Intramolecular and solvent dynamics in femtosecond pump–probe spectroscopy

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(Received 24 May 1990; accepted 15 June 1990)

A density-matrix theory is applied to the calculation of femtosecond pump–probe experiments on solvated polyatomic molecules. Specific calculations are performed for a two-mode system, in which an optically active solute mode is represented by a pair of harmonic oscillators in the state representation, and the solute is modeled as an overdamped harmonic mode, using the Wigner phase space representation. No restrictions are placed on the relative time scales of the solute vibrational period, the solvent relaxation time scale and the pump pulse duration. The calculations demonstrate the physical phenomena observed in recent experiments on solvated dyes, both in the hole-burning limit, where the pump pulse is long compared to the relevant solute and solvent time scales, and the impulsive limit, for which the pump is short compared to the solute vibrational period.

I. INTRODUCTION

Recent developments in laser technology have made pulses as short as 6 femtoseconds (fs) available for use in chemical experiments. It is thus possible to make real-time observations of chemical events, using pulses shorter than or comparable to molecular vibrational periods; indeed, such pulses are comparable even to the inverse absorption linewidths of many condensed-phase systems. As such, there is strong motivation to provide a theory for molecular nonlinear optical line shapes which allows for arbitrary solvent, solute, and laser pulse time scales, so that a broad range of experiments can be described by a single model. Such a theory has been presented recently; the present work provides specific application of that theory for some realistic experimental situations.

Many recent experiments have used femtosecond pulses to observe real-time vibrational dynamics in room-temperature condensed phase systems. Experiments of this nature can be either resonant, e.g. impulsive pump–probe absorption, or nonresonant, as in an impulsive scattering configuration. A nonresonant experiment reveals only ground-state dynamical information about the molecule of interest, whereas in a resonant experiment, both ground-state and excited-state dynamics play an important role. One advantage to such time-resolved experiments is that they present a picture of vibrational dynamics which is largely unhindered by electronic dephasing.

Another important time-resolved experiment is dynamic hole-burning. Hole-burning differs from impulsive pump–probe spectroscopy only in that the former typically utilizes a pump beam which is spectrally narrow compared to the vibrational energy level spacing of the optically active mode of interest; in the latter, the opposite is true. Other than that, the two techniques are essentially the same; however, the information given by the two experiments is very different. In hole-burning, the experiment selectively excites a small portion of the inhomogeneously broadened absorption line, and we may see vibronic structure in the initial spectrum, due to one or more high-frequency optically active modes. Over time, the solvent relaxes, and any vibronic structure initially present becomes masked by the solvent broadening. In impulsive pump–probe, however, we coherently excite two or more vibronic levels of one or more optically active modes. In this case, we see evidence of the vibronic eigenstates in the time domain, as time-dependent oscillations ("quantum beats") in the probe absorption signal.

In modeling dynamic hole-burning experiments, one must include a means of incorporating solvent-induced phenomena (Stokes shift, line broadening) observed in the experiment. One method which has been used in modeling solvent effects in time-resolved fluorescence experiments is a generalization of the Onsager cavity model, in which the solute is represented by a point dipole in a spherical cavity, and the solvent is modeled by a dielectric continuum. A limitation of this treatment is that, although it successfully models the time-dependent Stokes shift, it does not properly describe the solvent-induced time-dependent broadening of the hole profile. Time-resolved fluorescence is similar to hole-burning, except that the former gives only information pertaining to the excited electronic state, whereas the latter has contributions from both ground-state and excited-state dynamics. Loring et al. successfully incorporated both the Stokes shift and the broadening effects seen in fluorescence and hole-burning experiments by incorporating solvent effects collectively, using a solvation coordinate. Their work was extended by Kinoshita to include electronic level relaxation.

Solvents are, in general, characterized by many relaxation time scales, which may be from ~0.1 to ~100 ps. If we consider a frequency-dispersed detection scheme, the entire probe absorption spectrum is measured at each delay time; solvent relaxation may well be important in such an experiment. We will therefore consider solvent relaxation to be a potentially important process on the time scale of the impulsive pump–probe experiment.
One way to theoretically model such experiments would be to describe the molecular system’s evolution in terms of wave packets made up of harmonic oscillator wave functions. 22,23 The main limitation of such an approach is that it does not allow for any simple, realistic means of incorporating the effects of the solvent. Furthermore, incorporation of finite-temperature effects may make the calculation of the spectrum very complicated. An alternative method would be to use the optical Bloch equations as the theoretical starting point. 7,11,14,24,25 For this approach, each vibronic population and coherence is considered separately, and solvent effects are added to this model via phenomenological dephasing and level relaxation terms. A serious limitation of this method is that for experiments in which many vibronic levels are important, the calculation of the spectrum becomes very complicated. Furthermore, the characterization of the solvent by these means is very limited—all solvent motions are taken to be either infinitely fast or infinitely slow.

