

Vibrational structure of the S_2 ($1B_u$) excited state of diphenyloctatetraene observed by femtosecond stimulated Raman spectroscopy

Philipp Kukura ^a, David W. McCamant ^a, Paul H. Davis ^b,
Richard A. Mathies ^{a,*}

^a Department of Chemistry, University of California, Berkeley, CA 94720, USA

^b Department of Chemistry, Santa Clara University, Santa Clara, CA 95053, USA

Received 3 September 2003; in final form 14 October 2003

Published online: 6 November 2003

Abstract

Femtosecond time-resolved stimulated Raman spectroscopy (FSRS) is used to study the vibrational structure and dynamics of the S_2 state of diphenyloctatetraene. Strong vibrational features at 1184, 1259 and 1578 cm^{-1} whose linewidths are determined by the S_2 electronic lifetime are observed at early times after photoexcitation at 397 nm. Kinetic analysis of the integrated Raman intensities as well as the transient absorption reveals an exponential decay of the S_2 state on the order of 100 fs. These results demonstrate the ability of FSRS to study the vibrational structure of excited state and chemical reaction dynamics on the femtosecond timescale.

© 2003 Elsevier B.V. All rights reserved.

1. Introduction

Time-resolved vibrational spectroscopy is a powerful tool for monitoring ultrafast structural and reactive dynamics in chemical and biological systems [1]. In contrast to electronic spectroscopy, vibrational spectroscopic techniques reveal time-resolved structural information about reacting molecular species [2]. The most prominent time-resolved ultrafast vibrational techniques include

direct IR-probing and picosecond resonance Raman spectroscopy. While the former has entered the femtosecond time domain [3,4] it is usually limited to a narrow ($\sim 200 \text{ cm}^{-1}$) preselected spectral region. Spontaneous Raman on the other hand can generate full vibrational spectra but suffers from the pulse duration/bandwidth transform limit which requires pulse durations greater than 600 fs to achieve acceptable spectral resolution [5–7]. As a consequence, only limited experimental data are available to date concerning the vibrational structure and thus the nature of potential energy surfaces of very short lived ($< 500 \text{ fs}$) excited electronic states. To circumvent these

* Corresponding author. Fax: +1-510-642-3599.

E-mail address: rich@zinc.cchem.berkeley.edu (R.A. Mathies).

intrinsic limitations, we [8,9] and others [10,11] have recently developed the technique of femto-second stimulated Raman spectroscopy (FSRS), which enables the capture of full Raman spectra with spectral resolution far exceeding the traditional transform limit.

Stimulated Raman scattering occurs any time two coherent optical fields (provided by a Raman pump, ω_p and Raman probe, ω_s) are incident on a sample that contains a molecular vibration of frequency $\omega_v = \omega_p - \omega_s$ (Fig. 1a). Stokes Raman transitions cause net attenuation in the pump and

net gain in the probe beam. In our experimental setup, the Raman pump consists of a narrow-bandwidth ($\sim 17\text{ cm}^{-1}$, $\sim 800\text{ fs}$) pulse while the Raman probe is provided by a 50-fs, broadband pulse to the red of the Raman pump, generating a continuous Stokes field for the simultaneous probing of vibrational frequencies from 600 to 2100 cm^{-1} . The spectral shapes of the two pulses are depicted in Fig. 1b where the Raman probe continuum is presented in both absence and presence of the Raman pump. Only when both optical fields are present does stimulated Raman scattering occur giving rise to the sharp gain features in the probe beam that report on the vibrational structure. The spectral resolution of this process is limited by the convolution of the Raman pump bandwidth, the inherent Raman linewidth and the resolution of the spectrographic system and is typically 25 cm^{-1} . We have recently shown that FSRS can be effectively used to study sub-pico-second vibrational relaxation dynamics in β -carotene [8] and that the intrinsic insensitivity of FSRS to fluorescence interference makes it a valuable analytical technique [9].

To study the time-resolved vibrational structure and dynamics of excited states with FSRS, we add a femtosecond actinic pump pulse and then vary the time-delay of the actinic pump relative to the Raman probe (Fig. 1c). The time-resolution of the experiment is thus only limited by the cross-correlation of these two femtosecond pulses which is in this case on the order of 170 fs. Simultaneous 25-cm^{-1} spectral and 170-fs temporal resolution represents a significant technical advancement in time-resolved vibrational spectroscopy.

