

Thermally Induced Limit Cycles in the Nonlinear Theory of Fluorescence Depolarization

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Received: February 24, 1994; In Final Form: April 27, 1994*

Electronic excitations in molecules can acquire nonlinearity in their transport as a result of strong interactions with vibrations, and stochasticity as a result of thermal fluctuations. The interplay of the nonlinearity and the stochasticity has the potential of producing dramatic effects in the behaviour of the excitations. Such effects, which involve thermally induced limit cycles and Hopf bifurcations, are presented in the specific context of fluorescence depolarization on the basis of a recent generalization of the discrete nonlinear Schroedinger equation.

1. Introduction

Many fields of chemical physics have been enriched by the work of Raoul Kopelman through the years: energy transfer, photosynthesis, excitation transport, and chemical kinetics, to name a few. One recalls the naphthalene "butterflies" in his slides of the 1970s through which he described his simulation studies of exciton percolation in molecular aggregates, his analysis of annihilation phenomena with powers far more exotic than 2, and his investigation of fractals in reaction dynamics. He has always been a valuable ally for the present author, not only in the initial battles to get generalized master equations accepted in the exciton transport community but also in attempts to survive against the onslaught of those who would pronounce "ex-CITE-on" without giving the quasiparticle its special due. It is a pleasure to dedicate this article to Raoul on his 60th birthday.

The article describes new predictions about fluorescence depolarization in molecular systems. The predictions arise from a nonlinear theory of the process when dissipation and thermal fluctuations are incorporated in the evolution of Frenkel excitations. In section 2, an evolution equation is introduced, which is a generalization of the so-called discrete nonlinear Schroedinger equation and which is capable of describing novel thermal effects including limit cycles and bifurcations. In section 3, the effects are described in relation to fluorescence depolarization. Concluding remarks are presented in section 4.

We begin with the questions: What is fluorescence depolarization? What is the discrete nonlinear Schroedinger equation? Why and how would one apply the equation to fluorescence depolarization? We deal with the first of the questions in the rest of this section.

Fluorescence depolarization is a tool useful in the study of excitation transport in molecular systems, the simplest prototype of the systems being a variable-distance noninteracting donor-acceptor pair of molecules.¹⁻⁵ A practical example is provided by the so-called "stick-dimers" in which poly-L-proline oligomers of controllable length are used to separate an α -naphthyl group at the carboxyl end—the donor—from the dansyl group at the imino end—the acceptor. The observational technique is to study the efficiency of energy transfer through measurements of fluorescence excitation, emission, and polarization spectra. Suppose, for simplicity, that the donor and the acceptor are identical molecules. On illumination, either of the molecules in the pair may undergo electronic excitation. The direction of the induced dipole moment produced on the molecule through the process of excitation depends on geometrical factors and is generally different for the two molecules in the pair. For simplicity, let us assume the two dipole moments to be mutually perpendicular. One could, in principle, create an excitation of

the dimer which is localized on one of the two molecules by shining (broad-band) light polarized in the direction of the dipole moment on that molecule. Varying the angle of the polarization of the incident light beam would result in varying the relative amplitude or probability of excitation of either molecule. If I_{\parallel} and I_{\perp} are the intensities of fluorescence polarized respectively parallel and perpendicular to the direction of the polarization of the incident light, the degree of fluorescence polarization f , defined as

$$f = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp}) \quad (1.1)$$

is a convenient experimental observable for the investigation of excitation transfer within the dimer. A detailed presentation of the basic formalism required for the analysis of this observable has been given by Rahman et al.² It is clear that the intensity of fluorescence in the direction of the unit vector e_{λ} is given by

$$I_{\lambda} = \sum_{m,n} \rho_{mn} (\mu_m \cdot e_{\lambda}) (\mu_n \cdot e_{\lambda}) \quad (1.2)$$

where the μ 's are the dipole moments, ρ 's are density matrix elements, and m, n represent states in a suitable basis, such as that of the localized molecular (site) states 1 and 2. Given the assumption of mutually perpendicular dipole moments that we have made for simplicity, it follows that

$$\mu_1 \cdot e_{\parallel} = \mu_2 \cdot e_{\perp} = \cos \phi; \quad -\mu_1 \cdot e_{\perp} = \mu_2 \cdot e_{\parallel} = \sin \phi \quad (1.3)$$

where ϕ is the angle made by the polarization of the incident light with the induced dipole moment on molecule 1. Equation 1.1 then yields

$$f = p \cos 2\phi + r \sin 2\phi \quad (1.4)$$

for f , the primary observable of this investigation, in terms of the combinations p and r of the density matrix elements in the site representation:

$$p = \rho_{11} - \rho_{22}; \quad r = \rho_{12} + \rho_{21}; \quad q = i(\rho_{12} - \rho_{21}) \quad (1.5)$$

We have also defined the additional quantity q in (1.5) for later use. As in our previous papers on this subject, the notation used above describes the degree of fluorescence of polarization by f rather than p and reserves the latter symbol for the probability difference, in keeping with standard usage in density matrix treatments.

