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Solvent Reorientation Process in the “Twisted” Intramolecular Charge-Transfer Process of Cyanophenyldisilane−(H_2O)$_2$ Cluster Investigated by Transient Infrared Spectroscopy

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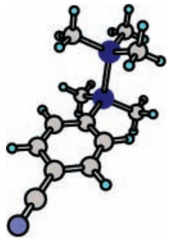
The solvent reorientation process of the intramolecular charge-transfer (ICT) process of the (*p*-cyanophenyl)-pentamethyldisilane−(H_2O)$_2$ (CPDS−(H_2O)$_2$) cluster in the excited-state was investigated by transient infrared (IR) absorption spectroscopy. It was found that there are at least two isomers in the charge-transfer (CT) state: one of the isomers exhibits a band of a π−hydrogen-bonded OH stretch of the water moiety. Analyses of the IR spectra in the dominant isomers revealed that water molecules are hydrogen-bonded with each other in the CT state. This indicates that the reorientation process of the water molecules takes place to form such a dimer structure during the ICT process.

Introduction

We have been carrying out laser spectroscopic studies on the jet-cooled (*p*-cyanophenyl)pentamethyldisilane (CPDS, Scheme 1) and its solvated clusters in the gas phase.[1−5] Phenyldisilane (PDS) and its derivatives are known to exhibit the excited-state intermolecular charge-transfer (ICT) process in solution.[6−15] The ICT mechanism of PDS expected[6−8] led to an analogue of the so-called twisted ICT (TICT) model in the case of *p*-dimethylaminobenzonitrile (DMABN).[16,17] An electron in the π orbital in the photoexcited ($\pi\pi^*$) state, which is referred to as a locally excited (LE) state, moves to the $\sigma_{\mathrm{Si-Si}}$ orbital and the charge-transfer (CT) $\sigma_{\mathrm{Si-Si}}\pi^*$ state is generated. During the ICT process, a 90° twist occurs around the single bond between the charge-donating disilanyl and -accepting cyanophenyl groups. In the LE state of CPDS, the molecular plane involving the disilanyl group is perpendicular to the phenyl ring, whereas it lies in the same plane as the phenyl ring in the CT state. Thus, the ICT mechanism of PDS seems to proceed in the opposite direction to that proposed in the case of the DMABN and related systems based on the structural conformation change. However, considering the role and the spatial distribution of the $\sigma_{\mathrm{Si-Si}}$ orbital of PDS and the n orbital of DMABN, the direction of the twist in the case of PDS is the same as in the case of DMABN. In this respect, the CT state of PDS can be referred to as a “twisted” CT state though its molecular configuration is in plane. The conformational change is an important issue of the ICT process. However, any clear spectroscopic evidence of the twist in the ICT process of PDS systems has not been reported. In our previous study, we have succeeded to measure infrared (IR) spectra of the CT state of the jet-cooled CPDS.[4] We recorded the transient IR spectrum of CPDS in the CH stretch region and found a large splitting of asymmetric CH stretch frequency in the CT state. A theoretical calculation assuming the “twisted” conformation of the CT state reproduced our observed spectrum. Therefore, our observation is known to be the first spectroscopic evidence that a twist occurs in the ICT process.

SCHEME 1: Structure of CPDS



Another important issue of the ICT process involves a reorientation of polar solvent molecules to stabilize the energy of the system. We also investigated the solvent reorientation in the ICT process of the CPDS−H_2O 1:1 cluster by transient IR spectroscopy.[5] We have found drastic spectral change in the IR spectrum in the OH stretch region of the water moiety. We have analyzed that the relative orientation of H_2O molecule with respect to the CPDS moiety in the ICT process. At first, the H_2O molecule is located at the side position of the CN group in the S_0 and the LE state. Once the CT state is formed, the H_2O molecule moves to the end of the CN group (a linear conformation). Then it moves to the top of the phenyl ring forming an on-ring type conformation. The time-constant of the transition from the linear to the on-ring conformations was found to be about 2 ns. Thus, our transient IR spectroscopic measurement turns out to be a promising technique to obtain detailed structural information of the ICT process. In the present study, we have extended our study to some hydrogen-bonded clusters of CPDS to obtain a detailed insight into the microscopic solvation effect on the ICT process.

