

High pressure effect on the ultrafast energy relaxation rate of LDS698 (C₁₉H₂₃N₂O₄Cl) in a solution

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Abstract: Effects of high pressure in a range of up to 1.7 GPa on ultrafast energy relaxation of LDS698 (C₁₉H₂₃N₂O₄Cl) molecules in solution have experimentally been illustrated by a method of femtosecond time-resolved absorption spectroscopy. The rates of the intramolecular and intermolecular energy relaxations show quite different pressure dependences. The observed results are in good agreement with the theoretical interpretation based on the pressure influences on the molecular energy gaps, the intermolecular H-bond interaction, and the solution viscosity.

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OCIS codes: (300.6500) Spectroscopy, time-resolved; (320.7130) Ultrafast processes in condensed matter, including semiconductors.

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1. Introduction

Vibrational energy relaxation of polyatomic molecules in solution under ambient condition has been widely investigated by using various ultrafast spectroscopic techniques [1-6]. These studies demonstrate that the internal conversion (IC) and intramolecular vibrational redistribution (IVR), taking place in a time range of sub-picosecond, are the most important intramolecular relaxation processes [2-4], and the excited molecule can also be cooled through the intermolecular interaction, such as hydrogen bonding and collision, with a relative long time scale of several ps to a few ten ps [5,6]. However, effects of high pressure on molecular vibrational energy relaxation is still ambiguous and only the temperature effect has been carried out experimentally [7,8]. It has long been recognized that pressure can cause changes in molecular electronic and vibrational structures [9-12], intermolecular interaction [13-16], and solution viscosity [17]. In principal, pressure can also affect the rates of molecular energy relaxation processes, like temperature, under extreme conditions. A theoretical calculation on the rate constants involving the pressure effects is also complex [18]. Laser spectroscopy has been recognized to be a powerful tool in high pressure studies [19]. A purpose of the present paper is to report our investigations of the pressure tuning of optical properties and optical processes of organic molecules. Molecular absorption and radiationless transition will be chosen as examples. The mechanism of the pressure tuning of optical spectroscopies and photophysical processes will be briefly discussed. Experimentally, femtosecond (fs) time-resolved optical absorption of LDS698 (pyridine, $C_{19}H_{23}N_2O_4Cl$), a dye molecule, in methanol-ethanol solution has been measured under a pressure up to 1.7 GPa generated in a gem anvil cell (GAC). The observations have been interpreted in terms of the theoretical model developed and the results demonstrate clearly that pressure can significantly affect the molecular energy relaxation through changing the intramolecular energy gaps of molecular levels and the intermolecular interaction.

2. Experimental setup

The experimental setup is shown in Fig. 1. A sample of dye LDS698 (Exciton Chemical Company), dissolved in methanol-ethanol mixture (the ratio of volume, 4:1) with a concentration of 3×10^{-4} mol/L, is filled in a 1mm diameter cuvet GAC which generates a pressure up to 2 GPa with a tardy change of pressure in solution phase. The pressure is calibrated by a standard technique of ruby fluorescence. A regenerative amplified Ti:sapphire laser (Spectra-Physics) is used to generate a 90 fs, 788 nm linearly polarized laser pulse with 1 kHz repetition rate. The majority of the intensity from the fundamental output of the fs laser is doubled through a 0.5 mm-thick β -BaB₂O₄ (BBO) crystal to provide 394 nm pump beam for

the electronic excitation from S_0 to both the lower vibrational levels of S_2 and higher vibrational levels of S_1 . The residual 788 nm laser beam acts as a probe beam for the transient absorption of $S_2 \rightarrow S_3$ and $S_1 \rightarrow S_3$, as shown in Fig. 2. The time delay between the pump and probe beams is realized by a computer-controlled translation stage with 6.6 fs for each step. The intensity ratio of pump to probe beam is about 10:1. Before running the time-resolved experiment we carefully measure the transient absorption signals from the sample irradiated long time by the laser with different intensity and finally choose a lower pump intensity of 10^8 W/cm² for avoiding photoinduced degradation of the sample. The detailed descriptions of the experimental setup are given in elsewhere [20].