The behavior of the degree of fluorescence polarization f thus depends on the time evolution of p and r . Over the years, such evolution has been treated through a multitude of theoretical approaches. In fluorescence depolarization studies, stochastic Liouville equations were used in the original treatment of Rahman et al.,² and the discrete nonlinear Schroedinger equation was

* Abstract published in *Advance ACS Abstracts*, June 15, 1994.

used in a later nonlinear treatment.^{3,4} In the recent past, the discrete nonlinear Schroedinger equation has been generalized to produce a new evolution equation^{7,8} which can describe, in a reasonably unified manner, nonlinear effects arising from strong interactions of the excitation with vibrations, dissipation effects originating in bath interactions, and bifurcation effects stemming from thermal fluctuations. The origin, meaning, and form of the new equation are described in the following section in the fluorescence depolarization context.

2. Evolution Equation

The evolution of the amplitudes c_m of occupation of Wannier-like localized sites m by a Frenkel excitation generally obeys the standard Schroedinger equation

$$i\hbar \frac{dc_m}{dt} = \sum_n V_{mn} c_n + E_m c_m \quad (2.1)$$

where the E 's and the V 's are respectively the diagonal and off-diagonal matrix elements of the Hamiltonian in the localized basis. If interactions with vibrations are present, the V 's and E 's are dependent on the vibrational coordinates x . For simplicity, let us take V_m to be independent of x , and E_m to depend linearly only on the internal coordinate x_m at site m . In the absence of interactions, x_m might evolve sinusoidally with frequency ω and equilibrium position 0. In the presence of interactions, however, the equilibrium position of the oscillator is changed by an amount proportional to the probability that site m is occupied by the quasiparticle. Furthermore, dissipation effects acting on the vibrations as well as the corresponding thermal fluctuation effects would be represented by

$$\frac{d^2 x_m}{dt^2} + \gamma \frac{dx_m}{dt} + \omega^2 x_m = -\text{const.} |c_m|^2 + R_m(t) \quad (2.2)$$

where bath interactions give rise to the damping parameter γ , and fluctuations are described by the random force term $R_m(t)$. For simplicity, we will assume that the damping parameter is large enough to justify the neglect of the second derivative of the oscillator displacements. Then, if $\omega \rightarrow \infty$, $\gamma \rightarrow \infty$, and $\omega^2/\gamma = \Gamma$, the evolution of the oscillator displacements toward their equilibrium positions proceeds at a single characteristic "vibrational relaxation" rate Γ . For fluorescence depolarization of dimers, we need restrict the analysis only to a two-site system. Then, with y denoting the difference $x_1 - x_2$ except for proportionality constants, we can write the evolution of the density matrix elements p, q, r defined in (1.5) as

$$\frac{dp}{dt} = 2Vq; \quad \frac{dq}{dt} = -2Vp - \chi yr; \quad \frac{dr}{dt} = \chi yq \quad (2.3a)$$

$$\frac{dy}{dt} = -\Gamma(y - p) + F(t); \quad F(t) = 2\Gamma(kT/\omega^2)\delta(t) \quad (2.3b)$$

where k is the Boltzmann constant and T the temperature. Equations 2.3 constitute a Langevin set. Standard techniques allow the derivation⁹ of an exact Fokker-Planck equation for the distribution function in p, q, r, y space, an approximate but useful Fokker-Planck equation for the distribution function in p, q, r space, and a closed evolution equation for the thermal averages of p, q, r obtained through a contraction analysis.⁷ The latter equation is

$$\frac{dp}{dt} = 2Vq \quad (2.4a)$$

$$\frac{dq}{dt} = -2Vp - \chi pr + \frac{2V\chi}{\Gamma} qr - \alpha q \quad (2.4b)$$

$$\frac{dr}{dt} = \chi pq - \frac{2V\chi}{\Gamma} q^2 - \alpha(r - r_{\text{eq}}) \quad (2.4c)$$

where the symbols p, q, r now represent averages over a thermal ensemble of the vibrations, $r_{\text{eq}} \equiv \tanh(V/kT)$ is the thermal equilibrium value of r , and α is a rate which attempts to drive the system to the thermal state. A high-temperature expression⁷ for this rate is $\alpha = (2\chi/\Gamma)kT$.