We shall employ the multimode density matrix formalism for the calculation of nonlinear optical spectroscopies. 26,27 This treatment allows for arbitrary solvent timescales and, in principle, an arbitrary number of solute and solvent modes. It is based on the Liouville-space propagation of the nuclear density matrix, using either the vibronic state representation or the Wigner phase space representation, 28 whichever allows for the simplest calculation. In fact, as will be shown presently, a combination of the two representations may be the most convenient for the systems of interest. 4,19

We shall specialize to a pump–probe experiment on a solvated polyatomic molecule, e.g., a dye molecule. 1,5–7,9–11 In this paper, we will choose a relatively simple model system, and apply the doorway–window formalism of Ref. (4) for the calculation of a pump–probe experiment on that system. In doing so, we will make as few approximations as possible regarding the relative time scales of the solute, the solvent, and the pump pulse.

The doorway–window picture of pump–probe spectroscopy allows the density matrix formula for the probe absorption to be cast in a physically appealing form. The basic picture of the pump–probe experiment is as follows. 4,29 The pump pulse interacts with the material system, creating an initial doorway state. This doorway state propagates for a time \( \tau \), at which point the spectrum is calculated by taking the overlap of the propagated doorway state with the window state, created by the probe pulse.

The rest of this paper is organized as follows. In Sec. II, we present a two mode model system for pump–probe calculations. The solute mode of interest will be treated as harmonic, in the state representation; all other modes will be treated collectively by an overdamped harmonic mode in the phase space representation. 4,19,27 Although possible, additional contributions from purely homogeneous and purely inhomogeneous broadening will not be included, in order to be able to focus on time-dependent solvent effects. In Sec. III, we perform calculations in the hole-burning limit, where the pump pulse is taken to be long compared to the inverse absorption linewidth. The effects of different solvent time scales will be studied. In Sec. IV, we perform calculations in the impulsive limit, where the pump pulse is short compared to the inverse vibrational spacing of the solute mode of interest. We shall then summarize our results in Sec. V.

II. PUMP–PROBE EXPERIMENTS ON SOLVATED MOLECULES: THEORY

A. The doorway–window picture

We shall consider a pump–probe experiment on a polyatomic molecule in its solvent environment. The experiment proceeds as follows: The molecule is subjected to a pump pulse, centered at time \( t = -\tau \), followed by a probe pulse, at \( t = 0 \). The transmitted probe is then dispersed through a monochromator. The probe difference absorption, defined as the probe absorption in the absence of the pump minus the probe absorption in the presence of the pump, is measured as a function of delay time (\( \tau \)) and detection frequency (\( \omega_2 \)).

We shall consider here the case in which there are only two relevant electronic levels. We can think of an ideal pump–probe experiment on such a system as proceeding as follows: The pump pulse transfers a portion of the equilibrium distribution of molecules to the excited electronic state, leaving a “hole” in the ground state distribution. The density matrix corresponding to this nonequilibrium system is called the “doorway state.” This doorway state then evolves for a time \( \tau \), and the spectrum is then given by its overlap with the “window state,” generated by the probe pulse and the detection apparatus. For overlapping pulses, however, this simple picture does not tell the whole story. When the pump and probe pulses overlap, there are additional contributions from the probe interaction occurring while the pump is preparing the initial state and before the pump prepares the initial state. These contributions to the signal are known collectively as the “coherent artifact.” 29,30 Time-domain pump–probe spectroscopy has the advantage of allowing one to separate the pump and probe temporally, and thus retain only that spectral information corresponding to the doorway–window contribution to the signal. This simplifies the interpretation considerably.

The theory used here applies equally well to both the doorway–window and the coherent artifact contributions to the total spectrum; however, we shall focus in this work on the information provided by the doorway–window part. We may thus write the probe difference absorption in the form:

\[
S(\Omega_1;\omega_2,\tau) = \text{Tr} \left[ \rho_w(\Omega_1;\omega_2) \mathcal{G}_w(\tau) \rho_p(\Omega_1) \right] + \text{Tr} \left[ \rho_w(\Omega_2;\omega_2) \mathcal{G}_w(\tau) \rho_p(\Omega_1) \right].
\]

(2.1)

Here \( \rho_p^m \) and \( \rho_w^m \) (m = g, e) are the doorway and window states, respectively. \( \mathcal{G}_w(\tau) \) and \( \mathcal{G}_w(\tau) \) describe the propagations of the ground and excited-state contributions to the doorway state during the delay time, \( \tau \), between the pulses. \( \Omega_1 \) and \( \Omega_2 \) are the pump and probe center frequencies, respectively. For the calculations presented here, we shall assume our probe pulse to be a delta-function in time; although this may seem a harsh approximation, it actually places no real restrictions on the relevant time scales of a dispersed-detection experiment. Thus, making such an approximation does not restrict the scope of our calculations significantly.
The probe center frequency then drops out of the calculation.

