Time-Resolved Impulsive Stimulated Raman Studies of 1,1′-Binaphthyl in the Excited State: Low-Frequency Vibrations and Conformational Relaxation

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The conformational relaxation of excited-state 1,1′-binaphthyl in solution was investigated by using femtosecond time-resolved absorption and time-resolved time-domain Raman spectroscopy. Femtosecond time-resolved absorption measurements confirmed that the first transient (the "unrelaxed" S_1 state) is generated in a subpicosecond time scale after photoexcitation and that it undergoes a relaxation with a time constant of 16 ps (in cyclohexane) to form the second transient (the "relaxed" S_1 state). Time-domain Raman experiments provided low-frequency Raman data of the relaxed S_1 state for the frequency region of 0−400 cm^{-1}. The obtained Raman data of the relaxed S_1 state were significantly different from the low-frequency S_0 spectrum in solution. The relaxed S_1 spectrum resembles the spectrum of the crystalline form that has a dihedral angle of 69°, whereas the S_0 Raman spectrum in solution coincides well with that of the crystalline form having a dihedral angle of 103°. The time-domain Raman measurements provided vibrational data that support a conformational change occurring in 1,1′-binaphthyl in the S_1 state.

1. Introduction

Molecules consisting of two aromatic rings connected by a C−C single bond are model compounds for the study of a conformational relaxation because the arrangement of the two aromatic rings is sensitive to the perturbation from surrounding environments. 1,1′-Binaphthyl is one of the molecules having such a structure (Figure 1). This molecule consists of two naphthyl rings linked by a C−C single bond, and its conformation (dihedral angle between the two naphthyl rings θ) has been studied under various conditions for the ground and excited states. Friedel et al. noted that the absorption spectrum of 1,1′-binaphthyl is similar to that of naphthalene[1] and pointed out that the π-conjugation between the two naphthyl rings is weak in the S_0 state. They concluded that the dihedral angle of S_0 1,1′-binaphthyl is nearly 90° in solution. The conformation in the excited state has been argued on the basis of the fluorescence properties. Fluorescence of 1,1′-binaphthyl in solution at room temperature shows a large Stokes shift with respect to its absorption, indicating that a structural relaxation takes place in the excited state. The Stokes shift becomes small in low-temperature glasses, which implies that the structural relaxation involves a large motion such as the change of the dihedral angle.[2] The dynamics of the conformational change taking place in the excited state was investigated by time-resolved spectroscopy. It was reported that the transient absorption due to the lowest excited singlet (S_1) state in solution showed a biexponential rise with time constants of a few picoseconds and a few tens of picoseconds.[3] The faster rise time was independent of the solvent, whereas the slower rise time varied from 11 to 41 ps, depending on the solvent viscosity.[4,5] The slower rise time has been assigned to the relaxation time to the equilibrated conformation in the S_1 state.

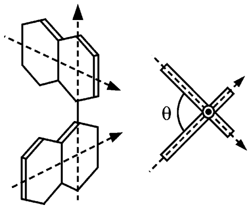

Figure 1. Molecular structure of 1,1′-binaphthyl. The dihedral angle between naphthyl rings θ is indicated.

Vibrational spectra contain much information about the molecular structure, and therefore time-resolved Raman spectroscopy has been widely used for the study of the structure of short-lived transients. In particular, time-resolved Raman spectra in the low-frequency region are expected to provide unique information about the relaxation process of 1,1′-binaphthyl since low-frequency vibrational spectra are often sensitive to the large amplitude conformational change. However, the observation of low-frequency Raman spectra of the excited states are generally difficult because of disturbance of strong Rayleigh scattering. Recently, we reported time-resolved impulsive stimulated Raman scattering (TR-ISRS) measurements of excited-state polyatomic molecules for the first time and demonstrated that time-resolved "time-domain" Raman spectroscopy can be an alternative method for obtaining Raman spectra of the excited state.[6] Experiments based on a similar concept but using a different optical process was reported also by Cerullo et al. very recently.[7] TR-ISRS spectroscopy has a high potential, especially for the measurements of transient Raman spectra in the low-frequency region. Therefore, it is highly desirable to apply TR-ISRS spectroscopy to 1,1′-binaphthyl to obtain new information about the relaxation process in the excited state.

