 150 ns and 5 μs was, respectively, 1500 and 2200 cm^{-1} for 4-acetylamino-*N*-methylphthalimide in isobutanol at 233 K.

Using this method Pavlovich and Zablotskii⁽¹⁸⁾ showed that not only does collapse take place in the process of evolution, but also vibrational destructurezation as well. This effect of intensity redistribution of vibrational bands in the TDF spectrum had been observed previously for an isobutanol solution of 2-acetylanthracene and interpreted in Ref. 18.

In this paper we discuss TDF shift in terms of Landau free energy and use the model of the band structure of electronic levels for polar probes in polar solutions.^(23–26) We examine collective photoinduced molecular dynamics as the motion of a quasi-particle called a *hison*.⁽²⁴⁾ The purpose of this work was to develop a simple theoretical method for understanding new results mentioned in the Introduction. From this point of view, we focus our attention on the mechanisms of non-Debye shift and collapse of the TDF spectrum. For further discussion, more accurate experiments and theoretical considerations are clearly needed.

STATISTICAL THEORY

Orientalional Number and Landau Free Energy

Let us consider the ensemble of clusters the nuclei of which are luminescent probe molecules and solvation shells consisting of N molecules of a disordered medium with translational r_0 and orientational ψ_0 coordinates. We choose the values of clusters large enough that the properties of the cluster ensemble reproduce the statistical properties of the probe + solvent system. The electronic energy of a cluster nucleus for the n th state can be written approximately as a sum,

$$E_n(N, r_0, \psi_0) = E_n^0 + T_n(N, r_0) + W_n(N, r_0, \psi_0) \quad (1)$$

where E_n^0 is the electronic energy of the bare probe molecule, and T_n and W_n are the translational and orientational components of solvation energy. W_n depends on the instantaneous angle coordinates ψ_0 of molecules in clusters. T_n includes dispersion and induction solute–solvent interactions, which, as suggested, depend weakly on the orientational coordinates. Here we disregard the fluctuations of the number N of solvent molecules in clusters and of their coordinates r_0 . Therefore, below N and r_0 are the ensemble-averaged values.

The orientational component of solvation energy includes dipole–dipole interactions and is defined by an electric field \mathbf{R} , acting on the probe from N solvent mol-

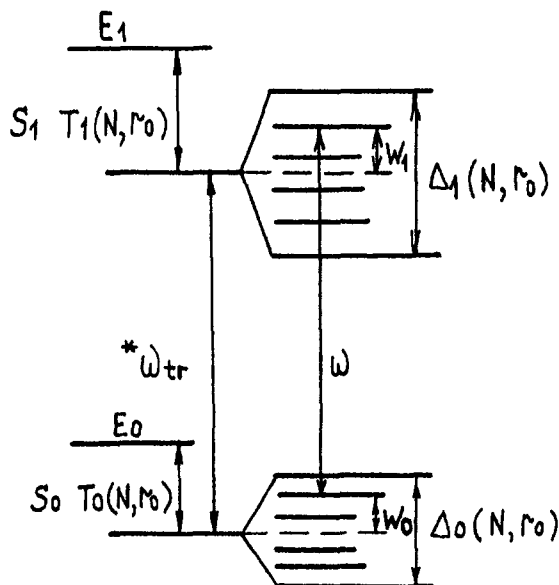


Fig. 1. Structure of electronic levels of a polar probe in a polar disordered medium (for details, see text).

ecules placed in the solvation shell. Thus

$$W_n(N, r_0, \psi_0) = -m_n R \\ = -m_n R(N, r_0, \psi_0) \cos \phi_n = -m_n R_{mn} \quad (2)$$

where m_n is the dipole moment of the probe molecule in the n th electronic state, ϕ_n is the angle between m_n and R , and R_{mn} is the component of R in direction m_n .

