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# Conformational Change in Azobenzene in Photoisomerization Process Studied with Chirp-Controlled sub-10-fs Pulses

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Negatively and positively chirped pulses were used to selectively excite vibrationally coherent wave packets in the ground and the excited states, respectively, in an azobenzene derivative molecule in solution. Strong dynamic mode coupling between the N═N and C−N stretching modes is observed in real time at ∼1400 and ∼1150 $cm^{-1}$ in the excited state of the molecule, but it is relatively week in the ground state. Instantaneous frequencies of N═N and C−N stretching modes around 1400 and 1150 wavenumbers (corresponding to ∼24 and ∼29 fs vibrational periods, respectively, in both of the states) were found to be modulated on the basis of time-frequency analysis of transmittance-change traces with high time-resolution of a few femtoseconds. In the excited state, the modulation periods of N═N and C−N stretching modes are ∼510 and ∼390 fs, respectively, directly indicating the existence of at least one more mode other than the torsion mode coupled to either or two of these stretching modes during the photoisomerization.

## 1. Introduction

Ultimate understanding of chemical reaction mechanisms is to describe structural change and bond rearrangement in the reacting molecules. Sub-vibration-period pulses can provide the instantaneous vibrational frequency that offers structural information during the chemical reaction by impulsive excitation of molecular vibrarion in the excited or ground state. Ultrafast spectroscopic method using much shorter pulse than the molecular vibration period with a controlled chirp can provide such information. Among various chemical reactions, *trans*−*cis* photoisomerization is one of the most important and widely investigated unimolecular photochemical reactions. It triggers conformational changes in retinoid proteins, such as rhodopsin[1] and bacteriorhodopsin,[2,3] relevant to vision and ATP synthesis, respectively. Azobenzene and its derivatives are known to form a group of molecules showing the *trans-to-cis* or *cis-to-trans* photoisomerization and are studied for the basic understanding of fundamental chemistry. These are also widely investigated for various photonics applications such as optical switches and high-density optical memory storage devices.[4,5] Because azobenzene has lone-pair electrons on the nitrogen atoms, the n−$\pi$* electronic transition is observed in addition to the $\pi$−$\pi$* transition, which may result in a different isomerization mechanism from that of widely investigated stilbene. It has been proposed that the photoisomerization mechanism of *trans*-azobenzene depends on the excitation wavelength.[6,7] Figure 1a shows the schematic of a generally accepted model. According to this model, after $\pi$−$\pi$* excitation, isomerization proceeds with a rotated phenyl ring (Φ) around the N═N double bond in the rotation mechanism. On the other hand, after n-$\pi$* excitation, it takes place in the mechanism of in-plane inversion at one of the two nitrogen atoms maintaining a semilinear configuration. However, there is still an argument about the model.[8,9] The arguments made in the papers of refs 7 and 8 are limited to the discussion made on the basis of the probe time dependence of the electronic transition intensity obtained by pump−probe experiment. It is difficult to obtain information about the structural change of molecules associated with chemical reactions, even though the time dependence of the population of intermediate species can be obtained relatively precisely. On the other hand, in the experiment of time-resolved Raman spectroscopy, vibrational spectra at several decay times were used for the discussion in ref 9. They can be precisely determined, but their population dynamics are difficult to be determined precisely.

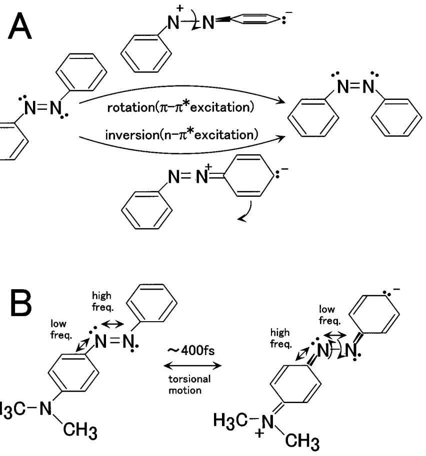

**Figure 1.** (a) Generally accepted model of photoisomerization in azobenzene composed of the rotation and inversion pathways. (b) Dynamic mode-coupling mechanism of DMAAB between the N═N and C−N stretching modes via a torsional mode in the $S_2$($\pi$−$\pi$*) excited state. The structures show those contributing only partially to quantum-mechanical resonance structure corresponding to the intermediate structures. Electronic structures are exaggerated to show the quantum-mechanical resonance configurations.