Equation 2.4 will form the point of departure for the analysis in this paper. It describes the combined phenomena of transfer, nonlinearity, dissipation, and thermal fluctuation and is a special (two-site) case of the general evolution equation⁸

$$i\hbar \frac{d\rho_{mn}}{dt} = [V, \rho]_{mn} - \chi(\rho_{mm} - \rho_{nn})\rho_{mn} - i\frac{\chi}{\Gamma}\rho_{mn}([V, \rho]_{mm} - [V, \rho]_{nn}) - i\alpha(1 - \delta_{mn})(\rho_{mn} - \rho_{mn}^{\text{eq}}) \quad (2.5)$$

We draw the reader's attention to the physical significance of the various terms on the right-hand side of (2.5). The first term describes the transfer of the electronic excitation. Along with the last term, which describes thermal and dephasing effects, it goes to make the ordinary stochastic Liouville equation¹⁰ used in an augmented form in the fluorescence depolarization analysis of ref 2. The nonlinearities that can arise from strong interactions of the moving excitation with vibrations are represented by the second and third terms in (2.5). Equation 2.5 with just the first two terms on the right-hand side is nothing other than the discrete nonlinear Schroedinger equation⁴ or its formal equivalent, the discrete self-trapping equation,¹¹ written in von Neumann notation. It has formed the basis of the fluorescence depolarization investigation of ref 3. The finiteness of vibrational relaxation is responsible for the third term on the right-hand side of (2.5), as shown in ref 12. The simple form of (2.5), or of its dimer counterpart (2.4), is convenient in that the various terms discussed above appear in an additive manner. Needless to say, such simplicity is dependent on the use of judicious approximations. The limitations of the approximation scheme are discussed in refs 7 and 8. Space constraints prevent us from elaborating further on these and related matters. We state in passing that (2.5) or (2.4) can indeed be taken to apply to the standard Hamiltonian used in countless earlier¹³ investigations of similar systems:

$$H = \sum_m \epsilon_m a_m^\dagger a_m + \sum_{m,n} V_{m,n} a_m^\dagger a_n + \sum_q \hbar \omega_q (b_q^\dagger b_q + 1/2) + N^{-1/2} \sum_q \hbar \omega_q g_q \exp(iqR_m)(b_q + b_{-q}^\dagger) a_m^\dagger a_m \quad (2.6)$$

Excepting (2.1) and (2.6), all the equations in this paper have been written down with \hbar set equal to 1. Equation 2.6 uses standard notation which we will not detail here, except for stating that a and b refer respectively to the moving excitation and the vibrations with which it interacts strongly, that the V 's denote intermolecular transfer, and that the sum of $g_q^2 \omega_q$ over all modes q essentially provides the nonlinearity parameter χ appearing in (2.4) or (2.5).

3. Fluorescence Depolarization

We will now investigate the quantity f as given by (1.4) by substituting in it the solution of p and r from (2.4) for various cases. Throughout the analysis in this paper, except in eqs 3.2 and 3.4, the lifetime of the excitation has been assumed to be infinite.

Case 1. Linear Undamped Dimer. If the interactions with both the vibrations and the damping bath are negligible, one has $\chi = 0$ and $\alpha = 0$ in (2.4). The molecular system is thus a linear undamped dimer. One obtains

$$f(t) = \sin^2 2\phi + (\cos^2 2\phi) \cos 2Vt \quad (3.1)$$

The quantity f oscillates from the initial value 1 at frequency $2V$ around the value $\sin^2 2\phi$. This latter value depends on the inclination of the plane of polarization of the incident light to the dipole moment on molecule 1. If the excitation decays with lifetime τ , the steady-state fluorescence polarization $f_s = (1/\tau) \int_0^\infty f(t) e^{-t/\tau} dt$ is given by

$$f_s = \frac{\cos^2 2\phi}{1 + 4V^2\tau^2} + \sin^2 2\phi \quad (3.2)$$

These are standard and expected results.

