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Non-Markovian correlation effects in time-delayed femtosecond absorption spectroscopy

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The dependence of the electronic absorption spectrum of a dye molecule on the time of delay between the excitation of the molecule by a pump-laser pulse and the probing of the absorption by a test-laser pulse is studied. The effect of dephasing of the molecular transition arising from the interaction with dissipative systems is described by a stochastic modulation of the electronic transition frequency. It is shown that in the case when the two laser pulses are short compared with the correlation time of the frequency modulation and when the spectral linewidth of the pump-laser light is smaller than the bandwidth of the equilibrium absorption spectrum, hole burning appears although the molecules have equal mean transition frequencies. This effect arises from non-Markovian correlations between the dephasings of the molecule during the actions of the pump- and the test-laser pulse. With increasing delay time the holes are smoothed out and disappear when the delay time exceeds the correlation time. Such effects were found in recent femtosecond absorption experiments by Shank *et al.* [in *Ultrafast Phenomena V,* edited by G. R. Fleming and A. E. Siegman (Springer, Berlin, 1986), p. 179].

I. INTRODUCTION

Femtosecond spectroscopy is a helpful tool for studying ultrafast phenomena in complex atomic systems, such as solids or large dye molecules. In particular, femtosecond laser pulses are nearly ideal light sources for measuring time-resolved absorption spectra in order to study the behavior of excited atomic systems. Recently, the following pump-probe-type measurement was performed.[1] An amplified 60-fs optical pulse was split into two parts. One part was used to optically excite a sample of dye molecules, while the other part was compressed to 10 fs. The shorter pulse was then used to probe the absorption spectrum by passing through the excited sample into a spectrometer and a photodetector.

It was found that the absorption profile sensitively depends on the time of delay between pump- and test-laser pulse. In the case when the pump and the probe are coincident in time, hole burning is observed. With increasing delay time, the holes are washed out and the line profile of the observed (nonequilibrium) absorption spectrum approaches the profile of the equilibrium absorption spectrum, with the nonequilibrium spectrum, of course, being uniformly reduced below the equilibrium level, as long as the delay time remains smaller than the longitudinal relaxation time. Equivalently, for short delay times, the differential absorption line (equilibrium absorption spectrum minus nonequilibrium absorption spectrum) is narrower than the equilibrium absorption line. With increasing delay time, the differential absorption spectrum becomes more and more flat and, for sufficiently long delay times, its linewidth approaches the linewidth of the equilibrium absorption spectrum.

To understand this dependence of the absorption line shape on the time of delay between pump and probe, we note that the molecular levels are strongly coupled to dissipative systems. This coupling gives rise to a dephasing of the molecular transitions and leads to a corresponding level broadening. In many cases, it is sufficient to treat the dephasing within a Markovian relaxation theory by introducing dephasing rates into the molecular density-matrix equations of motion, which, in these cases, takes the familiar form of (multilevel) Bloch equations. In such an approach to the problem of dephasing, the main assumption is, that the correlation time of the interaction between the molecular quantum states and the levels of the dissipative system is short compared with all other characteristic times, so that memory effects can be disregarded. With respect to the pump-probe experiment described above, the consequence would be that the dephasing during the excitation of the molecule by the pump-laser pulse is decorrelated from the dephasing during the probing of the absorption spectrum and, therefore, the profile of the absorption spectrum should be independent of the delay time. The observed dependence of the absorption line shape on the delay time is obviously a (non-Markovian) effect of finite correlation time, since, on the (femtosecond) time scale of the pulse lengths and the delay time, the correlation time cannot be regarded as a short time.

In the present paper we develop a theory for calculating the absorption spectrum as a function of the time of delay between the generation of the nonequilibrium level populations of the molecule by the pump-laser pulse and the probing of the absorption spectrum by the test-laser pulse. For simplicity, we restrict ourselves to an electronic two-level transition and treat its dephasing by using the model of stochastic modulation of the transition frequency.[2,3] The basic equations for calculating the absorption spectrum and the molecular density-matrix elements needed are briefly derived in Sec. II. In Sec. III a detailed analysis of the non-Markovian limiting case is given. It is shown that the dependence of the line shape of the absorption spectrum on the delay time is indeed an effect of finite correlation time. In particular, for the case when the spectrum of the pump-laser light may be approximated by a Gaussian, the explicit dependence of the linewidth of the differential absorption spectrum on the delay time is given. Finally, in Sec. IV, the main results are briefly summarized and some concluding remarks are given.

II. BASIC EQUATIONS

Let us consider a localized two-level system, which is irradiated by two ultrashort laser pulses delayed to one another. The first pulse (pump pulse) is used to resonantly excite the two-level system, while the second pulse (test pulse), which is also assumed to be in resonance with the two-level transition, is used to probe the absorption spectrum. That is, after having passed the two-level system, the test pulse is transmitted through a spectrometer and passed into a photodetector. The directions of propagation of the two pulses are assumed to be separated by the angle θ, the direction of propagation of the test pulse being the x axis. We therefore may assume that the range of observation is outside the pump pulse.

From Glauber's theory of photodetection, the number of photoelectron counts n is given as follows:[4,5]

$$n=\alpha\int dt\langle\hat{E}^{(-)}(x,t)\hat{E}^{(+)}(x,t)\rangle\ , \tag{2.1}$$

where $\hat{E}^{(+)}$ and $\hat{E}^{(-)}$, respectively, are the positive- and negative-frequency parts of the operator of the electric field strength

$$\hat{E}(x,t)=\hat{E}^{(+)}(x,t)+\hat{E}^{(-)}(x,t)\ , \tag{2.2}$$

$$\hat{E}^{(-)}(x,t)=(\hat{E}^{(+)}(x,t))^{\dagger}\ , \tag{2.3}$$

and α is the photoefficiency of the photodetector. The operator of the electric field strength, which obeys the Maxwell equations, may be decomposed into two parts, viz.,

$$\hat{E}^{(+)}(x,t)=\hat{E}_s^{(+)}(x,t)+\hat{E}_{\text{free}}^{(+)}(x,t)\ . \tag{2.4}$$

Here, the first term represents the source field attributed to the two-level system. The second term is the free field observed in the case when the two-level system is absent. It simply describes the unperturbed laser fields. Inserting Eq. (2.4) together with Eq. (2.3) into Eq. (2.1) yields

$$\begin{aligned} n=n_{\text{free}}&+\alpha\left[\int dt\langle\hat{E}_s^{(-)}(x,t)\hat{E}_{\text{free}}^{(+)}(x,t)\rangle+\text{c.c.}\right]\\ &+\alpha\int dt\langle\hat{E}_s^{(-)}(x,t)\hat{E}_s^{(+)}(x,t)\rangle\ , \end{aligned} \tag{2.5}$$

where

$$n_{\text{free}}=\alpha\int dt\langle\hat{E}_{\text{free}}^{(-)}(x,t)\hat{E}_{\text{free}}^{(+)}(x,t)\rangle\ . \tag{2.6}$$

We now assume that the source field is weak compared with the free field, so that the third term on the right-hand side of Eq. (2.5) becomes small in comparison with the second one and therefore may be neglected. From Eq. (2.5), we thus obtain

$$\Delta n=n_{\text{free}}-n=-\alpha\left[\int dt\langle\hat{E}_s^{(-)}(x,t)\hat{E}_{\text{free}}^{(+)}(x,t)\rangle+\text{c.c.}\right]\ , \tag{2.7}$$

which may be regarded as the relevant quantity for studying absorption.

