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Determination of the Equilibrium Structure of the Charge-transfer State of (*p*-Cyanophenyl)pentamethyldisilane by Means of Transient Infrared Spectroscopy

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An equilibrium structure of the charge-transfer (CT) state of (*p*-cyanophenyl)pentamethyldisilane was determined by transient infrared absorption spectroscopy of its CH stretching vibration region, and by the spectral simulation with quantum chemical calculations. It was found that a pattern of the CH stretching vibration bands of the CT state is substantially different from that of the S_0 state. This band feature of the CT state was well reproduced assuming the planar $\sigma_{\mathrm{Si-Si}}\pi^*$ state, where the disilanyl group and the phenyl ring lie in the same plane. Considering that the disilanyl group in the S_0 and the locally excited $\pi\pi^*$ states lie in the plane perpendicular to the phenyl ring, an occurrence of a twisting-type structural change during the ICT process was experimentally identified in the present study.

The intramolecular charge-transfer (ICT) process is one of the most fundamental processes in photochemical reactions. Since the first report of a dual emission of *p*-(dimethylamino)-benzonitrile (DMABN),[1] a vast number of spectroscopic studies have been carried out, mainly in the condensed phase.[2] The most widely accepted mechanism is a twisted intramolecular charge transfer (TICT) model.[3] In this model, a 90° twist of a dimethylamino group with respect to the phenyl ring occurs during the ICT process. However, other mechanisms such as a planar ICT (PICT)[4] and a rehybridized ICT (RICT),[5] where such a twist is not expected, are also proposed. Thus, a determination of an equilibrium structure of the charge-transfer (CT) state is the most direct way to elucidate the mechanism of the ICT process. For this purpose, many transient infrared (IR) or Raman spectroscopic studies in solution were carried out, so far.[6] In these studies, mainly vibrational modes within a cyanophenyl group were investigated. However, a clear agreement between the observed and calculated vibrational frequencies and intensity patterns has not been obtained yet. One of the main difficulties is that differences in frequencies predicted on the basis of the TICT model compared with the PICT model are not so large and depend on levels of calculations. Recently, Dobkowski and co-workers examined the TICT-type structural change by observing a syn−anti photoisomerization of 2-(*N*-methyl-*N*-isopropylamino)-5-cyanopyridine, which is a desymmetrized analogue of DMABN, by ^{1}H NMR spectroscopy.[7] The authors claimed that the syn−anti isomerization must proceed through a twisted CT state. Though this observation strongly supported the TICT model, it was not a direct observation of the CT state.

We have been carrying out laser spectroscopic studies on jet-cooled phenyldisilanes and their solvated clusters to elucidate details of the ICT process.[8−10] Phenyldisilanes are known to exhibit a dual emission in solution.[11,12] Similar to the DMABN system, an occurrence of a 90° twist of a disilanyl group with respect to the phenyl ring in the ICT process has been one of the main issues in this system.[13] In our previous studies, it was found that (*p*-cyanophenyl)pentamethyldisilane (CPDS) exhibits a dual emission even in a jet-cooled isolated condition and that a CT emission yield depends on vibrational levels.[8,9] We also determined an electronic configuration of the CT state of CPDS as the $\sigma_{\mathrm{Si-Si}}\pi^*$ type and claimed that a local structure of the pentamethyldisilanyl group of the CT state should be much different from that of the S_0 state.[9] Though the main difference is an elongation of the Si−Si bond length, it affects on the structure of methyl groups attached to the silicon atoms. Thus, it is expected that CH stretching (ν_{CH}) band of the CT state should exhibit some changes in frequency and/or intensity pattern. In the present paper, we report results of our transient IR measurement in the ν_{CH} region and a determination of the equilibrium structure of the CT state.

In the present study, transient IR spectra were recorded by ultraviolet (UV)−infrared double resonance spectroscopy.[14] First, a UV pulse excites molecules to a locally excited (LE) $\pi\pi^*$ state, and the molecules are successively irradiated by an IR pulse. When the IR absorption by the electronically excited molecule occurs, a fluorescence yield decreases due to some nonradiative decay processes in the vibrationally excited levels. Thus, the IR absorption of the electronically excited molecules can be detected as a depletion of the fluorescence intensity. Temporal pulse widths of the UV and IR pulses were ∼3 and ∼4 ns, respectively.

Before results of the present transient IR study are reported, the ICT process of CPDS is briefly described here. Figure 1a shows a fluorescence excitation spectrum of jet-cooled CPDS.