Case 2. Linear Dimer in Stochastic Interaction with Bath. If interactions with vibrations continue to be not strong enough to introduce nonlinearities into the evolution, but if a bath interaction introduces damping, specifically if $\chi = 0$ but $\alpha \neq 0$, one gets from (2.4)

$$f(t) = (\cos^2 2\phi) e^{-\alpha t/2} [\cos \Omega t + (\alpha/2\Omega) \sin \Omega t] + (\sin 2\phi) \{r_{\text{eq}} + [\sin 2\phi - r_{\text{eq}}] e^{-\alpha t}\} \quad (3.3)$$

where $\Omega = [4V^2 - (\alpha/2)^2]^{1/2}$. If this quantity, which arises from a combination of the transfer interaction and the damping interaction, is real (imaginary), the evolution of f is underdamped (overdamped). The degree of fluorescence polarization evolves from an initial value of 1 to the quantity $(\sin 2\phi)r_{\text{eq}} = (\sin 2\phi) \tanh(V/kT)$ which depends on the polarization angle ϕ . Thus, if the incident light has its plane of polarization parallel to the induced dipole moment on one of the molecules (and perpendicular to that on the other molecule), the degree of fluorescence polarization f vanishes at large times. For other inclinations of the incident polarization plane, f does not vanish at long times. The steady-state f is given by

$$f_s = \frac{4 \cos^2(2\phi)(1 + \alpha\tau)}{(2 + \alpha\tau)^2 + (16V^2 - \alpha^2)\tau^2} + \frac{\sin(2\phi)}{1 + \alpha\tau} (\sin(2\phi) + \alpha\tau r_{\text{eq}}) \quad (3.4)$$

These results agree with the analysis of ref 2. The effect of the relative magnitudes of the transfer interaction and the damping rate are clear in (3.3) and (3.4).

Case 3. Nonlinear Dimer in the Adiabatic Limit (Infinitely Fast Relaxation) at $T = 0$. If the interactions with vibrations are strong enough, behavior inaccessible to the linear treatments of refs 2, 5, and 6 is predicted by the present theory. One now has $\chi \neq 0$. Let bath interactions be absent, i.e., $\alpha = 0$, and let vibrational relaxation be infinitely fast, i.e., $\Gamma \rightarrow \infty$. We then have

$$f(t) = (\cos^2 2\phi) cn(ut|\sigma) + (\sin 2\phi) [\sin 2\phi - \sigma(\cos^2 2\phi) sn^2(ut|\sigma)] \quad (3.5a)$$

$$u = 2V\xi \cos 2\phi; \quad \sigma = \xi\chi/4V; \quad \xi = (\cos 2\phi)[1 + (\chi/2V) \sin 2\phi]^{-1/2} \quad (3.5b)$$

The Jacobian elliptic functions cn and sn present in the evolution of f describe a number of interesting physical features in this case including the occurrence of abrupt transitions (e.g., the cn - dn transition⁴). The crucial parameter which controls these transitions is σ . It is determined not only by the relative ratio of the nonlinearity and the transfer interaction but also by the polarization angle. This is an important feature which should not be missed. It suggests the possibility of experimental control over the effective nonlinearity of the system through a mere variation of the inclination of the polarization of incident light. Unfortunately, a fixed inclination has little meaning in a disordered aggregate or solution, and finding an experimentally appropriate crystal is not an easy task. Nevertheless, it is useful to stress that

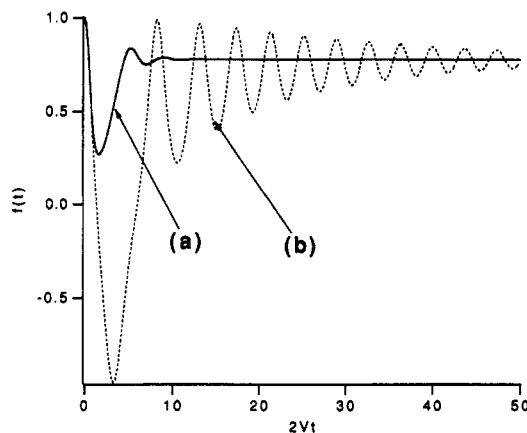


Figure 1. Effect of finite vibrational relaxation on $f(t)$, the degree of fluorescence depolarization. Plotted is f as a function of the dimensionless time $2Vt$ for two values of the vibrational relaxation rate Γ : (a) 1 and (b) 10 in units of $2V$. The effective dissipation is clearly more pronounced in (a). The other parameters are $\phi = 9^\circ$, $\chi/2V = 2$, and $\alpha = 0$. This choice signifies a nonlinear system at zero temperature with a degree of nonlinearity high enough to cause symmetry breaking. The lifetime of the excitation has been assumed infinite in all the plots of this paper.

the experimental technique of fluorescence depolarization can modify a sensitive parameter in the observations without changing the system property χ .