In the process of solvent dynamics the chance field R is defined by the instantaneous orientational configuration and the value R is variable from 0 to R_{\max} . R_{\max} is the greatest possible field produced by solvent molecules in the position of the probe. The value R_{\max} is realized when the dipole moments of solvent molecules are oriented strictly in the direction of the electric field produced by the probe dipole m_n . Varying in Eq. (2) the angle ϕ_n from 0 to π and R from 0 to R_{\max} , we obtain that the orientational sublevels fill in the energetic bands with width

$$\Delta_n(N, r_0) = 2m_n R_{\max}$$

Therefore, Eq. (2) can be also written as

$$W_n(N, r_0, \psi_0) = \mu_n m_n R_{\max} \quad (3)$$

Thus, Eq. (1) gives

$$E_n(N, r_0, \psi_0) = E_n^0 + T_n(N, r_0) + \mu_n m_n R_{\max}$$

From Eq. (3) and the last expression it follows that the effect of the electric field of the medium on the probe leads to symmetric splitting of electronic levels and to

the formation of energetic bands. The orientational energy (3) conforms to the internal linear Stark effect and is defined by the former orientational quantum number μ_n (for simplicity, the orientational number), which takes continuous meaning from -1 to $+1$. The orientational sublevels form a quasi-continuum confined by the width of band Δ_n .

The structure of electronic levels for the S_0 and S_1 states is illustrated in Fig. 1.

According to the Franck–Condon principle the transitions between orientational sublevels of bands of different electronic states allow, when the orientational energy W or number μ satisfies the following conditions,

$$W_u/W_n = \Delta_u \cos \alpha_{nu} / \Delta_n \\ = m_u \cos \alpha_{nu} / m_n, \quad \mu_u / \mu_n = \cos \alpha_{nu} \quad (4)$$

where n and u are the indexes of the initial and final states, respectively, for transitions with absorption or emission; α_{nu} is the angle between the dipole moments of the probe in the n and u states. These selection rules are discussed in detail in Refs. 23–26.

The distribution of clusters on orientational sublevels in the equilibrium state follows the Boltzmann law:

$$\rho_n(W_n) = C_n g_n(W_n) \exp(-W_n/k_B T) \quad (5)$$

where k_B is the Boltzmann constant and T the temperature. Here and below, C_n are the normalization constants. The statistical weight in (5) is the Gaussian function^(23–25)

$$g_n(W_n) = C_n G_n \exp(-W_n^2/2m_n^2 \eta^2) \quad (6)$$

where G_n is the number of orientational microstates and η^2 is the variance (standard deviation) of chance field R . Thus, we have

$$\rho_n(W_n) = C_n \exp[-(W_n - *W_n)^2/2d_n^2] \quad (7)$$

where the ensemble-averaged orientational energy $*W_n$ is given by

$$*W_n = -d_n^2/k_B T \quad (8)$$

and d_n^2 is the variance of W_n . Using the Onsager model,⁽²⁷⁾ Eq. (8) can be written as

$$*W_n = -m_n R_0 = -2m_n^2 a^{-3} (\epsilon - 1)/(2\epsilon + 1) \quad (9)$$

where R_0 and a are the Onsager field and radius, respectively, and ϵ is the dielectric constant. In accordance with definition (3), the average orientational number $*\mu_n$ is given by

$$*\mu_n = 2*W_n/\Delta_n \\ = -2m_n a^{-3} (\epsilon - 1)/(2\epsilon + 1) R_{\max} \quad (10)$$

In the equilibrium state the free energy of the sys-

tem, or subsystem, *F_n can be written

$$\begin{aligned} {}^*F_n &= -k_B T \ln {}^*Z_n \\ &= -k_B T \ln \int_{-\infty}^{+\infty} g_n(W_n) \exp(-W_n/k_B T) dW_n \end{aligned} \quad (11)$$

where *Z_n is the statistical sum. From (5), (6), (7), and (9), it follows that the integrand $K(W_n)$ in (11) is given by

$$K(W_n) = C_n G_n \exp({}^*W_n^2/2d_n^2) \exp[-(W_n - {}^*W_n)^2/2d_n^2] \quad (12)$$