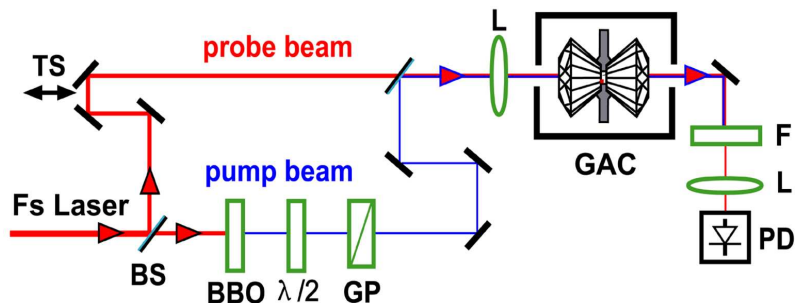


Fig. 1. The schematic diagram of the experimental setup. BS, beam splitter; TS, translation stage for optical delay; GP, Glan prism; L, focusing lens; F, filter for 788 nm passing through; PD, sensitive p-i-n Si photodiode; GAC, gem anvil cell.

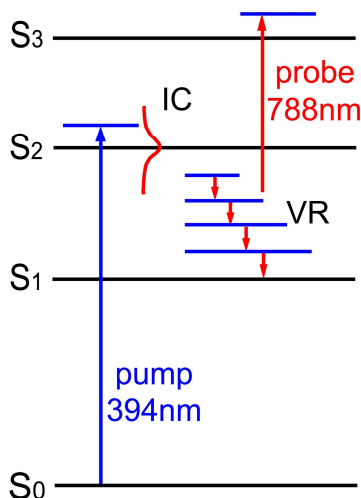


Fig. 2. An illustration for the dynamic processes involved in the observed transient absorption of LDS698 molecules. IC is the internal conversion process and VR is the vibrational relaxation process.

3. Experimental results and discussions

Transient absorption spectra of LDS698 under different pressures are shown in Fig. 3. These spectra reflect the relaxation of the molecules from the photo excited potential surface S_1 or S_2 . Under different pressures the absorption curves have the same trend in time evolution, showing a fast increasing within the first several hundred femtoseconds and a relative slow increasing in a time scale of about ten picoseconds. With increasing pressure, the magnitude of the absorption decreases gradually due to the pressure induced shift of the molecular levels [11,21], which has also been implied by the color change of the dye solution during

uploading, that is, the color of the dye fades away with the pressure increasing because of the shift in its fluorescent transition $S_1 \rightarrow S_0$ from visible to infrared region. Following a general treatment in pump-probe experiment [20,22], the transient absorption signal $\Delta I(\tau)$ can be obtained by $\Delta I(\tau) = \int S(t)R(t-\tau)dt$, a convolution between a pump-probe correlation function $R(t-\tau)$ and an absorption decay function $S(t)$, with τ the delay time between the pump and the probe pulses. The measured function $S(t)$ at different pressure exhibits a biexponential decay behavior and thus is expressed as $S(t) = a_0 + a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2)$, in which a_0, a_1, a_2 are the parameters, τ_1, τ_2 are the time constants of the decay processes, which can be obtained from a fit of the measured curve for each pressure. The rates $k_1 = 1/\tau_1, k_2 = 1/\tau_2$ of two relaxation processes are determined from these time constants as given in Fig. 4(a) and 4(b). For the fast process, the rate k_1 increases with pressure and can be assigned more likely to the IC ($S_2 \rightarrow S_1$) and IVR in S_1 of the excited molecules. Another process is relative slow and its rate k_2 decreases with pressure. This process may involve some intermolecular energy relaxations, such as vibrational energy relaxation, in addition to IC ($S_1 \rightarrow S_0$). Under pressure the process IC ($S_2 \rightarrow S_1$) with a rate constant of k_1 plays a primary role. This is because the IC between these two electronic states is an ultrafast process due to the small energy gap between S_2 and S_1 , according to the Kasha rule, taking place in sub-picosecond time scale. Even at ambient pressure in the range of early delay time the IVR in S_1 is the dominating process, under pressure the intermolecular hydrogen bond interaction is enhanced, which might accelerate the IC ($S_2 \rightarrow S_1$) process. The lifetime of S_1 depends on the vibrational level of the S_1 state (see Fig. 2) in our case. At a high vibrational level of the S_1 state, the single-vibronic level IC will compete with vibrational relaxation (VR) which usually takes place in picosecond range. At a lower level of the S_1 state, the single-vibronic level IC rate of the S_1 state is slower than VR; in this case vibrational equilibrium is established before the IC takes place and the S_1 state lifetime is of the order of nanoseconds.

