

Chirped molecular vibration after impulsive Raman excitation in a stilbene derivative molecule in solution

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Abstract. The vibrational dynamics in 4-methoxy-4'-nitrostilbene in a condensed phase was studied by femtosecond pump-probe spectroscopy and quantum-chemical calculation. Transient changes in absorbance due to bleaching exhibit oscillations reflecting chirped molecular vibrational on the potential surface.

1. Introduction

Stilbene and its derivative have been extensively studied as a reference system for cis/trans photoisomerization ([1-3]). Even though the photoisomerization of stilbene is considered to involve 72 modes, the relaxation process in the molecule can be simplified to be described in a two-dimensional view, involving θ (double bond torsion angle) and ϕ (phenyl ring rotation) torsion angle [4-6]. Reaction toward twisting can be monitored by ultrafast spectroscopy, and nuclear motions on the excited state surface are followed with high temporal resolution [7]. In the present work, we report the ultrafast spectroscopy of stilbene derivative.

2. Experimental Methods

Reagent grade 4-methoxy-4'-nitrostilbene (MONS) was dissolved in solvents (benzene, acetonitrile, and methanol). All samples had an optical density about 1.0 at 395 nm in a 1-mm quartz cell. A Ti: sapphire laser amplifier system was used for pump-probe experiment [8,9]. The output fundamental pulse was frequency doubled to generate a 395 nm pulse having a width of 40 fs at a 1-kHz repetition rate. All measurements were performed at room temperature (294K).

3. Results and Discussion

The probe delay time dependence of MONS in benzene solution is shown in Fig. 1. It shows the change in the electronic absorption intensity with some vibrational signal with a few vibrations. It could be well described by the following chirped oscillation of transient absorption due to molecular vibration first utilized by Zewail and others [7].

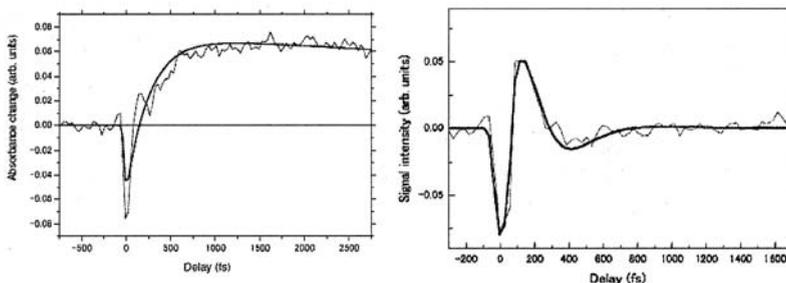


Fig. 1. (a) Probe delay time dependence of ΔA (real-time trace) observed for MONS in benzene. Smooth line is the best fit. (b) Data obtained from (a) after removal of slowly varying time dependence due to electronic dynamics.

The most stable structures of MONS were calculated using MP2/6-31G* and CIS/6-31G* level in the ground and the lowest excited states. The structure is twisted in the ground state with the angle of ϕ being -25.9° . However, in the excited state, the angle of ϕ is 0° . Structure of the potential energy surface (PES) of MONS was also calculated in the ground state (Fig. 2).

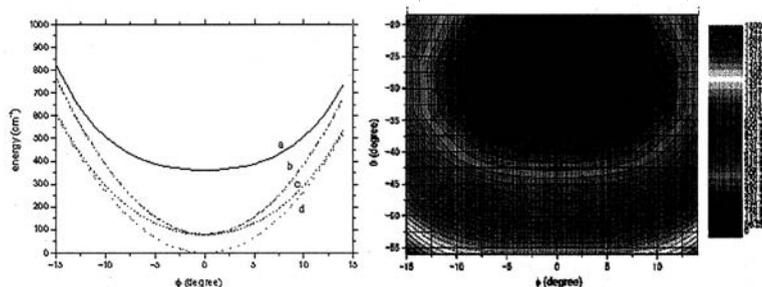


Fig. 2. Calculated potential energy surface (PES). Lines in the left figure show the results when ϕ are (a)- 41° , (b)- 33.5° , (c)- 26° and (d)- 18.5° , respectively.

From the calculation it was found that when the MONS molecule in the ground state is excited to the Franck-Condon region, it starts to increase the angle of ϕ bound for the most stable structure of the excited state. As a reaction of the movement of the excited state, the MONS molecule in the ground state starts to

decrease the angle of ϕ . Fig. 2 shows when ϕ decreases in the ground state the curvature of the PES also decreases, which causes the chirp in the molecular vibration frequency as seen in Fig. 1.

4. Conclusions

In conclusion, we could for the first time observe the chirped molecular vibration on the excited state potential surfaces associated with photoisomerization in a condensed phase. The different rates are well explained in terms of the differences in the dielectric constant and/or proticity of the solvent.

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References

- 1 D. H. Waldeck, in *Chemical Review*, 91, 415, 1991.
- 2 T. Kobayashi, E. O. Degenkolbl, and P. M. Rentzepis, in *Journal of Applied Physics*, 50, 3118, 1979.
- 3 K. Ishii, S. Takeuchi, and T. Tahara, in *Chemical Physics Letters*, 398, 400, 2004.
- 4 J. C. Polanyi and A. H. Zewail, in *Accounts of Chemical Research*, 28, 119, 1995.
- 5 M. Terauchi, and T. Kobayashi, in *Chemical Physics Letters*, in *Chemical Physics Letters*, 137, 319, 1987.
- 6 A. B. Myers, and R. A. Mathies, in *Journal of Chemical Physics*, 81, 1552, 1984.
- 7 A. H. Zewail, M. Dantus, R. M. Bowman, and A. Mokhtari, in *Journal of Photochemistry and Photobiology*, 62, 301, 1992.
- 8 T. Taneichi, T. Fuji, Y. Yuasa, and T. Kobayashi, in *Chemical Physics Letters*, 394, 377, 2004.
- 9 T. Fuji, H. J. Ong, and T. Kobayashi, in *Chemical Physics Letters*, 380, 135, 2003.