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ARTICLE *in* INTERNATIONAL JOURNAL OF QUANTUM CHEMISTRY · APRIL 1986

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Semiclassical Time-dependent Theory of Two-photon Spectroscopy. The Effect of Dephasing in the Virtual Level on the Two-photon Excitation Spectrum of Isotachysterol

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Abstract

It is commonly assumed that the nonlinear absorption of two photons is a process involving the simultaneous capture of two radiation quanta. The purpose of this paper is to evaluate semiclassically the spectroscopic consequences of relaxing this assumption by permitting dephasing in the virtual level. Semiclassical wave-packet propagation theory is used to model the vibronic consequences of finite, virtual-state population times. We demonstrate that extremely short virtual-state lifetimes (1–10 femtoseconds) can have a profound effect on two-photon excitation line shapes and total vibronic envelopes. We provide experimental evidence suggesting that virtual state dephasing has an important influence on the two-photon excitation spectrum of the polyene chromophore of isotachysterol. Our analysis suggests that dephasing in the virtual state is of potential importance in defining the vibronic development of two-photon spectra of many polyatomic molecules in solution.

Introduction

The current quantum theoretical treatments of the two-photon absorption process have their origins in the Dirac dispersion theory [1]. The quantum mechanical description of nonlinear spectroscopy does not require the explicit assignment of the temporal properties of the virtual level [1–3], and, in effect, the absorption of two photons is assumed to be a simultaneous process (see Fig. 1). It would be incorrect, however, to assume that the assumption of simultaneous photon absorption inherent in the prevailing theories represents an endorsement of simultaneity. There is growing experimental and theoretical evidence to suggest that this assumption is naive, and a number of recent papers have addressed the potential importance of a finite virtual-state lifetime on Raman line shapes [4, 5] and two-photon absorption spectra [6–8]. It is particularly important to consider this question with respect to nonlinear absorption processes, because the interaction of a molecule with a coherent radiation field invariably leads to a finite virtual-state lifetime (see below). We will present both theoretical and experimental justification for the hypothesis that the two-photon

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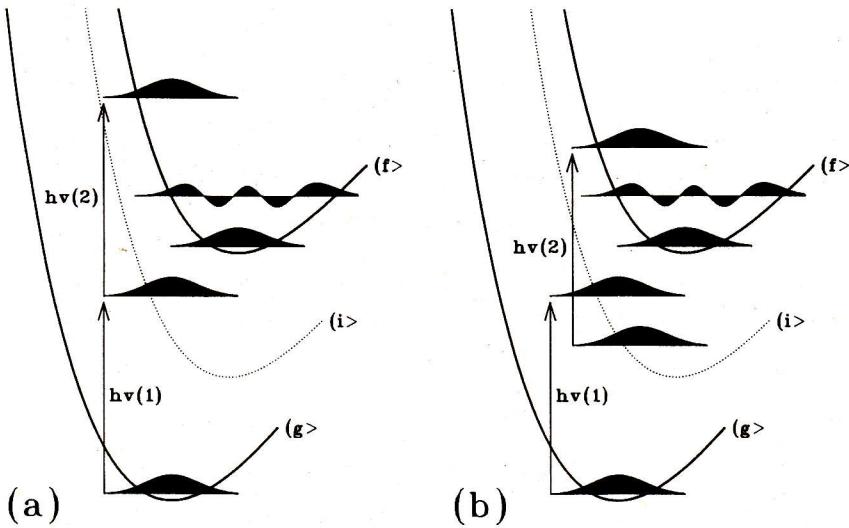


Figure 1. A schematic representation of the two-photon absorption event for a single-oscillator system using wave-packet propagation theory to semiclassically describe the time-dependent process. Insert (a) depicts a simultaneous two-photon absorption in which the wave packet is not allowed to propagate in the virtual level. Insert (b) depicts a two-photon absorption in which propagation (dephasing) of the wave packet in the virtual level occurs prior to injection onto the final excited-state surface. If virtual-state dephasing is pure T'_2 , there is no loss in the kinetic energy of propagation, and the final vibronic spectrum differs only to the extent that the virtual state differs from the final excited-state surface. If virtual-state dephasing includes a T_1 component, however, a portion of the kinetic energy of propagation in the virtual state is lost to the environment (bath), resulting in a blue shift in the line-shape centroid. The calculations reported in this paper assume equal T_1 and T'_2 dephasing unless indicated otherwise.

absorption process is mediated via a virtual state with a finite lifetime. We will further demonstrate that a finite virtual-state lifetime can have a profound influence on the two-photon absorption line shapes and vibronic envelopes.

Theoretical

The semiclassical treatment of the two-photon absorption process will be presented from two perspectives. The development in the following few paragraphs briefly outlines the electronic component and introduces the concept of the effective virtual-state lifetime. Following this, the description of the vibronic spectrum using semiclassical wave-packet propagation theory is presented. The latter represents the theoretical emphasis of this paper and provides a basis for describing the effect of virtual-state dephasing on vibronic line shapes and total vibronic envelopes.

The number of molecules transferred into the final excited state following two-photon absorption, N_f , can be calculated using Eq. (1) [8],

$$N_f = N^2 \sigma_{\lambda}^{f \leftarrow i} \sigma_{\lambda}^{i \leftarrow o} C(Z_{o2}/\pi W_{o2}^2) \exp(-\langle t_{\text{rad}} \rangle/\tau_i), \quad (1)$$

where N is the number of photons in the laser pulse, $\sigma_{\lambda}^{i \leftarrow o}$ and $\sigma_{\lambda}^{f \leftarrow i}$ are the cross sections for single-photon processes from the ground state (o) to the virtual state (i) and from the virtual state (i) to the final state (f), respectively, C is the concentration of the solute, Z_{02} and W_{02} define the confocal distance and the beam radius of the focused irradiation (see Ref. 10, pp. 135–138), τ_i is the intrinsic lifetime of the virtual state, and $\langle t_{rad} \rangle$ is the expectation value of the effective lifetime of the virtual state in the radiation field. For simplicity we assume that the molecule is irradiated with pure monochromatic radiation of wavelength λ .

The exponential term in Eq. (1) represents the fractional occupation of the virtual state manifold that is present upon the arrival of the second photon. This term is invariably less than unity, because a portion of the ensemble of virtual states does not remain populated long enough for the second photon to arrive at the molecule prior to the “decay” of the virtual state (see Fig. 2). An estimate of the intrinsic lifetime of the virtual state, τ_i , can be obtained using Heisenberg’s uncertainty principle and the single intermediate state approximation [11],

$$\tau_i = h(4\pi \Delta \tilde{\nu}_{i\lambda})^{-1}, \quad (2)$$

where h is Planck’s constant and $\Delta \tilde{\nu}_{i\lambda}$ is the difference in energy between the photon energy and the stationary energy of the appropriate low-lying strongly allowed singlet state. For a “typical” molecule and “typical” experimental conditions, $\Delta \tilde{\nu}_{i\lambda}$ will be on the order of 10^4 cm^{-1} , yielding an intrinsic virtual-state lifetime of about $3 \times 10^{-16} \text{ s}$. This time period, which is on the same order as that required to excite a molecule via a one-photon process into a stationary excited state, is too short to have vibronic consequences. In other words, if a second photon arrives at the molecule within 0.3 fs of the first, it is physically reasonable to view the two-photon absorption process as “simultaneous.”