Experimental Section

Since details of our experimental apparatus is described in our previous report,[5] we describe our experimental and computational methods briefly. In the present study, a conventional supersonic jet apparatus and a nanosecond pulsed laser system

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were used. CPDS was synthesized using a previously described method.[7] CPDS was heated to 350 K to create sufficient vapor pressure. The CPDS vapor seeded in He gas was supersonically expanded into a vacuum chamber through a pulsed nozzle with an orifice 0.8 mm in diameter. Before entering the nozzle, the buffer He gas passed a bottle partially filled with water cooled at 270 K and picked up water vapor. Transient IR spectra were recorded by a fluorescence depletion type of the ultraviolet (UV)−infrared (IR) double resonance technique[5,18] as follows. First, the UV laser pulse excites the CPDS clusters to the LE state. Then, UV-excited clusters were pumped by the IR light pulse for the vibrational excitation. When the IR absorption by the electronically excited molecule occurs, the fluorescence yield decreases due to the enhancement of nonradiative decay processes, such as internal conversion, intersystem crossing, and vibrational predissociation in the vibrationally excited levels. IR absorption spectra of the electronically excited clusters can be detected as a depletion of the fluorescence intensity. When IR spectra of the S_0 state were measured, the IR light pulse was introduced ~20 ns prior to the UV light pulse. In this case, vibrational excitation in the S_0 state was detected as a decrease in the fluorescence intensity, which also reflects the population of the vibrational ground level of the S_0 state. The IR light pulse was generated by a difference frequency mixing by a $LiNbO_3$ crystal between the second harmonics of the Nd:YAG (Continuum Powerlite 8000) and the output of a dye laser (Continuum ND6000). IR laser wavenumbers were calibrated based on the IR absorption spectra of H_2O vapor (3500−3800 cm^{-1}).[19] The temporal pulse widths of the UV and IR pulses were ~3 and ~4 ns, respectively. The delay time between the UV and the IR pulses was controlled by a digital delay generator (SRS DG535).

Results

Fluorescence Excitation and Dispersed Fluorescence Spectra of the CPDS−$(H_2O)_2$ Cluster. Before reporting the results of the present study, we will briefly review our previous spectroscopic study on the ICT process of the CPDS−H_2O system.[1−3] Figure 1(a) shows a fluorescence excitation spectrum of the CPDS−H_2O system. The origin band of the S_1−S_0 origin of the CPDS monomer appears at 35519.0 cm^{-1}. The bands appearing at 35456.5 cm^{-1} and 35394.3 cm^{-1} are assigned as the origin of the S_1−S_0 transition of CPDS−H_2O and CPDS−$(H_2O)_2$, respectively. As seen in the figure, a clear low-frequency progression was assigned as a torsional motion of the disilanyl group with respect to the phenyl ring.[2] This vibrational mode is denoted as "τ" in Figure 1. The appearance of a very similar torsional progression suggests that the H_2O molecule is bound to the CN group side and thus has no significant influence on the Si−Si bonding site of the molecule. No progression assignable to an intermolecular vibrational motion appeared in the spectrum. This indicates that the relative orientation between the CPDS and the H_2O moieties in the LE state is quite similar to that in the S_0 state. Figures 1(b−d) show dispersed fluorescence spectra measured by exciting the origin band of each species. In the case of the CPDS monomer, an emission consists of sharp bands starting from the laser-excited wavenumber and a broad emission whose band maximum is subject to a large Stokes shift, with no vibrational structure observed. The former is assigned as the LE emission whereas the latter is the CT emission, as in the emission spectra measured in solution. In the case of water clusters, the intensity of the CT emission becomes very strong. In the case of the CPDS−$(H_2O)_2$, no trace of the LE emission was observed. The Stokes shift of the CT emission was found to increase with the number of the water molecule increases. The Stokes shifts of the CT emission were about 7900 cm^{-1} and 9000 cm^{-1} for the CPDS−H_2O and −$(H_2O)_2$ clusters, respectively. These results indicated that the water solvation on the CPDS molecule takes place in a step-by-step way.