It is often convenient, from a computational point of view, to combine the intermediate propagation step with the preparation of the doorway state; in general, we may write:

\[ G_{ee} (\tau) \rho^d (\Omega_1) = \sum_{b,d} D_{ab} (\Omega_1, \tau) \langle d | b \rangle, \]  

(2.2a)

\[ G_{ee} (\tau) \rho^b (\Omega_1) = \sum_{a,c} D_{cb} (\Omega_1, \tau) |c \rangle \langle a |, \]  

(2.2b)

\[ \rho^d_\nu (\omega_2) = \sum_{b,d} W_{db} (\omega_2, \Gamma) |d \rangle \langle b |, \]  

(2.2c)

\[ \rho^b_\nu (\omega_2) = \sum_{a,c} W_{ca} (\omega_2, \Gamma) |c \rangle \langle a |. \]  

(2.2d)

In Eqs. (2.2), we have partitioned the propagated doorway and the window states into two parts. Those modes which are relatively fast (e.g., optically active modes) we express in terms of their relevant eigenstates; we adopt the convention that \( a, c \ldots \) represent vibrational levels of the ground electronic state and \( b, d \ldots \) represent vibrational levels of the excited electronic state. We treat slow modes (e.g., many solvent nuclear reorientation processes) in terms of the relevant phase space variables, \( \Gamma \) (here \( \Gamma \) is a vector containing the coordinates, \( q_i \), and momenta, \( p_j \), of the slow modes considered).

In principle, then, we may express our doorway and window functions for the total solute-solvent system in terms of an arbitrary number of modes, each of which may be represented using either eigenstates or its coordinate and momentum. We choose the representation for a given mode based on the ease of calculating the trace in Eq. (2.1). In a high frequency vibrational mode, for example, it may be the case that only a few vibronic levels are experimentally accessible. We would then represent this degree of freedom using vibronic eigenstates. If, on the other hand, many levels are experimentally accessible in a given mode, we use the Wigner phase space representation. In this case, we no longer have to sum over states; the doorway and window states will be relatively smoothly varying functions of position and momentum, and the appropriate integrations \( d \beta \) will be relatively simple to perform.

We are now ready to introduce a specific model for calculation of a pump–probe experiment on a solvated polyatomic molecule.

**B. A single optically active mode in a solvent**

We shall consider here a two-mode system: one optically active solute mode and one solvent mode. The solvent mode represents the collective contributions of the solvent and those other modes of the solute molecule which contribute to the signal only through broadening processes. Each mode will be modeled using a harmonic surface whose equilibrium position changes upon electronic excitation.

We treat the solute mode in the vibronic state representation. Because we do not introduce a direct coupling between the solute mode and the solvent mode, vibrational dephasing will be included via a phenomenological exponential decay, \( \exp(-\gamma_{vd} t) \), where \( v \) and \( v' \) are vibration states in the same electronic manifold. We neglect vibrational level relaxations, assuming that they take place on a time scale which is much longer than that of the experiment. No electronic level relaxation is included, for the same reason.

The expressions developed earlier for the doorway and the window states [Eqs. (7.1) together with (A.6) of Reference 4] allow the incorporation of solvent inertial effects by treating its motion in phase space. For simplicity we specialize to the overdamped (Smoluchowski) limit whereby the moment is no longer a relevant variable and may be eliminated. The solvent dynamics may then be expressed in terms of the solvent coordinate, \( U \equiv (H_v - H_d) / \hbar \). Vibrational solvent effects have been previously studied in impulsive experiments using ultrashort pulses where the theory is greatly simplified.\(^{12,31}\)

For this model, the doorway–window part of the differential absorption spectrum is given by:

\[ S(\Omega_1; \omega_2, \tau) = \int dU W_{db} (\omega_2, U) D_{ab} (\Omega_1, \tau, U) + \sum_{c,a} \int dU W_{ca}^* (\omega_2, U) D_{ca} (\Omega_1, \tau, U), \]  

(2.3)

with

\[ D_{ab} (\Omega_1, \tau; U) = \exp(-i \omega_{ab} \tau - \gamma_{ab} \tau) \int_0^\infty dt_1 \int_{-\infty}^\tau dt_0 \sum_a P(a) \mu_{da} \mu_{ab} \{ E_\uparrow (t') E_\downarrow (t' - t_1) \exp[i(\Omega_1 - \omega_{ba}) t_1 + i \omega_{ab} t'] \times F_c (t_1, t - t'; U) + E_\downarrow (t' - t_1) E_\uparrow (t' - t_1) \exp[-i(\Omega_1 - \omega_{ba}) t_1 - i \omega_{ab} t'] F_c^* (t_1, t - t'; U) \}, \]  