In order to describe the effect of the spectrometer, which is in front of the photodetector, we follow the theory given in Refs. 6–8. In dipole and rotating wave approximation, the source field at the point x (behind the spectrometer) $\hat{E}_s^{(-)}(x,t)$ can be related to quantities of the spectrometer and the two-level systems situated, with respect to the x axis, at x_0 (in front of the spectrometer) as follows:[6-8]

$$\begin{aligned} \hat{E}_s^{(-)}(x,t)=-\frac{i}{\hbar}\beta d_{21}\int dt'T^*(t-t'-\Delta t)&\\ \times\hat{A}_{21}\left[t'-\frac{x-x_0}{c}\right]&\ , \end{aligned} \tag{2.8}$$

where $T(t)$ is the transmission response function of the spectrometer and $\hat{A}_{21}(t)$ is the atomic flip operator defined by $\hat{A}_{21}=|2\rangle\langle 1|$, $|1\rangle$ and $|2\rangle$ being the ground and the excited quantum state of the two-level system, respectively. Furthermore, d_{21} is the transition dipole moment and β is a geometry factor. The time correction $\Delta t=(d_{\text{opt}}-d)/c$ reflects the fact that the geometrical path d through the spectrometer is different from the optical one d_{opt}.

The free field $\hat{E}_{\text{free}}^{(+)}(x,t)$ can be related to quantities of the spectrometer and the free field $\hat{\mathcal{E}}_{\text{free}}^{(+)}(x,t)$ in the case without spectral filtering. The only part of $\hat{\mathcal{E}}_{\text{free}}^{+}(x,t)$ that can contribute to the expectation value in Eq. (2.7) obviously comes from the field $\hat{\mathcal{E}}_{\text{free}}^{(+)}(t-x/c)$ propagating in the x direction. The spectrally filtered version of it is just the relevant part of $\hat{E}_{\text{free}}^{(+)}(x,t)$ in Eq. (2.7),[8]

$$\hat{E}_{\text{free}}^{(+)}(x,t)\,\hat{=}\int dt'T(t-t'-\Delta t)\hat{\mathcal{E}}_{\text{free}}^{(+)}\left[t'-\frac{x}{c}\right]\ . \tag{2.9}$$

Inserting Eqs. (2.8) and (2.9) into Eq. (2.7), we arrive at

$$\Delta n=\frac{i}{\hbar}\alpha\beta d_{21}\int dt\int dt_1\int dt_2T^*(t-t_1-\Delta t)T(t-t_2-\Delta t)\left\langle\hat{A}_{21}\left[t_1-\frac{x-x_0}{c}\right]\hat{\mathcal{E}}_{\text{free}}^{(+)}\left[t_2-\frac{x}{c}\right]\right\rangle+\text{c.c.} \tag{2.10}$$

Introducing the Fourier decompositions

$$T(t)=\frac{1}{2\pi}\int d\omega\, e^{-i\omega t}\underline{T}(\omega)\ , \tag{2.11}$$

$$\hat{\mathcal{E}}^{(+)}_{\text{free}}\left(t-\frac{x}{c}\right)=\frac{1}{2\pi}\int d\omega \exp\left[-i\omega\left(t-\frac{x}{c}\right)\right]\underline{\hat{\mathcal{E}}}^{(+)}_{\text{free}}(\omega)\ , \tag{2.12}$$

$$\hat{A}_{21}(t)=\frac{1}{2\pi}\int d\omega\, e^{i\omega t}\underline{\hat{A}}_{21}(\omega)\ , \tag{2.13}$$

we may rewrite Eq. (2.10) as

$$\Delta n=\alpha\int d\omega\,|\,\underline{T}(\omega)\,|^2 S(\omega)\ , \tag{2.14}$$

where

$$S(\omega)=\frac{i}{2\pi\hbar}\beta d_{21}\exp\left(i\omega\frac{x_0}{c}\right)\langle\,\underline{\hat{A}}_{21}(\omega)\underline{\hat{\mathcal{E}}}^{(+)}_{\text{free}}(\omega)\rangle+\text{c.c.} \tag{2.15}$$

Note that $S(\omega)$ may be regarded as the intrinsic absorption spectrum. In particular, if the passbandwidth of the spectrometer $\Delta\Omega$ is sufficiently small, so that $S(\omega)$ becomes slowly varying within the interval $\Omega-\Delta\Omega/2\ldots\Omega+\Delta\Omega/2$, Ω, being the setting frequency of the spectrometer, the reduction of the number of photoelectron counts Δn is proportional to $S(\Omega)$,

$$\Delta n\sim\Delta\Omega S(\Omega)\ . \tag{2.16}$$

Now let us study $S(\omega)$ in more detail. For simplicity, we assume that both the pump-laser pulse and the test-laser pulse may be approximated by coherent states. Remembering that, because of the scheme of observation studied, the light detected arises from the test-laser pulse, we may simplify Eq. (2.15) as follows:

$$S(\omega)=\frac{i}{2\pi\hbar}\beta d_{T21}\exp\left(i\omega\frac{x_0}{c}\right)\underline{\sigma}_{12}(\omega)\underline{\mathcal{E}}^{(+)}_{T}(\omega)+\text{c.c.} \tag{2.17}$$

Here and in the following, the symbols T and P indicate that the corresponding quantities are related to the test-laser pulse and the pump-laser pulse, respectively. In particular, the c numbers $\mathcal{E}^{(+)}_{T(P)}$ and $\mathcal{E}^{(-)}_{T(P)}$, respectively, are the positive- and negative-frequency parts of the (coherent) electric field strength of the (unperturbed) test (pump) laser pulse and, according to Eq. (2.12), we have

$$\mathcal{E}^{(\pm)}_{T(P)}\left(t-\frac{\mathbf{e}_{T(P)}\cdot\mathbf{r}}{c}\right)=\frac{1}{2\pi}\int d\omega\exp\left[\mp i\omega\left(t-\frac{\mathbf{e}_{T(P)}\cdot\mathbf{r}}{c}\right)\right]\underline{\mathcal{E}}^{(\pm)}_{T(P)}(\omega)\ , \tag{2.18}$$

where $\mathbf{e}_{T(P)}$ is the direction of propagation of the test- (pump-) laser pulse (note that $\mathbf{e}_T\cdot\mathbf{r}=\mathbf{e}_x\cdot\mathbf{r}=x$). Furthermore, $\underline{\sigma}_{12}(\omega)$ is the Fourier transform of the density-matrix element $\sigma_{12}(t)$ of the two-level system. Note that in Eq. (2.17), the relation $\langle\,\hat{A}_{21}(t)\rangle=\sigma_{12}(t)$ is used.