In this paper, the real-time dynamics of molecular vibration was investigated in the excited state of a derivative of azobenzene, *trans*-DMAAB [methyl yellow; 4-(dimethylamino) azoben-

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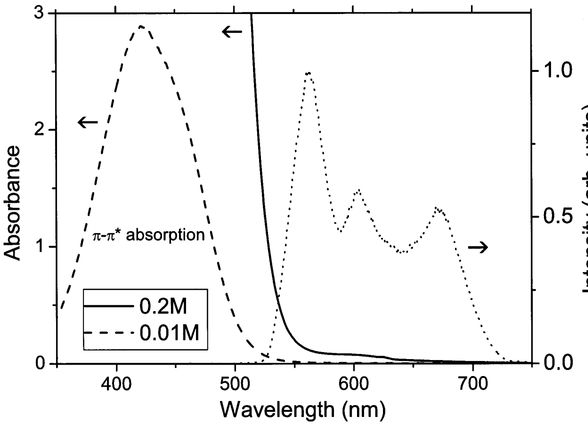

**Figure 2.** Absorption spectra of DMAAB/DMSO at 0.2 (solid curve) and 0.01 (dashed curve) mol dm$^{-3}$ in a 0.1 mm-thick homemade cell with a microscope cover-glass plate (front window) and a slide-glass plate (back window). The spectrum of NOPA (noncollinear optical parametric amplifier) output (dotted curve) used for both pump and probe pulses. The wavelength dependence (double dot dashed curve) of the intensity of light being absorbed by the probe light.

zene], in solution by pump−probe spectroscopy using sub-5-fs visible pulsed laser developed by our group.[10,11] The vibrational frequencies of N=N and C−N stretching modes are found to be modulated quasi-periodically, which can be explained in terms of coupling between the two modes via an ∼80 cm$^{-1}$ (∼400 fs) torsion mode. A small frequency difference between the two modulations was found by a more detailed analysis, leading to the conclusion that the reaction does not proceed by either the pure rotation or pure inversion mechanism (vide infra). This experiment can only be done with the use of the short and stable enough pulsed laser to determine the change in the molecular vibrational period due to the modulations by as small as 5% of the period corresponding to a few femtoseconds.

## 2. Experimental Section

The absorption spectrum of DMAAB solution dissolved in dimethyl sulfoxide (DMSO) has a peak around 420 nm that is assigned to a strongly allowed $\pi-\pi^*$ transition (Figure 2). The substitution of azobenzene by *p*-amino groups shifts $\pi-\pi^*$ band to longer wavelengths.[12] The peak of weak $n-\pi^*$ absorption band centered on 460 nm in azobenzene is known to be relatively insensitive to solvent.[12] Samples of 0.2 mol dm$^{-3}$ concentration was used for the pump−probe experiments. The pulse spectrum has a larger overlap with the second lowest excited state ($S_2$ ($\pi-\pi^*$)) absorption band resulting in the dominant excitation of about 70% of the state with a residual excitation of $S_1$ (n-$\pi^*$).