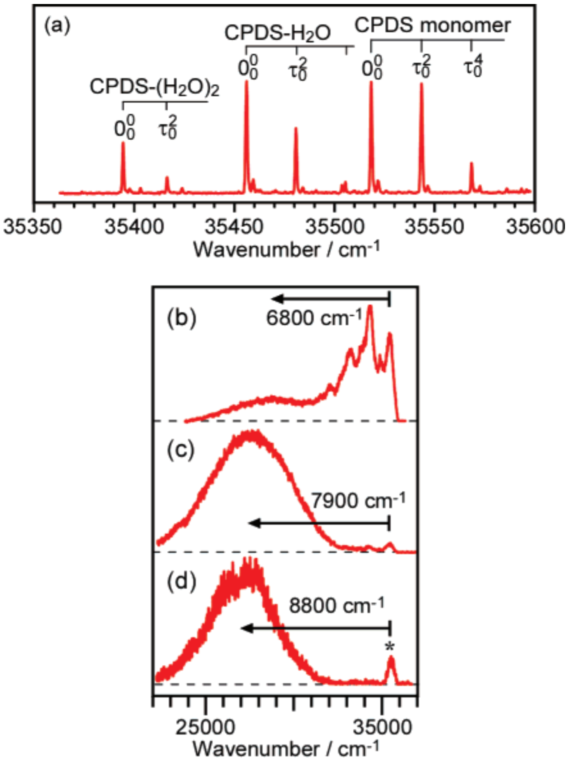

Figure 1. (a) Fluorescence excitation spectrum of jet-cooled CPDS−H_2O system. (b−d) Dispersed fluorescence spectra of CPDS monomer, CPDS−H_2O, and CPDS−$(H_2O)_2$, respectively. The dispersed fluorescence spectrum was measured exciting each origin band. The asterisk in trace d indicates the scattered light.

Transient IR Spectra of the CPDS−$(H_2O)_2$ Cluster in the ν_{OH} Region. IR spectra in the OH-stretching region of the CPDS−$(H_2O)_2$ cluster are shown in Figure 2. The UV laser was tuned to its origin band at 35394.3 cm^{-1}. It was confirmed that there is only one isomer of the S_0 state of the CPDS−$(H_2O)_2$ cluster under our experimental condition by a UV−UV hole-burning spectroscopy. The IR spectrum of the S_0 state is displayed in the top trace for comparison. The band pattern of this spectrum is quite similar to that of the benzonitrile(BN)−$(H_2O)_2$ cluster.[20] Thus, it is expected that the solvation structure of water molecules in CPDS−$(H_2O)_2$ is a ring structure similar to that of BN−$(H_2O)_2$. By comparing the assignment in the case of BN−$(H_2O)_2$, the bands at 3721 and 3718 cm^{-1} are assigned as the free OH-stretch vibrations, whereas the bands at 3544 and 3496 cm^{-1} are hydrogen-bonded OH-stretch vibrations. Figures 2(b−d) show transient IR spectra of CPDS−$(H_2O)_2$, where the delay times between the UV and the IR laser pulses are 1, 3, and 6 ns, respectively. In Figure 2(b), sharp bands appear at 3531 and 3486 cm^{-1}, in addition to the bands of the S_0 state. Since these bands disappear rapidly with the time evolution, they should be hydrogen-bonded OH stretch bands in the LE state. A relatively sharp band that appears at 3720 cm^{-1} in all spectra can be assigned as the free OH stretch band. Another band appears at 3623 cm^{-1}, and three rather broad bands appear below 3550 cm^{-1} in Figure 2(c) and 2(d). These bands can be assigned as hydrogen-bonded OH stretch bands of the CT state, since the LE state disappears within a time delay of 6 ns where the spectrum in Figure 2(d) is measured.

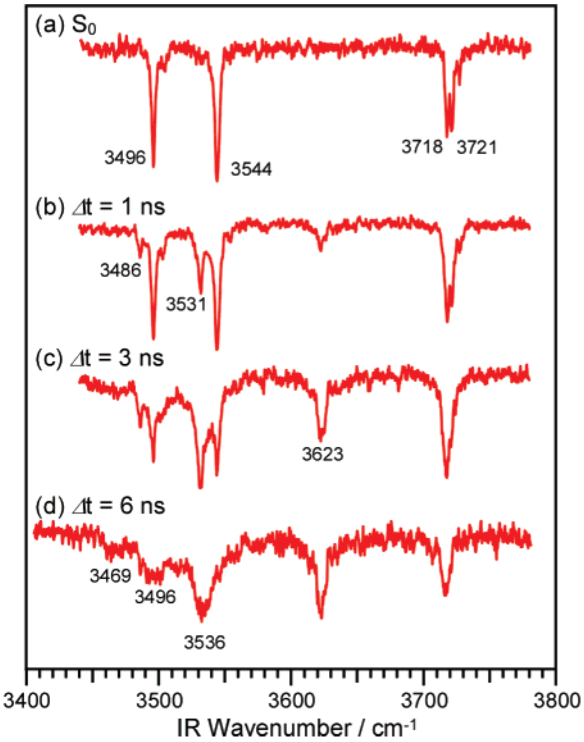

Figure 2. IR spectra of CPDS−$(H_2O)_2$ in the OH-stretching vibration region. Trace a is an IR spectrum of the S_0 state, whereas traces b−d are transient IR spectra. The delay times between the UV and IR laser pulses are indicated in the figure.