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In this paper, we report our TR-ISRS study of 1,1′-binaphthyl in solution. We measured Raman spectra of the "relaxed" S_1 state in the range of 0−400 cm^{-1} in the time domain. Referring to the low-frequency Raman data of the ground state in the crystalline phase, we discuss the conformational change of 1,1′-binaphthyl in the excited state from the viewpoint of vibrational spectroscopy.

2. Experimental Section

The experimental setup and principle of the TR-ISRS measurements have been described in detail previously.[6] The setup was based on a femtosecond Ti:sapphire regenerative amplifier system (Clark-MXR, CPA-1000) that was operated at 1 kHz. The amplified pulse having a 100-fs duration was divided into two parts. One portion was converted to the third harmonic (267 nm, 550 fs) by using 1.0-mm-thick LiB_3O_5 and 0.5-mm-thick β-BaB_2O_4 crystals. The generated ultraviolet pulse was used as a pump pulse and focused into a 300-μm-thick filmlike jet stream of the sample solution. At the sample position, the energy of the pump pulse was 4 μJ, and its spot diameter was ∼300 μm. The other portion was converted to a near-infrared pulse (1340 nm) in an optical parametric amplifier (Quantronix, TOPAS) and then frequency doubled in a 0.5-mm-thick β-BaB_2O_4 crystal. The generated visible pulse was compressed in time by using a prism pair, and it was used for TR-ISRS measurements. The compressed visible pulse (670 nm, 39 fs) was divided into three by beam splitters in the present experiment, although we used a phase mask[8,9] in the previous work.[6] The visible pulses were focused into the photoexicted portion of the sample jet with a standard BOXCARS geometry. The first and second pulses (P_1 and P_2) were simultaneously introduced to generate a transient grating after a delay time (ΔT) with respect to the pump pulse. The third pulse (P_3) was irradiated after a delay time (t_d) with respect to the P_1 and P_2 pulses to monitor the amplitude of the transient grating in the sample. The TR-ISRS signal scattered into the phase-matched direction was detected by a photodiode (Hamamatsu Photonics, S1337−1010BQ), and its output was processed on a shot-to-shot basis by using a boxcar integrator (Stanford Research Systems). At the sample position, the energies of the P_1, P_2, and P_3 pulses were 0.6 μJ, 0.6 μJ, and 0.2 μJ, respectively, and their spot diameter was ∼200 μm. Polarizations of the three probe pulses (P_1, P_2, and P_3) were set parallel with one another. The pump polarization was set at the magic angle (54.7°) with respect to the probe polarization.

Subpicosecond time-resolved absorption measurements were carried out using a setup reported previously.[10] The light source was the same regenerative amplifier system as used for the TR-ISRS measurements, but the system was operated with a 100 Hz repetition rate. The third harmonic of the amplified pulse was used as a pump pulse (550 fs, 5 μJ) to photoexcite the sample. A white-light continuum pulse generated in D_2O was divided into two, and they were used as a probe and a reference pulse. Spectra of the probe and reference pulses were simultaneously measured by a CCD detector that was synchronized with the laser pulse. The measurements with the magic-angle condition (54.7°) were achieved by rotating the pump polarization with respect to the probe polarization. Kerr gate signals of the solvent (cyclohexane) were also measured to correct the effect of the group velocity dispersion of the probe light on the time-resolved absorption spectra.

Raman spectra were recorded by a commercial Raman spectrometer (LABRAM 1B, Dior) using the 514.5-nm line of a CW argon ion laser. The frequency resolution of the Raman measurements was 2.5 cm^{-1}.

1,1′-Binaphthyl was purchased from Tokyo Kasei and used as received. Liquid-chromatography grade cyclohexane and chloroform were received from Wako Pure Chemical Industries, and they were used without further purification. The concentration of the sample solution was 5.5×10^{-3} mol dm^{-3} for the TR-ISRS as well as time-resolved absorption measurements. All the measurements were carried out at room temperature. Crystalline 1,1′-binaphthyl was prepared according to the reported procedures.[11,12] In the crystalline state, 1,1′-binaphthyl exists in two forms. One form that has a dihedral angle of 68.9° ("69°-form") was obtained by slowly cooling a saturated hexane solution of 1,1′-binaphthyl. Another form having a dihedral angle of 103.1° ("103°-form") was prepared by a rapid crystallization in hexane. The 103°-form crystal was dried in vacuo and subsequently heated at 150 °C for 4 h in N_2-atmosphere. This treatment ensured that residual 69°-form crystals were converted to the 103°-form.[11] The melting points of the obtained crystals (148 °C for the 69°-form, 161 °C for 103°-form) agreed with the reported values.[11]