(2.4a)

\[ D_{ca} (\Omega_1, \tau; U) = \exp(-i \omega_{ca} \tau - \gamma_{ca} \tau) \int_0^\infty dt_1 \int_{-\infty}^\tau dt_0 \sum_a \mu_{cd} \mu_{ac} \times \{ P(a) E_\uparrow (t') E_\downarrow (t' - t_1) \exp[i(\Omega_1 - \omega_{ca}) t_1 + i \omega_{ac} t'] \times F_c (t_1, t - t'; U) + P(c) E_\downarrow (t' - t_1) E_\uparrow (t' - t_1) \exp[-i(\Omega_1 - \omega_{ca}) t_1 - i \omega_{ac} t'] F_c^* (t_1, t - t'; U) \}, \]  

(2.4b)

\[ W_{db} (\omega_2; U) = \sum_c \mu_{dc} \mu_{ba} \{ G(\omega_2 - \omega_{bc}; U) + G^* (\omega_2 - \omega_{bc}; U) \}, \]  

(2.5a)

\[ W_{ca} (\omega_2; U) = \sum_c \mu_{cb} \mu_{ba} \{ G(\omega_2 - \omega_{bc}; U) + G^* (\omega_2 - \omega_{bc}; U) \}. \]  

(2.5b)
For simplicity, we have invoked the Condon approximation for the solvent mode; that is, the transition dipole operator is taken to be independent of the solvent nuclear coordinates. $F_m$ and $G_m$ ($m = g, e$) give the solvent contributions to the doorway and window functions, respectively; they are given by

$$F_m(t_1; t - t', U) = (2\pi \Delta^2)^{-\frac{1}{2}} \times \exp \left[ -\frac{1}{2\Delta^2} (U - \bar{U}_m)^2 - g(t_1) \right]$$  

$$G(\omega; U) = \int_0^\infty dt_2 \exp \left[ -iUc(t_2) - b(t_2) + i\omega t_3 \right],$$

where

$$\bar{U}_m = (1 - 2\xi)\lambda [1 - M(\tau - t')] + \lambda M(\tau - t') \times M(t_1) - 2\Delta^2 M(\tau - t') \int_0^{t_1} d\tau' M(\tau'),$$

$$g(t_1) = i\lambda \int_0^{t_1} d\tau' M(\tau')$$

$$+ \Delta^2 \int_0^{t_1} d\tau' \int_0^{\tau'} d\tau'' M(\tau''),$$

$$b(t_1) = \Delta^2 \int_0^{t_1} d\tau' \int_0^{\tau'} d\tau'' M(\tau' - \tau'') [1 - M^2(\tau'')]$$

$$c(t_3) = \int_0^{t_3} d\tau' M(\tau').$$

Here

$$\lambda = \bar{U}(t = -\infty)$$

and

$$\Delta^2 = \bar{U}^2(t = -\infty) - \bar{U}^2(t = -\infty) \approx 2\lambda k_B T$$

are static parameters related to the Stokes shift magnitude and the absorption linewidth, respectively.\(^{27}\) In Eq. (2.8a), $\xi$ is equal to 0 for ground-state propagation ($m = g$) and 1 for excited-state propagation ($m = e$). $M(t)$ is the normalized two-time correlation function of the solvation coordinate; it is given, for an overdamped mode, by:

$$M(t) = \exp \left[ -t/\tau_e \right].$$

$\tau_e$ is the time scale on which, for example, the spectral diffusion processes observed in hole-burning experiments take place. The solvent mode is thus characterized by a correlation time, $\tau_e$, a coupling strength, $\Delta$, and a reorganization energy, $\lambda$. In contrast to those broadening processes which are very fast (homogeneous) or very slow (inhomogeneous) compared to the time scale of the experiment, the present treatment allows for an arbitrary solvent time scale, $\tau_e$. To also include another mode, for purely homogeneous broadening, would be straightforward.

In addition to the quantities $\lambda$, $\Delta$, and $\tau_e$, we introduce the absorption linewidth (FWHM), $\Gamma$, which is approximately related to $\tau_e$ and $\Delta$ by:

$$\Gamma = \Delta \frac{2(\Delta \tau_e) + 2.67(\Delta \tau_e)^2}{1 + 0.96(\Delta \tau_e) + 1.136(\Delta \tau_e)^2}.$$  

$\Gamma$ is the total absorption linewidth due to the solvent mode, and is thus related to the inverse of the time scale of the dephasing caused by the solvent. The quantities $\tau_e, \lambda, \Delta$, upon which the solvation mode depends, are thus all experimentally measurable quantities.