We show here that FSRS can be used to study the vibrational spectra and dynamics of the S_2 excited state of diphenyloctatetraene (DPO). Diphenylpolyenes have been studied extensively in the past [12–14] because of the similarity of their electronic structure to biologically important chromophores such as β -carotene and retinal. A simplified energy level diagram is given in Fig. 1a depicting the two low lying excited electronic states, S_2 ($1B_u$) and S_1 ($2A_g$) of DPO. The very fast 100-fs decay time of S_2 places the observation of its vibrational structure beyond the scope of conventional time-resolved spontaneous Raman

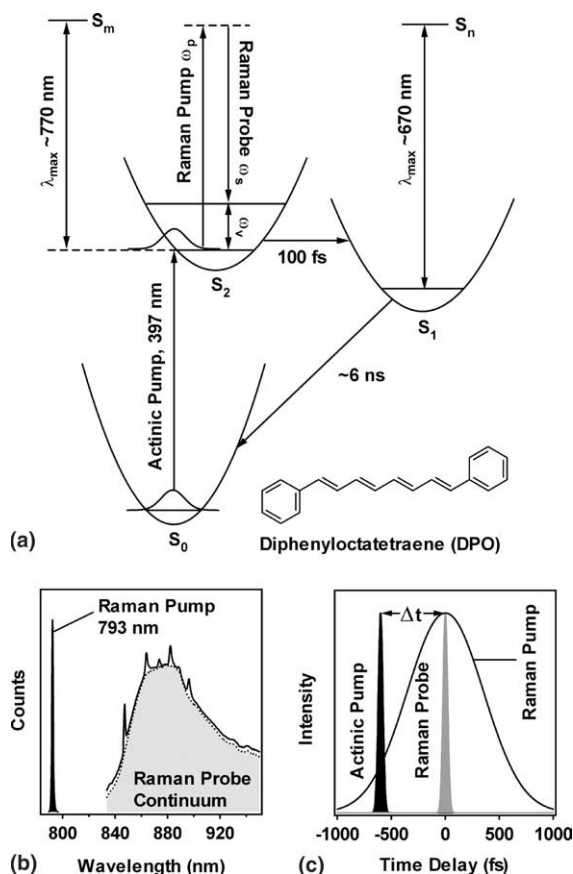


Fig. 1. (a) Energy level diagram for DPO including the pump and probe pulses used to perform femtosecond stimulated Raman spectroscopy (FSRS). After excitation by the actinic pump, the vibrational spectrum of S_2 is probed by the narrow bandwidth Raman pump and the Raman probe continuum pair. (b) Raman pump and probe spectra for a typical FSRS measurement on cyclohexane with clearly visible Raman features in the Raman-pump-on spectrum (solid). (c) Schematic representation of the pulse durations and timing employed.

spectroscopy. However, by use of FSRS we can observe very clear Raman features whose 100-fs decay demonstrates that they are due to the S_2 excited state. These results are the first reported Raman spectra whose resolution is determined by the electronic lifetime of the studied species rather than the resolution of the spectrographic laser system.

2. Experimental

DPO (1,8-diphenyl-1,3,5,7-octatetraene, Aldrich) was recrystallized from benzene. A 0.4 mM solution of DPO in carbon tetrachloride (10 mL) was recirculated through a 0.5 mm path length cell at a rate sufficient to replenish the illuminated volume between shots. The concentration of the sample was chosen to give an OD of 1 per 0.5 mm at the 397 nm actinic pump wavelength.

The apparatus and method used to perform FSRS has been described by McCamant et al. [8]. A Ti:sapphire oscillator seeds a regenerative amplifier to produce 45 fs, 800 μ J pulses (1 kHz) centered at 795 nm with a 23 nm FWHM. The Raman pump (\sim 800 fs, 17 cm^{-1}) is produced by passing 80% of the amplifier output through two narrow band-pass interference filters. The actinic pump (\sim 50 fs, 397 nm) is generated by doubling a fraction of the amplifier output in a 1 mm BBO crystal. Focusing the remaining amplifier output into a 3 mm thick sapphire plate generates the Raman probe continuum. Raman pump and Raman probe pulses are temporally centered on one another while the delay of the actinic pump relative to the Raman probe is varied by means of a computer controlled translation stage. The instrument response is \sim 170 fs as measured by optical Kerr effect cross-correlation (OKE-XC) of the Raman probe with the actinic pump [15] with less than 5 fs chirp in the continuum.