3. Results and Discussion

3−1. Time-Resolved Absorption Measurements and Kinetics. The ultrafast relaxation kinetics of 1,1′-binaphthyl has been discussed on the basis of picosecond time-resolved absorption data measured at one probe wavelength.[3−5] To clarify the overall behavior of transient absorption, we first measured time-resolved absorption spectra with a subpicosecond time-resolution. Figure 2a shows transient absorption spectra of 1,1′-binaphthyl measured in cyclohexane with 267-nm excitation. Just after photoexcitation, a weak structureless absorption appears. Then, the transient absorption intensity increases and shows two broad peaks around 480 and 630 nm. The double-peaked spectrum shows no significant change after the delay time of 30 ps. The spectrum after the initial change agrees very well with that reported in a nanosecond absorption study.[13] Figure 2b shows the temporal behavior of the transient absorption at 630 nm. The transient absorption was well fitted with a biexponential function convoluted with the instrumental response. The fit indicates that the transient absorption shows an instrumental-limited "instantaneous" rise (the fast rise) and a subsequent slow rise having a time constant τ_{relax} of 16 ps (the slow rise). The fast rise corresponds to the appearance of the weak structureless absorption band observed immediately after photoexcitation. The slow rise corresponds to the spectral change from this initial absorption to the absorption that shows two peaks around 480 and 630 nm. This temporal behavior is basically the same as that reported in a previous study performed with pump at 308 nm and probe at 615 nm[3]. However, the time constant of the fast rise, which was claimed to be 2.5 ps in the previous study, was not resolved in our measurements although the time resolution was high enough. At least with excitation at 267 nm, the transient absorption appeared with a time constant much shorter than 2.5 ps (<0.5 ps).

Figure 3a illustrates the observed kinetics of excited-state 1,1′-binaphthyl in cyclohexane. Our time-resolved spectral measurements clarified that the overall spectral feature significantly changes in the first tens of picoseconds. The observed large spectral change confirmed the existence of two distinct transient species. Moreover, the relaxation time (τ_{relax} = 16 ps) of the first transient is apparently longer than a typical lifetime of highly excited states of aromatic compounds (<1 ps),[14−16] indicating that the first transient is the S_1 state. Since the second transient is also assignable to the S_1 state of binaphthyl from the fluorescence spectrum[2] and lifetime,[13] the spectral change

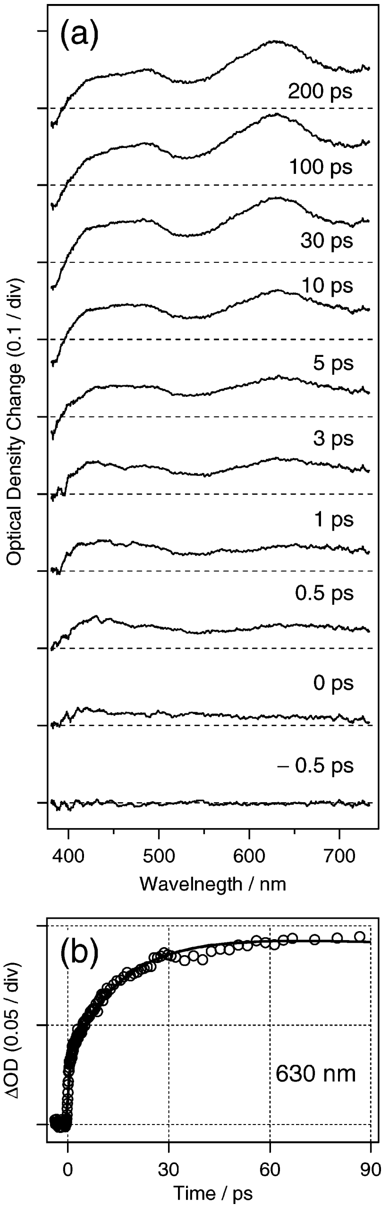

Figure 2. (a) Time-resolved absorption spectra of 1,1′-binaphthyl in cyclohexane (5×10^{-3} mol dm^{-3}) in the range from −0.5 to 200 ps after 267-nm excitation. The time delays are shown on the right. (b) Temporal change of the transient absorption signal probed at 630 nm.

of transient absorption is safely ascribable to the relaxation process from the "unrelaxed" S_1 state to the "relaxed" S_1 state. This process has been attributed to the conformational relaxation around the dihedral angle on the basis of the solvent viscosity dependence of the τ_{relax}.[4,5] To obtain further evidence from the viewpoint of vibrational spectroscopy, we carried out TR-ISRS measurements for the relaxed S_1 state.