A density matrix approach is ideal for treating a complex system such as the one considered here. The density matrix approach allows for a realistic and simple method of including relaxation processes, which is not possible using wave functions. In adopting the doorway–window picture, we include the electronic coherence evolutions in the doorway and window states themselves. This provides us with a simple physical picture of the molecular dynamics, while allowing for the full computational advantage of the density-matrix treatment.

There is also a calculational advantage to the doorway–window picture over the traditional density-matrix treatment for the pump–probe spectrum. The full expression for the signal [given by Eq. (A.5) of Ref. (4)] involves a fourfold integration. Previous works\(^{19,27}\) have gotten around this problem by making suitable approximations regarding pulse duration and solvent time scales. In the doorway–window approach, however, we may break up this quadruple integration, and obtain a more general result for the differential absorption signal.

The calculations to be shown in the following two sections were performed by evaluating Eqs. (2.3)–(2.7) numerically. The double integrals in Eqs. (2.4) were performed with a two-dimensional FFT routine. Calculation time was less than two hours on a Cray-2 for all of the figures to follow. For simplicity, the vibrational dephasing was taken to be the same for all pairs of levels; we used $\gamma_{v'v} = 900$ fs for all $v \neq v'$. The pump pulse envelope was taken to be a Gaussian:

$$E_p(t) = \exp \left[ -t^2/2\tau_p^2 \right].$$

III. DYNAMIC HOLE BURNING

An ideal hole burning experiment provides detailed information as a function of both delay time and detection frequency. This combination is due to the pump pulse duration being long compared with the electronic dephasing time scale, $\tau_e^{-1}$, and short compared with the solvent relaxation time scale, $\tau_s$. It is furthermore typically the case that both the pump and the solvent relaxation time scale are long compared with the inverse vibrational spacing of the solute mode, providing us with eigenstate resolution at short times; this is not normally present in the ordinary absorption spectrum.

It is often said that a hole-burning experiment separates homogeneous from inhomogeneous broadening. Such a statement must be made with care, as we must be sure exactly what is meant by "homogeneous" and "inhomogeneous" broadening. A homogeneous process, in a context such as this, is one which occurs on a faster time scale than is experimentally measurable. Thus, a homogeneous process manifests itself in the form of a broadening of the initial line. Inhomogeneous broadening, on the other hand, will be taken here to mean processes which are slow compared to the time scale of the experiment.
Consider, now, a hole-burning experiment in which homogeneous and inhomogeneous broadenings are present, in addition to a solvent mode which relaxes on the experimental time scale. We may derive an approximate expression for the hole-burning linewidth by considering an ideal experiment, for which the pump pulse is long compared to $\Gamma^{-1}$ and short compared to $\tau_c$. We further take the homogeneous and inhomogeneous broadenings to be Gaussian distributions with standard derivations $\sigma_H$ and $\sigma_I$, respectively. In this case, an analytic expression may be derived for the hole-burning line shape. The time-dependent hole-burning linewidth is then given by:

$$\sigma(\tau) = \left\{ (\sigma_H^2 + \Delta^2 + \sigma_I^2) - [\Delta^2 M(\tau) + \sigma_I^2] \right\}^{1/2}.$$  \hspace{1cm} (3.1)

Here $\sigma(\tau)$ is the variance of the (Gaussian) hole profile; the full width at half maximum (fwhm) is given by $\sigma(\tau)/2.355$.

When the inhomogeneous broadening is large compared with the pulse spectral width and the other broadening processes ($\sigma_I^2 \gg \tau_p^{-2} + \sigma_H^2 + \Delta^2$), Eq. (3.1) becomes:

$$\sigma(\tau) = \left\{ \tau_p^{-2} + 2\sigma_H^2 + 2\Delta^2 [1 - M(\tau)] \right\}^{1/2}.$$  \hspace{1cm} (3.2)

Thus, we see a $\tau = 0$ hole width of $\{\tau_p^{-2} + 2\sigma_H^2\}^{1/2}$ and a $\tau = \infty$ width of $\{\tau_p^{-2} + 2\sigma_H^2 + 2\Delta^2\}^{1/2}$.

In this work, we shall not explicitly include homogeneous and inhomogeneous broadenings, in order to focus on that part of the broadening which is time-dependent on the experimental time scale. In this case (setting $\sigma_H = \sigma_I = 0$), the hole width is given by

$$\sigma(\tau) = \Delta \left[ 1 - \frac{\Delta^2 M(\tau)}{\tau_p^{-2} + \Delta^2} \right]^{1/2}.$$  \hspace{1cm} (3.3)

If the solvent is slow compared to the experimental time scale, $M(\tau) = 1$ throughout the experiment, and we have $\sigma(\tau) = \tau_p^{-1}$, provided the pulse is spectrally narrow compared to $\Delta$. In this limit, the solvent broadening appears inhomogeneous. If, on the other hand, the solvent relaxes on a time scale fast compared to that of the experiment, we have $M(\tau) = 0$; hence, $\sigma(\tau) = \Delta$, and the solvent’s broadening is constant (homogeneous) throughout the hole-burning experiment.