Combining (11) and (12) after calculation, using (8), we obtain

$${}^*F_n = {}^*W_n/2 - k_B T \ln G_n \quad (13)$$

Since the number of orientational microstates G_n is defined by the structure of clusters in which N and r_0 are fixed, it is evident that $G_n = G_0$ and the orientational component of equilibrium entropy ${}^*\sigma_n$ should be the same for any electronic state,

$${}^*\sigma_n = {}^*\sigma_u = k_B \ln G_0 \quad (14)$$

In the equilibrium state any system, or subsystem, has the minimum free energy *F_n . In the nonequilibrium state we consider the free energy F_n as a deviation from *F_n ,

$$F_n = {}^*F_n + \Delta F_n \quad (15)$$

According to the Franck–Condon principle, under excitation only the solute–solvent dipole–dipole interactions are changed. The solvent–solvent interactions are not changed. Therefore, on the one hand, we may write the probability of formation of a nonequilibrium state in the form

$$P_n(W_n) = \exp[-(W_n - {}^*W_n)^2/2d_n^2] \quad (16)$$

Equation (16) follows from Eq. (7) after substitution of microscopic W_n for macroscopic W_n and after removal of C_n . Thus, here and below W_n and μ_n are the macroscopic values.

On the other hand, for this state P_n can be written as

$$P_n(\Delta F_n) = \exp(-\Delta F_n/k_B T) \quad (17)$$

According to (16), (17), and (8), the variation of the free energy ΔF_n is equal to

$$\Delta F_n = -(W_n - {}^*W_n)^2/2{}^*W_n \quad (18)$$

Using (13), (14), (15), and (18), for F_n in the nonequilibrium state, we obtain

$$F_n = {}^*W_n/2 - (W_n - {}^*W_n)^2/2{}^*W_n - k_B T \ln G_0 \quad (19)$$

Since

$$\Delta F_n = \Delta H_n - T\Delta\sigma_n \quad (20)$$

and

$$\Delta H_n = {}^*W_n - {}^0W_n$$

for the variation of entropy in the photoinduced process of orientational relaxation, we obtain from (13), (19), and (20),

$$\Delta\sigma_n = ({}^*W_n^2 - {}^0W_n^2)/2{}^*W_n T \quad (21)$$

where the upper indexes 0 and * indicate the initial, nonequilibrium, and the equilibrium states, respectively. Relation (21) was used for thermodynamic classification of orientational relaxation processes in Ref. 26.

The free energy of the nonequilibrium state, expressed as a function of the minimization parameter, have been called by Kittel⁽²⁸⁾ the Landau free energy. From (2), (3), and (19) it follows that, in our case, the parameters of minimization of F_n may be the component of \mathbf{R} in direction \mathbf{m}_n , the component μ_n in the direction \mathbf{R} , the orientational energy W_n , and the number μ_n .

The convenient parameter of minimization is the orientational number μ_n . Thus, for the ground and excited states the Landau free energy can be written

$$F_0 = b(\mu_0 - {}^*\mu_0)^2/2 \quad (22)$$

$$F_1 = b(\mu_1 - {}^*\mu_1)^2/2 + h{}^*\omega_{tr} \quad (23)$$

with

$$b = a^3 R_{\max}^2 (2\epsilon + 1)/2(\epsilon - 1) \quad (24)$$

where h is Planck's constant and ${}^*\omega_{tr}$ is the ensemble-averaged frequency of electronic transitions between translational sublevels of ground and excited states.

The F diagrams for transitions between the S_0 and the S_1 states, and the ground- and excited-state relaxations in the μ -coordinate model, are presented in Fig. 2. The absorption and fluorescence in the F -diagrams are reproduced according to selection rule (4), which we copy here in the form

$${}^0\mu_u = {}^*\mu_n \cos\alpha \quad (25)$$

where for fluorescence and absorption from equilibrium states, $n = 1, u = 0$, and $n = 0, u = 1$, respectively; $\alpha = \alpha_{01}$. Absorption from the equilibrium state is realized under excitation in the band maximum (see Ref. 26).

As follows from (25) the orientational number μ is not changed when angle $\alpha = 0$, only in this case the transitions between F terms take place vertically. This condition is fulfilled only for probe molecules of C_{2v} ,

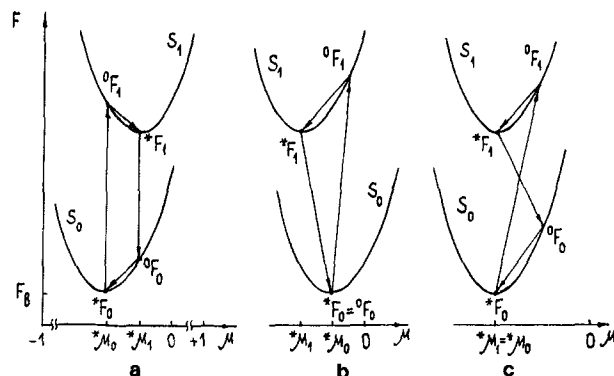


Fig. 2. F diagrams with Frank-Condon transitions between F potentials of the S_0 and S_1 states as well as schematic relaxation processes in the case $m_1 < m_0$, $\alpha = \alpha_{01} = 0$ (a), $m_1 = 2m_0$, $\alpha = \pi/3$ (b), and $m_1 = m_0$, $\alpha = \pi/3$ (c) under excitation in the maximum of the absorption band.