3−2. TR-ISRS Measurements and Low-Frequency Raman Data. The schematic diagram of the TR-ISRS measurement is shown in Figure 3b. In the present measurement, we set the delay time between the pump and probe pulses (ΔT) at either −200 or 200 ps. Since the spectral evolution of transient absorption is completely finished at 200 ps, we expect to observe ISRS signal of the relaxed S_1 state in the measurement at ΔT = 200 ps. To obtain a resonance enhancement, we tuned the probe wavelength to 670 nm. The TR-ISRS signals were measured by scanning the delay time (t_d) between the P_1, P_2 pulses and the P_3 pulse.

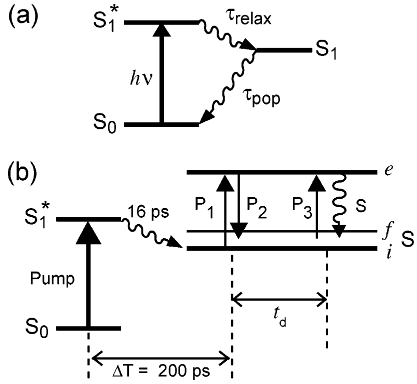

Figure 3. (a) Schematic diagram of the relaxation kinetics of 1,1′-binaphthyl after photoexcitation: S_1* and S_1 denote the unrelaxed and relaxed S_1 states, τ_{relax} is the relaxation time constant from S_1* to S_1, τ_{pop} is the lifetime of relaxed S_1 state. (b) Experimental scheme of the TR-ISRS measurement of the relaxed S_1 binaphthyl.

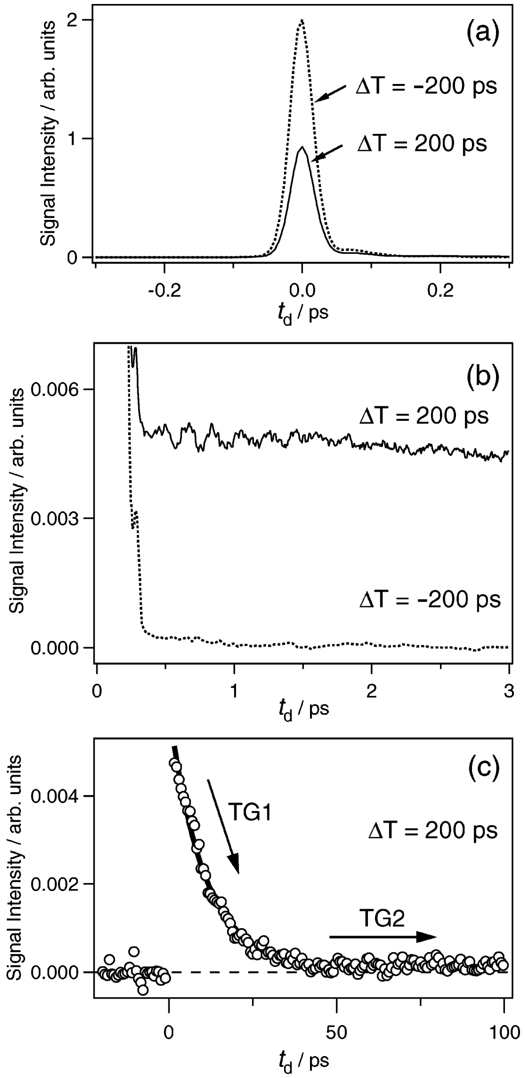

Figure 4. TR-ISRS signals of 1,1′-binaphthyl in cyclohexane at ΔT = +200 ps and −200 ps after photoexcitation (pump 267 nm; probe 670 nm; 5×10^{-3} mol dm^{-3}). (a) −0.3 ∼ 0.3 ps, (b) 0 ∼ 3 ps, and (c) −20 ∼ 100 ps. In a and b, solid curves indicate the signals at ΔT = +200 ps and dotted curves represent the signal at ΔT = −200 ps.

