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Nanosecond Time-resolved Infrared Spectra and Structure of the Charge-transfer State of 9,9′-Bianthryl in Acetonitrile

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Nanosecond time-resolved infrared spectra of photoexcited 9,9′-bianthryl (BA) and its deuterated derivative (BA-d_{18}) were recorded in acetonitrile-d_3 and cyclohexane-d_{12}. The charge-transfer (CT) bands observed at the 1200–1400 $\mathrm{cm^{-1}}$ region are contributed mostly by the intra- and inter-ring CC stretch vibrations. The intrinsic frequency of the inter-ring CC stretch falls within the 1200–1400 $\mathrm{cm^{-1}}$ region, which is consistent more with a twisted structure than with a fully conjugated planar structure of the CT state.

Photoinduced charge transfer (CT) is a fundamental chemical reaction. The intramolecular CT state formation in 9,9′-bianthryl (BA) has attracted attention since its proposal in 1968.[1] A large number of spectroscopic experiments on the CT reaction in BA have been performed in the UV–visible region in clusters,[2–4] in solutions,[5–12] or in ionic liquids.[13,14] When BA is irradiated by UV light, it is excited to the locally excited (LE) state in which one of the anthracene moieties is electronically excited. The CT reaction proceeds between the two anthracene moieties after the UV irradiation in polar solvents, while it is widely accepted that the complete CT reaction does not proceed in nonpolar solvents. Our previous time-resolved near-IR absorption experiments[15–18] have revealed that an intermediate, "partial CT (PCT)" state, is formed in the CT reaction. The PCT state has a transition dipole moment parallel to the inter-ring CC bond as the CT state does.[17] The PCT state is also observed in nonpolar solvents, where it is in equilibrium with the LE state.[17,18]

Structural information on BA in the CT and PCT states is required for elucidating the detailed mechanism of the CT reaction. Internal rotation is proposed as one of the key factors that determine the reaction kinetics. The internal rotation process around the central CC bond is presumable, because a non-perpendicular dihedral angle is favorable for effective inter-ring interaction. For examining the molecular structure of BA in the CT and PCT states, time-resolved IR and Raman spectroscopy is an effective method, because the internal rotation will affect the position and the strength of the inter-ring CC stretch band. To the best of our knowledge, however, there has been no study reported on time-resolved vibrational spectroscopy of the excited state of BA in solution, except for a time-resolved CARS/CSRS experiment.[19] The CSRS signals of BA in the CT state were all assigned to ring vibrations, whereas no vibrational band predominated by the inter-ring CC stretch was reported.

In this letter, nanosecond time-resolved IR spectra of BA and its deuterated derivative, BA-d_{18}, are reported. We assign the observed spectra to the CT state of BA and discuss the origin of the IR bands.

Transient absorption spectra were measured with a nanosecond time-resolved IR absorption spectrometer.[20,21] Briefly, sample solutions were photoexcited by the third harmonic of a pulsed Q-switched Nd:YAG laser (IB LASER DiNY pQ355, 355 nm, 250 Hz, 40 μJ/pulse, 7 ns) or by the second harmonic of a DCM dye laser (345 nm). Probe radiation in the IR region from a ceramic infrared light emitter (JASCO) was focused onto sample solution. Transmitted probe light was introduced to a dispersive monochromator (JASCO CT-50TFP) with a pair of off-axis ellipsoidal mirrors and was detected by a photovoltaic MCT detector with a preamplifier (Kolmar Technologies KISDP11-1J1/DC). Sample solutions were circulated with a peristaltic pump through a $\mathrm{BaF_2}$ flow cell with a 100- or 500-μm optical path length.

Steady-state IR absorption spectra were measured with an FT-IR spectrometer (JASCO FTIR-670). The spectral resolution was set to be 1 $\mathrm{cm^{-1}}$. Samples were dispersed in KBr disks.

We synthesized 9,9′-bianthryl (BA-h_{18}) by reducing anthraquinone with zinc powder in hydrochloric acid and acetic acid.[22] Anthraquinone-d_8, hydrochloric acid-d, and acetic acid-d_4 were used for synthesis of perdeuterated 9,9′-bianthryl (BA-d_{18}). The products were recrystallized from acetic acid. Steady-state UV–visible absorption spectra of purified BA-h_{18} and BA-d_{18} were identical with those in the literature.[1,9]

Anthracene (ANT-h_{10}) and anthracene-d_{10} (ANT-d_{10}) were purchased from Wako Pure Chemical Industries, Ltd. and ISOTEC, respectively. Acetonitrile-d_3 (99.6 atom %D) and cyclohexane-d_{12} (99.6 atom %D) were purchased from Aldrich Chemical Co., Inc. The solvents were used without further purification.