symmetry. No minimization parameters are available for which vertical transitions take place for molecules of C_s symmetry as well as C_{2v} symmetry in the case $\alpha = \pi$.

Histons

The orientational number μ is the generalized coordinate at the parabolic F potentials (22) and (23). Thus, we have shown that the solution of the problem of molecular dynamics in the cluster system—in a system of many particles—may be reduced to the consideration of the motion of a certain particle along the μ -coordinate or, in other words, in one-dimensional space. This collective nonequilibrium molecular dynamics can be examined as the motion of a quasi-particle called a histon.

The word *histon* comes from a Belarussian word meaning “swing.”

In the S_1 state of interest to us the histon motion is described by the equation

$$\Delta \dot{\mu}_1 + 2\gamma \Delta \mu_1 + \Omega_0^2 \Delta \mu_1 = 0 \quad (26)$$

where $\Delta \mu_1 = \mu_1 - \mu_1^*$, γ is the damping constant, and Ω_0 is the circular frequency of harmonic vibration of histon. Without going into detail we write the relations for the histon moment of inertia, J_h , and mass, M_h , presented in more detail in Ref. 24:

$$J_h = 2m_1^2 a^{-3} \Omega_0^{-2} (\epsilon - 1)/(2\epsilon + 1), \quad M_h = J_h M_s / J_s$$

where M_s and J_s are the mass and moment of inertia of the solvent molecule (or other kind of dipole under consideration).

To understand what histons are, let us return to the solvation motion and consider it as a microscopic process. It is well-known that in liquids, low-temperature glasses, and other disordered polar media, the orientational motion includes the librations and jump reorientations of dipoles. Under equilibration after pulse excitation the jump reorientation process is characterized by changes in the time-varying settling positions. It is described by time-varying equilibrium coordinates ψ_0 . At the same time libration relaxation takes place, which is defined by coordinates ψ , provided $\psi = \psi_0 + \Delta\psi$, where $\Delta\psi$ is an angle deviation. From the mathematical point of view the origin of the chance field R in relations (2), as well as of the orientational energy W_n and orientational number μ_n in relations following (2), is of no importance: it could be a combination of ψ_0 coordinates or angle deviations $\Delta\psi$ under fixed ψ_0 . That is, the libration relaxation and jump reorientational processes are appreciably independent. Furthermore, this mathematical formality makes it possible to use the F term (23) with a common b (24) for examination of both cases. However, we consider that either of these processes is described by Eq. (26) with different frictions γ and frequencies Ω_0 . Thus, we can distinguish l - and j -histons. At every instant, if necessary, one can refer to the conclusion that, for l - and j -histons, b is alike and use the condition $\Omega_{0l} = \Omega_{0j}$.

One may conclude that in the solvation shell of the excited solute probe, not only synchronous librations but also cooperative jump reorientations of solvent molecules take place, and their damped motion is caused by localized dielectric friction.

It should be particularly emphasized that there are many kinds of dipole motions in polar solutions and other disordered objects, which can be considered motions of the histons. In associated liquids, like alcohols, we may take into account the motion of entire molecules as well as OH groups. The photoinduced dynamics of polar fragments in polymers, proteins, and biopolymers, polar probes adsorbed on the surface, and others can also be considered histon motion. The fluctuations of cluster structures, the number of particles N , and their space coordinates r_0 lead to the frequency distributions of histons. There are dispersion bands of histons in real polar disordered media.