Figure 4a shows the TR-ISRS signals of 1,1′-binaphthyl measured in cyclohexane. Before photoexcitation (ΔT = −200 ps), the signal shows only a spikelike response around the time origin (t_d = 0 ps). The response can be assigned to the electronic

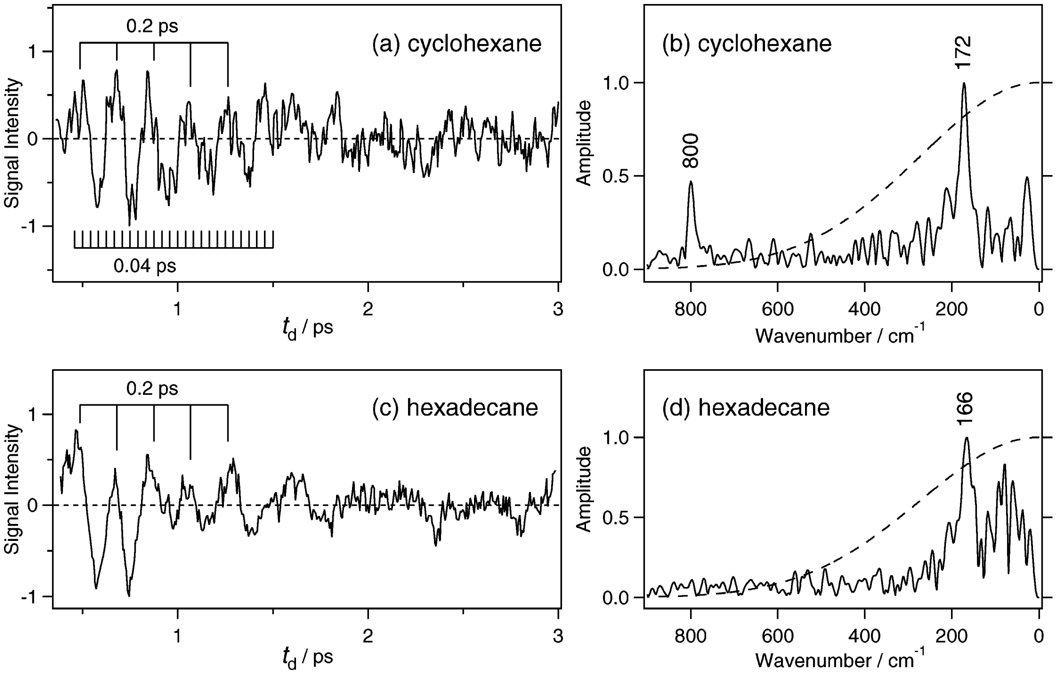

Figure 5. Oscillatory ISRS components of 1,1′-binaphthyl in cyclohexane (a) and hexadecane (c). Fourier amplitude spectra of the oscillatory components in cyclohexane (b) and hexadecane (d). The sensitivity curve in the frequency domain is shown with a broken curve in figure b and d (see note 25).

response of cyclohexane because it is almost identical to the electronic response obtained from pure cyclohexane. The temporal shape of the electronic response has an fwhm of 40 fs, which corresponds to the instrumental response function. Compared with the ISRS signal taken at $\Delta T = -200$ ps, the intensity of the signal measured after photoexcitation ($\Delta T = +200$ ps) was much lower. It arises from the self-absorption effect because of the S_1 transient absorption. In both traces, the electronic response of the solvent dominates the signal, so that the ISRS signal at $\Delta T = +200$ ps and $\Delta T = -200$ ps looks very similar to each other. However, there are significant differences between these two ISRS traces, especially in the region of a few picoseconds. The TR-ISRS signal in the 0−3-ps region is expanded in Figure 4b. In addition to the spikelike feature around the time origin, the signal taken after photoexcitation ($\Delta T = +200$ ps) exhibits an oscillatory feature and a slowly decaying offsetlike component, whereas the signal measured before photoexcitation ($\Delta T = -200$ ps) is almost none after t_d of 0.3 ps.

