# Vibrational relaxation dynamics in transient grating spectroscopy studied by rate equations based on time-dependent correlation function*

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A modified model, a set of rate equations based on time-dependent correlation function, is used to study vibrational relaxation dynamics in transient grating spectroscopy. The dephasing, the population dynamics, and the vibrational coherence concerning two vibrational states are observed respectively in organic dye IR780 perchlorate molecules doped polyvinyl alcohol matrix. The result shows that in addition to the information concerning system-environment interaction and vibrational coherence, the vibrational energy transfer can be described by this modified model.

**Keywords:** transient grating, population dynamics, vibrational energy transfer

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## 1. Introduction

The vibrational relaxation dynamics is a common way to investigate energy redistributions in some processes such as isomerization,[1,2] photoluminescence,[3,4] and photoinduced charge-transfer.[5,6] Therefore, the investigations concerning vibrational relaxation dynamics are helpful for understanding the mechanisms of these processes. A great amount of research has studied vibrational relaxation dynamics in gas phase and solution regimes.[7−16] Experimental results show that the time scale of vibrational relaxation is dependent on the interaction between the molecular system and the local environment. So it can be predicted that the vibrational relaxation of molecules doped in solid film is much faster than that in gas phase and solution regimes because the system-environment interaction is much stronger in film.

With the development of ultrafast laser, a third-order nonlinear spectroscopy, the TG spectroscopy, proves to be a powerful method to detect vibrational relaxation.[17−20] The time-dependent correlation function is usually used to characterize third-order nonlinear signal response. And the information concerning system-environment interactions and vibrational coherence is obtained by this correlation function.[19,21−23] However, population dynamics of each vibrational state is considered to be isolated in this model. To our knowledge, population transition among vibrational states has not been introduced in this model. Therefore, the information concerning vibrational energy transfer (VET) is unable to be obtained by the time-dependent correlation function mentioned above.

To solve this problem, we introduce a set of rate equations based on the time-dependent correlation function. In this modified model, population transition among vibrational states is considered. To start with, the dephasing, the population dynamics, and the vibrational coherence are separated by time-dependent correlation function, and then the kinetic curves concerning population dynamics are fitted with the numerical solutions of rate equations to obtain the information about the population transition among vibrational states. In this paper, the transient grat-

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ing (TG) spectroscopy is used to study vibrational relaxation dynamics in organic dye IR780 perchlorate doped polyvinyl alcohol (PVA) film. With this modified model, we confirm the route and time constant concerning VET between two vibrational modes.

## 2. Method and material

The experimental setup for femtosecond TG is displayed in Fig. 1. The ultrashort pulses ($\sim$ 100 fs, 800 nm, 1 kHz) generated by a Ti:sapphire regeneration amplified laser system (Spectra-Physics, Spitfire) are split into three beams which have the same polarizations. Two of them ($\boldsymbol{k}_1$ and $\boldsymbol{k}_2$) act as the excitation pulses while the third one ($\boldsymbol{k}_3$) acts as the probe pulse. The intensity of the excitation pulse is about $1\times10^9$ W/cm$^2$ and that of the probe pulse is $7\times10^8$ W/cm$^2$. The three pulses spatially cross at one point on the sample forming folded box geometry. The interval between two excitation pulses ($t_{12}$) is set to be zero and the interval between excitation and probe pulses ($t_{23}$) is scanned by an optical delay line. The TG signal along the phase-matched direction $\boldsymbol{k}_4 = -\boldsymbol{k}_1+\boldsymbol{k}_2+\boldsymbol{k}_3$ is captured by a spectrometer (Bruker, Optics 250IS/SM) equipped with an intensified charge-coupled device (Andor iStar, DH720).

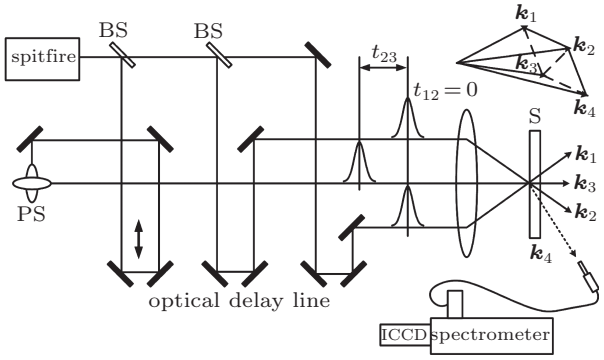



**Fig. 1.** Schematic diagram of experimental setup. BS: beam splitter, PS: periscope, S: sample.

In sample preparation, IR780 perchlorate (Aldrich, Dye content 99%) ethanol solution and PVA water solution were evenly mixed, and then the mixture was spun on a glass substrate to produce the film which has good optical properties and the thickness of the film is about 5 μm.