To calculate $S(\omega)$, the density-matrix equations for the two-level system are needed. As mentioned in Sec. I, the two-level system is a model for an electronic transition in a large dye molecule in solution at room temperature. The transition frequency may therefore be supposed to be strongly modulated by the thermal motion of the surrounding solvent molecules and internal degrees of freedom of the dye molecule. Assuming that the overall number of degrees of freedom participating in the frequency modulation is sufficiently large and the resulting effect strong, we approximately treat the frequency modulation by introducing a classical stochastic transition frequency $\omega_{21}(t)$ (Refs. 2 and 3). In dipole approximation and rotating-wave approximation, the density-matrix equations of motion are then derived to be

$$\dot{\sigma}_{12}=[i\omega_{21}(t)-\gamma]\sigma_{12}-\frac{i}{\hbar}\left[d_{P12}\mathcal{E}^{(-)}_{P}\left(t-\frac{\mathbf{e}_p\cdot\mathbf{r}_0}{c}\right)+d_{T12}\mathcal{E}^{(-)}_{T}\left(t-\frac{\mathbf{e}_T\cdot\mathbf{r}_0}{c}\right)\right](\sigma_{11}-\sigma_{22})\ , \tag{2.19}$$

$$\dot{\sigma}_{21}=\dot{\sigma}^{*}_{12}\ , \tag{2.20}$$

$$\frac{d}{dt}(\sigma_{11}-\sigma_{22})=-2\gamma(\sigma_{11}-\sigma_{22})+2\gamma+\left\{-\frac{2i}{\hbar}\left[d_{P21}\mathcal{E}^{(+)}_{P}\left(t-\frac{\mathbf{e}_P\cdot\mathbf{r}_0}{c}\right)+d_{T21}\mathcal{E}^{(+)}_{T}\left(t-\frac{\mathbf{e}_T\cdot\mathbf{r}_0}{c}\right)\right]\sigma_{12}+\text{c.c.}\right\}\ . \tag{2.21}$$

By using the arguments given in the derivation of Eq. (2.17), the source-field contributions are omitted in Eqs. (2.19)–(2.21). Note that $\mathbf{e}_P\cdot\mathbf{r}_0$ is different from $\mathbf{e}_T\cdot\mathbf{r}_0=x_0$, $\mathbf{r}_0$ being the position vector of the two-level system. Furthermore, the relaxational transition from the upper quantum state into the lower one is taken into account by the rate of depopulation 2γ.

Equations (2.17) and (2.19)–(2.21) may be regarded as basic equations for determining the absorption spectrum sought. Practically, the calculation consists of three stages. At the first stage, the density-matrix equations of motion as given in Eqs. (2.19)–(2.21) are solved. At the second stage, the resulting solution for $\sigma_{12}(t)$ is averaged with respect to the transition frequency $\omega_{21}(t)$. In particular, in the case of finite correlation time of the frequency modulation, this averaging is expected to lead to an effect of correlation between the level populations at the time of excitation by the pump-laser pulse and the off-diagonal density-matrix elements at the time of probing these nonequilibrium level populations by the test-laser pulse. At the third stage, the Fourier transform of the (averaged) off-diagonal density-matrix element $\bar{\sigma}_{12}(t)$ is calculated and the result is inserted into Eq. (2.17).

III. EFFECT OF FINITE CORRELATION TIME OF FREQUENCY MODULATION

Because of their stochastic character, the density-matrix equations of motion as given in Eqs. (2.19)–(2.21) are, in general, hard to solve. However, to understand the effect of finite correlation time of frequency modulation on the nonequilibrium absorption spectrum, it is sufficient to treat the problem within the framework of perturbation theory.

From Eq. (2.19), together with the initial condition $\sigma_{12}(-\infty)=0$, we derive

$$\sigma_{12}(t)=-\frac{i}{\hbar}\int_{-\infty}^{t}dt_1\left[d_{T12}\mathcal{E}_T^{(-)}\left(t_1-\frac{\mathbf{e}_T\cdot\mathbf{r}_0}{c}\right)+d_{P12}\mathcal{E}_P^{(-)}\left(t_1-\frac{\mathbf{e}_P\cdot\mathbf{r}_0}{c}\right)\right]\times\exp\left[-\gamma(t-t_1)+i\int_{t_1}^{t}d\tau\,\omega_{21}(\tau)\right][\sigma_{11}(t_1)-\sigma_{22}(t_1)]\,. \tag{3.1}$$

Analogously, from Eq. (2.21), together with the initial conditions $\sigma_{11}(-\infty)=1$ and $\sigma_{22}(-\infty)=0$, we derive

$$\sigma_{11}(t)-\sigma_{22}(t)=1-\left\{\frac{2i}{\hbar}\int_{-\infty}^{t}dt_1\left[d_{T21}\mathcal{E}_T^{(+)}\left(t_1-\frac{\mathbf{e}_T\cdot\mathbf{r}_0}{c}\right)+d_{P21}\mathcal{E}_P^{(+)}\left(t_1-\frac{\mathbf{e}_P\cdot\mathbf{r}_0}{c}\right)\right]\times\exp[-2\gamma(t-t_1)]\sigma_{12}(t_1)+\text{c.c.}\right\}. \tag{3.2}$$

Inserting Eq. (3.1) into Eq. (3.2), solving the resulting integral equation by successive approximation, and retaining only terms up to the second order in the laser field strengths, we arrive at

$$\sigma_{11}(t)-\sigma_{22}(t)=1-D_{PP}(t)-D_{TT}(t)-D_{TP}(t)-D_{PT}(t)\,, \tag{3.3}$$

where

$$D_{NM}(t)=\frac{2}{\hbar^2}d_{N21}d_{M12}\int_{-\infty}^{t}dt_1\int_{-\infty}^{t_1}dt_2\,\mathcal{E}_N^{(+)}\left(t_1-\frac{\mathbf{e}_N\cdot\mathbf{r}_0}{c}\right)\mathcal{E}_M^{(-)}\left(t_2-\frac{\mathbf{e}_M\cdot\mathbf{r}_0}{c}\right)\times\exp[-2\gamma(t-t_1)]\exp\left[-\gamma(t_1-t_2)+i\int_{t_2}^{t_1}d\tau\,\omega_{21}(\tau)\right]+\text{c.c.}\,, \tag{3.4}$$

N (and M) being T or P. Combining Eqs. (3.1), (3.3), and (3.4) yields the result of perturbation theory for $\sigma_{12}(t)$, which is valid up to the third order in the laser field strengths, so that the absorption spectrum, according to Eq. (2.17), becomes valid up to the fourth order in the laser field strengths.