Output pulses from the pulse-front-matched noncollinear optical parametric amplifier (NOPA)[10,11] with 4.7 fs width and 5 $\mu$J energy at 1 kHz repetition rate were used as both pump and probe pulses. Negatively chirped (NC), positively chirped (PC), and transform-limited (TL) pulses for sample excitation were prepared by changing the insertion amount of a prism pair in the NOPA. For the pulse characterization, second-harmonic generation frequency-resolved optical gating (SHG-FROG) measurement[17,18] was used. The full width at half-maximum-(fwhm) of the NC, PC, and TL pulses are 9.6, 8.4, and 7.4 fs, respectively. The "TL" pulse was broader than 4.7 fs, the fwhm of the pulse just at the output of the NOPA. This is mainly due to smearing effect induced by finite angle of pump and probe pulses (2.5°) and higher order chirp caused by a front cell-wall glass or a thin beam splitter, which separates pump and probe beams. The quadratic phase term $\Phi''(\nu)$ of the NC, PC, and TL pulses were determined from the FROG traces to be −930, 990, and 330 fs$^2$, respectively. The chirp rate to generate a wave packet on the ground state most efficiently by stimulated Raman process is calculated as −1000 fs$^2$ using the potential curves of the ground and excited states. The detailed analysis is to be published elsewhere. Laser pulse energies of the pump and probe pulses are about 20 and 2 nJ, respectively. The pump beam was mechanically chopped at 500 Hz in synchronization with the laser pulse at 1 kHz. The probe pulse intensity was measured with a Si photodiode attached to a monochromator with 4-nm resolution. Change in transmitted probe intensity induced by the pump was detected with a lock-in amplifier. All the measurements were performed at room temperature (298 ± 1 K).

## 3. Results and Discussion

Figure 3a shows the traces of the transient transmittance change [$\Delta T/T$ ($t$)] of DMAAB/DMSO at 570 nm induced by the pump pulse against the pump−probe delay time up to 1.8 ps in the case of PC- and NC-pulse excitations. They show very complicated but clear and reproducible oscillating features in all of the cases.

The positive transmittance change averaged over the several oscillation periods due to the ground-state bleaching does not decay to zero in the measured delay-time range because the decay of the excited state followed by the ground-state thermalization takes place for about 50 ps.[13] The averaged transmittance change ($\Delta T$) over the 50−1800 fs delay-time range was nearly proportional ($\Delta T = aI_p^{(0.9\pm0.2)}$, $a$ is proportionality constant) to the pump pulse intensity $I_p$, indicating the signal is a linear regime of one-photon excitation process.

The chirped pulse excitations were performed to study the wave packet dynamics separately in the excited and ground states.[14−16] It is well-established that the excited-state wave packet is dominantly generated when the ratio of the pulse width to the vibrational period is substantially small as in the present case of sub-5-fs pulse. In the present study the PC (chirp rate of 990 fs$^2$)-pulse excitation and NC (−930 fs$^2$)-pulse excitation cases mainly reflect the dynamics of the excited-state and the ground-state wave packets, respectively.

In the case of PC-pulse excitation probed at 620 nm, the time trace (not shown) has a fast decaying component with a time constant of 0.7 ± 0.2 ps. The amplitude of the decaying component probed at 670 nm (not shown) is larger than that of the 620 nm probe because of a negligibly small contribution of the growth of the ground-state bleaching. The time constants correspond to the lifetime of the $S_2$ ($\pi-\pi^*$) including relaxation due to *trans*−*cis* photoisomerization. The time constants are close to the reported values between 0.8 and 1.4 ps in solutions by a 400 nm excitation depending on the excitation wavelength and the polarity of the solvent.[19] The values are consistent if we take into account of the longer probe wavelength corresponds to the transition from the more relaxed state to the nearly constant energy final state because of the highly deformed excited state initially prepared.

In the case of PC-pulse excitation probed at 570 nm, this decay does not clearly appear because of the cancellation with the growing component of ground state bleaching. Because the following discussion on the molecular vibration probed by the transmittance change is mainly up to the delay of 0.8 ps, the relevant excited state is the $S_2$ ($\pi-\pi^*$) after predominant excitation of the state.

Figure 3b shows the Fourier power spectra of oscillating components of the transmittance-change traces. For all of the