Correlation Functions

The correlation function is defined as

$$c(t) = \langle xx(t) \rangle / \langle x^2 \rangle$$

and follows immediately from the solutions of Eq. (26),

which depend on the relation between γ and Ω_0 . Let us now examine the solvation dynamics as a result of the motion of l - and j -histons. As pointed out, these motions are independent processes. Therefore, the full correlation function $c_{ij}(t)$ is

$$c_{ij}(t) = [c_i(t) + c_j(t)]/2 \quad (27)$$

where $c_i(t)$ and $c_j(t)$ must satisfy Eq. (26) under $\gamma = \gamma_i$, $\Omega_0 = \Omega_{0i}$ and $\gamma = \gamma_j$, $\Omega_0 = \Omega_{0j}$, respectively.

The friction and damping constant γ_i are very low because the properties of l -histons, as collective synchronous librations, are determined by the properties of rotational vibrations into localized potential wells. For this kind of molecular dynamics in real systems, as a rule the relation $\gamma_i < \Omega_{0i}$ is fulfilled over a wide temperature interval and γ_i depends only weakly on the temperature.

In the case $\gamma_i < \Omega_{0i}$ damped oscillational motion of histons takes place, and from Eq. (26) we have

$$c_i(t) = \exp(-\gamma_i t) \cos(\Omega_i t - \varphi_0 - \nu_i) \quad (28)$$

where Ω_i is the circular frequency of damped vibrations of l -histons

$$\Omega_i = (\Omega_{0i}^2 - \gamma_i^2)^{1/2}$$

φ_0 is the initial phase, and ν_i is the analogue of the loss angle in the theory of electric polarization,

$$\tan \nu_i = \gamma_i / \Omega_i = \gamma_i (\Omega_{0i}^2 - \gamma_i^2)^{-1/2}$$

When $\varphi_0 = 0$ we have

$$c_0(t) = \exp(-\gamma t) (\cos \Omega t + \gamma_i \Omega_i^{-1} \sin \Omega t)$$

It must be emphasized that Fleming and co-workers⁽¹⁵⁾ and, earlier, Van der Zwan and Hynes⁽⁸⁾ obtained the function $c_0(t)$ in the form given above. In Ref. 15 a model of independent polarization modes was used and a correlation function was obtained as a solution of the generalized Langevin equation.

A different situation arises with the motion of j -histons. j -Histons describe the collective jump reorientations between localized wells, thus their behavior depends strongly on the temperature. One can use the Arrhenius relation for damping constant γ_j in the case

$$\gamma_j = \gamma_{0j} \exp(-E_a/k_B T)$$

where γ_{0j} is a preexponential factor and E_a is the averaged activation energy on the excited ensemble. Now the form of correlation functions is defined by three types of solutions of Eq. (26). When $\gamma_j < \Omega_{0j}$ such solutions have forms like Eq. (28).

Dephasing of Histons

There is an initial phase φ_0 in solution (28) of Eq. (26). The behavior of this parameter is crucial to understanding the properties of l -histons as well as to describing the shape evolution of TDF spectra. The reason is that l -histons interact with random localized phonons and with random translational vibrations of the probe. These interactions cause a dephasing of l -histons. At $t = 0$ after excitation the phase equals zero, and in a short time, several periods of phonon or probe vibrations, it is uniformly distributed in the interval from 0 to π . To calculate the contribution of l -histons in the full correlation function (27), we must average (28) over φ_0 . Therefore, it is apparent that after short-time dephasing, the l -component in (27) equals zero. We do not discuss here the statistic of dephasing and, following Maroncelli,⁽¹¹⁾ introduce the Gaussian l -component as a result of expression (28) in a series. On the retention of only two terms after changing from Ω_l to Ω_g , one obtains

$$c_l(t) = \exp(-\Omega_g^2 t^2 / 2) \quad (29)$$

When the condition $\gamma_j < \Omega_{0j}$ is realized, one can say that dephasing of j -histons is a result of their interaction with jump translational motion of molecules in the solvation shell. This is a very slow-response process observed in long-time evolution experiments. Some aspects of the translational component in solvation dynamics have been discussed by Chandra and Bagchi.^(9,10) Long-time measurements of TDF spectra have been made in Refs. 17–19. Much of this problem is not understandable.