Ground-state structure of BA was investigated by FT-IR spectroscopy. Steady-state IR spectra of ANT-h_{10}, BA-h_{18}, ANT-d_{10}, and BA-d_{18} are shown in Figure 1. The IR spectra of BA-h_{18} and BA-d_{18} are similar to those of ANT-h_{10} and ANT-d_{10}, respectively. The symmetry species and peak positions of the strong IR bands of ANT-h_{10} and ANT-d_{10} are listed in Table 1.[23–25] These bands show low-frequency shifts by 36–

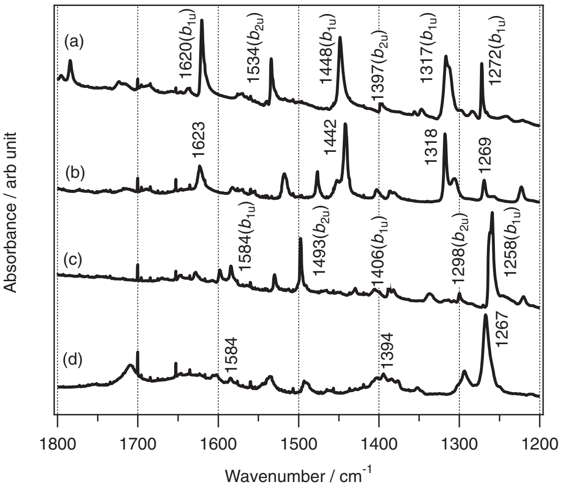

Figure 1. FT-IR spectra of (a) anthracene-h_{10}, (b) bianthryl-h_{18}, (c) anthracene-d_{10}, and (d) bianthryl-d_{18} from 1200 to 1800 cm^{-1}. The samples are dispersed in KBr disks. The symmetry species for major bands of anthracene are shown in the figure (refs 23–25).

Table 1. Peak positions and symmetry species of observed IR bands of anthracene-h_{10}, anthracene-d_{10}, bianthryl-h_{18}, and bianthryl-d_{18} in the 1200–1800 cm^{-1} region

Symmetry[a]	ANT-h_{10}	ANT-d_{10}	BA-h_{18}	BA-d_{18}	Description[b]
b_{1u}	1620	1584	1623	1584	ring CC str.
	1448	1406	1442	1394	ring CC str.
	1317	1258	1318	1267	ring CC str.
	1272	—[c]	1269	—[c]	in-plane CH bend
b_{2u}	1534	1493			ring CC str.

[a] Refs 23–25. [b] Ref 24. [c] Out of the wavenumber range.

100 cm^{-1} with the deuteration. The deuteration of BA results in similar degree of spectral shifts to anthracene. This result suggests that the ring stretch modes mainly contribute to the IR spectrum of the ground state in the 1200–1800 cm^{-1} region.

Transient IR spectra of BA-h_{18} and BA-d_{18} in the CT state in acetonitrile-d_3 were recorded with nanosecond time-resolved IR spectrometer. Transient IR spectra at 20 ns after the photoexcitation are shown in Figure 2, together with a transient IR spectrum of BA-h_{18} in cyclohexane-d_{12} at 20 ns. Strong absorption is observed in the spectra of BA-h_{18} and BA-d_{18} in acetonitrile-d_3, while intensities of all the IR bands for BA-h_{18} in cyclohexane-d_{12} are under the detection limit. Because the transient IR bands are clearly observed only in a polar solvent acetonitrile-d_3, they are assigned to the CT state.

Time-dependent spectral changes of BA-h_{18} and BA-d_{18} in acetonitrile-d_3 were observed for supporting the assignment to the CT state. The results are shown in Figure 3. Relative band intensity does not change in a set of time-resolved spectra for either BA-h_{18} or BA-d_{18}. This indicates that all the observed bands are assigned to only one species. Time profile of the 1352-cm^{-1} band of BA-d_{18} is shown in Figure 4. The decay time constant is determined to be (28 ± 8) ns by the least-

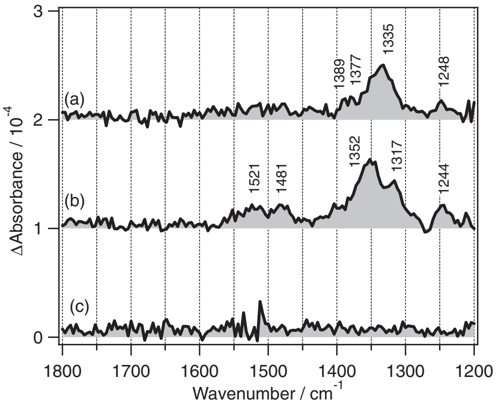

Figure 2. Transient IR spectra of (a) bianthryl-h_{18} in acetonitrile-d_3, (b) bianthryl-d_{18} in acetonitrile-d_3, and (c) bianthryl-h_{18} in cyclohexane-d_{12} at 20 ns. The samples were photoexcited at 345 nm.