For a clear picture of the solvent’s effects on the differential absorption spectrum, it is convenient to look first at the solvent mode alone. In Fig. 1, we have plotted (linear) absorption line shapes [given by Eq. (5.6a) of Ref. (4)] for the solvent mode for two different values of $\tau_c$. The temperature is taken to be 300 K, and $\Gamma = 3000$ cm$^{-1}$. The solid and dashed curves correspond to the $\tau_c = 200$ ps and $\tau_c = 100$ fs, respectively; $\Delta = 1300$ cm$^{-1}$ for both curves. Notice that the line shapes are essentially the same. As we increase $\tau_c$, the linear absorption line shape changes from an inhomogeneously broadened Gaussian to a homogeneously broadened Lorentzian.$^{21}$ This effect is most pronounced in the wings of the line shape; in Fig. 1, it is too small to be clearly visible.

Hole burning, however, is much more sensitive to the solvent time scale. Figure 2 gives the $\tau = 200$ fs hole burning line shapes for the solvent mode; the linear absorption signal is indicated by the outermost dashed line. The innermost dashed line in the figure is the pump pulse power spectrum. The solid lines, from the inside out, are the $\tau = 200$ fs differential absorption line shapes for $\tau_c = 100$ ps, 10 ps, 1 ps, and 100 fs; $\Delta = 1300$ cm$^{-1}$ for all curves. The line shapes have FWHMs of 260, 610, 1700, and 2950 cm$^{-1}$, respectively [as predicted by Eq. (3.3)]. The pump pulse envelope is given by Eq. (2.13), with $\tau_p = 62$ fs. In order to clearly show the linewidths, we have included only the ground-state propagation of the doorway state, and normalized all the curves to the same maximum height.

Because we are considering a delay of $\tau = 200$ fs, and because the doorway state is prepared over a finite time, we see that the linewidths in Fig. 2 vary, depending upon the solvent timescale. If $\tau_c$ is very large, then the solvent is slow, and the initial hole-burning linewidth is dictated by the pulse.
the pump–pulse duration, should we wish to probe the dynamics of the spectral diffusion.

Figure 3(a) gives the differential probe absorption for the solvent mode only as a function of delay time, using the parameters $\tau_e = 3.5$ ps, $\Gamma = 1200$ cm$^{-1}$, and $\tau_p = 62$ fs. The temperature is taken to be 300 K. We choose $\tau = 200$ fs to be our initial time for the following reason. Since we are neglecting those terms in the signal which are due to the coherent artifact, we effectively require that the doorway state is created before the arrival of the probe pulse. When the pulses are overlapping in time, this assumption would require an unphysical “chopping off” the pump pulse at the probe. Thus, the doorway–window picture only gives the full signal when the pulses do not overlap in time. In Fig. 3(a), we see that the hole profile broadens as a function of time, and begins to separate into ground-state and (Stokes-shifted) excited-state components.

The effects are more clear if we look at just the initial ($\tau = 200$ fs) and long-time ($\tau = 50$ ps) spectra for those same solvent parameters, shown in Fig. 3(b). The solid line in the figure gives the $\tau = 200$ fs line shape, which has a width of approximately 540 cm$^{-1}$ FWHM. The long-dashed line gives the long-time value of the spectrum, with the contributions from the ground- and excited-state propagated doorways plotted separately using the short-dashed lines. Each of these components has a linewidth of 1200 cm$^{-1}$, which is equal to that of the absorption spectrum.

Figure 4 gives the differential absorption spectrum for a faster solvent, $\tau_e = 700$ fs. All other parameters are the same spectral width. In the other extreme, for small values of $\tau_e$, the solvent equilibrates completely during the preparation of the doorway state and the first 200 fs of propagation; in this case, the pulse “burns” the whole absorption line, and the solvent mode can be thought of as purely homogeneous broadening. Thus, $\tau_e$ provides us with an upper bound for

![Figure 3](image-url)

**FIG. 3.** The pump–probe signal for the solvent mode, with $\tau_e = 3.5$ ps, $\Delta = 510$ cm$^{-1}$ ($\Gamma = 1200$ cm$^{-1}$), $\tau_p$ is 62 fs, and the pump pulse is tuned 600 cm$^{-1}$ to the blue of the 0–0 transition. (a) The time- and frequency-dependent differential absorption spectrum. (b) Solid line: the initial ($\tau = 200$ fs) line shape for the system of Fig. 3. Long-dashed line: the long-time ($\tau = 50$ ps) line shape; the ground- and excited-state contributions are shown separately, using the short-dashed lines.