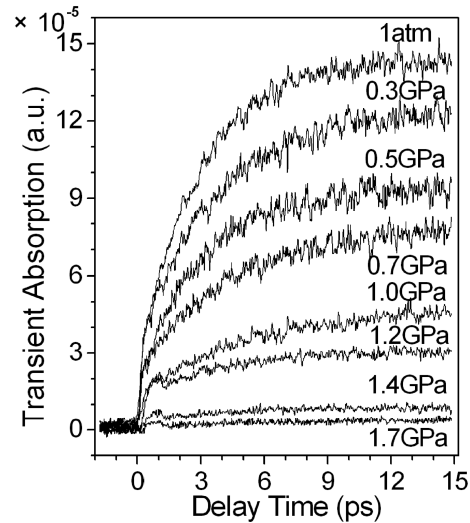


Fig. 3. The transient absorption spectra of LDS698 in solution at different pressures. The spectrum at ambient pressure was also taken from a 1 mm quartz cell for comparison.

The measured k_1 , as a function of pressure P , is given in Fig. 4(a). The best fitting can be achieved by a straight line with a slope of 0.24 in this semi-logarithmic plot, indicating an exponential dependence of k_1 on pressure P . Theoretically, using the Born-Oppenheimer approximation as a basis set, the absorption coefficient for the electronic transition $a \rightarrow b$ can be expressed as

$$\alpha(\omega) = \frac{4\pi^2\omega}{3\hbar c} \sum_{\nu} \sum_{\nu'} P_{\nu\nu'} \left| \langle \Psi_{\nu\nu'} | \bar{\mu} | \Psi_{\nu\nu'} \rangle \right|^2 \delta(\omega_{\nu\nu',av} - \omega), \quad (1)$$

where $\bar{\mu}$ denotes the dipole operator and $\psi_{\nu\nu'}$, $\psi_{\nu\nu'}$ represent the vibronic wavefunctions. Notice that in the B-O approximation

$$\left| \langle \Psi_{\nu\nu'} | \bar{\mu} | \Psi_{\nu\nu'} \rangle \right|^2 = \left| \langle \Phi_b \oplus_{\nu\nu'} | \bar{\mu} | \Phi_a \oplus_{\nu\nu'} \rangle \right|^2 = \left| \langle \Phi_b | \bar{\mu} | \Phi_a \rangle \right|^2 \left| \langle \oplus_{\nu\nu'} | \oplus_{\nu\nu'} \rangle \right|^2 = \left| \bar{\mu}_{ba} \right|^2 \left| \langle \oplus_{\nu\nu'} | \oplus_{\nu\nu'} \rangle \right|^2. \quad (2)$$

Here $\bar{\mu}_{ba}$ denotes the electronic transition moment and $\left| \langle \oplus_{\nu\nu'} | \oplus_{\nu\nu'} \rangle \right|^2$ represents the molecular Franck-Condon factor which in turn can be expressed in terms of the F-C factors of vibrational modes,

$$\left| \langle \oplus_{\nu\nu'} | \oplus_{\nu\nu'} \rangle \right|^2 = \prod_i \left| \langle X_{\nu\nu'_i} | X_{\nu\nu'_i} \rangle \right|^2, \quad (3)$$