## 3. Results and discussion

The excitation pulse wavelength lies in the absorption band of the IR780 perchlorate doped PVA film as shown in Fig. 2, which indicates that the molecular system is resonantly stimulated from electronic ground state to excited state. Compared with the excitation pulse, the TG signal has a blue shift caused by the coupling of the vibrational modes. This result indicates that the TG signal contains the information concerning vibrational states on the electronic excited state. However, frequencies of vibrational modes which are related to these vibrational states cannot be obtained in frequency domain because the TG spectroscopy is lacking in spectral resolution.

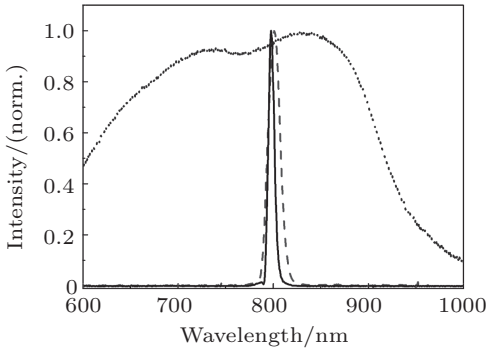



**Fig. 2.** TG signal (solid line), excitation pulse (dash line), and absorption (dot line) spectra.

The information about vibrational modes is usually confirmed from time-resolved spectrum in TG spectroscopy by using the Fourier transform. The time-resolved spectrum can be described by a time-dependent correlation function $M(t)$. This correlation function is usually separated into three parts to describe population relaxation, dephasing, and vibrational coherence. The three processes are represented with a sum of exponentials and a damped cosinusoid respectively.[19] So the $M(t)$ can be expressed as

$$M(t) = A_1\exp(-t/T_1) + A_2\exp(-t/T_2) + B\exp(-t/\tau)\cos(\omega t + p). \quad (1)$$

In Eq. (1), the first term describes the population relaxation with an amplitude $A_1$ and a time constant $T_1$; the second term expresses the dephasing with an amplitude $A_2$ and a time constant $T_2$; the third term represents vibrational coherence where $B$, $\tau$, $\omega$, and $p$ are the amplitude, the time constant, the frequency, and the initial phase of oscillations in time-resolved spectrum respectively.

As shown in Fig. 3(a), the time-resolved TG spectra are fitted with Eq. (1). An oscillation with a frequency of 150 cm$^{-1}$ is observed on the kinetic curve at 797 nm. This oscillation is the result of vibrational coherence between two vibrational states denoted by $v_1$ and $v_2$. And the vibrational modes related to the

vibrational states $v_1$ and $v_2$ can be confirmed by Raman calculation with Gaussian 03.[24] As shown in Fig. 3(b), the vibrational state $v_1$ belongs to vibrational mode with 190 $cm^{-1}$ which roots in N–$CH_3$ bond rotation, and the vibrational state $v_2$ belongs to vibrational mode with 350 $cm^{-1}$, which is assigned to the out-of-plane distortion of molecules.

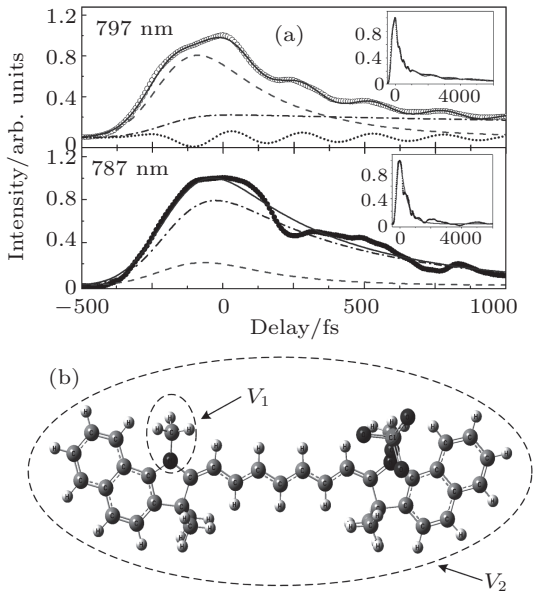



**Fig. 3.** (a) Time-resolved spectra of TG signal. The experimental data (open and solid circles) can be fitted with Eq. (1) (solid line). And each dynamic curve contains several components: dephasing (dash line), population relaxation (dash–dot line), and intramolecular vibration (dot line). (b) Molecular structures of IR780 perchlorate. The balls denote nitrogen, carbon, and hydrogen atoms, respectively.

The dephasing and the population relaxation are different at 787 nm and 797 nm. The kinetic curve at 797 nm has a fast component with 285 fs and a slow component with about 3527 fs. The kinetic curve at 787 nm has a fast component with 250 fs and a slow component with 508 fs. Both of the fast components (about 200 fs) are due to dephasing, and the slow component (about 3500 fs) is attributed to population relaxation. Note that the slow component with 508 fs at 787 nm is much faster than that at 797 nm. We suggest that the component with 508 fs is caused by population transition between the vibrational states $v_1$ and $v_2$. However, the time constant of this process cannot be obtained with the time-dependent correlation function described by Eq. (1).