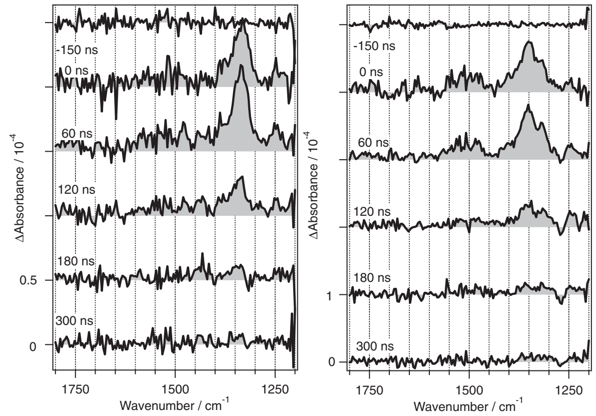

Figure 3. Nanosecond time-resolved IR spectra of bianthryl-h_{18} (left) and bianthryl-d_{18} (right) photoexcited at 345 nm in acetonitrile-d_3.

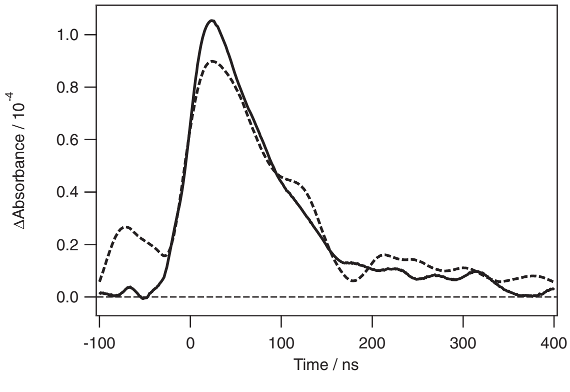

Figure 4. Time profile of absorption intensity of bianthryl-d_{18} at 1352 cm^{-1} with photoexcitation at 345 nm (solid line). Broken trace represents the model function: a single exponential decay function convoluted with an observed instrumental response function.

squares fitting analysis. The model function was a single exponential decay function convoluted with an observed instrumental response function. The 1352-cm^{-1} band is assigned to the CT state of BA-d_{18}, because the lifetime of the CT state in acetonitrile has been estimated to be between 30 and 40 ns by time-resolved fluorescence and UV–visible spectroscopy.[26]

The magnitude of the isotope shift provides valuable information on the assignment of the observed IR bands. The spectral pattern for the CT state of BA-h_{18} and BA-d_{18} does not change as much as the pattern for the ground state does. The IR bands observed for the CT state have smaller contribution from the CH stretch or CH bending vibrations. A vibrational mode with large contribution from the intra- and inter-ring CC stretch will form such a mode. Infrared intra-ring CC stretch bands are reported for the cation and anion radicals of anthracene.[24,27,28] The inter-ring CC stretch vibration can be significantly IR active, because the charge separation results in symmetry breaking of the two anthracene moieties with opposite charges.

It has been suggested that charge separation affects the IR absorption intensity by coupling of molecular vibrations with charge fluxes due to exchanges between resonance structures.[28–30] The observed absorbance change of the CT band of BA-h_{18} at 1335 cm^{-1} is as large as ca. 5×10^{-5} at 0 ns, while the depletion of the ground state absorption is below the noise level of the spectrometer of 1×10^{-5}. The CT absorption band at 1335 cm^{-1} is enhanced by at least five times compared with the IR bands of the ground state. The other bands of the CT state of BA-h_{18} are also larger than the strongest band of the ground state absorption at 1442 cm^{-1}. Similar results are obtained in its deuterated derivative. Most probably, vibrational modes associated with the inter-ring CC stretch are observed with large intensity in the transient IR spectra.

Although more detailed experiments are required to investigate the precise structure of the CT state of BA, one of the strong bands of the CT state observed in this study is probably assigned to the inter-ring CC stretch vibration. When BA is planar, a simple structural formula of BA in the CT state has a complete C=C bond at the center. As BA is twisted from the planar structure, the bond order of the central CC bond decreases from two. In the case of simple alkenes, IR bands originating from C=C stretch vibrations are observed between 1600 and 1700 cm^{-1}. If one of the IR bands that we observe in the 1200–1400 cm^{-1} region is predominated by the inter-ring CC stretch vibration, the inter-ring bond is not a complete C=C bond nor a complete C–C bond, which implies that BA takes a twisted but nonplanar structure.

In the present study, the nanosecond time-resolved IR spectra of 9,9′-bianthryl-h_{18} and 9,9′-bianthryl-d_{18} in acetonitrile-d_3 and in cyclohexane-d_{12} have been observed. The IR band intensities of the CT state are stronger than those of the LE and ground states. The isotope shifts of the IR bands in the CT state are smaller than the shifts in the ground state. IR bands observed in 1200–1400 cm^{-1} for the CT state most probably have large contribution from the inter-ring CC stretch.

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