In order to pick out the relevant terms in the resulting expression for $\sigma_{12}(t)$, we note that each field strength

$$\mathcal{E}_{T(P)}^{(\pm)}(t-\mathbf{e}_{T(P)}\cdot\mathbf{r}_0/c)$$

gives rise to a phase factor

$$\exp[\pm i\omega_L\mathbf{e}_{T(P)}\cdot\mathbf{r}_0/c]\,,$$

ω_L being the laser frequency. Supposing that many molecules situated at different positions are involved in the absorption observed, we may assume that only those terms of $\sigma_{12}(t)$ substantially contribute to the absorption spectrum $S(\omega)$ [Eq. (2.17)], the phase factors of which together with the phase factor

$$\exp(i\omega_L\mathbf{e}_T\cdot\mathbf{r}_0/c)$$

in Eq. (2.17) compensate each other, whereas the contribution of the rest is negligibly small. In this sense, we therefore may write

$$\sigma_{12}(t)=-\frac{i}{\hbar}\int_{-\infty}^{t}dt_1\exp\left[-\gamma(t-t_1)+i\int_{t_1}^{t}d\tau\,\omega_{21}(\tau)\right]$$
$$\times\left[d_{T12}\mathcal{E}_T^{(-)}\left[t_1-\frac{\mathbf{e}_T\cdot\mathbf{r}_0}{c}\right][1-D_{PP}(t_1)-D_{TT}(t_1)]-d_{P12}\mathcal{E}_P^{(-)}\left[t_1-\frac{\mathbf{e}_P\cdot\mathbf{r}_0}{c}\right]D_{PT}(t_1)\right]\ . \tag{3.5}$$

From an inspection of Eq. (3.5) together with Eqs. (3.3) and (3.4), we see that the integral with $D_{PP}(t_1)$ $[D_{TT}(t_1)]$ simply describes the effect of the change of the level populations caused by the action of a single pump (test) laser pulse on the off-diagonal density-matrix element $\sigma_{12}(t)$. At this point, we note the test laser pulse may be assumed to be weak compared with the pump-laser pulse so that the term with D_{TT} can be omitted. The integral with $D_{PT}(t_1)$ describes the effect of superposition of pump- and test-laser pulse. It can be readily seen that, because of the time hierarchy, this term can become relevant only in cases when the two pulses overlap. In the following, we ignore such overlap effects and assume that the two pulses are effectively separated from each other. From these arguments, we may simplify Eq. (3.5) as follows:

$$\sigma_{12}(t)=-\frac{i}{\hbar}d_{T12}\int_{-\infty}^{t}dt_1\exp\left[-\gamma(t-t_1)+i\int_{t_1}^{t}d\tau\,\omega_{21}(\tau)\right]\mathcal{E}_T^{(-)}\left[t_1-\frac{\mathbf{e}_T\cdot\mathbf{r}_0}{c}\right][1-D_{PP}(t_1)]\ . \tag{3.6}$$

We now turn to the problem of averaging Eq. (3.6). For this purpose, we make the ansatz

$$\omega_{21}(t)=\omega_0+\delta(t)\ , \tag{3.7}$$

where ω_0 is the mean value of the transition frequency and $\delta(t)$ (with mean value of zero) is the modulating part underlying an Ornstein-Uhlenbeck process:[9]

$$\overline{\delta(t)\delta(t')}=s^2\exp(-\gamma_c\,|\,t-t'\,|\,)\ . \tag{3.8}$$

In this equation, $s=(\overline{\delta^2})^{1/2}$ is the amplitude of the frequency modulation and $\gamma_c^{-1}=\tau_c$ is its correlation time. The averaging of Eq. (3.6) may now be performed by using standard methods. After some lengthy calculations, we arrive at the following result:

$$\bar{\sigma}_{12}(t)=-\frac{i}{\hbar}d_{T12}\int_{-\infty}^{t}dt_1\mathcal{E}_T^{(-)}\left[t_1-\frac{\mathbf{e}_T\cdot\mathbf{r}_0}{c}\right]\exp[i\omega_0(t-t_1)]\{F^{(0)}(t-t_1)-[F_-^{(1)}(t-t_1;t_1)+F_+^{(1)}(t-t_1;t_1)]\}\ , \tag{3.9}$$

where

$$F^{(0)}(t)=\exp\left[-\gamma t-\Gamma t+\frac{\Gamma}{\gamma_c}(1-e^{-\gamma_c t})\right]\ , \tag{3.10}$$

$$F_\pm^{(1)}(t;t')=\frac{2}{\hbar^2}\,|\,d_{P12}\,|^2\int_{-\infty}^{t'}dt_1\int_{-\infty}^{t_1}dt_2\exp[-2\gamma(t'-t_1)]\mathcal{E}_P^{(\pm)}\left[t_2-\frac{\mathbf{e}_P\cdot\mathbf{r}_0}{c}\right]$$
$$\times\mathcal{E}_P^{(\mp)}\left[t_1-\frac{\mathbf{e}_P\cdot\mathbf{r}_0}{c}\right]\exp[\mp i\omega_0(t_1-t_2)]F^{(0)}(t_1-t_2)$$
$$\times K_\pm(t,t_1-t_2,t'-t_1)F^{(0)}(t)\ , \tag{3.11}$$

and

$$K_\pm(t,t',t'')=\exp\left[\pm\frac{\Gamma}{\gamma_c}e^{-\gamma_c t''}(1-e^{-\gamma_c t'})(1-e^{-\gamma_c t})\right]\ . \tag{3.12}$$

In Eqs. (3.10)–(3.12), Γ is a measure for the strength of the frequency modulation

$$\Gamma=\frac{s^2}{\gamma_c}\ . \tag{3.13}$$

Note that in the Markovian approximation the quantity $\Gamma+\gamma$ is equal to the dephasing rate of the electronic transition.