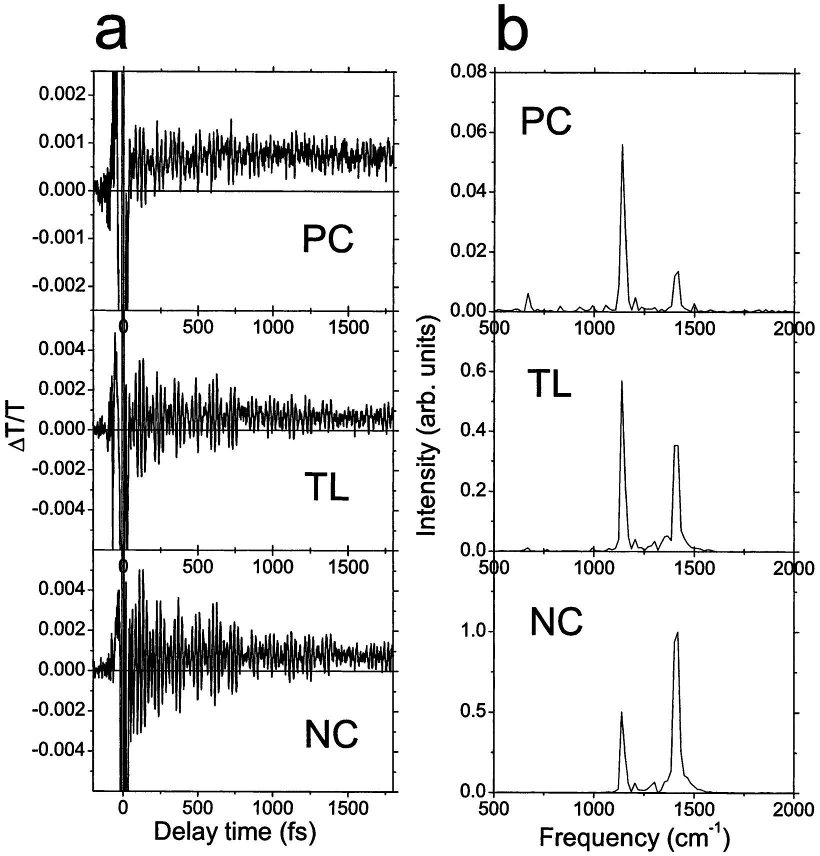

**Figure 3.** Transient normalized transmittance changes [$\Delta T/T(t)$] of DMAAB/DMSO probed at 570 nm using (a) PC, TL, and NC pulses, and (b) their corresponding Fourier power spectra.

NC-, PC- and TL-pulse excitations, two strong vibrating components are commonly observed in the Fourier power spectra. The peaks at ~1400 and ~1150 cm$^{-1}$ (more precise determination of the frequencies in the excited and ground states are discussed later) are attributed to the N=N and C−N stretching modes, respectively, from the IR[20,21] and Raman[8,21−23] spectra of azobenzene derivatives in the literature. The conventional ground-state Raman frequencies of the N=N and C−N stretching modes of DMAAB are 1423 and 1138 cm$^{-1}$, respectively.[21] The Fourier power spectra of the transmittance changes probed at 620 and 670 nm were found to have essentially the same profile as those of 570 nm.

The N=N stretching frequencies in the ground and the excited states are calculated to be 1410±2 and 1403±8 cm$^{-1}$, respectively, by averaging over the probe delay time between 200 and 850 fs. The C−N stretching frequencies are also determined in the same way to be 1143±2 and 1146±8 cm$^{-1}$ in the ground and the excited state, respectively. Hence the frequency difference between the two modes in the excited state (257 cm$^{-1}$) is 10 cm$^{-1}$ smaller than that in the ground state (267 cm$^{-1}$). This indicates that the bond-order difference between N=N and C−N bonds are reduced in the more $\pi$-electron delocalized excited states. The small difference in the N=N stretching frequency between the excited and the ground states may also be due to the substantial mixing of the excited state with n−$\pi$* character induced by the charge-transfer donative dimethylamino group to the Φ-N=N-Φ group as expected from the charge-transfer theory.[24] This mixing reduces the difference in the N=N stretching frequency between the ground and the excited states. The difference is slightly smaller than the results obtained by the time-resolved Raman experiment.[8] This may also be explained by difference in the probe time-range between the two experiments. In the present paper we are probing the instantaneous vibrational frequencies, while the average frequencies of molecular vibration in the excited state were observed in the time-resolved Raman spectroscopy. The latter can have larger difference in the frequency between the ground and excited states because more extensive relaxation after thermalization in the excited state may have taken place.