To solve this problem, a set of rate equations is introduced based on the time-dependent correlation function. As shown in Fig. 4(a), a vibrational state $v_0$ in the electronic ground state $S_0$ and two vibrational states $v_1$ and $v_2$ in the electronic excited state $S_1$ are involved in the population dynamics. So the population dynamics can be described by a set of rate equations concerning three-level system

$$dn_0/dt = -(W_{01} + W_{02})n_0 + A_{10}n_1 + A_{20}n_2, \quad (2)$$

$$dn_1/dt = W_{01}n_0 - A_{10}n_1 + S_{21}n_2, \quad (3)$$

$$dn_2/dt = W_{02}n_0 - A_{20}n_2 - S_{21}n_2, \quad (4)$$

where $n_i$ ($i = 0, 1, 2$) represent the population of the corresponding vibrational state; $W_{0i}$, $A_{i0}$ ($i = 1, 2$), and $S_{21}$ refer to probabilities of pumping, population relaxation, and population transition from vibrational state $v_2$ to $v_1$. As shown in Fig. 4(b), the time constants concerning population transition between vibrational states $v_1$ and $v_2$ can be obtained while the kinetic curves about population dynamics are fitted by the numerical solutions of Eqs. (2), (3), and (4). Here, $W_{0i}$ ($i = 0, 1, 2$) are the Gaussian functions which are related to the pulse width of the excitation pulse and absorption cross section of molecular

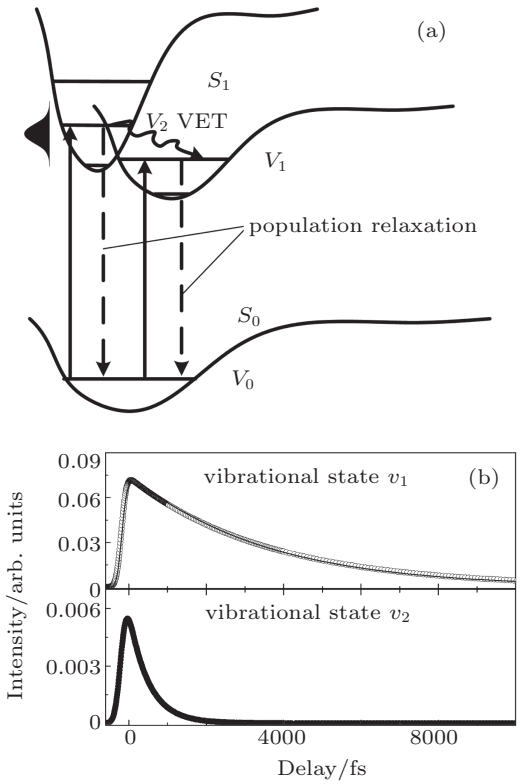



**Fig. 4.** (a) Sketch of potential energy surfaces involved in vibrational dynamics. The solid vertical arrows represent pumping of excitation pulses. The Gaussian envelope refers to the bandwidth of the excitation pulse. (b) Contributions concerning population dynamics (open and filled circles) in kinetic curves. The population kinetic curve of each vibrational state is fitted with the numerical solutions (solid line) of Eqs. (2), (3), and (4).

system itself; and $1/A_{10}$ is equal to 3527 fs according to the result obtained from the fitting of time-resolved

TG spectra with Eq. (1). As a result, $1/A_{20} = 5500$ fs and $1/S_{21} = 450$ fs are obtained through the fitting of population dynamics with the numerical solutions of the rate equations. So the population transition from vibrational state $v_2$ to $v_1$ holds on 450 fs and that from vibrational state $v_2$ to ground state relaxes holds on 5500 fs.

Therefore, the information concerning vibrational relaxation dynamics in IR780 perchlorate-doped PVA film system can be clearly described with a set of rate equations based on the time-dependent correlation function. The photons from excitation pulses will excite the molecular system from an electronic ground state to an excited state. And the populations are formed in vibrational states $v_1$ and $v_2$ because the bandwidth of the excitation pulse covers the two vibrational states which belong to N–$CH_3$ bond rotation and out-of-plane distortion of the molecule respectively. Then the system-environment interaction will cause the dephasing and the population relaxation in the molecular system. The dephasing makes the populations lose their coherences and this process holds on about 200 fs. The population relaxation makes the excess energy of each vibration state transfer to the surrounding environment and this process holds on several picoseconds. In addition, the VET from N–$CH_3$ bond to the whole molecule is also involved in this molecular system and this process relaxation holds on 450 fs.

# 4. Conclusion

Introducing a set of rate equations based on the time-dependent correlation function, the information concerning population transition among vibrational states is obtained in analysing time-resolved TG signal. Two vibrational modes, N–$CH_3$ bond rotation and the out-of-plane distortions, are coupled in IR780 perchlorate-doped PVA film and the VET exists between the two vibrational modes. Therefore, we suggest that when one of the two vibrational modes is selectively stimulated, the energy of this vibrational mode will preferentially transfer to the other mode.

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