Now we remember that the test-laser pulse should be extremely short. In particular, we may assume that it is short compared with all other characteristic times. We therefore may replace $F_\pm^{(1)}(t-t_1;t_1)$ by $F_\pm^{(1)}(t-t_1;t_T)$ in the integral in Eq. (3.9), t_T being the time of probing the two-level system by the test laser pulse. In this approximation, the integral in Eq. (3.9) is a convolution integral, so that its Fourier transform is simply the product of the Fourier transforms of the corresponding functions in the time domain. Thus, combining Eqs. (3.9) and (2.17), the absorption spectrum $S(\omega)$ is easily derived to be

$$S(\omega)=S^{(0)}(\omega)-S^{(1)}(\omega)\ , \tag{3.14}$$

$$S^{(0)}(\omega)=\beta\,|\,d_{T12}\,|^2\frac{1}{2\pi\hbar^2}S_T(\omega-\omega_T)f^{(0)}(\omega-\omega_0)\ , \tag{3.15}$$

$$S^{(1)}(\omega)=\beta\,|\,d_{T12}\,|^2\frac{1}{2\pi\hbar^2}S_T(\omega-\omega_T)f^{(1)}(\omega-\omega_0)\ , \tag{3.16}$$

where

$$f^{(0)}(\omega)=\int_0^\infty dt\, e^{-i\omega t}F^{(0)}(t)+\text{c.c.}\ , \tag{3.17}$$

$$f^{(1)}(\omega)=\int_0^\infty dt\, e^{-i\omega t}[F_-^{(1)}(t;t_T)+F_+^{(1)}(t;t_T)]+\text{c.c.}\ , \tag{3.18}$$

$$S_T(\omega-\omega_T)=\,|\,\mathcal{E}_T^{(-)}(\omega)\,|^2\ , \tag{3.19}$$

$\omega_{T(P)}\approx\omega_L\approx\omega_0$ being the test- (pump-) laser frequency.

$S^{(0)}(\omega)$ obviously represents the equilibrium absorption spectrum. The effect of the nonequilibrium generated by the pump-laser pulse is included in $S^{(1)}(\omega)$. We note that $f^{(0)}(\omega-\omega_0)$ and $f^{(1)}(\omega-\omega_0)$ are the relevant spectral functions determining the absorption profile of the molecular transition under consideration. Because of the assumed shortness of the test-laser pulse, its spectrum $S_T(\omega-\omega_T)$ is sufficiently flat in the relevant range of frequency, in which $f^{(0)}(\omega-\omega_0)$ and $f^{(1)}(\omega-\omega_0)$ are sharply peaked.

From Eqs. (3.11) and (3.12), it is seen that the functions $K_\pm(t,t_1-t_2,t_T-t_1)$ (note that t' is fixed at t_T) may give rise to a correlation of the line shape of the nonequilibrium absorption spectrum probed by the test-laser pulse at time t_T to the generation of the nonequilibrium level populations by the pump-laser pulse at time t_P. In the rigorous Markovian case, when the decay of the correlation of the modulation of the electronic transition frequency of the molecule is sufficiently fast [γ_c/Γ, $\gamma_c\tau_P$, $\gamma_c\tau_T\gg 1$, $\tau_{T(P)}$ being the length of the test- (pump-) laser pulse], this effect, of course, vanishes ($K_\pm\approx 1$). In this approximation, the functions $F_\pm^{(1)}(t;t_T)$ are proportional to $F^{(0)}(t)$ and, according to Eqs. (3.17) and (3.18), the spectral function $f^{(1)}(\omega-\omega_0)$ is simply proportional to $f^{(0)}(\omega-\omega_0)$. That is, the absorption profile is given by the equilibrium line shape and the effect of the nonequilibrium level populations (population of the upper quantum state at the expense of the lower quantum state) is, as expected, a homogeneous reduction of the absorption below its equilibrium level.

Correlation effects of the type described above are therefore non-Markovian effects. The stronger the non-Markovian features become, the more pronounced the correlation effects are. To clarify them, we therefore confine ourselves to the case when the non-Markovian features are the dominant ones (γ_c/Γ, $\gamma_c\tau_P$, $\gamma_c\tau_T\ll 1$). For simplicity, let us assume that γ_c/Γ tends to zero, whereas $\gamma_c\Gamma$ remains finite. Expanding the upper exponentials in Eqs. (3.10) and (3.12) into power series and retaining only terms proportional to $\gamma_c\Gamma$, we may approximate $F^{(0)}(t)$ and $K_\pm(t,t',t'')$ as follows:

$$F^{(0)}(t)=\exp(-\gamma t-\tfrac{1}{2}\gamma_c\Gamma t^2)\ , \tag{3.20}$$

$$K_\pm(t,t',t'')=\exp(\pm\gamma_c\Gamma e^{-\gamma_c t''}t't)\ . \tag{3.21}$$

Inserting Eq. (3.20) into Eq. (3.17), combining Eqs. (3.11), (3.20), and (3.21), and inserting the resulting expression for $F_\pm^{(1)}(t;t_T)$ into Eq. (3.18), we may readily perform the time integrations in Eqs. (3.17) and (3.18). To simplify the calculations and to avoid rather lengthy formulas, we make the realistic assumption that the energy relaxation of our two-level system is slow compared with the phase relaxation [$\gamma\ll(\gamma_c\Gamma/2)^{1/2}$], so that the term γt in the exponential of $F^{(0)}(t)$ [Eq. (3.20)] may be suppressed. Furthermore, we assume that the pump-laser pulse is tuned to the transition frequency ω_0, viz.,

$$\mathcal{E}_P^{(\pm)}\left[t-\frac{\mathbf{e}_P\cdot\mathbf{r}_0}{c}\right]=\exp\left\{\mp i\left[\omega_0\left[t-\frac{\mathbf{e}_P\cdot\mathbf{r}_0}{c}\right]+\varphi_P\right]\right\}\times\tilde{\mathcal{E}}_P(t-t_P)\ , \tag{3.22}$$

where $\tilde{\mathcal{E}}_P(t-t_P)$ is the slowly varying (real) amplitude of the pump-laser pulse, the maximum being at $t=t_P$, and φ_P is an appropriately chosen phase. Performing the time integrations in Eqs.(3.17) and (3.18) yields

$$S^{(0)}(\omega)\propto f^{(0)}(\omega-\omega_0)=\left[\frac{2\pi}{\gamma_c\Gamma}\right]^{1/2}\exp\left[-\frac{(\omega-\omega_0)^2}{2\gamma_c\Gamma}\right]\ , \tag{3.23}$$

$$\begin{aligned}S^{(1)}(\omega)\propto f^{(1)}(\omega-\omega_0)=\frac{4}{\hbar^2}\,|\,d_{P12}\,|^2 f^{(0)}(\omega-\omega_0)\\ \times\int_{-\infty}^{t_T-t_P}dt_1\int_{-\infty}^{t_1}dt_2\tilde{\mathcal{E}}_P(t_1)\tilde{\mathcal{E}}_P(t_2)\exp[-2\gamma(t_T-t_P-t_1)]\\ \times\exp(-\tfrac{1}{2}\gamma_c\Gamma\{1-\exp[-2\gamma_c(t_T-t_P-t_1)]\}(t_1-t_2)^2)\\ \times\cos\{\exp[-\gamma_c(t_T-t_P-t_1)](\omega-\omega_0)(t_1-t_2)\}\ .\end{aligned} \tag{3.24}$$