The problem with the above analysis is that it assumes that the intrinsic lifetime of this virtual state is identical to the effective lifetime of the virtual state in the radiation field (i.e., $\tau_i = \langle t_{rad} \rangle$). In fact, a detailed analysis indicates that $\langle t_{rad} \rangle$ is usually an order of magnitude larger [8]:

$$\langle t_{rad} \rangle = -\tau_i \ln \left[\left(\frac{36}{\pi^2} \right) \left(\frac{1}{c \Gamma} \right) \left(\frac{\tilde{\nu}_\lambda}{(\Delta \tilde{\nu}_{i\lambda})^2} \right) \right], \quad (3)$$

where c is the speed of light, Γ is the pulse width of the laser (assuming a Gaussian pulse; see pp. 120–121 of Ref. 10), and $\tilde{\nu}_\lambda$ is the wavenumber of the laser. Equation (3) is a very simplified expression for the effective lifetime, and details of its derivation may be found in [8]. Key assumptions in the derivation are (1) Gaussian optics and a Gaussian excitation pulse shape, (2) negligible ground-state depletion, and (3) a single intermediate state [8]. If we arbitrarily assume $\tilde{\nu}_\lambda = \Delta \tilde{\nu}_{i\lambda} = 10^4 \text{ cm}^{-1}$ and $\Gamma = 10 \text{ ns}$, then the term in brackets equals approximately 10^{-7} , and

$$\langle t_{rad} \rangle \approx 16\tau_i \approx 5 \text{ fs}$$

We will demonstrate below that a virtual-state occupation time of about 5 fs is sufficient to dramatically change the vibronic line shapes and total vibronic envelope

of a two-photon excitation spectrum if T_1 dephasing occurs during virtual-state population.

Semi-classical Wave-packet Propagation Theory of Two-photon Absorption

Wave-packet propagation equations which describe two-photon vibronic absorption spectra are derived below for two cases that allow the wave packet to propagate in the virtual state. In Case 1 the wave packet is not allowed to dephase via T_1 processes while in the virtual state. In Case 2 the wave packet is allowed to dephase via T_1 (energy loss) processes.

Case 1. No T_1 dephasing in the virtual state

The analysis of the vibronic spectrum for a two-photon allowed electronic transition is inherently more complicated than that for a one-photon allowed electronic transition. The added complexity is due to the potential involvement of virtual intermediate electronic states and their vibrational-state manifolds in a two-photon electronic transition.

The present analysis assumes that (1) the two photons which excite the molecule have the same polarization (e) and energy (E), (2) the two-photon transition begins from the lowest energy vibrational state of the ground electronic state, and (3) the

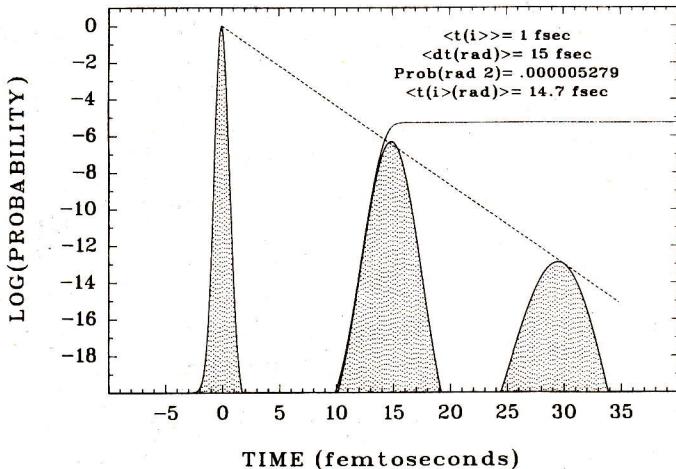


Figure 2. Schematic representation of the interaction of coherent laser light with an ensemble of virtual states. The calculation was carried out assuming arbitrarily that the lifetime of the virtual state [Eq. (2)] is 1 fs and that the expectation value for the virtual-state lifetime in the field of the radiation [Eq. (3)] is 14.7 fs. Approximately 5.3×10^{-6} of the virtual states initially prepared remain populated upon arrival of the second photon (dashed and dotted lines). The three curves filled with dots represent the probability of the first, second, and third photons being scattered by a virtual level, arbitrarily assuming that the probability of the first photon is unity and that the arrival time (x axis) of the first photon is at time zero.

Franck-Condon approximation holds. The two-photon tensor for a transition from the ground electronic state (o) to the n th vibrational level of the final electronic state (f) is [10-11]

$$S_{fn,oo} = 2 \sum_j (e \cdot \mu_{fj}) (e \cdot \mu_{jo}) \sum_k \frac{\langle \chi_{fn} | \chi_{jk} \rangle \langle \chi_{jk} | \chi_{oo} \rangle}{(E_k + E'_{jo}) - E - i\hbar\Gamma_j}, \quad (4)$$

where j counts over intermediate electronic states and k over vibrational states of the j th intermediate electronic state. The terms μ_{fj} and μ_{jo} are the one-photon transition dipoles between the f and j , and j and o pairs of electronic states. Vibrational states are represented as $\chi_{\mu\lambda}$, where the subscripts μ and λ designate the λ th vibrational level of the μ th electronic state. The explicit nuclear coordinate dependence of $\chi_{\mu\lambda}$ is assumed but not shown. The vibronic resonance energy between χ_{jk} and χ_{oo} is given by the term $E_k + E'_{jo}$, where E_k is the energy of the k th vibrational level of the j th electronic intermediate state, and E'_{jo} is the difference in energy between the minimum of the j th electronic state and the lowest vibrational level of the ground electronic state. The symbol Γ_j is the intrinsic line width associated with the j th electronic intermediate state.

The lowest-lying two-photon allowed electronic state in a linear polyene is the $1^{\text{a}1}\text{A}_g^* \pi\pi^*$ state [9]. Previous theoretical studies of the two-photon properties of nonpolar linear polyenes [11] have shown that the two-photon absorption into the $1^{\text{a}1}\text{A}_g^* \pi\pi^*$ state (hereafter designated as the A state) is mediated by a virtual state with properties determined by the strongly one-photon allowed $1^{\text{b}1}\text{B}_u^* \pi\pi^*$ state (hereafter designated as the B state). If we let f be A, and we let B represent the only intermediate electronic state in Eq. (4), then the two-photon tensor becomes

$$S_{An,oo} = 2(e \cdot \mu_{AB}) (e \cdot \mu_{Bo}) \sum_k \frac{\langle \chi_{An} | \chi_{Bk} \rangle \langle \chi_{Bk} | \chi_{oo} \rangle}{(E_k + E'_{Bo}) - E - i\hbar\Gamma_B}. \quad (5)$$

This tensor is further simplified by adopting all approximations used in the simplest Franck-Condon analysis of one-photon allowed electronic absorption spectra described in [14]. As a result, the vibrational wave functions are those for a harmonic oscillator, one harmonic mode is assumed to be vibronically active (this restriction will be relaxed later), the fundamental frequencies of this mode in the ground (o), B, and A electronic states are equal to ω , $E_k = (k + \frac{1}{2})\hbar\omega$, and $E'_{Bo} = E_{Bo} - \frac{1}{2}\hbar\omega$, where E_{Bo} is the difference in energy between the minima of the B and o electronic states.