The Raman pump power (30 nJ/pulse) is chosen to minimize depletion of the S_2 population while maintaining an acceptable signal-to-noise ratio. The actinic pump power is set at 30 nJ/pulse to eliminate possible artifacts due to higher electronically excited states while generating sufficient excited state population. A broadband beam splitter

is used to separate the continuum into probe and reference pulses and simultaneously make the three beams collinear before they are focused onto the sample. The beam diameters at the sample point are \sim 50 μ m for the actinic pump and Raman probe beams and \sim 100 μ m for the Raman pump beam. The probe is separated from the other pulses after the sample by two colored glass filters and then focused alongside the reference onto the slit of a spectrograph (Roper Scientific, DPDA-1024). Both probe and reference are dispersed and imaged onto a dual-diode array detector producing spectra as shown in Fig. 1b. Baseline oscillations due to cross-phase modulation [16] caused by the high power Raman pump were removed by vibrating the Raman pump retroreflector during data acquisition by a small motor at a frequency of \sim 110 Hz. Electronic shutters are used both to record Raman-pump-on and -off spectra in sequential exposures as well as to limit the exposure time of the detector to 100 ms to avoid saturation. All spectra consist of an average of 400 such exposures giving rise to acquisition times of 90 s per time point unless otherwise stated.

Spectra are calculated by first subtracting the dark background and then normalizing by the reference spectrum to compensate for any instabilities in the continuum. The Raman gain is then determined as

Raman gain

$$= \frac{[(\text{probe} - \text{bkgnd}) \div (\text{ref} - \text{bkgnd})]_{\text{RamanPumpOn}}}{[(\text{probe} - \text{bkgnd}) \div (\text{ref} - \text{bkgnd})]_{\text{RamanPumpOff}}}.$$

A spline fit was used to remove baseline features in the Raman gain spectrum caused by the near-infrared absorption band of DPO's S_2 state. This baseline subtraction is the major contributor to the error limits given in the kinetic fits. Transient transmission spectra are conveniently calculated from the attenuation of the probe spectrum in the actinic-pump-on/Raman-pump-off data in a similar fashion to the Raman gain.

3. Results and discussion

Time-resolved femtosecond stimulated Raman spectra of DPO in carbon tetrachloride are

presented in Fig. 2. The S_2 spectrum in Fig. 2a ($\Delta t = +100$ fs) was obtained using identical Raman and actinic pump powers of 30 nJ/pulse. At such low pump powers no features can be observed for time delays >500 fs due to S_1 or the ground state, which both lack resonance enhancement at the 793 nm Raman pump wavelength. The 2–30 ps S_1 spectrum is an average of