In our previous TR-ISRS measurement on S_1 *trans*-stilbene,[6] we observed the signal that consists of (1) a spikelike electronic response around the time origin, (2) oscillatory ISRS components, and (3) slowly decaying traditional transient grating (TG) components. The origin of the traditional TG components was the transient absorption change that was induced by the irradiation of the P_1 and P_2 pulses in the probe process. Since the probe wavelength was resonant with the $S_n \leftarrow S_1$ absorption, the P_1 and P_2 pulses excited the S_1 state to the S_n state. Some portion of the generated S_n state was relaxed to the S_1 state to produce the vibrationally hot S_1 state whereas the other was relaxed directly to the S_0 state. Consequently, two components having two different lifetimes appeared in TG signal. One was the TG signal reflecting the vibrational cooling process in the S_1 state (TG1) and the other was the “bleaching grating” (TG2). The signal observed in the present experiment for 1,1′-binaphthyl exhibits corresponding three components, although the relative amplitudes are different from that observed for S_1 *trans*-stilbene. Therefore, the physical origin of these components in the S_1 1,1′-binaphthyl signal are safely considered the same.

To confirm the origin of the slowly decaying TG component, we carried out the measurements for a long-time range up to 100 ps. The obtained signal is shown in Figure 4c. The signal was well fitted by a single-exponential function (TG1) with a small constant (TG2). The time constant of the fitted exponential was ~10 ps, which means that the lifetime of the TG1 component was ~20 ps because the measurement was performed with homodyne detection. We also carried out TR-ISRS measurements of 1,1′-binaphthyl in hexadecane under the same experimental condition. The TG1 lifetime in the hexadecane solution was evaluated as 26 ps. The observed lifetimes agreed fairly well with the vibrational cooling times in both solvents.[17,18] This assured that the TG1 component arises from the transient absorption change that reflects the vibrational cooling process in the relaxed S_1 state.[19] The TG2 component, which is assignable to the bleaching grating, is seen as almost constant in Figure 4c. It is because the lifetime of the relaxed S_1 state is as long as ~4 ns.[13]

In the present measurement, the oscillatory ISRS component was observed with the slowly decaying TG component. In this case, the TG component acts as a local oscillator, and the oscillatory ISRS component is practically heterodyned even if the measurement was carried out with homodyne detection.[6,20,21] Thus, we can directly transform the time-domain oscillation into a vibrational spectrum by Fourier transform analysis.[22,23] To extract the oscillatory component, we first fitted a quadratic polynomial function to the TG component and subtracted it from the raw data. The extracted oscillatory component is shown in Figure 5a. This component exhibits underdamped oscillations with periods of ~0.2 ps and ~0.04 ps. By Fourier transform analysis,[24] we obtained Fourier amplitude spectrum shown in Figure 5b. (In the same figure, we also plotted the “effective sensitivity curve” of the present measurement that was calculated from the instrumental response.[25]) The Fourier transform shows

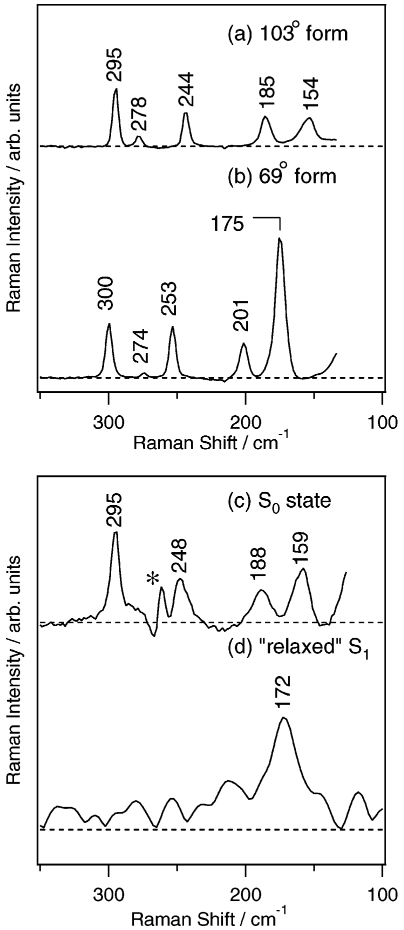

Figure 6. S_0 Raman spectra of 1,1′-binaphthyl crystalline, (a) 103°-form and (b) 69°-form. (c) S_0 Raman spectrum of 1,1′-binaphthyl in $CHCl_3$ at room temperature. The $CHCl_3$ bands were already subtracted from the spectrum, and the artifact generated by the subtraction procedure is marked by an asterisk. (d) Fourier amplitude spectrum of the TR-ISRS signal of the relaxed S_1 state.