The energy-dependent denominator in Eq. (5) can be replaced by a time-dependent half-Fourier transform, an algebraic identity:

$$\begin{aligned} S_{An,oo} &= 2(e \cdot \mu_{AB}) (e \cdot \mu_{Bo}) (i/\hbar) \int_0^\infty \sum_k \\ &\times \left\{ \langle \chi_{An} | \chi_{Bk} \rangle \langle \chi_{Bk} | \chi_{oo} \rangle \exp \left[-i(E_k + E_{Bo} - \frac{1}{2}\hbar\omega - E - i\hbar\Gamma_B) \frac{t_B}{\hbar} \right] \right\} dt_B. \end{aligned} \quad (6)$$

Because

$$\langle \chi_{Bk} | e^{-i(E_k + E_{Bo})t_B/\hbar} = \langle \chi_{Bk} | e^{-iH_B t_B/\hbar},$$

where H_B is the vibrational Hamiltonian for the B intermediate electronic state, Eq. (6) can be written as

$$S_{An,oo} = C_1 \left(\frac{i}{\hbar} \right) \int_0^\infty \sum_k \{ \langle \chi_{An} | \chi_{Bk} \rangle \langle \chi_{Bk} | e^{-iH_B t_B / \hbar} | \chi_{oo} \rangle \times \exp[i(E + \frac{1}{2}\hbar\omega + i\hbar\Gamma_B)t_B / \hbar] \} dt_B, \quad (7)$$

where $C_1 = 2(e \cdot \mu_{AB})(e \cdot \mu_{Bo})$. If we consider the time propagator $e^{-iH_B t_B / \hbar}$ to operate on the right side of the integral, then

$$e^{-iH_B t_B / \hbar} | \chi_{oo} \rangle = | \chi_{oo}(t_B) \rangle. \quad (8)$$

Eq. (9) is obtained by using the completeness relation to remove the sum over k :

$$S_{An,oo} = C_1 \left(\frac{i}{\hbar} \right) \int_0^\infty \langle \chi_{An} | \chi_{oo}(t_B) \rangle \exp \left[i(E + \frac{1}{2}\hbar\omega + i\hbar\Gamma_B) \frac{t_B}{\hbar} \right] dt_B. \quad (9)$$

The two-photon vibronic spectrum for state A as a function of E [$\varepsilon_2(E)$] is

$$\varepsilon_2(E) = C_2 E^2 \sum_n S_{An,oo}^* S_{An,oo} \delta[2E - (E_n + E_{Ao} - \frac{1}{2}\hbar\omega)], \quad (10)$$

where C_2 is a constant, n counts over all vibrational states of the A electronic state, $E_n = (n + \frac{1}{2})\hbar\omega$, and E_{Ao} is the difference in energy between the minima of the A and ground electronic states. After replacing the delta function by its integral formulation and inserting the expressions for $S_{An,oo}^*$ and $S_{An,oo}$ given in Eq. (9), Eq. (10) becomes

$$\begin{aligned} \varepsilon_2(E) = c E^2 & \int_{-\infty}^{\infty} \int_0^{\infty} \int_0^{\infty} \sum_n \{ \langle \chi_{oo}(t'_B) | \chi_{An} \rangle \langle \chi_{An} | \chi_{oo}(t_B) \rangle \\ & \times \exp[i(E + \frac{1}{2}\hbar\omega)(t_B - t'_B)/\hbar] \exp[-\Gamma_B(t_B + t'_B)] \\ & \times \exp[i(2E + \frac{1}{2}\hbar\omega - E_n - E_{Ao})t_A/\hbar] \} dt_B dt'_B dt_A, \end{aligned} \quad (11)$$

where $c = C_1^* C_1 C_2$. Because

$$\langle \chi_{An} | e^{-i(E_n + E_{Ao})t_A / \hbar} = \langle \chi_{An} | e^{-iH_A t_A / \hbar},$$

where H_A is the vibrational Hamiltonian for the A electronic state, Eq. (11) becomes

$$\begin{aligned} \varepsilon_2(E) = c E^2 & \int_{-\infty}^{\infty} \int_0^{\infty} \int_0^{\infty} \sum_n \{ \langle \chi_{oo}(t'_B) | \chi_{An} \rangle \langle \chi_{An} | e^{-iH_A t_A / \hbar} | \chi_{oo}(t_B) \rangle \\ & \times \exp[i(E + \frac{1}{2}\hbar\omega)(t_B - t'_B)/\hbar] \exp[-\Gamma_B(t_B + t'_B)] \\ & \times \exp[i(2E + \frac{1}{2}\hbar\omega)t_A/\hbar] \} dt_B dt'_B dt_A. \end{aligned} \quad (12)$$

If we consider the time propagator $e^{-iH_A t_A / \hbar}$ to operate on the right side of the integral, then

$$e^{-iH_A t_A / \hbar} | \chi_{oo}(t_B) \rangle = | \chi_{oo}(t_A, t_B) \rangle. \quad (13)$$

Eq. (14) arises by employing the completeness relation to remove the sum over n :

$$\begin{aligned} \varepsilon_2(E) = cE^2 \int_{-\infty}^{\infty} \int_0^{\infty} \int_0^{\infty} & \{ \langle \chi_{oo}(t'_B) | \chi_{oo}(t_A, t_B) \rangle \\ & \times \exp[i(E + \frac{1}{2}\hbar\omega)(t_B - t'_B)/\hbar] \exp[-\Gamma_B(t_B + t'_B)] \\ & \times \exp[i(2E + \frac{1}{2}\hbar\omega)t_A/\hbar] \} dt_B dt'_B dt_A. \end{aligned} \quad (14)$$

Note that the integral $\langle \chi_{oo}(t'_B) | \chi_{oo}(t_A, t_B) \rangle$ is equivalent to $\langle \chi_{oo}(0) | \chi_{oo}(-t'_B, t_A, t_B) \rangle$, where

$$|\chi_{oo}(-t'_B, t_A, t_B)\rangle = e^{-iH_B(-t'_B)/\hbar} e^{-iH_A t_A/\hbar} e^{-iH_B t_B/\hbar} |\chi_{oo}(0)\rangle. \quad (15)$$

Our evaluation of $\langle \chi_{oo}(0) | \chi_{oo}(-t'_B, t_A, t_B) \rangle$ is based on analyzing the dynamics of a Gaussian wave packet in the $-t'_B$, t_A , and t'_B time domains—i.e., successively applying the three time propagators shown in Eq. (15). This analysis is outlined below for a single harmonic mode that is vibronically active.