Case 4. The General Case: Finite Nonlinearity, Relaxation Rate, and Temperature. We will now consider the general case $\chi \neq 0$, $\alpha \neq 0$, $1/\Gamma \neq 0$ from which all the above results may be derived under special conditions. New results pertain to additional subcases, e.g., $\chi \neq 0$, $\alpha \neq 0$, $1/\Gamma = 0$, signifying the adiabatic nonlinear system in the presence of bath interactions, and $\chi \neq 0$, $\alpha = 0$, $1/\Gamma \neq 0$, signifying the zero-temperature (no bath interactions) case of the nonadiabatic system. Equation 2.4 must be solved numerically in the general case. Figures 1–3 show the solution numerically. Only the time dependence of f is shown. In units of $2V$, the nonlinear parameter $\chi = 2$ in all the plots. Because the range of validity of the high-temperature expression $\alpha = (2\chi/\Gamma)kT$ is not known with precision, we have treated α as an independent parameter here. We have set the equilibrium value of r to be 1, for simplicity.

Comparison of the time dependence of the degree of fluorescence polarization in case 1 (eqs 3.1 and 3.2) and case 2 (eqs 3.3 and 3.4) reveals their prime difference to be persistent oscillations in the former case and their damping to the value $(\sin 2\phi)r_{\text{eq}} = (\sin 2\phi) \tanh(V/kT)$ in the latter case. This has already been clear from the analysis of Rahman et al.² We see here a similar relation between the adiabatic results of Kenkre and Tsironis³ and the present analysis. Figure 1 shows the appearance of an effective damping of the nonlinear oscillations. In units of $2V$, we have taken the relaxation rate Γ to be 1 in Figure 1a but 10 in Figure 1b and have set the polarization angle $\phi = \pi/20$ and the fluctuation rate $\alpha = 0$. The effective damping in the present analysis relative to that of ref 3 arises from the finiteness of vibrational relaxation. This subtle point has been explained in the context of the general evolution by Kenkre and Wu.¹⁰ Briefly stated, finiteness of vibrational relaxation appears as dissipation in the evolution of the fictitious classical oscillator whose displacement represents the probability difference p of the quantum mechanical excitation and forces the system into the stationary states of the adiabatic system. The effective damping is much more transparent in Figure 1a than in Figure 1b.

An even more remarkable feature that arises from (2.4) consists of limit cycles into which the system settles provided the thermal fluctuations are small enough. These limit cycles manifest themselves as oscillations of the degree of fluorescence polarization. They represent an unusual steady state of the system. Normal oscillations of $f(t)$, such as in cases 1 and 2 above, decay

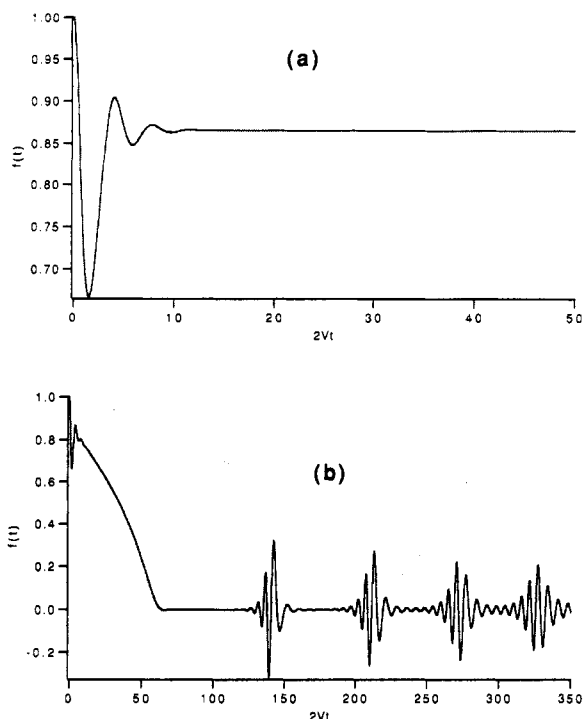


Figure 2. Bifurcation effects in $f(t)$ arising from thermal fluctuations. Plotted is f as a function of the dimensionless time $2Vt$ for two values (in units of $2V$) of the thermal fluctuation rate α : (a) 0 which signifies zero temperature and (b) 0.01. Other parameters are $\phi = 0^\circ$, $\chi/2V = 2$, and $\Gamma/2V = 1$. Dramatic bursts of $f(t)$ occur in (b).