In our previous work[25] of polydiacetylene, we found that the instantaneous frequencies of molecular vibrations are modulated in time exhibiting "dynamic" mode coupling. To investigate the frequency modulation of these modes, in the present work, the time-frequency distributions[26](TFD) free from an artificial mode mixing was performed for these two oscillating components to study in relation with chemical reactions. The TFD indicates the energy content of a signal as a function of both time and frequency. There are many construction methods of TFD such as a short-time-Fourier transform (spectrogram)[25,27] and a Wigner distribution. We have adopted an adaptive optimal kernel (AOK) method,[28,29] which suppresses artificial interference caused when the signal contains many frequency components or a large amount of noise. This method can represent the instantaneous frequencies of frequency-modulated complicated signals more properly than other methods. The instantaneous frequencies $\omega$ ($t_d$) at delay time $t_d$ for N=N and C−N stretching modes calculated from the TFD obtained for the excited and ground states by PC- and NC-pulse excitations are respectively shown in parts a and b of Figure 4. The error limits (standard deviation of $\omega$ ($t_d$) at 200 < $t_d$ < 850 fs caused by the noise and systematic errors) are estimated to be 8 and 2 cm$^{-1}$ in the case of PC- and NC-pulse excitations, respectively. Figures 4c and 4d are corresponding Lissajou's figures to show the correlation between two instantaneous frequencies of N=N and C−N stretching modes. The values of correlation are −0.8 and 0.35 in the case of PC- and NC-pulse excitations,