$\omega_{\nu\nu',av}$ in Eq. (1) can be written as

$$\hbar\omega_{\nu\nu',av} = \hbar\omega_{ba} + \sum_i \left[\left(\nu_i + \frac{1}{2} \right) \hbar\omega_i - \left(\nu_i + \frac{1}{2} \right) \hbar\omega_i \right], \quad (4)$$

where $\hbar\omega_{ba}$ represents the electronic energy gap. It follows that

$$\alpha(\omega) = \frac{4\pi^2\omega}{3\hbar c} \left| \bar{\mu}_{ba} \right|^2 \sum_{\nu} \sum_{\nu'} P_{\nu\nu'} \prod_i \left| \langle X_{\nu\nu'_i} | X_{\nu\nu'_i} \rangle \right|^2 \delta(\omega_{\nu\nu',av} - \omega). \quad (5)$$

And the transition probability of IC for the electronic transition $a \rightarrow b$ can be expressed as [4]

$$W_{a \rightarrow b} = \frac{2\pi}{\hbar} \sum_{\nu} \sum_{\nu'} P_{\nu\nu'} \left| \langle \psi_{\nu\nu'} | \hat{H}'_{BO} | \psi_{\nu\nu'} \rangle \right|^2 \delta(E_{\nu\nu'} - E_{\nu\nu'}), \quad (6)$$

where $P_{\nu\nu'}$ is the Boltzmann weighting factor, \hat{H}'_{BO} is the perturbation Hamiltonian in the Born-Oppenheimer approximation, $E_{\nu\nu'}$, $E_{\nu\nu'}$ and $\psi_{\nu\nu'}$, $\psi_{\nu\nu'}$ are the energies and wave-functions of the molecules in the initial and final states, and δ is the Dirac delta function. Using the same argument Eq.(6) can be written as

$$W_{a \rightarrow b} = \frac{2\pi}{\hbar} R_{ba}(i) \sum_{\nu} \sum_{\nu'} P_{\nu\nu'} \prod_i \left| \langle X_{\nu\nu'_i} | X_{\nu\nu'_i} \rangle \right|^2 \delta(E_{\nu\nu'} - E_{\nu\nu'}), \quad (7)$$

where $R_{ba}(i)$ is the electronic matrix element of the i th promoting mode and be expressed as

$$R_{ba}(i) = \frac{\omega_i}{2\hbar} \left\langle \Phi_a \left| \hbar^2 \frac{\partial}{\partial Q_i} \right| \Phi_b \right\rangle, \quad (8)$$

Q_i and ω_i being the normal coordinate and vibrational frequency of the i th mode. In the low temperature range $W_{a \rightarrow b}$ reduces to

$$W_{a \rightarrow b} = \frac{R_{ba}(i)}{\hbar^2} \sqrt{\frac{2\pi}{\bar{\omega}\omega_{ab}}} \exp\left[-S - \frac{\omega_{ab}}{\bar{\omega}} \left(\ln \frac{\omega_{ab}}{S\bar{\omega}} - 1\right)\right], \quad (9)$$

where ω'_{ab} is the electronic energy gap, and S and $\bar{\omega}$ represent the Huang-Rhys factor and average vibrational frequency, respectively [23].