Full Correlation Functions

At low temperatures or in very viscous solvents the condition $\gamma_j > \Omega_{0j}$ is fulfilled. The j -component $c_j(t)$ is predicted from Eq. (26) to be two-exponential. In this case after pulse excitation, j -histons, as quasi-particles, may asymptotically come close to equilibrium. The full correlation function (27) is given by

$$c_{ij}(t) = [\exp(-\Omega_g^2 t^2 / 2) + A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t)] / 2 \quad (30)$$

with

$$A_1 = \lambda_2 / (\lambda_2 - \lambda_1), \quad A_2 = \lambda_1 / (\lambda_1 - \lambda_2)$$

$$\lambda_1 = \gamma_j - (\gamma_j^2 - \Omega_{0j}^2)^{1/2}, \quad \lambda_2 = \gamma_j + (\gamma_j^2 - \Omega_{0j}^2)^{1/2}$$

where $\lambda_2 > \lambda_1 > 0$ and $A_2 < 0$.

With heating under $\gamma_j = \Omega_{0j}$, the Debye process is observed:

$$c_j(t) = [\exp(-\Omega_g^2 t^2/2) + \exp(-\gamma_j t)]/2 \quad (31)$$

Then, with increasing temperature, $\gamma_j < \Omega_{0j}$. Debye relaxation is replaced by an underdamped oscillational process, whereas the Gaussian contribution (29) from l -histons should remain as before because condition $\gamma_l < \Omega_{0l}$ still stands. We have

$$c_j(t) = [\exp(-\Omega_g^2 t^2/2) + \exp(-\gamma_j t) (\cos\Omega_j t + \tan\upsilon_j \sin\Omega_j t)]/2 \quad (32)$$

Fluorescence Response Functions

TDF Stokes shift has been used extensively to study solvation dynamics [1,13]. It is characterized by the normalized response function

$$s(t) = [\omega(t) - \omega(\infty)]/[\omega(0) - \omega(\infty)] \quad (33)$$

$$= [v_1(t) - v_1(\infty)]/[v_1(0) - v_1(\infty)]$$

In this expression $\omega(t)$ is the time-dependent ensemble-averaged frequency of 0-0 transitions between the S_1 and the S_0 states and $v_1(t)$ is the first moment of the spectrum obtained experimentally.

Let us determine the relation between $c(t)$ and $s(t)$. As shown in Fig. 1 the frequency ω follows from the relation

$$h(\omega - {}^*\omega_{tr}) = W_1 - W_0$$

which, using (3), may be written in the form

$$h(\omega - {}^*\omega_{tr}) = (\mu_1 m_1 - \mu_0 m_0) R_{\max} \quad (34)$$

where ${}^*\omega_{tr}$ is constant. According to Eqs. (26) and (34) the motion of histons modulates the frequency ω . The selection rule (25) gives the magnitude of orientational number deviation under excitation ${}^0\Delta\mu_1 = {}^*\mu_0 \cos\alpha - {}^*\mu_1$. Thus

$$\mu_1(t) = {}^*\mu_1 + ({}^*\mu_0 \cos\alpha - {}^*\mu_1) c(t) \quad (35)$$

because $c(t)$ is a solution of Eq. (26). Figure 2 shows that the fluorescence takes place between orientational sublevels of the S_1 and S_0 , thus obtaining the adequate combination of equilibrium and nonequilibrium states. Taking this fact into account, with the help of rule (25), we get

$$\mu_0(t) = {}^*\mu_0 + ({}^*\mu_1 \cos\alpha - {}^*\mu_0)[1 - c(t)] \quad (36)$$

After substitution of (35), (36) in (34), using (10), one finds that

$$\omega(t) = {}^*\omega_{10} + \Delta\omega_s(t) = {}^*\omega_{10} + \Delta\omega_s c(t) \quad (37)$$

where $\Delta\omega_s(t)$ is the time dependence of the Stokes shift, ${}^*\omega_{10}$ is the mean frequency 0-0 transitions of equilib-

rium fluorescence,

$$h{}^*\omega_{10} = h{}^*\omega_{tr} + 2(m_0 m_1 \cos\alpha - m_1^2) a^{-3} (\epsilon - 1)/(2\epsilon + 1) \quad (38)$$

and $\Delta\omega_s$ is the magnitude of the Stokes shift defined by Lippert's formula (see, e.g., Ref. 29), which, in the approximation of rigid dipoles, used here for simplicity, has the form

$$h\Delta\omega_s = 2(m_1 - m_0)^2 a^{-3} (\epsilon - 1)/(2\epsilon + 1)$$

Determining $\omega(0)$ and $\omega(\infty)$ from (37) after substitution of these results and (37) in (33), one gets

$$s(t) = c(t)$$

There is also a need to examine here the next significant aspect of the behavior of steady-state and time-resolved spectra. With result (27), the value $\omega(t)$, defined by (37), becomes

$$\omega_j(t) = {}^*\omega_{10} + 2\Delta\omega_s c_j(t) \quad (39)$$

because l - and j -histons produce the same contribution to the Stokes shift.