1. Solve

$$H_B \chi_{oo}(t_B) = i\hbar \partial \chi_{oo}(t_B) / \partial t_B, \quad (16)$$

where

$$H_B = (\hbar\omega/2)[p^2 + (q - \Delta_B)^2 + E_{Bo}], \quad (17)$$

and

$$\chi_{oo}(t_B) = (1/\pi)^{1/4} \exp\{-\alpha(t_B)[q - q(t_B)]^2 + ip(t_B)[q - q(t_B)] + i\gamma(t_B)\}. \quad (18)$$

Equation (17) defines the vibrational Hamiltonian for the B intermediate electronic state expressed in terms of momentum coordinates (p) and the ground-electronic-state position coordinates (q) [14]. The term Δ_B is the displacement of the equilibrium position of the potential energy surface for the B state with respect to that for the ground state. Equation (18) defines the time-dependent Gaussian wave packet in the t_B domain [14]. When the fundamental frequencies of the o, B, and A states are equivalent, as in our theoretical analysis, $\alpha(t_B) = \alpha(t_A) = \alpha(-t'_B) = \frac{1}{2}$ [14]. This result means that the wave packet does not spread or rotate in time. The initial conditions for the dynamics of the wave packet in the t_B domain are $q(t_B = 0) = 0$, $p(t_B = 0) = 0$, and $\gamma(t_B = 0) = 0$. These conditions reflect an adiabatic or Franck-Condon transition between the o and B states. Solution of Eq. (16) yields

$$q(t_B) = \Delta_B(1 - \cos \omega t_B), \quad (19)$$

$$p(t_B) = \Delta_B \sin \omega t_B, \quad (20)$$

$$\gamma(t_B) = -(\Delta_B^2/2) \sin \omega t_B \cos \omega t_B - (\hbar\omega/2 + E_{Bo})t_B/\hbar. \quad (21)$$

2. Solve

$$H_A \chi_{oo}(t_A, t_B) = i\hbar \partial \chi_{oo}(t_A, t_B) / \partial t_A, \quad (22)$$

where

$$H_A = (\hbar\omega/2)[p^2 + (q - \Delta_A)^2] + E_{Ao}, \quad (23)$$

and

$$\chi_{\text{oo}}(t_A, t_B) = (1/\pi)^{1/4} \exp\{-\frac{1}{2}[q - q(t_A, t_B)]^2 + ip(t_A, t_B)[q - q(t_A, t_B)] + \gamma(t_A, t_B)\}. \quad (24)$$

Equation (23) defines the vibrational Hamiltonian for the A electronic state [14]. The term Δ_A is the displacement of the equilibrium position of the potential energy surface for the A state relative to that for the ground state. Equation (24) defines the time-dependent Gaussian wave packet in the t_A and t_B domains. The initial conditions for the dynamics of the wave packet in the t_A domain are $q(t_A = 0, t_B) = q(t_B)$, $p(t_A = 0, t_B) = p(t_B)$, and $\gamma(t_A = 0, t_B) = \gamma(t_B)$. These conditions reflect a Franck-Condon transition between the B and A states.

Solution of Eq. (22) yields

$$q(t_A, t_B) = C_{1A} \cos \omega t_A + C_{2A} \sin \omega t_A + \Delta_A, \quad (25)$$

$$p(t_A, t_B) = -C_{1A} \sin \omega t_A + C_{2A} \cos \omega t_A, \quad (26)$$

$$\gamma(t_A, t_B) = -\frac{1}{4}(C_{1A}^2 - C_{2A}^2) \sin 2\omega t_A + C_{1A} C_{2A} \cos 2\omega t_A - (\hbar\omega/2 + E_{A0})t_A/\hbar + C_{3A}, \quad (27)$$

where

$$C_{1A} = q(t_B) - \Delta_A, \quad (28)$$

$$C_{2A} = p(t_B), \quad (29)$$

$$C_{3A} = \gamma(t_B) - C_{1A} C_{2A}. \quad (30)$$

3. Solve

$$H_B \chi_{\text{oo}}(-t_B, t_A, t_B) = i\hbar \partial \chi_{\text{oo}}(-t'_B, t_A, t_B) / \partial(-t'_B), \quad (31)$$

where

$$\begin{aligned} \chi_{\text{oo}}(-t'_B, t_A, t_B) &= (1/\pi)^{1/4} \exp\{-\frac{1}{2}[q - q(-t'_B, t_A, t_B)]^2 \\ &\quad + ip(-t'_B, t_A, t_B)q(-t'_B, t_A, t_B) + i\gamma(-t'_B, t_A, t_B)\}. \end{aligned} \quad (32)$$

The Hamiltonian H_B is given in Eq. (17). Equation (32) defines the time-dependent Gaussian wave packet in the $-t'_B$, t_A , and t_B domains. The initial conditions for the dynamics of the wave packet in the $-t'_B$ domain are $q(-t'_B = 0, t_A, t_B) = q(t_A, t_B)$, $p(-t'_B = 0, t_A, t_B) = p(t_A, t_B)$, and $\gamma(-t'_B = 0, t_A, t_B) = \gamma(t_A, t_B)$. These conditions reflect a Franck-Condon transition between the A and B states. Solution of Eq. (31) yields

$$q(-t'_B, t_A, t_B) = C_{1B} \cos \omega(-t'_B) + C_{2B} \sin \omega(-t'_B) + \Delta_B, \quad (33)$$

$$p(-t'_B, t_A, t_B) = -C_{1B} \sin \omega(-t'_B) + C_{2B} \cos \omega(-t'_B), \quad (34)$$

$$\begin{aligned} \gamma(-t'_B, t_A, t_B) &= -\frac{1}{4}(C_{1B}^2 - C_{2B}^2) \sin 2\omega(-t'_B) + C_{1B} C_{2B} \cos 2\omega(-t'_B) \\ &\quad - (\hbar\omega/2 + E_{B0})(-t'_B)/\hbar + C_{3B}, \end{aligned} \quad (35)$$

where

$$C_{1B} = q(t_A, t_B) - \Delta_B, \quad (36)$$

$$C_{2B} = p(t_A, t_B), \quad (37)$$

$$C_{3B} = \gamma(t_A, t_B) - C_{1B} C_{2B}. \quad (38)$$

4. The closed-form solution of $\langle \chi_{oo}(0) | \chi_{oo}(-t'_B, t_A, t_B) \rangle$ is

$$\begin{aligned} \langle \chi_{oo}(0) | \chi_{oo}(-t'_B, t_A, t_B) \rangle = \exp & \left[-\frac{q(-t'_B, t_A, t_B)^2}{4} - i \frac{p(-t'_B, t_A, t_B)q(-t'_B, t_A, t_B)}{2} \right. \\ & \left. - \frac{p(-t'_B, t_A, t_B)^2}{4} + i\gamma(-t'_B, t_A, t_B) \right]. \end{aligned} \quad (39)$$

By inserting the expressions for $q(-t'_B, t_A, t_B)$, $p(-t'_B, t_A, t_B)$, and $\gamma(-t'_B, t_A, t_B)$ given in Eqs. (33)–(35) into Eq. (39) and performing some algebraic manipulations, we obtain

$$\begin{aligned} \langle \chi_{oo}(0) | \chi_{oo}(-t'_B, t_A, t_B) \rangle &= \exp \left\{ -\frac{\Delta_A^2}{2} (1 - e^{-i\omega t_A}) + \frac{\Delta_B}{2} [(1 - e^{-i\omega t_B}) + (1 - e^{i\omega t'_B})] \right. \\ &\quad \times [\Delta_A (1 - e^{-i\omega t_A}) - \Delta_B] + \frac{\Delta_B^2}{2} (1 - e^{-i\omega t_B}) (1 - e^{i\omega t'_B}) e^{-i\omega t_A} \Big\} \\ &\quad \times \exp \left\{ -i \left[(\hbar\omega/2) (t_B + t_A - t'_B) + E_{Bo} t_B + E_{Ao} t_A - E_{Bo} t'_B \right] \right\}. \end{aligned} \quad (40)$$

Note that if t_B and $t'_B = 0$, then

$$\langle \chi_{oo}(0) | \chi_{oo}(-t'_B, t_A, t_B) \rangle = \exp\{-(\Delta_A^2/2)(1 - e^{-i\omega t_A})\} \exp\{-i \left[\frac{\hbar\omega}{2} + E_{Ao} \right] t_A / \hbar\},$$

i.e., the dynamics of the wave packet are determined solely by the potential energy surface of the A electronic state.