The number of the hydrogen-bonded OH stretch bands indicates that there should be at least two isomers in the CT state. The band position of 3623 cm^{-1} is a typical frequency of the π-hydrogen-bonded OH stretch.[21] This is clear evidence that there is an isomer where the H_2O molecule is on the phenyl ring. Thus, a reorientation of water molecules from the side position of the CPDS to the top of the phenyl ring is expected to occur during the ICT process. Unfortunately, since the intensity of the IR bands of the CT state rises within our temporal resolution, any temporal information is not obtained in the present study.

Discussion

In the previous study, possible conformations of the CPDS−H_2O clusters in the CT state were examined based on the theoretical calculation of CASSCF(8,8)/cc-pVDZ level, where the π, σ_{Si-Si}, π^*, and d_π orbitals were chosen as active orbitals in the calculations.[5] However, the number of the atoms and electrons are much larger in the present system so that the same level of calculations cannot be performed. The CT state of the CPDS monomer and the CPDS−H_2O cluster is well described by a one-electron excitation model from the σ_{Si-Si} to the π^* orbitals. Thus, CASSCF(6,5)/cc-pVDZ calculations, where the six electrons are distributed in the five active orbitals, π, σ_{Si-Si}, and π^*, have been carried out to find possible isomers by using the Gaussian 03 program package.[22] We have confirmed that there is no major difference in the optimized structure in the case of the CPDS monomer and the CPDS−H_2O cluster. Since vibrational calculations require more memory space, the basis set was limited to the 6-31G(d), except for the hydrogen atoms in H_2O. The 6-31G(d,p) basis set was used for them for a better description of the hydrogen bonds.

The isomers of CPDS−$(H_2O)_2$ obtained in the present study are shown in Figure 3 together with configurations of the S_0 and LE states. On the basis of the IR spectra, water molecules are found to make a ring configuration around the CN group in the S_0 and the LE state. For the CT state, six isomers were found in the optimization calculations. Each of them is labeled according to the positions of water molecules as indicated in the figure. In three of them, (c), (d), and (e), water molecules are independently attached to the CPDS moiety. The positions of the water molecule are almost the same as those found in CPDS−H_2O. In the other three isomers, water molecules are hydrogen bonded to one another, as in a water dimer. The relative energy and the value of the dipole moment of each isomer are also indicated in Figure 3. The most stable isomer is the π−disilanyl type configuration. In this configuration, one of the waters is directed to the disilanyl group by the dipole−dipole interaction while the other water is π−hydrogen bonded to the phenyl ring. The second most stable configuration is the CN−π isomer. In this isomer, one of the water molecules is