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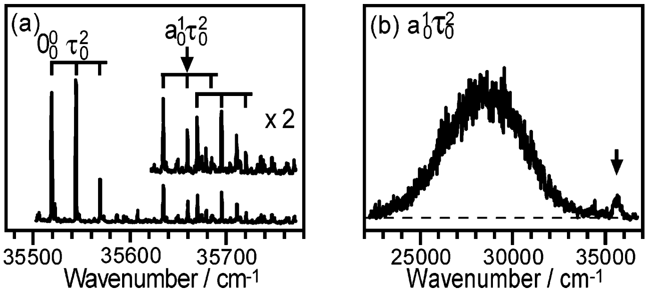

Figure 1. Fluorescence excitation (a) and dispersed fluorescence (b) spectra of jet-cooled CPDS. An arrow indicates the excitation band used in measuring the dispersed fluorescence spectrum.

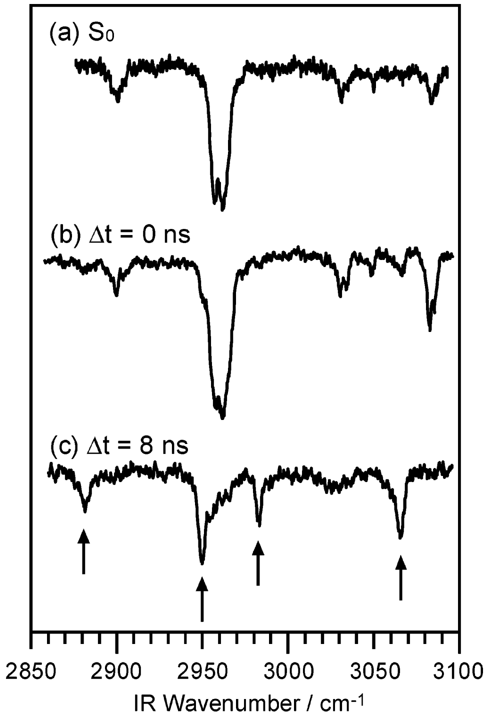

Figure 2. Observed transient IR spectra of CPDS: (a) IR spectrum of the S_0 state; (b) and (c) transient IR spectra. The delay time between the UV and IR pulses is indicated in each spectrum.

The origin band of CPDS is located at 35 519 cm^{-1}. A clear progression with an interval of 25 cm^{-1} denoted as "τ" appears in the figure. Several bands appearing about 120 cm^{-1} above the origin band also accompany the same progression. The low-frequency vibration forming this progression has been assigned as a torsional motion of the disilanyl group with respect to the phenyl ring.[9] A vibrational assignment of the mode denoted as "a" in Figure 1a has not yet been determined, because there are many low-frequency vibrational modes in the case of CPDS. Figure 1b shows dispersed fluorescence (DF) spectra of the CPDS monomer measured by exciting the $a_0{}^1\tau_0{}^2$ band. A broad and Stokes-shifted emission was observed. The amount of the shift was 6700 cm^{-1}. This band has already been assigned as an emission from the CT state in our previous studies. A decay time constant of the CT emission was found to be ~8 ns. Because the LE emission that appears at around 35 000 cm^{-1} is very weak, the ICT reaction rate should be very fast. In the following transient IR measurements, the $a_0{}^1\tau_0{}^2$ band was used as a pump transition.

Transient IR spectrum of the CPDS monomer measured in the present study is shown in Figure 2. For comparison, an IR absorption spectrum of the S_0 state is also exhibited in the top trace of Figure 2. Bands whose frequencies are higher than 3000 cm^{-1} are assigned as the CH stretching vibrations of the phenyl ring. The strongest band at 2960 cm^{-1} is assigned as an asymmetric CH stretch of the methyl groups, and a small peak at 2900 cm^{-1} is assigned as a symmetric CH stretch.

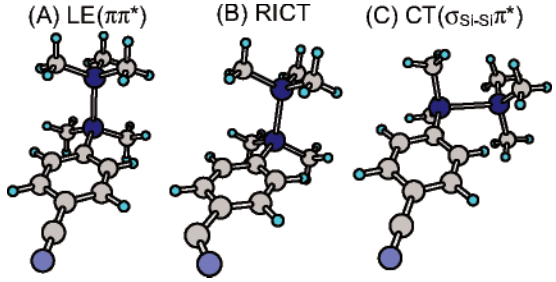

Figure 3. Equilibrium structures of the CT states obtained by ab initio calculations.