Therefore, the multimode expression for $\varepsilon_2(E)$ is [14]

$$\begin{aligned} \varepsilon_2(E) = cE^2 \int_0^\infty & \int_0^\infty \int_{-\infty}^\infty dt_A dt_B dt'_B \exp \left[\frac{i(E - E_{Bo})(t_B - t'_B)}{\hbar} \right] \exp[-\Gamma_B(t_B + t'_B)] \\ & \times \exp \left[\frac{i(2E - E_{Ao})t_A}{\hbar} \right] \exp(-\Gamma_A|t_A|) \\ & \times \prod_m \exp \left\{ -\frac{\Delta_{Am}^2}{2} (1 - e^{-i\omega_m t_A}) + \frac{\Delta_{Bm}}{2} [(1 - e^{-i\omega_m t_B}) + (1 - e^{i\omega_m t'_B})] \right. \\ & \quad \times [\Delta_{Am} (1 - e^{-i\omega_m t_A}) - \Delta_{Bm}] + \frac{\Delta_{Bm}^2}{2} \\ & \quad \left. \times (1 - e^{-i\omega_m t_B}) (1 - e^{i\omega_m t'_B}) e^{-i\omega_m t_A} \right\}, \end{aligned} \quad (41)$$

where m counts over all vibronically active harmonic modes, ω_m is the fundamental frequency for each mode m , Δ_{Bm} and Δ_{Am} are the coordinate displacements for the B and A states for mode m , and $\exp(-\Gamma_A|t_A|)$ is an exponential decay function describing the relaxation of the wave packet on the potential energy surface of the A electronic state with a lifetime of $1/\Gamma_A$. It is noted that this relaxation could also be described with a Gaussian function.

The multimode expression for $\varepsilon_2(E)$ in Eq. (41) can be rearranged to better indicate the contributions of the wave-packet dynamics in the B (virtual) and A (final) electronic states:

$$\begin{aligned} \varepsilon_2(E) = & cE^2 \int_0^\infty \int_0^\infty dt_B dt'_B \exp\left[\frac{i(E - E_{Bo})(t_B - t'_B)}{\hbar}\right] \exp[-\Gamma_B(t_B + t'_B)] \\ & \times \prod_m \exp\left\{-\frac{\Delta_{Bm}^2}{2}(1 - \exp(-i\omega_m(t_B - t'_B)))\right\} \\ & \times \int_{-\infty}^\infty dt_A \exp\left[\frac{i(2E - E_{Ao})t_A}{\hbar}\right] \exp(-\Gamma_A|t_A|) \\ & \times \prod_m \exp\left\{-\frac{\Delta_{Am}^2}{2}[1 - \exp(-i\omega_m t_A)]\right\} \\ & \times \left\{1 - \frac{\Delta_{Bm}}{\Delta_{Am}}[1 - \exp(-i\omega_m t_B)]\right\} \left\{1 - \frac{\Delta_{Bm}}{\Delta_{Am}}[1 - \exp(i\omega_m t'_B)]\right\}. \end{aligned} \quad (42)$$

The term defining the dynamics of the wave packet solely for the B state is

$$\exp\left[\frac{i(E - E_{Bo})(t_B - t'_B)}{\hbar}\right] \prod_m \exp\left\{-\frac{\Delta_{Bm}^2}{2}[1 - \exp(-i\omega_m(t_B - t'_B))]\right\} \equiv X$$

in Eq. (42). This term makes a significant contribution only if E equals E_{Bo} . In other words, if the incident photons are in one-photon resonance with the B state, then X is a significant term. Because we assumed in our derivation of Eq. (42) that E will never equal E_{Bo} , X can be deleted from the expression for $\varepsilon_2(E)$. Consequently, the expression for $\varepsilon_2(E)$ can be approximated by

$$\begin{aligned} \varepsilon_2(E) \approx & cE^2 \int_0^\infty \int_0^\infty dt_B dt'_B \exp[-\Gamma_B(t_B + t'_B)] \int_{-\infty}^\infty dt_A \exp\left[\frac{i(2E - E_{Ao})t_A}{\hbar}\right] \\ & \times \exp[-\Gamma_A|t_A|] \prod_m \exp\left\{-\frac{\Delta_{Am}^2}{2}[1 - \exp(-i\omega_m t_A)]\right\} \\ & \times \left\{1 - \frac{\Delta_{Bm}}{\Delta_{Am}}[1 - \exp(-i\omega_m t_B)]\right\} \left\{1 - \frac{\Delta_{Bm}}{\Delta_{Am}}[1 - \exp(i\omega_m t'_B)]\right\}. \end{aligned} \quad (43)$$

In the absence of wave-packet propagation in the B state, the integral

$$\int_{-\infty}^\infty dt_A \exp\left[\frac{i(2E - E_{Ao})t_A}{\hbar}\right] \exp[-\Gamma_A|t_A|] \prod_m \exp\left\{\left(-\frac{\Delta_{Am}^2}{2}\right)[1 - \exp(-i\omega_m t_A)]\right\}$$

would define the vibronic spectrum for a two-photon electronic transition. However, Eq. (43) shows that with wave-packet propagation in the B state, the $(-\Delta_{Am}^2/2)$ ·

$[1 - \exp(-i\omega_m t_A)]$ component of the above integral is modified by the term

$$\left\{ 1 - \frac{\Delta_{Bm}}{\Delta_{Am}} [1 - \exp(-i\omega_m t_B)] \right\} \left\{ 1 - \frac{\Delta_{Bm}}{\Delta_{Am}} [1 - \exp(i\omega_m t'_B)] \right\} \equiv Y.$$

The contribution of Y is determined by the lifetime $(1/\Gamma_B)$ of the B state expressed through $\exp[-\Gamma_B(t_B + t'_B)]$.

Because the effective lifetime of the virtual (B) state is short (on the order of femtoseconds), the Y term can only have a significant impact when t_B and t'_B are small. However, for small values of t_B and t'_B both $[1 - \exp(-i\omega_m t_B)]$ and $[1 - \exp(i\omega_m t'_B)]$ approximately equal zero, and hence $Y \approx 1$. Thus, Y has very little impact on the calculated vibronic spectrum for a two-photon electronic transition. This observation is supported by numerical evaluations of Eq. (43) which reveal the minor importance of Y . As a result, the Y term can be deleted from the expression for $\varepsilon_2(E)$ in Eq. (43), and a new approximation of $\varepsilon_2(E)$ can be defined as

$$\begin{aligned} \varepsilon_2(E) \approx cE^2 & \int_0^\infty \int_0^\infty dt_B dt'_B \exp[-\Gamma_B(t_B + t'_B)] \int_{-\infty}^\infty dt_A \exp\left[\frac{i(2E - E_{A0})t_A}{\hbar}\right] \\ & \times \exp[-\Gamma_A|t_A|] \prod_m \exp\left\{\left(-\frac{\Delta_{Am}^2}{2}\right)[1 - \exp(-i\omega_m t_A)]\right\}, \end{aligned} \quad (44)$$

where

$$c = C_2 |2(e \cdot \mu_{AB})(e \cdot \mu_{Bo})|^2.$$

The basic form of Eq. (44) is identical to that of Eq. (42) when $t_B = t'_B = 0$ —i.e., for no wave packet propagation in the B state. We conclude that *the propagation of the wave packet in the virtual state with no T_1 dephasing has no (or very little) effect on the calculation of vibronic spectra for two-photon electronic transitions if the potential surfaces for the A and B states are identical (or similar)*. This conclusion is supported by numerical evaluations of Eqs. (42) and (44) which yield nearly identical results.