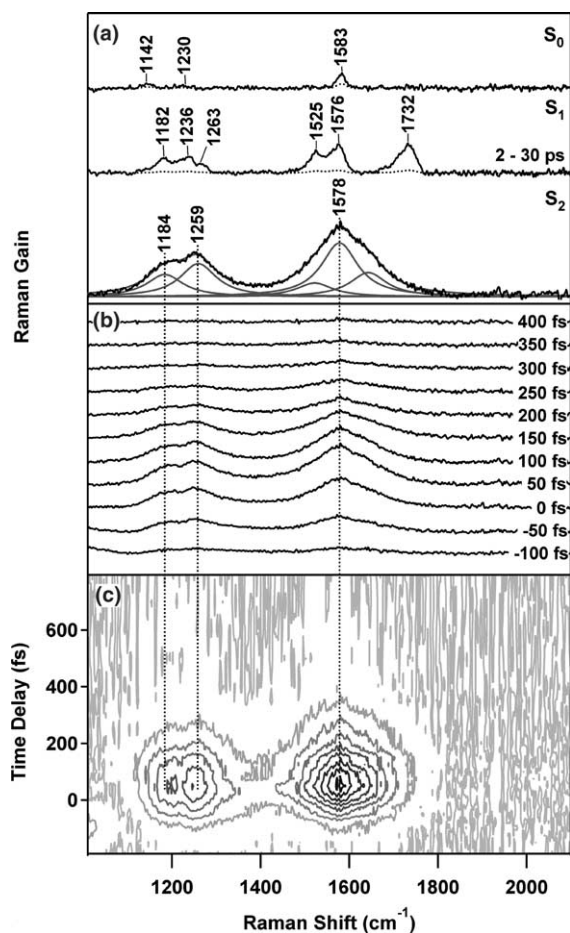


Fig. 2. (a) Selected FSRS spectra of DPO's three lowest lying electronic states (S_2 , S_1 , S_0) in carbon tetrachloride. The solvent spectrum and baselines have been subtracted and the spectra vertically offset for clarity. Included in grey is a decomposition of the 100-fs spectrum into 5 peaks. The FWHM for all features were fixed to the lifetime limit (~ 105 cm^{-1}) while their position was allowed to vary resulting in peaks centered at 1184, 1259, 1522, 1578 and 1643 cm^{-1} . (b) Temporal evolution of the vibrational structure of S_2 from -100 to 400 fs in 50 fs steps. (c) Contour plot of S_2 spectra from -200 fs to $+800$ fs.

six spectra (100 exposures each) at time delays between 2 and 30 ps, during which time no spectral changes were observed, with the actinic and Raman pump increased to 100 nJ/pulse. This spectrum can be confidently assigned to the first excited state of DPO (S_1) due to Raman features growing in at times >300 fs and persisting for long times (>30 ps) as would be expected for S_1 [17] and the similarity of the observed Raman shifts due to C–C stretching vibrations (1200 cm^{-1} region) and C=C stretching vibrations (1500 – 1700 cm^{-1} region) with those routinely observed in polyenes [18]. Scaling this spectrum to the lower pump powers used in the S_2 experiment yields the dotted S_1 spectrum, which would not be observable within the baseline noise of the S_2 spectra. The ground state spectrum is an average of four sets of 100 exposures with the actinic pump blocked and the Raman pump set at 100 nJ/pulse. The dotted spectrum represents the signal intensity expected at the 30 nJ/pulse Raman pump power of the S_2 experiment.

Strong, novel and very intense vibrational features are observed at 1184, 1259 and 1578 cm^{-1} within the first 300 fs after photoexcitation of DPO. The resonance enhancement of these Raman transitions in combination with their decay on the order of 100 fs strongly suggests that they are due to the S_2 state of DPO. These features are attributed to a pair of C–C stretching modes at 1184 and 1259 cm^{-1} and a C=C stretching mode at 1578 cm^{-1} . The lack of any changes in shape or position, e.g., due to vibrational cooling is dramatically demonstrated in the contour diagram presented in Fig. 2c. The constancy of the spectral shape is not surprising since the actinic pump has been chosen to coincide with the 0–0 transition of DPO at 397 nm. The 300-cm^{-1} bandwidth of the 50-fs excitation pulse provides insufficient excess energy to excite high frequency vibrational modes in the excited state.

A kinetic analysis of the temporal evolution of the S_2 absorption and its vibrational features during the first picosecond after photoexcitation is presented in Fig. 3. The vibrational peak kinetics are calculated using the integrated area under the 1200- and 1578- cm^{-1} bands. The data are fit to a convolution of the instrument response as mea-