![Figure 4](image-url)

**FIG. 4.** The differential absorption spectrum for a solvent mode with $\tau_e = 700$ fs. All other parameters are the same as in Fig. 3.
as in Fig. 3. We can see from the figure that the Stokes shift and the broadening occur on a time scale which is faster than that of Fig. 3(a).

Having demonstrated the effects of the solvent dynamics, we are now ready to add the solute mode to our calculations. Figure 5 gives the hole-burning spectrum for the two mode formula given in Eqs. (2.3)–(2.10). The solute mode is taken to have fundamental vibrational frequency 600 cm\(^{-1}\) in both the ground and excited states. The solute mode has the same parameters as in Fig. 3. The pump pulse is tuned to the |g,\(v = 0\rangle \rightarrow |e,\(v = 1\rangle\) vibronic transition. The ground and excited states of the solute mode are taken to have a relative displacement \(d = 1.2\) [cf. Eq. (4.3) of Ref. 4]; this relatively high value leads to the Franck-Condor progressions on either side of the 0–1 vibronic transition. We see that during the time scale of the figure, the vibronic peaks are washed out due to solvent relaxation processes. At long times, the spectrum will undergo the same broadening and Stokes shift phenomena seen in the solvent-only spectrum; however, the final linewidths will be much broader, due to the underlying vibronic structure.

Whether or not we can resolve individual eigenstates in a hole-burning experiment depends upon the relative time scales of the pulse, the solvent, and the vibrational period of the solute mode. This point is illustrated in Fig. 6, where we display the differential absorption spectrum for the same parameters as in Fig. 5, except that we now take the excited-state vibrational frequency to be 300 cm\(^{-1}\) and \(d = 0.85\). This value is smaller than the initial linewidth due to solvent broadening; hence, we see vibronic structure corresponding to the ground state and not the excited state. Based on Fig. 2, we can say that the effect would be the same were we to increase the pump spectral width to greater than 300 cm\(^{-1}\).

IV. THE IMPULSIVE LIMIT

We shall now consider the time dependent differential absorption spectrum for the case in which the pump pulse is short compared to the solute inverse vibrational energy spacings. In this limit, we no longer obtain frequency-resolved vibronic absorption lines in our spectrum; instead, the vibrational information obtained from the experiment manifests itself in the time domain, in the form of quantum beats.

Figure 7 represents the same solute-solvent system as Fig. 5. The only difference is that \(\tau_p\) is now 4.5 fs, and the pump pulse is centered at 900 cm\(^{-1}\) to the blue of the 0–0 transition. The solute contribution to the doorway state is now given by vibrational coherences in the ground and excited electronic manifolds. In Fig. 7(a), we see that the differential absorption maximum oscillates in frequency as a function of time. In contrast to the hole-burning spectra discussed in Sec. III, the time-dependence of the differential
absorption signal is now dominated by the effects of the solute, rather than the solvent. The solvent’s contribution to the signal is still visible in that the absorption maximum changes amplitude as a function of frequency; the signal peak is at its maximum when it coincides with the peak of the absorption line.

The time dependence of the solvent mode is still present in Fig. 7(a); however, for the parameters chosen, any broadening is effectively masked by the quantum beats, and the Stokes shift happens on a slower time scale than the one chosen for the figure. In Fig. 7(b), we extend the calculation to 5 ps. We can now see the Stokes shift occur, as in the calculations of the previous section.

In Fig. 7(c), we show three time-dependent “slices” of the differential absorption signal, at detection frequencies $\omega_2 - \omega_{eg} = 0 \text{ cm}^{-1}$, $600 \text{ cm}^{-1}$, and $-600 \text{ cm}^{-1}$. The oscillations in the figure have a period of 56 fs, which corresponds to our solute mode frequency of 600 cm$^{-1}$. The doorway state, in addition to the fundamental frequency, can have contributions from overtone beating; that is, oscillations due to vibrational coherences between vibronic states which are not adjacent to one another. This is the case in the 0 cm$^{-1}$ slice. For the parameters chosen here, however, the contributions from coherences between adjacent vibronic states dominate the signal.

Figure 8 demonstrates the effect of having different vi-
brational frequencies in the ground and excited electronic states. The parameters chosen are the same as in Fig. 7, except that the excited state has a vibrational frequency of 250 cm$^{-1}$ and $d = 0.77$. Low frequencies in the excited state are typical in systems undergoing photoisomerization, such as polyenes. Both the 250 cm$^{-1}$ excited-state and the 600 cm$^{-1}$ ground-state vibrations are clearly visible in Fig. 8(a).