As expected, in the non-Markovian limiting case the equilibrium absorption line shape given by $f^{(0)}(\omega-\omega_0)$ is a Gaussian [Eq. (3.23)]. From an inspection of Eq. (3.24), it is seen that in the case when the pump-laser pulse is long compared with the correlation time, the integral term in this equation becomes independent of the frequency $\omega-\omega_0$, and hence $f^{(1)}(\omega-\omega_0)$ becomes proportional to $f^{(0)}(\omega-\omega_0)$, so that the usual equilibrium absorption line shape is observed. Let us therefore study the more interesting case, when the pump-laser pulse is short compared with the correlation time: $\tau_P \ll \tau_c$. Clearly, the pump-laser pulse may also be assumed to be short compared with the time of energy relaxation: $2\gamma\tau_P \ll 1$. Since in Eq. (3.24) the t_1 integral effectively runs over the interval $-\tau_P/2 \lesssim t_1 \lesssim \tau_P/2$, we now may approximately write t_T-t_P instead of $t_T-t_P-t_1$ in the integrand in Eq. (3.24)

$$\begin{aligned}&\exp[-\gamma_c(t_T-t_P-t_1)]\approx\exp[-\gamma_c(t_T-t_P)] ,\\&\exp[-2\gamma(t_T-t_P-t_1)]\approx\exp[-2\gamma(t_T-t_P)] .\end{aligned} \tag{3.25}$$

Taking into account that in this approximation the integrand in Eq. (3.24) becomes a symmetric function of the arguments t_1 and t_2, we may rewrite this equation as follows:

$$\begin{aligned}S^{(1)}(\omega)\propto f^{(1)}(\omega-\omega_0)=&\frac{2}{\hbar^2}|d_{P12}|^2 f^{(0)}(\omega-\omega_0)\exp[-2\gamma(t_T-t_P)]\\&\times\int_{-\infty}^{+\infty}dt_1\int_{-\infty}^{+\infty}dt_2\tilde{\mathcal{E}}_P(t_1)\tilde{\mathcal{E}}(t_2)\\&\qquad\times\exp(-\tfrac{1}{2}\gamma_c\Gamma\{1-\exp[-2\gamma_c(t_T-t_P)]\}(t_1-t_2)^2)\\&\qquad\times\cos\{\exp[-\gamma_c(t_T-t_P)](\omega-\omega_0)(t_1-t_2)\} .\end{aligned} \tag{3.26}$$

In this equation, the integrals over t_1 and t_2 are extended to plus infinity (instead of t_T-t_P), since we are interested in the case when the two pulses do not overlap ($t_T-t_P \gtrsim \tau_P$).

The integrals in Eq. (3.26) may now be evaluated step by step by means of Fourier decompositions. After some mathematical manipulations, we arrive at the following result:

$$\begin{aligned}S^{(1)}(\omega)\propto f^{(1)}(\omega-\omega_0)=&\frac{2}{\hbar^2}|d_{P12}|^2\exp[-2\gamma(t_T-t_P)]f^{(0)}(\omega-\omega_0)\\&\times\left[\frac{\pi}{4}(\Delta\omega^{(0)})^2\{1-\exp[-2\gamma_c(t_T-t_P)]\}\right]^{-1/2}\\&\times\int d\omega' S_P(\omega')\exp\left[-\frac{4\{\exp[-\gamma_c(t_T-t_P)](\omega-\omega_0)-\omega'\}^2}{(\Delta\omega^{(0)})^2\{1-\exp[-2\gamma_c(t_T-t_P)]\}}\right] ,\end{aligned} \tag{3.27}$$

where

$$S_P(\omega-\omega_P)=|\mathcal{E}_P^{(-)}(\omega)|^2 \tag{3.28}$$

is the spectrum of the pump-laser light (note that $\omega_P=\omega_0$), and $\Delta\omega^{(0)}$ is the linewidth of the equilibrium absorption spectrum: $\Delta\omega^{(0)}=(8\gamma_c\Gamma)^{1/2}$.

The relevant term in Eq. (3.27) is the convolution of the spectrum of the pump-laser light with a Gaussian, both the line center

$$\exp[-\gamma_c(t_T-t_P)](\omega-\omega_0) ,$$

and the linewidth

$$\Delta\omega^{(0)}\{1-\exp[-2\gamma_c(t_T-t_P)]\}^{1/2} ,$$

of which sensitively depend on the time of delay $t_D=t_T-t_P$ between exciting the molecule and probing its absorption spectrum. To demonstrate this correlation effect, let us assume that $\gamma_c t_D$ is sufficiently small, so that the inequality

$$\left[\frac{\Delta\omega^{(0)}}{\Delta\omega_P}\right]^2(1-e^{-2\gamma_c t_D})\ll 1 \tag{3.29}$$

is valid, $\Delta\omega_P$ being the spectral linewidth of the pump-laser light. In this case, the Gaussian in the convolution integral in Eq. (3.27) is, in comparison with the spectrum of the pump-laser light, rapidly varying, and we may write

$$\begin{aligned}S^{(1)}(\omega)&\propto f^{(1)}(\omega-\omega_0)\\&=\frac{2}{\hbar^2}|d_{P12}|^2\exp(-2\gamma t_D)f^{(0)}(\omega-\omega_0)\\&\qquad\times S_P[e^{-\gamma_c t_D}(\omega-\omega_0)] .\end{aligned} \tag{3.30}$$

In particular, if the pump-laser pulse is immediately followed by the test-laser pulse ($t_D \gtrsim \tau_P$), we have

$$S^{(1)}(\omega)\propto f^{(1)}(\omega-\omega_0)$$

$$=\frac{2}{\hbar^2}\,|d_{P12}|^2 f^{(0)}(\omega-\omega_0)S_P(\omega-\omega_0)\ . \tag{3.31}$$