two peaks at 172 and 800 cm^{-1}, which correspond to the oscillatory components having periods of ~0.2 ps and ~0.04 ps, respectively. The band at 800 cm^{-1}, which appears at the edge of the sensitivity, is safely assigned to solvent (cyclohexane) because its frequency (800 cm^{-1}) is in excellent agreement with the frequency of a strong Raman band of pure cyclohexane (801 cm^{-1}, a_{1g}).[26] The band at 172 cm^{-1}, on the other hand, is attributed to a Raman active vibration of the relaxed S_1 state that was generated by photoexcitation.

To confirm this assignment, we carried out TR-ISRS experiments also in a hexadecane solution. Figure 5c and d shows the oscillatory component of the relaxed S_1 state in hexadecane (c) and the Fourier amplitude spectrum of the observed oscillation (d). A Raman band appears at 166 cm^{-1}, which corresponds to the 172 cm^{-1} band observed in the cyclohexane solution. The 800-cm^{-1} band assigned to a cyclohexane band was not observed in the signal obtained from a hexadecane solution.

Vibrational spectra contain much information about the molecular structure. For the S_0 state of 1,1′-binaphthyl, in fact, Raman spectra in the low-frequency region are very sensitive to the dihedral angle between two naphthyl rings (θ). Figure 6a and b shows the spontaneous Raman spectra of two crystalline forms of 1,1′-binaphthyl. X-ray analysis revealed that the most significant difference between the two forms is in the dihedral angle: The dihedral angle θ of one form is 103.1° ("103°-form") while the other is 68.9° ("69°-form").[11,27] As shown in Figure 6a and b, the low-frequency Raman spectra, especially those in the range of 140−210 cm^{-1}, are significantly different between the 103°-form (a) and 69°-form (b). This strongly indicates that the low-frequency Raman band can be a good indicator of the dihedral angle of 1,1′-binaphthyl. Figure 6c shows the Raman spectrum in solution. This spectrum is in excellent agreement with that of the 103°-form (Figure 6a). It manifests that the conformation of S_0 1,1′-binaphthyl in solution is also highly twisted. Lacey and Craven discussed the dihedral angle of the S_0 state in solution on the basis of the intensity ratio of the two Raman bands around 500 cm^{-1}. They concluded that the angle θ is approximately 90°.[12] Our conclusion based on the spectral feature below 250 cm^{-1} is consistent with their conclusion. Very high similarity between the spectra of the solution and the 103°-form seems to indicate that the conformation of the S_0 state in solution is slightly inclined from perpendicular to trans ("slightly trans") although it was argued that the conformation in solution is slightly cis in early literatures (vide infra).[2,3]

The low-frequency Raman data of the relaxed S_1 state obtained by the present TR-ISRS measurement (Figure 6d) is significantly different from the S_0 Raman spectra in solution (Figure 6c). In contrast, the frequency of the Raman band observed for the relaxed S_1 state (172 cm^{-1}) is in good agreement with that of the intense Raman band of the 69°-form at 175 cm^{-1} (Figure 6b). The low-frequency Raman data of the relaxed S_1 state indicate that the dihedral angle of the relaxed S_1 state is significantly different from that of the S_0 state in solution. Since it is natural to consider that the conformation of the S_1 state is initially close to that in the S_0 state after photoexcitation, the present ISRS data support that the conformational relaxation (the change in the dihedral angle) occurs in the S_1 state.