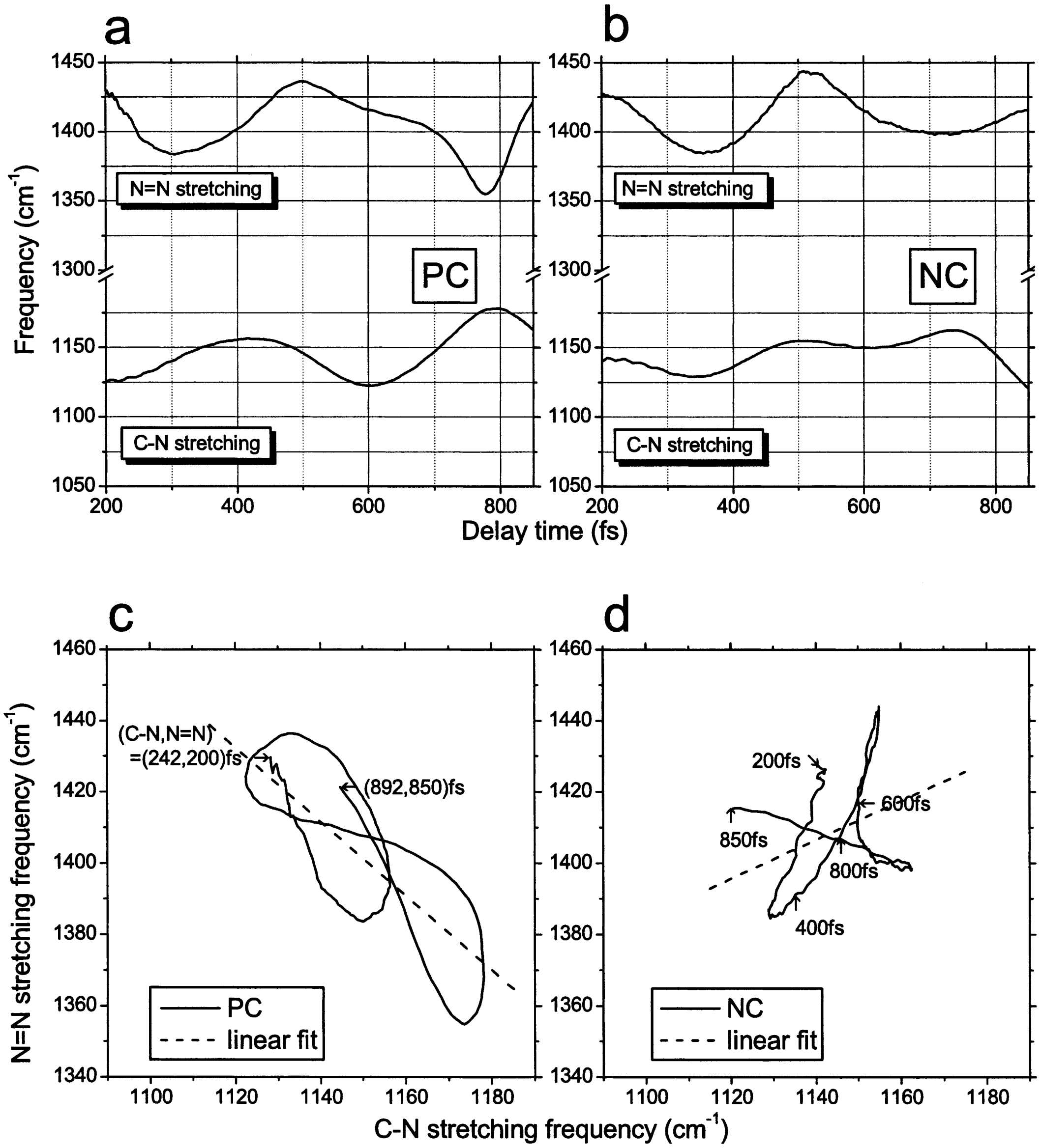

**Figure 4.** Time-delay dependencies (a and b) and Lissajou's figures (c and d) for instantaneous frequencies of N═N and C−N stretching modes calculated from the adaptive-optimal-kernel time-frequency distribution (AOK-TFD) of oscillating components of the $\Delta T/T(t)$ traces probed at 570 nm by using PC (a and c) and NC pulses(b and d). The correlation between the N═N and C−N stretching mode frequencies are maximized when the delay-time shifts are 42 and 0 fs in (c) and (d), respectively. The former delay-time shift of 42 fs used in the plot corresponds to ~0.8$\pi$ in the phase difference of two frequency modulations.

respectively. These correlations indicate that the N═N and C−N stretching modes are tightly coupled in the excited state, but there is much less correlation between the two in the ground state. This is because of the more pronounced anharmonicity induced by larger vibration amplitudes in the excited state than in the ground state.[14,15] Parts a and b of Figure 5 show the Fourier power spectra of the modulation frequencies of the two instantaneous frequencies of the molecular vibration modes in the excited and the ground states, respectively.

The modulation frequency spectra of N═N and C−N stretching frequencies in the ground-state induced by NC-pulse excitation shown in Figure 5b have peaks around 100 cm$^{-1}$ (~ 330 fs) and 65 cm$^{-1}$ (~ 510 fs), respectively. The modulation frequencies of the modes in the excited state by PC-pulse excitation are about 65 cm$^{-1}$ (~510 fs, N═N) and 100 cm$^{-1}$ (~330 fs, C−N). Furthermore the modulations of N═N and C−N stretching modes are nearly anti-phase with the phase difference of ~0.8$\pi$ (parts a and c of Figure 4). There is no well-defined correlation between the frequency modulations of N═N and C−N stretching modes in the ground state as shown in Figure 4d. Detailed dependence of the vibrational phase in the ground state on the probe wavelength is to be published elsewhere. The differences in the power spectra of modulation frequencies in both ground and excited states and the phase relations between the modulations of the two modes are explained in the following way.

The modulations at ~65 and 100 cm$^{-1}$ observed in the excited state are induced by the dynamic mode-coupling mechanism (Figure 1b) as discussed for a polydiacetylene in our previous papers.[11,25] In the conjugated polymer, excitation by transition to excitonic state in the conjugated electronic system triggers C═C stretching and C−C stretching mode vibrations. Their frequencies are modulated since the $\pi$ electron delocalization is associated with the conjugation of these bonds. From the normal-mode analysis in polydiacetylene, it is found that C−C and C═C double bonds are strongly coupled with each other through C═C−C in-plane bond-bending mode.[25] In the same way, N═N and C−N stretching modes are expected to be