at large times in any real system as a result of dissipation. This is quite clear from (3.3). Nonlinear oscillations arising in case 3 also decay for similar reasons for $1/\Gamma \neq 0$, $\alpha = 0$, as is apparent in Figure 1. By contrast, the interplay of nonlinearity ($\chi \neq 0$) with stochasticity ($\alpha \neq 0$) gives rise to nondecaying oscillations. For appropriate parameter values, the degree of fluorescence polarization can exhibit complex behavior consisting of initial oscillations, tendency to settle into a value corresponding to the stationary states of the system, and evolution into an apparently uninteresting state without oscillations, as well as the highly counterintuitive limit cycles. In Figure 2 we compare the evolution of f for no thermal fluctuations ($\alpha = 0$) with that for finite fluctuations ($\alpha = 0.01$). We have taken $\phi = 0$, $\chi = 2$, and $\Gamma = 1$ in these and all the subsequent plots in the paper. The curious bursts of the degree of fluorescence polarization in Figure 2b arise from Hopf bifurcations.¹⁴ For large times, the bursts bunch into limit cycles. The bunching tendency is clear on the right side of Figure 2b. In Figure 3, we have shown the evolution for the entire range of thermal fluctuations. The presence of nonlinearity in excess of the critical value ($\chi > 2V$) ensures the formation of symmetry-breaking stationary states. The fact that vibrational relaxation is finite forces the evolution to values of f corresponding to those stationary states, as is clear in Figure 3a. As soon as temperature is finite (α is finite), we see in Figure 3b ($\alpha = 0.01$) that the system is forced out of those stationary states by thermal fluctuations. As α is increased, bifurcation behavior depicted in Figure 1b occurs. In Figure 3c, one sees the clear onset of limit cycles ($\alpha = 1$). It should not be forgotten that the limit cycles are present in spite of dissipation. Indeed, they arise from a balance of nonlinearity and dissipation. For a large enough value of α , the cycles are destroyed as is obvious in Figure 3d ($\alpha = 4$). The condition for the destruction of the cycles is¹⁴

$$\alpha > (\chi/\Gamma)r_{\text{eq}} \quad (3.6)$$

If the high-temperature expression⁹ for the fluctuation rate is used in conjunction with (3.6), we obtain the simple condition for

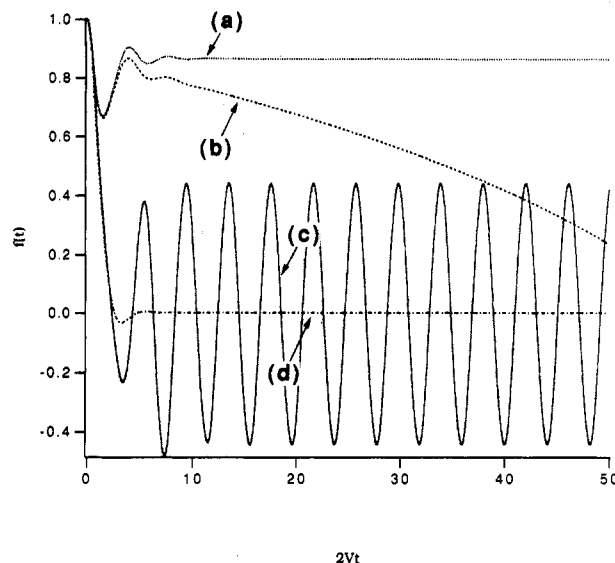


Figure 3. Limit cycles in $f(t)$ arising from thermal fluctuations. Plotted is f as a function of the dimensionless time $2Vt$ for several values (in units of $2V$) of the thermal fluctuation rate α : (a) 0 which shows straightforward evolution toward the stationary state, (b) 0.01 which shows the removal of the excitation from the stationary state as a result of thermal fluctuations, (c) 1 which exhibits limit cycles which do not ever decay, being maintained by a balance of nonlinearity and dissipation, and (d) 4 in which the limit cycles are destroyed. Other parameters are $\phi = 0^\circ$, $\chi/2V = 2$, and $\Gamma/2V = 1$. The system is in the strongly nonlinear regime.

the destruction of limit cycles in fluorescence depolarization to be

$$\frac{kT}{V} > \tanh\left(\frac{V}{kT}\right) \quad (3.7)$$

the critical temperature being thus $0.8336(V/k)$. Although this number is independent of the nonlinearity parameter χ , the phenomenon of limit cycles is itself absent unless χ exceeds the critical value $2V$. At the present stage of the analysis, the range of applicability of the α expression used to get (3.7) from (3.6) is unclear. However, if (3.7) is assumed to be valid, we see that systems with high excitation-vibration coupling (and consequently high degree of nonlinearity) could indeed exhibit the effects we have predicted to a measurable extent. Given typical values for the Davydov splitting in stick dimers, the temperatures under which the curious phenomenon of limit cycles might be observable could be of the order of a few tens of degrees kelvin. Under the assumption that the simple expression for the fluctuation rate which allows one to deduce (3.7) from (3.6) is valid, it is also possible to use a result derived by Kuš¹⁴ and obtain

$$\frac{kT}{V} > \tanh\left(\frac{V}{kT}\right) + \frac{2\Gamma}{\chi} \sqrt{1 + \frac{\chi}{2V} \tanh\left(\frac{V}{kT}\right)} \quad (3.8)$$

as the condition for the time evolution of $f(t)$ to be *monotonic* for large times.