If the pump-laser light is spectrally narrower than the equilibrium absorption spectrum ($\Delta\omega_P \ll \Delta\omega^{(0)}$), the linewidth of $S^{(1)}(\omega)$ is mainly determined by the linewidth of the spectrum of the pump-laser light, so that, in agreement with experiment,[1] hole burning is found. Remembering Eqs. (3.14) and (3.23), we obtain the following result:

$$S(\omega)\propto f^{(0)}(\omega-\omega_0)\left[1-\frac{2}{\hbar^2}\,|d_{P12}|^2 S_P(\omega-\omega_0)\right]\ . \tag{3.32}$$

As experimentally observed, this effect vanishes when the delay time becomes sufficiently large ($\gamma_c t_D\to\infty$). In this limiting case, the Gaussian in the convolution integral in Eq. (3.27) becomes independent of $\omega-\omega_0$, and hence $f^{(1)}(\omega-\omega_0)$ becomes proportional to $f^{(0)}(\omega-\omega_0)$. The line shape of the absorption spectrum is then given by the line shape of the equilibrium absorption spectrum. The only effect of the nonequilibrium level populations is that the overall absorption spectrum is homogeneously and uniformly reduced below the equilibrium level,

$$S(\omega)\propto f^{(0)}(\omega-\omega_0)\left[1-\frac{2}{\hbar^2}\,|d_{P12}|^2\rho\exp(-2\gamma t_D)\right]\ , \tag{3.33}$$

$$\rho=\frac{2}{\sqrt{\pi}\,\Delta\omega^{(0)}}\int d\omega' S_P(\omega')\exp\left[-\left[\frac{2\omega'}{\Delta\omega^{(0)}}\right]^2\right]\ . \tag{3.34}$$

It should be noted that in the further course of time, when the energy relaxation becomes substantial, the second term in the large parentheses in Eq. (3.33) decreases. Eventually, for sufficiently large delay ($2\gamma t_D\to\infty$), the nonequilibrium level populations tend to the equilibrium ones, and thus

$$S(\omega)=S^{(0)}(\omega)\propto f^{(0)}(\omega-\omega_0)\ .$$

To study in more detail the dependence of the linewidth of the differential absorption spectrum $S^{(1)}(\omega)$ on the time of delay between the excitation of the molecule and its probing by spectrally resolved absorption, knowledge of the spectrum of the pump-laser light is needed. Let us assume that this spectrum may be approximated by a Gaussian,

$$S_P(\omega-\omega_0)=S_P(0)\exp\left[-\left[\frac{2(\omega-\omega_0)}{\Delta\omega_P}\right]^2\right]\ . \tag{3.35}$$

Inserting Eq. (3.35) into Eq. (3.27), evaluating the convolution integral, we arrive after some mathematical manipulations at the following result:

$$S^{(1)}(\omega)\propto f^{(1)}(\omega-\omega_0)$$

$$=\frac{8\sqrt{\pi}}{\hbar^2\Delta\omega^{(0)}}\,|d_{P12}|^2 S_P(0)\exp(-2\gamma t_D)$$

$$\times\left[1+\left[\frac{\Delta\omega^{(0)}}{\Delta\omega_P}\right]^2(1-e^{-2\gamma_c t_D})\right]^{-1/2}$$

$$\times\exp\left[-\left[\frac{2(\omega-\omega_0)}{\Delta\omega}\right]^2\right]\ , \tag{3.36}$$

where the linewidth of $S^{(1)}(\omega)$ reads as

$$\Delta\omega=\Delta\omega^{(0)}\left[1-\frac{\exp(-2\gamma_c t_D)}{1+\left[\dfrac{\Delta\omega_P}{\Delta\omega^{(0)}}\right]^2}\right]^{1/2}\ . \tag{3.37}$$

We see that the line shape of the differential absorption spectrum depends on the delay time t_D, the relevant time scale being given by the correlation time $\tau_c=\gamma_c^{-1}$.

Immediately after the pump-laser pulse has passed the molecule ($t_D\approx\tau_P$), the linewidth of $S^{(1)}(\omega)$ is given by

$$\Delta\omega=\Delta\omega_P\left[1+\left[\frac{\Delta\omega_P}{\Delta\omega^{(0)}}\right]^2\right]^{-1/2}\ . \tag{3.38}$$

In particular, in the interesting case when the linewidth of the pump-laser light is small compared with the linewidth of the equilibrium absorption profile ($\Delta\omega_P\ll\Delta\omega^{(0)}$), we find that $\Delta\omega$ is approximately given by $\Delta\omega_P$ ($\Delta\omega\approx\Delta\omega_P$), and in the absorption spectrum $S(\omega)$, hole burning is observed. In the time domain, this condition, of course, implies that the pump-laser pulse must be long compared with the time of dephasing τ_{ph} [$\tau_{\text{ph}}=(2/\gamma_c\Gamma)^{1/2}=4/\Delta\omega^{(0)}$]. On the other hand, remembering the inequality $\tau_P\ll\tau_c$, we see that the correlation time, the time of duration of the pump-laser pulse, and the dephasing time must be sufficiently separated from each other, so that the inequalities $\tau_c\gg\tau_P\gg\tau_{\text{ph}}$ are valid. With increasing delay time, the differential absorption spectrum $S^{(1)}(\omega)$ becomes broader. Note that this broadening is accompanied, according to Eq. (3.36), by a decrease in the height of the line. Hence, with increasing value of the delay time, the effect of hole burning is more and more suppressed and, for $t_D\gg\tau_c$, it disappears. Clearly, in this case, the superposition of $S^{(0)}(\omega)$ and $-S^{(1)}(\omega)$ yields an absorption spectrum $S(\omega)$, the profile of which corresponds to that of $S^{(0)}(\omega)$. As long as the nonequilibrium level populations are not decayed ($2\gamma t_D\ll 1$), the values of $S(\omega)$ are below the values of $S^{(0)}(\omega)$.

IV. SUMMARY AND CONCLUSIONS

We have studied the spectrally resolved absorption of a dye molecule prepared by a pump-laser pulse and probed by a test-laser pulse after some time of delay. For this purpose, we have modeled the electronic transition of the dye molecule by a two-level system and have described the phase relaxation by a classical stochastic modulation of the transition frequency in the sense of an Ornstein-Uhlenbeck process. To simplify the calculations, we have assumed that the two pulses do not overlap, and have treated the reoccupation of the two quantum states caused by the action of the pump-laser pulse in the lowest order of perturbation theory. In this approximation, the absorption spectrum is represented in the form $S(\omega)=S^{(0)}(\omega)-S^{(1)}(\omega)$, where $S^{(0)}(\omega)$ is the equilibrium absorption spectrum and $S^{(1)}(\omega)$ reflects the nonequilibrium effect caused by the change of the level populations which is quadratic in the pump-laser field strength.