Concerning the detail of the conformational relaxation in the S_1 state, Shank et al. argued that it is a change from the almost perpendicular conformation (slightly cis) to a more coplanar conformation in the cis side ($90° > \theta > 0°$).[3] Post et al. calculated the π electronic SCF energies and showed that the stabilization energy that favors the coplanar conformation is larger in the S_1 state than in the S_0 state, which supports this argument.[28] On the other hand, Hochstrasser concluded that the conformation changes from slightly cis to a more coplanar state in the trans side crossing over the perpendicular configuration, which takes place in the S_1 state.[2] A CNDO/S calculation about the $S_n \leftarrow S_1$ spectral feature reported by Bigelow and Anderson suggested a rotation from cis to trans that has equal or less planarity,[29] being supportive for the latter assignment. In the present study, however, the low-frequency Raman spectrum of the S_0 state in solution resembles that of the 103°- crystalline form whereas the Raman data of the relaxed S_1 state show a similarity to the spectrum of the 69°-form. It seems that the low-frequency Raman data suggest that the conformational change in the S_1 state occurs from slightly trans to slightly cis, crossing over the perpendicular configuration. Obviously, the detail of the conformational change needs further investigation, including high-level theoretical calculations on the excited-state potential. We note that, in the early works, the initial configuration in the S_0 state in solution was assigned on the basis of the X-ray diffraction results for the 69°-form[27,30] which is slightly cis. The other crystalline form having the dihedral angle θ of 103° (103°-form), which is slightly trans, was reported later.[11] Therefore, we consider that even the conformation of the S_0 state in solution is an issue that requires re-examination.

The low-frequency vibrations of the relaxed S_1 state are influenced not only by the change of the dihedral angle θ but also by the electronic excitation. In this sense, it is highly desirable to measure the ISRS data of the unrelaxed S_1 state that exists immediately after photoexcitation and to compare them with the data of the relaxed S_1 state. We have tried to measure ISRS of the unrelaxed S_1 state but we have not succeeded yet so far. Probably, the ISRS signal of the unrelaxed S_1 state is very weak reflecting its weak transient absorption. The transient absorption of the unrelaxed S_1 state is quite flat over the whole visible region. Nevertheless, we might be able to have more chance to observe the ISRS signal of the unrelaxed S_1 state if we can optimize the probe wavelength.

In conclusion, we carried out time-resolved absorption and TR-ISRS measurements for the excited state of 1,1′-binaphthyl in nonpolar solvents. The observed time-resolved absorption spectra confirmed that the S_1 state of 1,1′-binaphthyl shows a 16-ps relaxation process in the S_1 state after photoexcitation. In the TR-ISRS measurements, the oscillatory features due to a Raman active vibration of the relaxed S_1 state was clearly observed. The Fourier transform of the observed TR-ISRS data provides vibrational spectra equivalent to time-resolved Raman spectra in the range of $0-400$ cm^{-1}. The low-frequency Raman data of the relaxed S_1 state is significantly different from that of the S_0 state in solution. The relaxed S_1 spectrum resembles the spectrum of the crystalline form that has a dihedral angle θ of 69°, whereas the low-frequency Raman spectrum of the S_0 state in solution coincides with the spectrum of the crystalline form having a dihedral angle θ of 103°. Therefore, the TR-ISRS data support, or are very consistent with, the argument that the 16-ps relaxation process occurring in the S_1 state after photoexcitation is the conformational relaxation with the change of the dihedral angle between two naphthyl rings.

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(19) We also considered a possibility that the relaxation of the S_n state generates the S_1 state having a different dihedral angle, e.g., the unrelaxed S_1 state. If so, the subsequent conformational relaxation induces a transient absorption change, which may give rise to the TG1 component. However, this is not likely because the lifetime of TG1 component does not significantly change in cyclohexane and hexadecane (~20 ps and ~26 ps), whereas the time constant of the conformational change from the unrelaxed S_1 state to the relaxed S_1 was 41 ps in hexadecane.[5]

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(24) To improve the apparent resolution in the frequency domain, we added zero data points from 3 to 20 ps in the time domain before Fourier transformation.

(25) The observed oscillation can be regarded as a heterodyne signal. In the heterodyne detection, the effective sensitivity in the frequency domain is determined by the intensity autocorrelation of the probe pulse. The width of the intensity autocorrelation (τ_{auto}) can be estimated from that of instrumental response ($\tau_{\mathrm{inst}} = 40$ fs, the homodyne signal of the electronic response), that is, the intensity cross-correlation of the probe pulse and the squared probe pulse. Assuming a Gaussian pulse shape, the width τ_{auto} was calculated as $\tau_{\mathrm{auto}} = (4/3)^{0.5} \times \tau_{\mathrm{inst}} = 46$ fs. Thus, the effective sensitivity was given by the Fourier transform of the calculated autocorrelation function having the fwhm of 46 fs.

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