Case 2. T_1 Dephasing in the Virtual State

In this section we derive the equation for wave-packet propagation in the virtual state with both T_1 and T'_1 dephasing.

The starting point for the derivation is the expression for $\varepsilon_2(E)$ given in Eq. (44). We note that if the wave packet is to dephase via a T_1 process or dissipate its energy while propagating in the virtual (B) state, an energy dissipation function should be included phenomenologically in the argument of $\exp[i(2E - E_{A0})t_A/\hbar]$. This function is defined as E_D , and has the general form

$$E_D = -f(t_B, t'_B)t_A. \quad (45)$$

One simple formulation of E_D that is linear in t_B and t'_B is

$$E_D = -D(t_B + t'_B)t_A,$$

where D is a constant defining the energy loss rate.

The expression for $\varepsilon_2(E)$ which includes dephasing in the B (virtual) state is then

$$\begin{aligned} \varepsilon_2(E) \cong cE^2 & \int_0^\infty \int_0^\infty dt_B dt'_B \exp[-\Gamma_B(t_B + t'_B)] \\ & \times \int_{-\infty}^\infty dt_A \exp\left[\frac{i(2E - E_{A0} - D(t_B + t'_B))t_A/\hbar}{\hbar}\right] \exp(-\Gamma_A|t_A|) \\ & \times \prod_m \exp\left\{\left(-\frac{\Delta_{Am}^2}{2}\right)(1 - \exp(-i\omega_m t_A))\right\}. \end{aligned} \quad (46)$$

Thus, as t_B and t'_B increase, the incident photon energy, E , is decreased by $D(t_B + t'_B)$, or, from another perspective, the "apparent" energy difference between the minima of the ground (o) and A electronic states is increased by $D(t_B + t'_B)$. Given t_B and t'_B , the contribution of the dephasing or energy dissipation term to the calculated Franck-Condon vibronic spectrum for a two-photon electronic transition is weighted by the effective lifetime of the virtual state expressed through $\exp[-\Gamma_B(t_B + t'_B)]$. As discussed in the following section, even extremely short virtual-state propagation times (on the order of femtoseconds) coupled with the above dephasing processes can lead to considerable changes in individual vibronic line shapes as well as global blue shifts in the total vibronic envelope.

In summary, there are two phenomenological relaxation terms which must be included in the theoretical treatment of vibronic spectra for two-photon electronic transitions. These terms are $\exp[-\Gamma_A|t_A|]$ and $\exp[-iD(t_B + t'_B)t_A/\hbar]$ in Eq. (46). The first term defines the intrinsic lifetime of the excited state. This exponential function or a related Gaussian function is the only phenomenological relaxation term generally included in the theoretical treatment of vibronic spectra for one-photon electronic transitions.

The second term, $\exp[-iD(t_B + t'_B)t_A/\hbar]$, is important when treating multiphoton phenomena involving virtual states. This term defines the dissipation of energy in the molecule to a surrounding bath while the molecule is in a short-lived virtual state. Clearly, the energy dissipation or T_1 dephasing term has the greatest impact for molecules in the condensed phase.

A final observation concerning the phenomenological relaxation terms is that they can be grouped as follows:

$$\exp[-\Gamma_A|t_A|] \exp[-iD(t_B + t'_B)t_A/\hbar] = \exp[-(\Gamma_A|t_A| + iD(t_B + t'_B)t_A/\hbar)]. \quad (47)$$

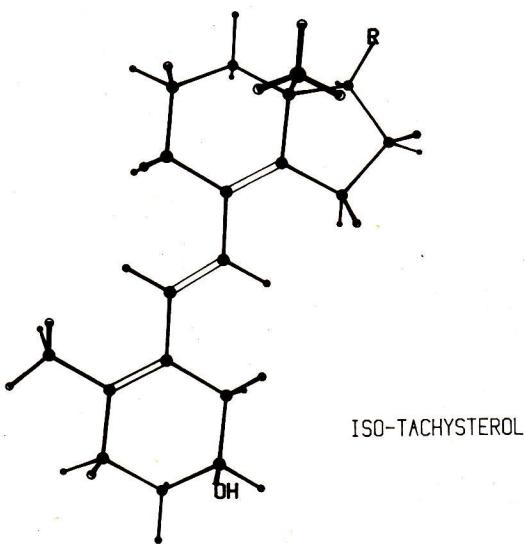
We see that the total contribution to the vibronic line shape for a two-photon electronic transition consists of a real, time-independent component (Γ_A) and an imaginary, time-dependent component ($D(t_B + t'_B)/\hbar$).

It is stressed that incorporating a phenomenological T_1 dephasing term into Eq. (46) defining the vibronic spectrum for a two-photon electronic transition was facilitated greatly by formulating this expression in terms of wave-packet dynamics.

The calculations reported in this paper were carried out on a CSPI 6420 64-bit array processor connected to a VAX 11/780. The integrals were solved numerically by using time increments of 0.1 fs in regions where the absolute value of the integrand was $>10^{-3}$, and by Gaussian quadrature outside of these regions. Test calculations were carried out to verify convergence.

Results and Discussion

Theoretical simulations of two-photon spectra are presented for two systems: an artificial polyene with two Franck-Condon active excited-state vibrational modes of 1200 ($\Delta = 1$) and 1600 ($\Delta = 2$) cm^{-1} (Fig. 3), and the lowest-lying $^1\text{A}_g^*$ -like state of isotachysterol (Figs. 4–5). A key assumption is that one-half (energetically) of the



dephasing in the virtual state is partitioned into T_1 (energy loss) processes (see Fig. 1). From a computational standpoint this means that one-half of the total “transferable” potential energy of the wave packet (which would, during the lifetime of the virtual state, be transferred into kinetic energy) is lost to the bath. There is no justification for adopting this ratio other than the fact that it lies at the energetic median of the two physical extremes. As noted in the previous section, if the wave packet were allowed to propagate without any T_1 dephasing, the resulting spectrum would be virtually identical to one generated with no dephasing (or zero propagation time) in the virtual state. In contrast, choosing a larger proportion of T_1 energy loss would only decrease the extent of virtual-state population time necessary to produce a given observed effect. Since the ratio of T_1 to T_2 dephasing is a function of solute, temperature, and solvent environment and accurate assignment of this ratio is not possible, our results are illustrative rather than quantitative.