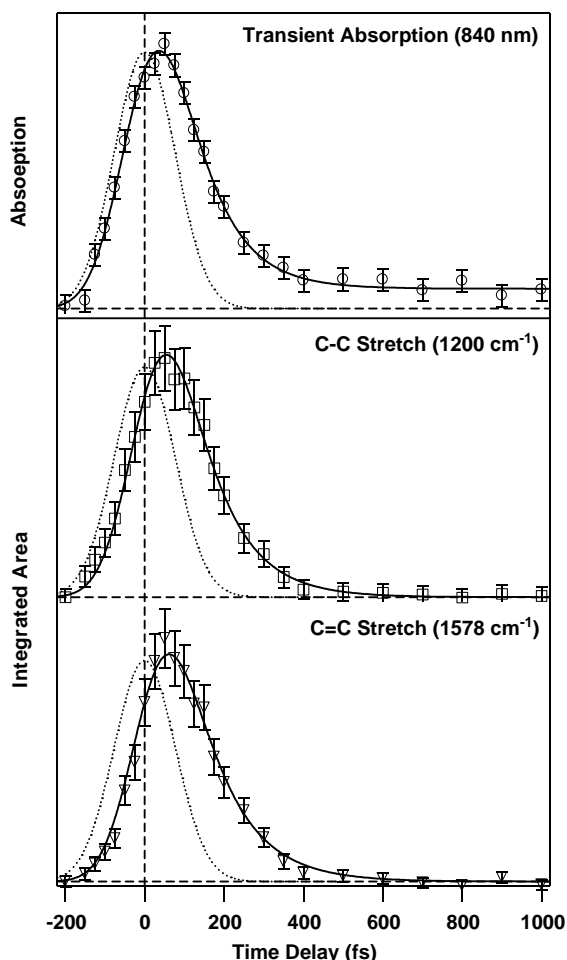


Fig. 3. Transient absorption kinetics (\circ) of DPO's S_2 state and the kinetic evolution of the integrated area of the C–C stretching region at 1200 cm^{-1} (\square) as well as the C=C stretching region at 1578 cm^{-1} (∇) from -200 to 1000 fs. All fits are a convolution of the 170 -fs instrument response (dotted line) and an exponential lifetime resulting in three similar decay times: 102 ± 15 fs (transient absorption), 102 ± 25 fs (1200 cm^{-1}) and 108 ± 25 fs (1578 cm^{-1}).

sured by OKE-XC (dotted line, 170 fs) and an exponential lifetime. The three fits give similar decay times of 102 ± 5 fs (transient absorption, \circ), 102 ± 3 fs (C–C stretch: 1200 cm^{-1} , \square) and 108 ± 4 fs (C=C stretch: 1578 cm^{-1} , ∇) supporting our proposal that the peaks observed during the first 500 fs are due to S_2 . The stated error limits are those due to statistical fitting errors only. Results from a series of experiments suggest that system-

atic variations in the baseline fitting process can cause these exponential lifetimes to vary by as much as 25 fs. Since no baseline has to be fit to the data in order to obtain transient absorption spectra, the error limits for the transient absorption kinetics are smaller (~ 15 fs). An additional long time constant was included in the fit of the transient absorption to account for the small S_1 absorption at long times.

The S_2 electronic lifetime determined in these experiments is significantly shorter than previously reported results [19–21]; this difference is most likely due to the poorer time resolution of the earlier experiments (>400 fs). There was no detectable delay in the onset of the transient absorption and the Raman peaks indicating a lack of delay between the creation of S_2 and the appearance of Raman features due to that state. The transient absorption kinetics (shown only for 840 nm) are consistent throughout the entire observation window from 830 to 960 nm.

The width of all vibrational features in the S_2 spectra is expected to be determined by the lifetime of the two participating quantum states in the Stokes transition, e.g., $v = 0$ and $v = 1$ of S_2 . Assuming that both the pure vibrational dephasing and the vibrational lifetime are much longer than the S_2 electronic state lifetime, we can calculate the expected lifetime broadening to be 105 cm^{-1} for the $v = 1 \leftarrow 0$ transition in S_2 [22,23]. In Fig. 2a we have included a possible decomposition of the S_2 Raman spectrum into such features for the $\Delta t = +100$ fs spectrum. In order to obtain satisfactory fits throughout the observation period, it is necessary to include a total of five peaks at 1191 ± 5 , 1265 ± 4 , 1511 ± 8 , 1577 ± 3 and $1650 \pm 6\text{ cm}^{-1}$, each with a fixed 105 cm^{-1} FWHM. The temporal evolution of the integrated peak areas for all five features agree quantitatively with the 100 -fs exponential lifetime determined by kinetic analysis of the transient absorption due to S_2 .