Figure 8(b) gives the three frequency components of the signal corresponding to the 0-0 transition frequency and 250 cm$^{-1}$ to the blue and to the red of the 0-0 transition frequency. The $-250$ cm$^{-1}$ slice appears significantly distorted, due to significant contribution from overtones of both the 250 and 600 cm$^{-1}$ vibrations. Figure 8(c) gives power spectra corresponding to the $-250$ cm$^{-1}$ component, calculated for delay times up to 800 fs (top frame) and 1600 fs (bottom frame). Clearly present are peaks due to overtones of both the 250 and 600 cm$^{-1}$ vibrations, as well as some combination bands. The ground and excited state frequencies in the solute mode are so drastically different that the Franck-Condon factors for the transition are all quite similar. Furthermore, the pulse is spectrally very broad compared to the excited state vibrational spacing. Hence, many vibrational levels contribute to the excited doorway state; furthermore, the similarity of the Franck-Condon factors facilitates the creation of ground-state vibrational coherences between nonadjacent levels. By comparing the two frames of Fig. 8(c), we can see that contributions from overtnote beating become less important at longer times; this point was made earlier.$^4$

In Sec. III, we discussed hole-burning, in which the solvent relaxation processes dictate the time-dependence of the probe differential absorption spectrum. We have considered here the impulse limited, in which the time-dependence of
the signal is dominated by quantum beats, due to the evolution of solute vibrational coherences. We do not wish to imply, by treating the two cases separately, that they are mutually exclusive. In Fig. 9, we demonstrate “impulsive hole-burning,” in which the pump pulse is long compared to the solvent time scale but short enough to create a solute vibrational coherence in the doorway state. The solvent parameters in the figure are the same as in Fig. 5 \( (\tau_c = 3.5 \text{ ps}, \Gamma = 1200 \text{ cm}^{-1}) \), \( \tau_p = 27 \text{ fs} \), and the solute mode has ground and excited state vibrational frequencies of 300 cm\(^{-1}\) (corresponding to a period of 112 fs). Quantum beats due to the vibrations of the solute mode are clearly present; in addition, the line is also visibly broadened due to the solvent. The inset shows the initial \( (\tau = 100 \text{ fs}) \) and final \( (\tau = 1 \text{ ps}) \) spectra in the figure, revealing that the differential absorption line shape has broadened considerably on the time scale of the figure. It is thus entirely conceivable that the solvent relaxation processes are important on the time scale of an experiment which displays quantum beats.

V. CONCLUSIONS

We have presented a multimode theory for calculation of a pump–probe experiment on a solvated polyatomic molecule. No limitations have been placed on the relative time scales of the solute, the solvent, and the pump pulse envelope. When the pump pulse is short compared to the vibrational frequency of the solute, solute information occurs in the time domain, in the form of quantum beats. For a pump pulse long compared to the solute vibrational frequency, the solute information occurs in the frequency domain, as resolved eigenstates.

Most density-matrix treatments of pump–probe spectroscopy add some sort of phenomenological dephasing term to the equation of motion of the density matrix. Thus, the solvent is treated as an effect on the system of experimental interest. By including a separate solvent mode in our calculations, we are treating the solvent explicitly as a part of the material system. This treatment allows us to focus directly on the solvent contributions to the spectrum, by considering the solvent mode only. It is the solute, and not the solvent, which determines whether or not we see the hole-burning effect. Thus, an “impulsive hole-burning” experiment, such as the one modeled in Fig. 9, should be possible for a suitable combination of solvent, solute, and pump pulse.

Condensed-phase systems are complicated, and may, in general, be characterized by a large number of solute and solvent modes, covering a broad range of time scales. A good experiment provides information about only a few of these modes; otherwise, the data become too complicated to interpret. The calculations presented here have only taken into account two modes, one for the solute and one for the solvent. The treatment of the solvent as a single overdamped mode is clearly an oversimplification but is sufficient for illustrating the interplay between the solvent time scale and the pulse duration, which is the main goal of the present study. A realistic solvent is usually characterized by many modes (both overdamped and underdamped). These modes reflect local solvation structure and dynamics and span a broad range of time scales. On the femtosecond time scale we expect some of these modes to show inertial effects. The general phase space expressions given in Ref. 4 allow the incorporation of additional solvent modes as well as inertial effects.

ACKNOWLEDGMENTS

We wish to thank Dr. Laurence Fried for many useful discussions, as well as for reading an earlier version of this manuscript. The support of the National Science Foundation, the Air Force Office of Scientific Research, and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Bosma, Yan, and Mukamel: Intramolecular and solvent dynamics

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