We have shown that the line shape of the absorption spectrum probed at time t_T by the test-laser pulse and the foregoing generation of the nonequilibrium level populations by the pump-laser pulse at time t_P are correlated to each other, provided that the (finite) correlation time of the dephasing process gives rise to substantial non-Markovian effects. In particular, in the case when the two pulses are short compared with the correlation time and, moreover, the dephasing time is short compared with the pump-laser pulse, we have found that the line shape of the absorption spectrum sensitively depends on the time of delay between the two pulses, the characteristic time scale being given by the correlation time. For example, if the delay time is short compared with the correlation time, $S^{(1)}(\omega)$ becomes proportional to the spectrum of the pump-laser light, which is, under the assumptions made, narrow compared with the equilibrium absorption spectrum $S^{(0)}(\omega)$, so that hole burning is observed. Clearly, in the case when the spectral linewidth of the pump-laser light is small compared with the linewidth of the equilibrium absorption spectrum, the pump-laser pulse may only reoccupy such quantum states of the combined system (consisting of the electronic two-level system and the dissipative system) for which the bandwidth of the corresponding transition frequencies is small compared with the bandwidth of the equilibrium absorption spectrum. Because of the shortness of the pump-laser pulse and the delay between pump and probe (both times are short compared with the correlation time), the remaining quantum states of the combined system with transition frequencies outside the spectral bandwidth of the pump-laser light cannot be involved in the reoccupation processes via equilibration of the quantum states of the dissipative system (decorrelation of the frequency modulation of the electronic transition frequency of the molecule). Hence, in this case the reduction of the absorption below the equilibrium level is restricted to the (small) frequency range of the pump-laser light, which gives rise to the hole burning. We therefore may say that in the case when the delay time (time of resolution) is smaller than the correlation time, the electronic transition of the molecule behaves like an inhomogeneously broadened transition. With increasing delay time, the effect of hole burning, of course, vanishes, owing to the now possible decorrelation of the frequency modulation. The calculations show that with increasing value of the delay time, the differential absorption spectrum $S^{(1)}(\omega)$, indeed, becomes more and more flat. Eventually, when the delay time is long compared with the correlation time, $S^{(1)}(\omega)$ becomes proportional to $S^{(0)}(\omega)$, so that the line shape of the observed absorption spectrum $S(\omega)$ is determined by the line shape of the equilibrium absorption spectrum $S^{(0)}(\omega)$, the value of $S(\omega)$ being, of course, reduced below the equilibrium values. In the further course of time, when the delay time becomes comparable with the longitudinal relaxation time of the two electronic quantum states of the molecule, $S^{(1)}(\omega)$ uniformly decreases, so that $S(\omega)$ approaches the equilibrium absorption spectrum $S^{(0)}(\omega)$. We therefore may say that in the case when the delay time (time of resolution) is longer than the correlation time, the electronic transition behaves like a homogeneously broadened transition.

These results are in good agreement with experimental observations.[1] It should be noted that we have applied our theory to the non-Markovian limiting case, which permits an analysis of the basic effects in an analytical way. The results found might therefore be expected to be somewhat overestimated in cases when the differences in the relations of magnitude of the characteristic times (correlation time, pulse lengths, and dephasing time) are less pronounced. Moreover, we have restricted our consideration to a single vibronic transition in the dye molecule. In general, the absorption bands of dye molecules in solution originate from several vibronic transitions. The line broadening is often so strong that these individual vibronic lines cannot be resolved even if the one or the other vibrational mode is strongly coupled to the electronic transition. Using the results derived above for a single transition, we may, at least qualitatively, discuss the pump-probe-type measurement performed with such more complex systems. For simplicity, we assume that only one vibrational mode (with frequency ω_v) is coupled to the electronic transition and that the $S_0 \rightarrow S_1$ absorption band is mainly composed of the vibronic lines $0 \rightarrow 1'$, $0 \rightarrow 0'$, and $1 \rightarrow 0'$ (the Franck-Condon factors of the remaining transitions are supposed to be small). Furthermore, let us assume that the three vibronic transition frequencies are modulated in nearly equal ways, so that the corresponding equilibrium linewidths are also nearly equal. Clearly, the theory developed above has to be applied to these individual transitions. Since the equilibrium overall profile of the absorption band shows no vibrational structure, we may conclude that for the individual linewidths, the relation $\Delta\omega^{(0)} \gtrsim \omega_v$ is valid, the vibrational frequency being typically in the order of magnitude 10^{14} s^{-1}. From the results and data given in Ref. 1, $\Delta\omega^{(0)}$ may be assumed to be 1.5×10^{14} s^{-1}, which corresponds to the dephasing time $\tau_{\mathrm{ph}} \approx 27$ fs. Furthermore, the length of the pump-laser pulse τ_P is about 60 fs, and the correlation time may be estimated to be $\tau_c \approx 150$ fs . Thus, the conditions $\tau_c \gg \tau_P \gg \tau_{\mathrm{ph}}$ used in our analytical calculations are fulfilled, at least in tendency. From the value given above, the value of γ_c/Γ is found to be 1.6×10^{-2}, which is consistent with the assumption of strong non-Markovian effects $(\gamma_c/\Gamma \ll 1)$. For a more quantitative comparison with the experimental results given in Ref. 1, numerical methods of calculation would be necessary.

At this point, we note that the theory developed above may also be used to study the absorption spectrum at early times when the effect of pulse overlap becomes substantial. In this case, in Eq. (3.5), the integral term D_{PT}, which describes the effect of superposition of pump- and test-laser pulse, must be taken into account. Clearly, the resulting spectrum is expected sensitively to reflect the structure of the edges of the two pulses and the phase relations between them. The numerical evaluation of the corresponding integrals therefore requires detailed knowledge of the pulse shapes. In particular, in the experiments described in Ref. 1, an "oscillatory" or "dispersionlike" structure of the absorption spectrum at earliest times was observed. The authors write that this structure was an artifact caused by the nonideal probing pulse, which had a tail owing to cubic phase distortions in the grating pulse compressor.[1] Since such effects may be suppressed by improved pulse compression, they are of less interest.

Finally, it should be pointed out that we have omitted in our calculations those contributions to the absorption spectrum which are mismatched in phase. The argument is that in the case of many molecules, when the characteristic linear extension of the interaction volume with the two laser pulses is large compared with the wavelength of the laser light, the averaged contribution of the phase-mismatched terms is negligibly small compared with the contribution of the phase-matched terms. In principle, the latter ones must also be averaged over the ensemble of molecules considered. Of course, this averaging could modify the correlation effects calculated, because the delay time varies from molecule to molecule. However, as long as the characteristic length of the interaction volume does not exceed c/τ_c, the results derived remain valid.

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