The results shown in Figure 3 demonstrate the two observable spectroscopic effects of virtual-state dephasing (assuming $T_1 = T_2$): (a) individual vibronic lines broaden, become unsymmetric, and their band maxima and integral centroids blue shift; and (b) the total vibronic envelope fills in and the maximum blue shifts. The effects listed in (b) are, of course, a result of those listed in (a). Many two-photon spectra do not display vibronic development [12, 13, 15], however, and effect (b) is all that can be observed experimentally. It is tempting to speculate that the unusually broad and blue-shifted ambient temperature two-photon excitation spectra of diphenyl polyenes

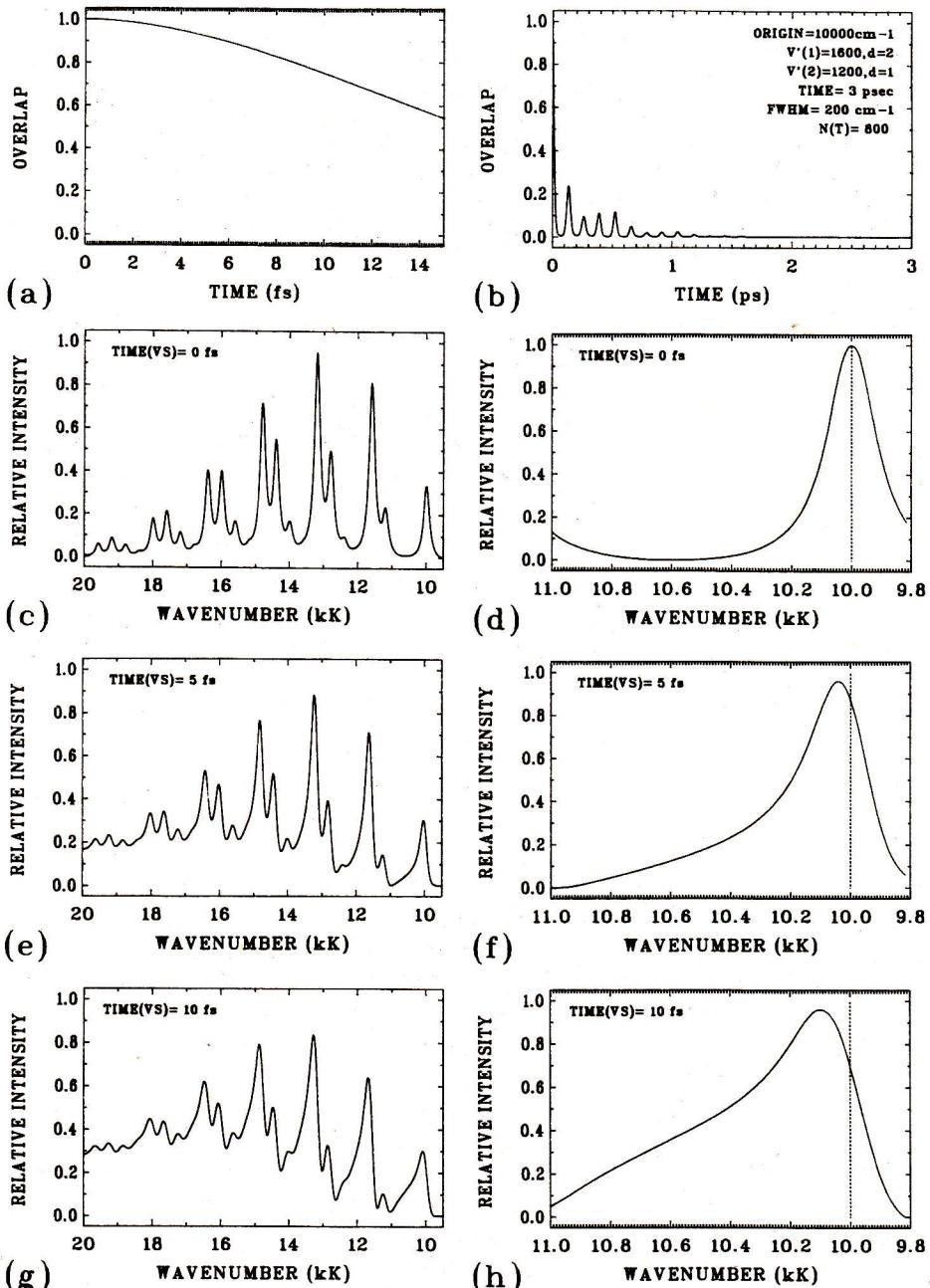


Figure 3. The effect of equal amounts of T_1 and T'_2 dephasing in the virtual level on the two-photon excitation spectrum of a simulated polyene with Franck-Condon active excited-state vibrational modes of 1200 ($\Delta = 1$) and 1600 ($\Delta = 2$) cm^{-1} . Inserts (c) and (d) show, respectively, the total vibronic spectrum and the system origin region in the absence of dephasing. Inserts (e-f) and (g-h) show the analogous regions for virtual-state population (dephasing) times of 5 and 10 fs, respectively. Note that the overlap between the ground-state wave function and the excited-state wave function as a function of time decreases rapidly as a function of time [insert (a)]. The overlap integral as a function of full simulation time is displayed in insert (b). These calculations assume the virtual-state surface is identical to the final-state surface.

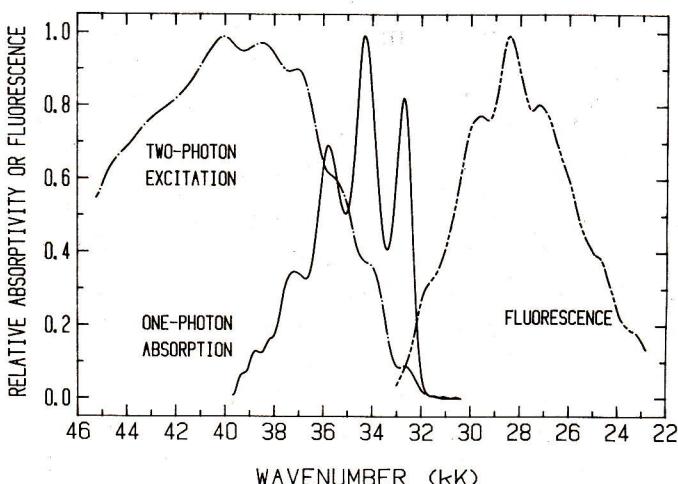


Figure 4. The one-photon absorption (—), two-photon excitation (- - - -), and uncorrected fluorescence (- · - -) spectra of isotachysterol in EPA (77 K). The two-photon excitation spectrum was taken using linearly polarized light and is plotted vs the combined energy of the two photons (see Ref. 9 for details).

observed by Holtom and McClain [15] display the consequences of virtual-state dephasing.

Isotachysterol

The two-photon excitation spectrum of the “ $^1A_g^{*-}$ ” $\leftarrow S_0$ transition of the polyene chromophore of isotachysterol is compared to the one-photon absorption and fluorescence spectra in Figure 4. Previous studies have demonstrated that the two-photon excitation and fluorescence spectra are both associated with transitions between the ground and “ $^1A_g^{*-}$ ” states. What remains to be explained, however, is the total lack of mirror image symmetry between the two-photon excitation and fluorescence spectra.

The simplest explanation is that two (or more) excited singlet states contribute to the blue region of the observed two-photon spectrum. Theoretical calculations, however, suggest that this is unlikely because only one two-photon allowed excited state is predicted in this region [11]. However, this possibility cannot be rigorously excluded. An alternative explanation, however, is that the discrepancy is due to an effective finite virtual-state lifetime. The following calculations illustrate that this assumption accounts adequately for the lack of mirror image symmetry. Furthermore, the anomalous “blue shift” of the “ $^1A_g^{*-}$ ” $\leftarrow S_0$ system origin is also explained.