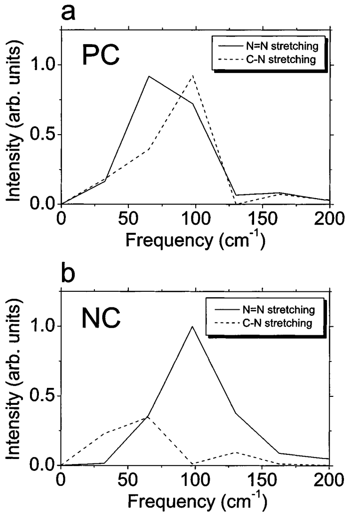

**Figure 5.** Fourier transform of the instantaneous frequencies of N═N stretching (solid lines) and C−N stretching (dashed lines) modes probed at 570 nm by using (a) PC and (b) NC pulses.

coupled through the N═N-Φ bond bending mode, since a change in the bond order of two bonds is expected to cause the bond-angle change. From the experimental results, N═N and C−N stretching modes are considered to be coupled through at least two modes including a Φ-N═N-Φ torsion-like motion from the values of ∼65 and 100 $\mathrm{cm}^{-1}$ because typical torsion frequency is in the range.

A simple model of reaction process based on the experimental results can be discussed as follows. The N═N and C−N stretching modes and their modulations due to torsion are related to a doorway to the photoisomerization. After several vibrations of the torsion-like mode, the isomerization reaction takes place by chance with a stochastic probability, which results in the reaction rate of about 1 ps.[19] The torsion motion is thus probed by the changes in the N═N and C−N stretching frequencies. Frequencies of in-plane bending modes relevant to the inversion mechanism are expected to be in the range of 800−1200 $\mathrm{cm}^{-1}$ and too high for the modulation frequencies to be attributed. Owing to the difference in the modulation frequencies of N═N and C−N stretching modes (∼65 and ∼100 $\mathrm{cm}^{-1}$, respectively), the above simple model is further refined. The slight difference of modulation frequencies is due to the difference in the amount of mixing of other modes. This result clearly indicates the multidimensionality of the potential surfaces relevant to the reaction in the excited state. In other words, the chemical reaction of *trans*−*cis* photoisomerization cannot be simply described either by "rotational" mechanism or "inversion" mechanism shown in Figure 1.

If the mechanism is either of the genuine "rotation" or "inversion", then the two stretching modes are coupled through the Φ-N═N-Φ torsion or in-plane bending, and the power spectra of the modulation frequencies are expected to be the same and the phase relation between the two modes to be $\pi$-out-of phase in both cases. For example, when one of the phenyl ring starts to rotate, the bond orders of N═N and C−N bonds synchronously decrease and increase, respectively, which means the frequency changes are $\pi$ out-of phase from each other. It is the same in the case of the inversion mechanism with a slight difference that the change in the N═N frequency should be smaller than the case of rotation mechanism because of the contribution of the $\mathrm{N{=}N^{+}{=}C}$ configuration in the transition state. The existence of the two apparent modulation frequencies (∼65 and ∼100 $\mathrm{cm}^{-1}$) indicates that there is at least one more mode coupled preferentially either or both of the two modes during photoisomerization. The difference between the two modulation frequencies can be explained in terms of a combined deformation mechanisms of the rotation and inversion in the initial stage of isomerization. It is a very interesting theoretical subject how much fraction of each mechanism contributes. This extra mode(s) may be attributed to the in-plane bending mode as in the case of stilbene,[30] N-Φ rotation and/or out-of plane pyramidal bending mode as expected in analogy with an ammonia molecule with a lone-pair electrons. Therefore the photoisomerization in azobenzene cannot be discussed either rotation or inversion mechanism. This is considered to be the case for stilbene as discussed theoretically.[30] The conclusion is very reasonable because even in the photoisomerization in a stilbene molecule, which does not have n-$\pi^*$ excitation, there are at least three angular coordinates (out of 72 modes) directly involved in the photochemical process. The small deviation of phase difference (∼0.8$\pi$) between N═N and C−N stretching frequency modulations from $\pi$ is also considered to be due to the contribution of the extra mode(s). The mode(s) contributes to the softening and hardening of the two stretching frequencies with slightly different frequency and phase between the N═N and C−N stretching modes.

It is concluded that the ultimately short visible pulses have revealed that the one-dimensional model via rotation or inversion is insufficient to describe the isomerization process of azobenzene derivatives. It must be described by the multidimensional model.

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