The position of steady-state spectrum $\omega_{st}(T)$ is defined by

$$\omega_{st}(T) = {}^*\omega_{10} + 2\Delta\omega_s \tau^{-1} \int_0^\infty c_j(t) \exp(-t/\tau) dt$$

where τ is the fluorescence lifetime. From (27), (39), and the relation for $\omega_{st}(T)$, it follows that the limiting positions of the steady-state spectrum observed at low temperatures and the TDF spectrum at $t \rightarrow 0$ are not equal because $\Omega_g^{-1} \ll \tau$ and the Gaussian component does not make a contribution to the steady-state spectrum. We have the relation

$$\omega_{st}(T \rightarrow 0) - {}^*\omega_{10} = [\omega_j(t \rightarrow 0) - {}^*\omega_{10}]/2$$

Collapse of the TDF Spectrum

The shape of the spectrum can be expressed in term of the ω -distribution $\xi_{nu}(\omega)$.⁽²³⁻²⁵⁾ The function $\xi_{nu}(\omega)$ characterizes the well-known inhomogeneous broadening due to fluctuations of dipole-dipole interactions. The equilibrium ω -distributions are Gaussian functions given by

$${}^*\xi_{nu}(\omega) = (2\pi)^{-1/2} D_{nu}^{-1} \exp[-h^2(\omega - {}^*\omega_{nu})^2/2D_{nu}^2]$$

with

$$h^2 D_{nu}^2 = 2(m_1 - m_0)^2 a^{-3} k_B T (\epsilon - 1)/(2\epsilon + 1) \quad (40)$$

where D_{nu}^2 is the equilibrium variance of ω and nu is

index 01 or 10 for transitions between the S_1 and the S_0 states. For emission ${}^* \omega_{10}$ is defined by (38), and for absorption it is expressed as

$$h {}^* \omega_{01} = h {}^* \omega_{10} + 2(m_0^2 - m_0 m_1 \cos \alpha) a^{-3} (\epsilon - 1)/(2\epsilon + 1)$$

It is clear from (40) that $D_{01}^2 = D_{10}^2$.

After pulse excitation on the frequency ν_{exc} at $t \rightarrow 0$, the shape of the fluorescence spectrum $w_0(\nu, \nu_{\text{exc}})$ is described by the Frank-Condon ω -distribution ${}^0 \xi_{10}(\omega, \nu_{\text{exc}})$. Since

$${}^0 \xi_{10}(\omega, \nu_{\text{exc}}) = {}^* \xi_{01}(\omega - {}^* \omega_{01}) \kappa(\nu_{\text{exc}} - \omega) \quad (41)$$

$w_0(\nu, \nu_{\text{exc}})$ can be written in the form

$$w_0(\nu, \nu_{\text{exc}}) = \int_0^\infty {}^* \xi_{01}(\omega - {}^* \omega_{01}) \kappa(\nu_{\text{exc}} - \omega) w(\nu - \omega) d\omega \quad (42)$$

In expressions (41) and (42) $\kappa(\nu - \omega)$ and $w(\nu - \omega)$ are the absorption and fluorescence spectra of clusters with the frequency of electronic transition ω , respectively. For equilibrium fluorescence we have

$$w_\infty(\nu) = \int_0^\infty {}^* \xi_{10}(\omega - {}^* \omega_{10}) w(\nu - \omega) d\omega$$

The evolution of the spectrum from $w_0(\nu, \nu_{\text{exc}})$ to $w_\infty(\nu)$ in the process of relaxation in the solvation shell can be characterized by the scheme

$${}^0 \xi_{10}(\omega, \nu_{\text{exc}}) \rightarrow \xi_{10}(\omega, \nu_{\text{exc}}, t) \rightarrow {}^* \xi_{10}(\omega) \quad (43)$$

where $\xi_{10}(\omega, \nu_{\text{exc}}, t)$ is an intermediate ω -distribution at time t . The evolution of the mean frequency $\omega(t)$ in scheme (43) is described by the j -histon component of the correlation function in relations (30), (31), and (32).