4. Conclusion

Femtosecond stimulated Raman spectroscopy has been used to observe the vibrational structure of the short lived S_2 ($1B_u$) excited state of

diphenyloctatetraene (DPO). To our knowledge this represents the highest time-resolution vibrational spectrum ever obtained by any method. Three strong Raman features are observed at 1184, 1259 and 1578 cm^{-1} within the first 300 fs after initiation of the photophysics. The temporal evolution of these features shows excellent agreement with the kinetics of S_2 as determined by transient absorption. The unique combination of 170-fs temporal and 25- cm^{-1} spectral resolution provided by FSRS marks these as the first Raman experiments whose *vibrational* spectral resolution is dominated by the 100-fs *electronic* lifetime of the observed species. The independence of temporal and spectral resolution intrinsic to FSRS in combination with its inherent insensitivity to fluorescence will make it an invaluable tool in studying vibrational spectra and reaction dynamics in ultrafast photochemical and photophysical processes.

Acknowledgements

We thank Soo Y. Lee for helpful discussions. PD thanks Atom Yee for helpful discussions and financial support. This work was supported by a grant from the National Science Foundation (CHE-9801651) and by the Mathies Royalty fund.

References

- [1] M.D. Fayer (Ed.), *Ultrafast Infrared and Raman Spectroscopy*, Marcel Dekker, New York, 2001.
- [2] S.E.J. Bell, *Analyst* 121 (1996) 107R (references therein).
- [3] I.V. Rubtsov, T.Q. Zhang, H. Nakajima, S. Aono, G.I. Rubtsov, S. Kumazaki, K. Yoshihara, *J. Am. Chem. Soc.* 123 (2001) 10056.
- [4] R. Diller, S. Maiti, G.C. Walker, B.R. Cowen, R. Pippenger, R.A. Bogomolni, R.M. Hochstrasser, *Chem. Phys. Lett.* 241 (1995) 109.
- [5] S.C. Hayes, C.L. Thomsen, P.J. Reid, *J. Chem. Phys.* 115 (2001) 11228.
- [6] D.W. McCamant, J.E. Kim, R.A. Mathies, *J. Phys. Chem. A* 106 (2002) 6030.
- [7] L. Song, M.A. El-Sayed, *J. Am. Chem. Soc.* 120 (1998) 8889.
- [8] D.W. McCamant, P. Kukura, R.A. Mathies, *J. Phys. Chem. A* 107 (2003) 8208.
- [9] D.W. McCamant, P. Kukura, R.A. Mathies, *Appl. Spectrosc.* 57 (2003) 1317.
- [10] M. Yoshizawa, Y. Hattori, T. Kobayashi, *Phys. Rev. B* 49 (1994) 13259.
- [11] M. Yoshizawa, H. Aoki, H. Hashimoto, *Bull. Chem. Soc. Jpn.* 75 (2002) 949.
- [12] M.T. Allen, D.G. Whitten, *Chem. Rev.* 89 (1989) 1691.
- [13] D.H. Waldeck, *Chem. Rev.* 91 (1991) 415.
- [14] B.S. Hudson, B.E. Kohler, K. Schulten, in: E.C. Lim (Ed.), *Excited States*, Academic Press, New York, 1982, p. 1.
- [15] S. Yamaguchi, H.O. Hamaguchi, *Appl. Spectrosc.* 49 (1995) 1513.
- [16] C. Hirlimann, in: C. Rulliere (Ed.), *Femtosecond Laser Pulses*, Springer, Berlin, Heidelberg, 1998, p. 47.
- [17] I.B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press, New York, 1971.
- [18] W.J. Buma, F. Zerbetto, *Chem. Phys. Lett.* 289 (1998) 118.
- [19] W.A. Yee, R.H. O'Neil, J.W. Lewis, J.Z. Zhang, D.S. Kliger, *J. Phys. Chem. A* 103 (1999) 2388.
- [20] Y. Hirata, K. Mashima, H. Fukumoto, K. Tani, T. Okada, *Chem. Phys. Lett.* 308 (1999) 176.
- [21] W.A. Yee, R.H. O'Neil, J.W. Lewis, J.Z. Zhang, D.S. Kliger, *Chem. Phys. Lett.* 276 (1997) 430.
- [22] J.M. Jean, G.R. Fleming, *J. Chem. Phys.* 103 (1995) 2092.
- [23] W.S. Struve, *Fundamentals of Molecular Spectroscopy*, Wiley, New York, 1989.