4. Concluding Remarks

The observable we have investigated in this paper is the degree of fluorescence polarization. Originally discussed by Knox in the application of excitation transfer theory to dimers, it was treated by him and his collaborators with the help of the stochastic Liouville equation in refs 2 and 6 and by others with the help of the discrete nonlinear Schrödinger equation in refs 3 and 4. Coherence and initial state preparation effects were among the targets of the former studies, and nonlinear effects were the goal of the latter studies. Recent work by Wynne and Hochstrasser⁵ has caused renewed interest in this field. In the present paper we have predicted entirely new effects, particularly limit cycles. Although space constraints have not permitted us to describe

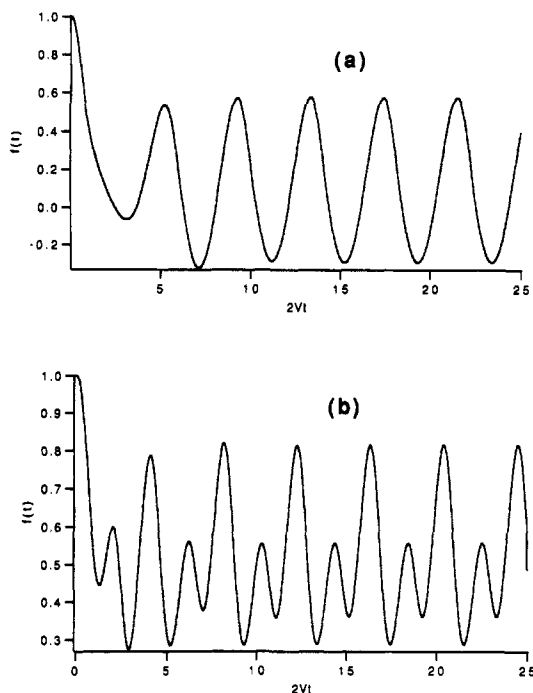


Figure 4. Effect of changing the inclination of the initial polarization. Plotted is f as a function of the dimensionless time $2Vt$ for $\alpha/2V = 1$, $\chi/2V = 2$, and $\Gamma/2V = 1$. The polarization angle ϕ equals 6° in (a) and 36° in (b).

them in detail, the figures we have provided from our numerical analysis should make the primary message clear. Thus, Figure 2 shows how increasing the temperature of the system might result in the experimental observation of the remarkable (a) \rightarrow (b) transition related to bifurcations, Figure 3 shows how increasing the temperature might result first in the observation of the limit cycles in (c) and then their destruction in (d), and Figure 4 shows how the structure in the observed time dependence of f could be made to change by varying the angle of polarization. For general aspects of the Hopf bifurcations of interest to this study we refer the reader to ref 14. Elucidation of further details in the fluorescence depolarization context, in particular the description of the steady-state quantity f_s and its angle average, which are generally of greater experimental relevance than the time-resolved f , will be provided in a forthcoming publication.

The observable f is accessible experimentally in its time-resolved form $f(t)$ or in its steady-state version f_s . Experiments to measure the steady-state quantity are easier to perform than their time-resolved counterparts. However, we have not provided the details of f_s here except in eqs 3.2 and 3.4 for cases 1 and 2, respectively, of section 3. A similar equation can be written down analytically in terms of an infinite expansion of the Jacobian elliptic functions appearing in (3.5) for case 3. For the general case 4, however, f_s must be supplied numerically. The analysis provided in the present paper has, as its aim, the description of the *qualitative* features of the new predicted effects. To make the predictions quantitative, it is important to take averages of the calculated observables over polarization angles. This is imperative in solutions where the dimer molecules constantly change their dipole moment angles with respect to a laboratory axis as a result of rotations. Angle averages would be unnecessary for the analysis of pure crystals. While the theory in refs 2, 3, 5, and 6 addresses two-site systems, a simple treatment for extended crystals has been given by the author in ref 4.

It might be useful to observe that, in contrast to the early attention given^{2,3} to the quantity f defined in (1.1), recent work in the chemical physics literature has focused on the degree of anisotropy $(I_{\parallel} - I_{\perp})(I_{\parallel} + 2I_{\perp})^{-1}$. Since the latter quantity is obtained from f as $2f(3 - f)^{-1}$, it is straightforward to examine its evolution with the help of the discussion presented in this paper.