Finally we consider the pressure effect on $\alpha(\omega)$ and $W_{a \rightarrow b}$. The pressure effect on the electronic parts $|\overline{\mu_{ba}}|^2$ and $R_{ba}(i)$ is the smallest because the electronic wavefunctions cannot easily be perturbed. Likewise the pressure effect on potential curves of intramolecular vibrations is also not significant; its effect on $\alpha(\omega)$ if significant will show up in the changes of spectral width and band shape. Therefore, we consider the pressure effect on ω'_{ab} . It is well known that the absorption maximum of $\alpha(\omega)$ can easily be shifted by solvents, that is, the solvent effect on ω'_{ab} , the electronic energy gap. This indicates that the pressure effect on ω'_{ab} will be significant, through intermolecular interactions. The intermolecular interactions between the solute molecule and solvent molecule which can be van der Waals type, polar interactions, hydrogen-bonding etc. depend on the intermolecular distance and can affect ω_a and ω_b . Thus we can expand ω'_{ab} as a power series of P , the external pressure. If we let $\omega'_{ab}(P) = \omega'_{ab}(0) + \Delta\omega'_{ab}P$, then the transition probability can be related with pressure P and the rate constant, k_1 , can be given by the ratio

$$\frac{W_{a \rightarrow b}(P)}{W_{a \rightarrow b}(0)} = \sqrt{\frac{\omega'_{ab}(0)}{\omega'_{ab}(P)}} \exp\left[-\frac{\Delta\omega'_{ab}P}{\omega'_{ab}(0)} \ln \frac{\omega'_{ab}(0)}{S\bar{\omega}}\right], \quad (10)$$

This indicates that the relationship of $\ln[W_{a \rightarrow b}(P)/W_{a \rightarrow b}(0)]$ vs P is linear, i.e.

$$\ln \frac{W_{a \rightarrow b}(P)}{W_{a \rightarrow b}(0)} = -\left(\frac{\Delta\omega'_{ab}}{\bar{\omega}} \ln \frac{\omega'_{ab}(0)}{S\bar{\omega}} + \frac{\Delta\omega'_{ab}}{2\bar{\omega}}\right)P. \quad (11)$$

From Eq. (11) we have shown that k_1 varies with P exponentially, just as obtained from the experimental measurement mentioned above in Fig. 4(a). The slope of $\ln k_1$ vs P is $-\frac{\Delta\omega'_{ab}}{\bar{\omega}} \ln \frac{\omega'_{ab}(0)}{S\bar{\omega}} - \frac{\Delta\omega'_{ab}}{2\bar{\omega}}$ theoretically. We can estimate $S\bar{\omega}$ from the absorption maximum of the S_2 spectra and $\omega'_{ab}(0)$ from the distance between the absorption maximum of the S_2 band and that of the S_1 band. In this way we obtain $-\Delta\omega'_{ab}/\bar{\omega} \approx 0.241$, in good agreement with the value by fitting the experimental measurements. Here $\Delta\omega'_{ab} < 0$, this implies that ω'_{ab} decreases with increasing pressure, that is to say, the gap between S_1 and S_2 decreases under pressure. And $\Delta\omega'_{ab}$ may be attributed to the pressure effect on vibronic coupling [10] and/or the intermolecular solvent effect enhanced by pressure.

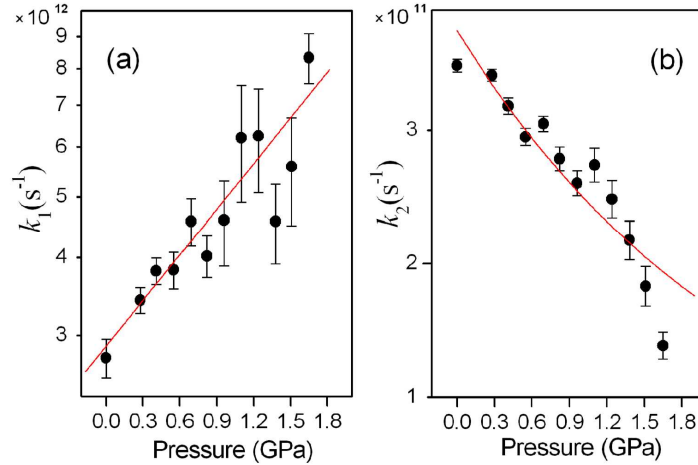


Fig. 4. (a) Semi-logarithmic plot of the rate constants k_1 of the intramolecular IC process of LDS698 solution versus pressure. The solid line is the result by a linear fitting, showing an exponential dependence of k_1 on P with a slope of 0.24. (b) Dependence of the rate constants k_2 of the vibrational energy relaxation process on pressure. The solid line is the fitting result by using Eq. (12) after considering intermolecular H-bond interaction and the viscosity of the solution.