Wave-packet propagation simulations in the two-photon excitation spectrum of isotachysterol are shown in Figure 5 for virtual-state population times of 0, 2, 4, and 6 fs. Intrinsic line widths of $\Gamma = 150 \text{ cm}^{-1}$ and 1200 cm^{-1} were used to demonstrate the effect of inhomogeneous broadening on the spectrum. The virtual-state “surface” was defined based on the properties of the low-lying strongly one-photon allowed “ $^1B_u^{*+}$ ” state [system origin at $32,730 \text{ cm}^{-1}$ (Fig. 4)]. The one-photon absorption spectrum of the “ $^1B_u^{*+}$ ” $\leftarrow S_0$ transition can be modeled to excellent precision us-

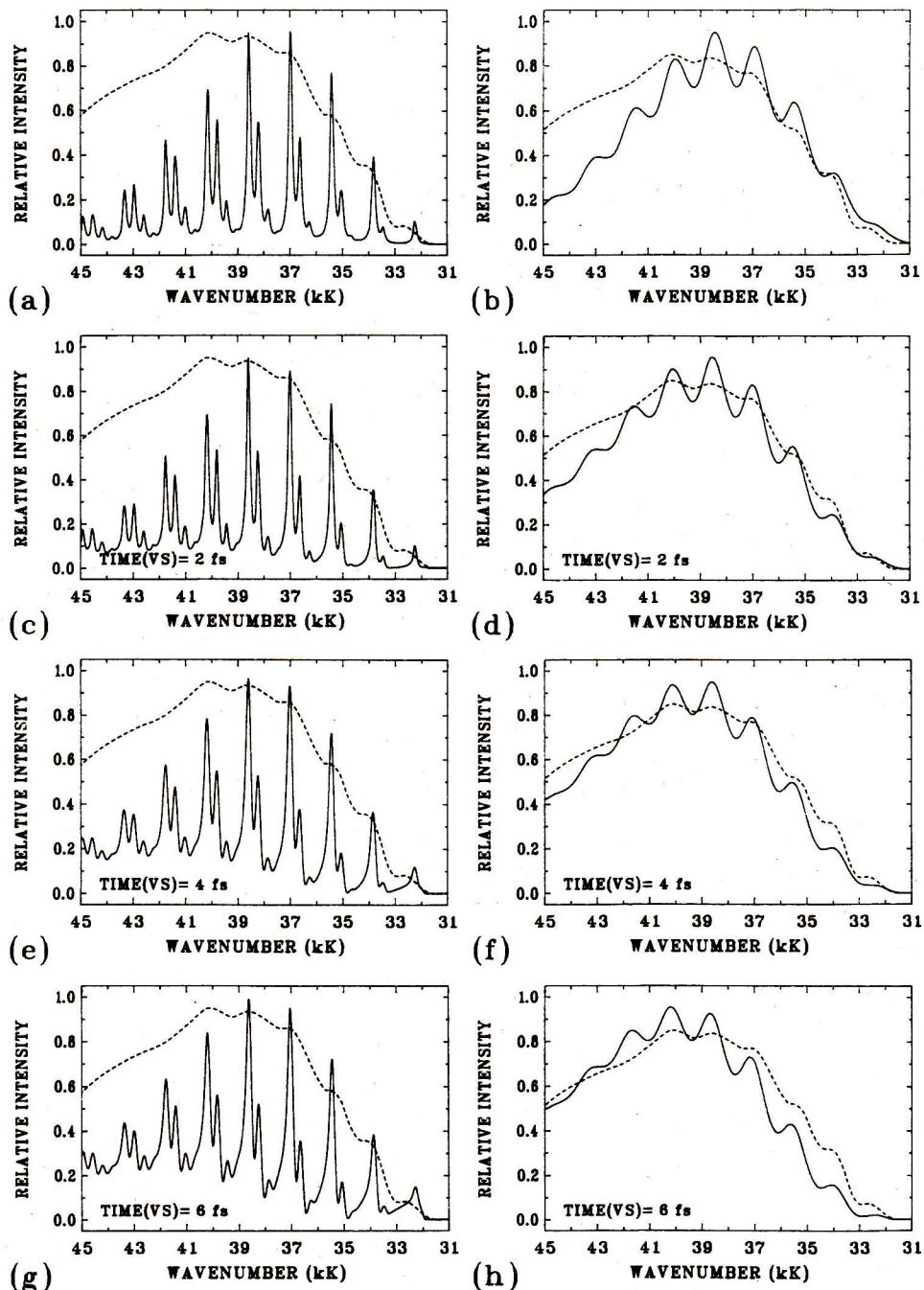


Figure 5. Simulation of the two-photon excitation spectra of isotachysterol as a function of dephasing time in the virtual state (a, b = 0; c, d = 2 fs; e, f = 4 fs; g, h = 6 fs). The calculations were carried out for intrinsic final-state line widths of 150 cm^{-1} (left-hand set) and 1200 cm^{-1} (right-hand set). The best-fit parameters yield a ($T_1 = T_2'$) dephasing time of 4.8 fs, two Franck-Condon active modes of 1216 cm^{-1} ($\Delta = 1.04$) and 1584 cm^{-1} ($\Delta = 2.7$), and a system origin of $32,250\text{ cm}^{-1}$.

ing only two Franck-Condon active modes [1670 cm^{-1} ($\Delta = 1.33$) and 1250 cm^{-1} ($\Delta = 1.05$)]. Our results agree well with previous studies of all-*trans* hexatriene [16, 17], although the system origin of isotachysterol is red shifted relative to all-*trans* hexatriene due to substituent effects.

As can be seen by reference to Figure 5, the assumption of T_1 and T'_2 dephasing processes and a virtual-state population time of 4–6 fs significantly improve the fit of the simulation to the observed spectrum [e.g., compare Fig. 5(f) to Fig. 5(b)]. It should also be emphasized that it is impossible to simultaneously fit both the two-photon excitation spectrum and the fluorescence spectrum without assuming virtual-state dephasing. The best-fit parameters [$\tilde{\nu}_{\infty} = 32,250\text{ cm}^{-1}$, $\tilde{\nu}_{C-C} = 1216\text{ cm}^{-1}$ ($\Delta \cong 1.04$, $\Delta r_{C-C} = 0.050 \pm 0.014\text{ \AA}$), $\tilde{\nu}_{C=C} = 1584\text{ cm}^{-1}$ ($\Delta \cong 2.7$, $\Delta r_{C=C} = 0.093 \pm 0.018\text{ \AA}$)] agree well with those theoretically predicted for all-*trans* hexatriene by Lasaga et al. ($\Delta r_{C-C} = 0.051\text{ \AA}$, $\Delta r_{C=C} = 0.081\text{ \AA}$) [18].

In summary, therefore, we have demonstrated that the anomalous Franck-Condon distribution observed in the two-photon excitation spectrum of isotachysterol can be fully explained by invoking a finite population time for the virtual level ($\sim 5\text{ fs}$) coupled with T_1 and T'_2 dephasing processes. It is important to recognize, however, that we have not proved that dephasing occurs—it is only a plausible possibility. Further experimental work is necessary to prove or disprove our hypothesis. In particular, the line shapes and total vibronic envelopes should display a laser-excitation pulse-width dependence [see Eq. (3)] provided negligible ground-state depopulation is maintained experimentally. Furthermore, the expected dependence of T_1 and T'_2 dephasing processes on temperature may provide an experimental window for observation of virtual-state dephasing. We hope that this preliminary study will stimulate further experimental and theoretical work on this interesting phenomenon.

Acknowledgments

This work was supported in part by grants to RRB from the National Institutes of Health (GM-34548) and the National Science Foundation (CHE-7916336). The authors gratefully acknowledge A. C. Albrecht, E. J. Heller, B. Honig, M. Llinas, A. B. Myers, D. W. Pratt, C. Sandorfy, and D. J. Tannor for interesting and helpful discussions.

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Accepted for publication October 4, 1985