Now we assume that at $t \rightarrow 0$ the variance of ω -distribution ${}^0 \xi_{10}(\omega, \nu_{\text{exc}})$, defined by (41), after excitation in the maximum of the absorption band, and that for equilibrium ω -distribution ${}^* \xi_{10}(\omega)$, defined by (40), are approximately alike,

$$D_j^2(t \rightarrow 0) \approx D_j^2(t \rightarrow \infty) = D_{10}^2 \quad (44)$$

where D_{10}^2 follows from (40), replacing index nu by 10. It is likely that this assumption is obeyed only by dyes exhibiting expanding structureless spectra. We do not discuss here the variance of intermediate ω -distribution $\xi_{10}(\omega, \nu_{\text{exc}}, t)$, for which this condition is not fulfilled.

The other reason for TDF broadening is due to l -histons. Dephasing of l -histons causes a sharp increase in the spectrum width in the time $\tau_g = 2^{-1/2} \Omega_g^{-1}$ [a

decrease in the Gaussian component $c_i(t)$ by a factor of e]. After dephasing, the full variance for emission is

$$D_{ij}^2 = D_l^2 + D_j^2 \quad (45)$$

where D_l^2 is the l -histon component and D_j^2 is the j -histon component of variance. The latter characterizes inhomogeneous broadening. The distinctive feature of l - and j -variances is that D_l^2 does not depend on the excitation frequency.

l -Histons produce the oscillational modulation of frequency ω according to relation (37), which can be rewritten as

$$\omega_l(t) = {}^* \omega_{10} + \Delta \omega_s \exp(-\gamma_l t) \cos(\Omega_l t - \varphi_0 - \nu_l) \quad (46)$$

Since

$$D^2 = \langle x^2 \rangle - \langle x \rangle^2 \quad (47)$$

and, in our case, $x \sim \omega_l(t)$, one can calculate the contribution of l -histons to the full variance (45) following (47) by averaging (46) over φ_0 in the interval from 0 to π . Taking into account that $\omega_l(t)$ is the ensemble-averaged, macroscopic value with magnitude variance D_{10}^2 as the statistical properties of l - and j -histons are alike, for $t \gg \tau_g$ we get

$$D_l^2(t) = D_{10}^2 \exp(-2\gamma_l t) \quad (48)$$

From relations (44), (45), and (48) it follows that at a short time, say $t \approx 5\tau_g$, the variance D_{ij}^2 is approximately two times greater than that at $t \rightarrow \infty$. For long-time studies when low-time resolution devices are used, we have

$$D_{ij}^2(t \rightarrow 0) \approx 2D_{ij}^2(t \rightarrow \infty) = 2D_{10}^2 \quad (49)$$

Variance determines the width of the TDF spectrum, and in long-time experiments one can detect compression of the band. This effect was experimentally observed in Refs. 17 and 18 and classified as *collapse* of the TDF spectrum. The approximate relation (49) was derived with several assumptions. However, as follows from the data presented in Ref. 17 for alcohol solutions of phthalimide derivatives, this result is in reasonably good agreement with the experimental.

The time dependence of the full variance is

$$D_{ij}^2(t) = D_{10}^2 [1 - \exp(-\Omega_g^2 t^2) + \exp(-2\gamma_l t)]/2 + D_j^2(t) \quad (50)$$

For the ultrafast scale from 0 to $t \approx 5\tau_g$ we have a sharp spectrum expansion as result of dephasing of l -histons:

$$D_{ij}^2(t \approx 5\tau_g) \approx 2D_{ij}^2(t \rightarrow 0) = 2D_{10}^2$$

The evolution of the j -component of the variance in (50) and the role of translational motion in l and j evolution processes have yet to be studied.

CONCLUSION

Histons provide a means to describe the macroscopic coherent orientational dynamics that appears against the background of thermal molecular motion in the solvation shell of the excited solute probe. This model has good perspectives for examination of the collapse and vibrational destructurezation of the band TDF spectra of polar solutions with increasing delay times. Reference 17 and 18 were the first to examine this behavior experimentally.

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