The picosecond relaxation process described by the rate constant k_2 can be attributed to the vibrational energy relaxation of the high vibrational levels in S_1 , which can be populated by either IC ($S_2 \rightarrow S_1$) process or pumping process $S_0 \rightarrow S_1$. The vibrational relaxation dynamics is quite complicated because that the excited energy levels of various vibrational modes are involved in high vibrational levels of S_1 , and k_2 may only represent the collective rate-determining step, including these processes of intramolecular IC ($S_1 \rightarrow S_0$), intramolecular and intermolecular vibrational energy relaxation. The intermolecular energy transfer (like cooling), if of the Förster type, will be very effective, because it is electronic-electronic transfer between the donor and acceptor molecule. The electronic-vibrational transfer cannot be very effective, because in the dipole-dipole interaction the transition dipole-moment is involved in the donor molecule (i.e. the excited molecule) while the ground state dipole moment is involved in the solvent molecule. Therefore, it is believed that intermolecular processes are dominant and mainly through intermolecular collision and/or H-bond interaction [7,8]. Under high pressure the solvent viscosity η will be increased, the relation can be described as $\eta \approx 1/\exp(aP^2 + bP + c)$ [17]. Thus, it is believed that this pressure effect can restrict the intermolecular collision and then lead to a decrease of the intermolecular energy relaxation rate, i.e. $k' \approx c''/\eta = 1/\exp(aP^2 + bP + c)$. On the other hand, the H-bond interaction between solute and solvent molecules changes with increasing pressure [13,14], which might affect the vibrational frequency of the promoting molecular mode. Taking the molecule as a spheroid, under pressure the H-bond distance between molecules can be expressed as $R = 2[3(V - \xi P)/4\pi]^{1/3}$ with V the volume of the solute molecule and ξ a constant related to compression. According to Förster expression [24], the energy transfer rate from an excited molecule to its nearest neighbor can be given by $k'' \approx d'/R^6 = d/(1 - eP)^2$, where e is the compression coefficient of the sample which decreases with rising pressure. Here e can be taken as a constant in the pressure range studied in present work because, when pressure is above 0.2 GPa, the decrease of e is very small [24]. Therefore, we can establish a relation

$$k_2 \approx k' + k'' = 1/\exp(aP^2 + bP + c) + d/(1 - eP)^2 \quad (12)$$

for fitting the experimentally measured rate constants k_2 , which decreases with pressure, and giving the solid line in Fig. 4(b). This fitting represents most parts of the experimental data, gives a compressibility e in the same order as given in the previous report [25], and therefore is reasonable even that it is approximate as the model is a macroscopic description. It should be noted that this fitting only adapts to the solution, i.e., in a pressure range lower than the solidification pressure (for the present sample, ~ 3 GPa) since the energy relaxation mechanism will be quite different for the solidified sample as shown in our previous study in pressure effect on molecular dynamics of solid sample [20].

4. Conclusion

We conclude, from the fs time-resolved spectroscopic experiment and theoretical interpretation, that the pressure influence on two components of the molecular ultrafast energy relaxation is significant through changing the energy gaps of molecular levels, the intermolecular H-bond interaction and the solution viscosity. Therefore we have experimentally shown that pressure can be taken as an important factor to alter a chemical dynamic process. In addition, the technique of combined fs time-resolved spectral measurement with high pressure generation used here can be applied to study optical spectroscopies and photophysical processes of liquids and solids at high pressure for exploring the fundamental of various interactions and understanding the properties of matter under extreme conditions.

Acknowledgements

This work is supported by the National Natural Science Foundation of China under Grant No. 10534010, 10974069, and National Basic Research Program of China under Grant No. 2005CB724400.