Variables in the fluorescence depolarization experiment which may be "dialed" to span the various effects considered are four: (i) the length L of the stick dimer, (ii) the temperature T of the system, (iii) the angle ϕ of the polarization of the excitation polarization, and (iv) possibly the angle between the induced dipole directions of the optically active molecules. Preparing the dimers with a variable number of optically inactive molecules separating the active ends would vary L and thereby the transfer interaction V . The effect could be substantial: this variation has as its consequence a change in the nonlinearity ratio $\chi/2V$ which is crucial to the onset of symmetry breaking in the system considered. Changes in the dial variable (ii), viz., the temperature T , would have two kinds of effects: a normal change in the relaxation rate and the striking consequences described above—bifurcations, the onset of limit cycles, and their destruction. Physically changing the direction of the exciting polarization would change ϕ . This change not only affects initial conditions as is known from the linear analysis² but also has substantial consequences in the nonlinear system as is clear from case 3 discussed in section 2 (see also Figure 4). This dial variable (iii) is, however, useless in solutions and disordered molecular aggregates where no unique ϕ exists. We have discussed in this paper only the case of mutually orthogonal dipole moments on the two molecules constituting the stick dimer. Our final dial variable (iv) corresponds to changes in the angle between the dipole moments which could possibly be brought about by geometrical selection, i.e., by making the constituents of the optically active molecular pair nonidentical or differently oriented.

The basis of the present study has been the nonlinear equation (2.5). Similar equations, typified by the discrete nonlinear Schrödinger equation, have existed for some time in the literature but were introduced only recently to the analysis of phenomena in molecular crystals and aggregates. The context of Davydov solitons^{15,16} has stimulated interest in these equations. The discrete nonlinear Schrödinger equation⁴ along with its formal equivalent, the discrete self-trapping equation put forward earlier by Eilbeck et al.,¹⁵ has been applied to a variety of experiments. (See refs 4 and 8 for a partial overview.) The basic evolution instrument used in the present paper is an extension^{7,8} of those nonlinear equations in the form of (2.5) capable of treating a blend of nonlinearity, dissipation, and thermal fluctuation.

Acknowledgment. I thank Robert S. Knox for introducing me many years ago to Raoul Kopelman, to whom this article is dedicated, as well as to the topic of fluorescence depolarization, which is the subject of the article. I also thank Marek Kuś for the bifurcation analysis and Mark Endicott and Srikanth Raghavan for discussions.

References and Notes

- (1) Stryer, S.; Haugland, R. P. *Proc. Natl. Acad. Sci. U.S.A.* **1967**, *58*, 719.
- (2) Rahman, T. S.; Knox, R. S.; Kenkre, V. M. *Chem. Phys.* **1979**, *44*, 197.
- (3) Kenkre, V. M.; Tsironis, G. P. *Chem. Phys.* **1988**, *128*, 219.
- (4) Kenkre, V. M. In *Singular Behaviour and Nonlinear Dynamics*; Pnevmatikos St., Bountis, T., Pnevmatikos, Sp., Eds.; World Scientific: Singapore, 1989; Vol. II.
- (5) Wynne, K.; Hochstrasser, R. M. *Chem. Phys.* **1993**, *171*, 179.
- (6) Knox, R. S.; Gulen, D. *Photochem. Photobiol.* **1993**, *57*, 40.
- (7) Kenkre, V. M.; Grigolini, P. Z. *Phys. B* **1993**, *90*, 247.
- (8) Kenkre, V. M. *Physica D* **1993**, *68*, 153.
- (9) Grigolini, P.; Wu, H.-L.; Kenkre, V. M. *Phys. Rev. B* **1989**, *40*, 7045.
- (10) See e.g.: Reineker, P. In *Exciton Dynamics in Molecular Crystals and Aggregates*; Hohler, G., Ed.; Springer: New York, 1983.
- (11) Eilbeck, J. C.; Lomdahl, P. S.; Scott, A. C. *Physica D* **1985**, *16*, 318.
- (12) Kenkre, V. M.; Wu, H.-L. *Phys. Rev. B* **1989**, *39*, 6907; *Phys. Lett. A* **1989**, *135*, 120.
- (13) See, e.g.: Rackovsky, S.; Silbey, R. *Mol. Phys.* **1974**, *23*, 124.
- (14) Kenkre, V. M.; Kuś, M. *Phys. Rev. B* **1994**, *49*, 5956.
- (15) Davydov, A. S. *J. Theor. Biol.* **1973**, *38*, 559; *Sov. Phys. Usp.* **1982**, *25*, 898.
- (16) *Davydov's Soliton Revisited*; Christiansen, P. L., Scott, A. C., Eds.; Plenum: New York, 1990.