It was found in the present transient IR measurement that a relative intensity ratio of the bands evolves drastically with time. In the case when the two laser pulses were temporally overlapped, the IR spectrum was similar to that of the S_0 state. In this case, vibrational bands of all the S_0, LE, and CT states can appear. However, in the case of $\Delta t = 8$ ns, a band pattern very distinct from that at $\Delta t = 0$ ns was observed. The most outstanding feature is a large splitting of the asymmetric CH stretch mode of the methyl groups (2980 and 2950 cm^{-1}). It is clear that intensities of four bands indicated by arrows in the figure increase with time, whereas those of the bands that strongly appeared at $\Delta t = 0$ ns decrease. On the basis of the DF spectrum, it is expected that a population of the LE state decreases within a few nanoseconds and that the CT state is dominant in population at the delay time of $\Delta t = 8$ ns. The intensity of these newly appeared bands decreases with the same time constant as the CT emission decay. Thus, we have assigned this splitting to the ν_{CH} bands of the CT state. It is also indicated that the ν_{CH} of the LE state do not change so much from those of the S_0 state, because no additional feature appeared at small Δt. This band pattern of the ν_{CH} observed here should provide us with a definitive clue to the determination of the structure of the CT state.

To determine the equilibrium structure of the CT state, ab initio calculations were carried out using a Gaussian 03 program package.[15] Results of CIS/cc-pVDZ calculations were used as initial points of CAS-SCF(8,8)/cc-pVDZ calculations. In the CASSCF calculation, eight orbitals, consisting of three π, one $\sigma_{\mathrm{Si-Si}}$, and four π^* type orbitals including $d_{\pi,\mathrm{Si-Si}}$, were used as active spaces. As a result, three low-lying singlet states were obtained: (A) the LE ($\pi\pi^*$) type, (B) the RICT type with a bent C$\equiv$N form, and (C) the planar $\sigma_{\mathrm{Si-Si}}\pi^*$ type. Structures of these states are schematically shown in Figure 3. The disilanyl group is perpendicular to the phenyl ring in (A) and (B), whereas the disilanyl group lies in the same plane with the phenyl ring in (C). In addition, the Si−Si bond length of the form (C) (2.81 Å) is much longer than those of the other forms (~2.4 Å). Among the simulated IR spectra in the ν_{CH} region of these three forms, the large splitting of the asymmetric CH stretch of the methyl groups was reproduced only in (C), as shown in Figure 4. To confirm whether the reproduction of this splitting is an intrinsic character of the form (C) rather than an artifact of the calculation, an IR spectrum was simulated on the basis of the CIS calculation, as shown in Figure 4c. It was clearly shown that the large splitting of asymmetric CH stretch of the methyl groups was well reproduced by different levels of calculations. Therefore, we concluded that the CT state of CPDS is the planar $\sigma_{\mathrm{Si-Si}}\pi^*$ type. This is a clear experimental

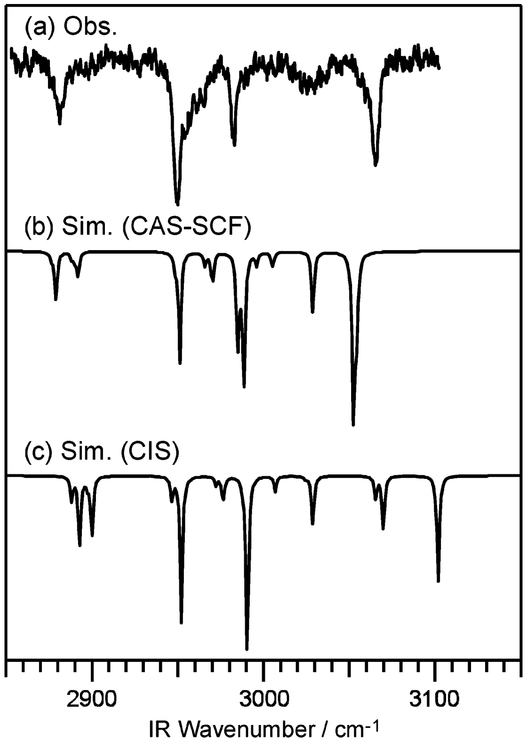

Figure 4. Simulated IR spectra of CPDS. (a) Same spectrum as Figure 3c reproduced for comparison. The IR spectra of the planar form obtained by (b) the CASSCF and (c) the CIS calculations, respectively.

identification of the twisting-type structural deformation during the ICT process.

In conclusion, we have succeeded in determining the equilibrium structure of the CT state of CPDS by transient IR spectroscopy. Our observation revealed the occurrence of a twisting-type structural change in the ICT process of CPDS. Though this result cannot be directly applied to the problem of DMABN and related species, it provides us with a new insight into the understanding of the ICT process.

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Supporting Information Available: A temporal profile of the transient IR band and details of the computational results. This material is available free of charge via the Internet at http://pubs.acs.org.

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