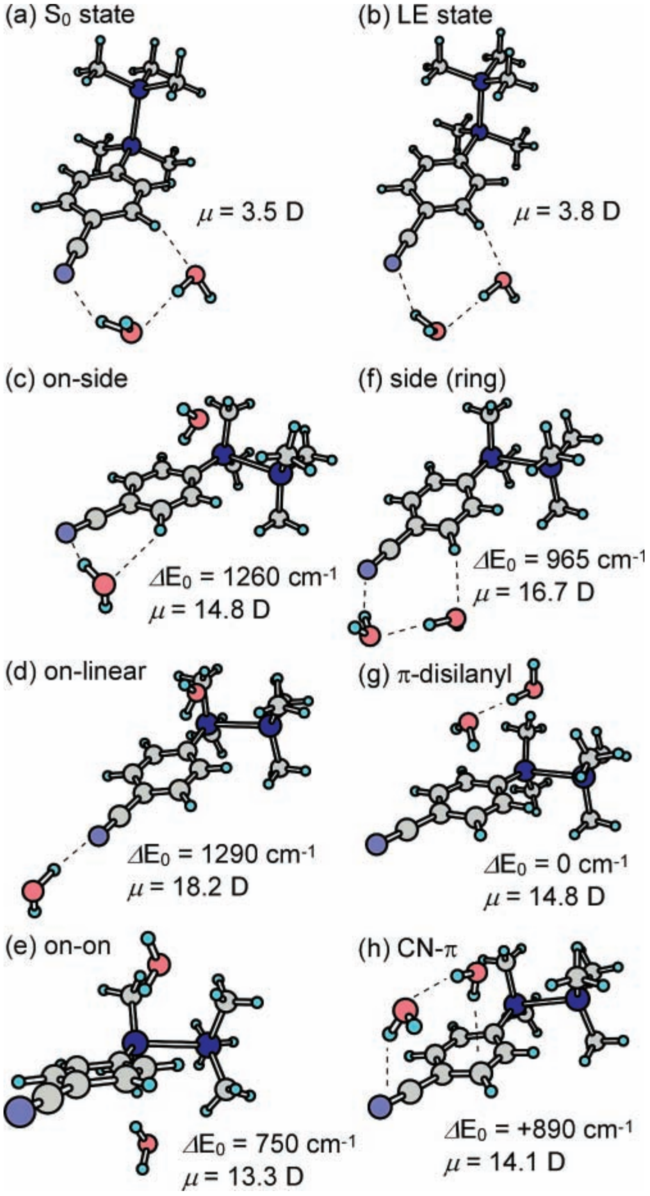

Figure 3. Optimized structures of CPDS−$(H_2O)_2$ in the CT state obtained by the theoretical calculation. For comparison, optimized structures of the S_0 and the LE states are also shown in a and b, respectively. Values of ΔE_0 indicate the energy difference measured from the vibrational ground level of the π-disilanyl isomer, which is the most stable one, whereas μ indicates the value of the dipole moment of each isomer.

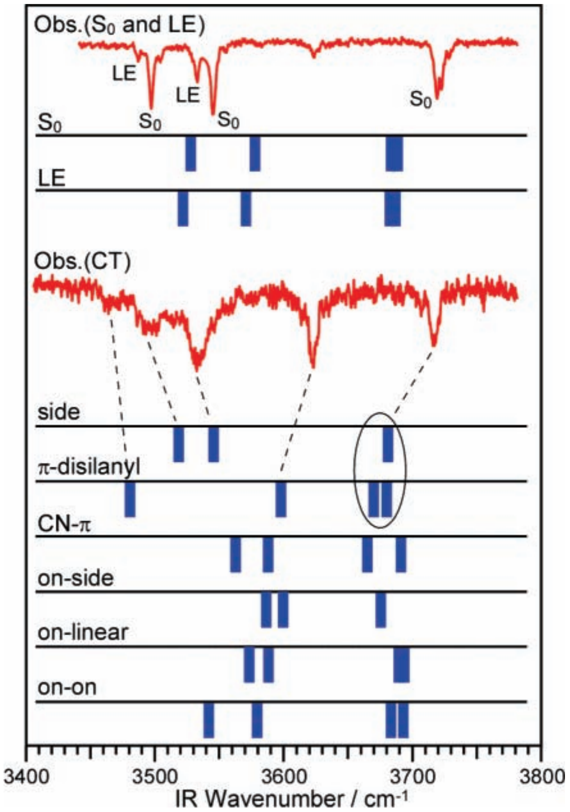

Figure 4. IR spectra of CPDS−$(H_2O)_2$. The observed IR spectra are displayed by a solid line, while the theoretical spectra are shown as a stick spectrum. The electronic states and the configurations of the carrier of each spectrum are also indicated in the figure. The scaling factor for the OH-stretch vibrations is 0.871, which is determined by averaging the differences between the theoretical and observed vibrational frequencies of all four OH stretching bands of the S_0 state.

attached to the phenyl ring by the π−hydrogen bond, while the other water is hydrogen-bonded to the π-orbital of the CN group. The third most stable isomer is the side configuration. The orientation of water molecules is very close to that in the S_0 and the LE state.

To assign the transient bands observed, vibrational frequencies of these six isomers found in the present calculation are examined. The calculated IR spectra are shown in Figure 4. The scale factor is 0.871, which is determined by averaging the differences between the theoretical and observed vibrational frequencies of all four OH stretching bands of the S_0 state. As shown in the figure, the observed spectrum is well reproduced by the superposition of OH bands of the π−disilanyl and the side isomers, considering the agreement in the case of the S_0 and the LE states. The band at 3623 cm^{-1} is assigned as the symmetric stretch of the π−hydrogen-bonded OH bond, whereas the antisymmetric stretch should be overlapped with the free OH stretch band. The 3469 cm^{-1} band is assigned as the hydrogen-bonded OH stretch of the molecule directed to the disilanyl group. The bands at 3536 and 3496 cm^{-1} are assigned as the hydrogen-bonded OH stretch in the side isomer. Our result indicates that the water molecules in the CPDS−$(H_2O)_2$ cluster move from the side to the π−disilanyl position holding the dimer structure of the water molecules. Such fine information on the solvent reorientation in the ICT process can be obtained owing to the experimental merit of the molecular cluster study.

Conclusion

The solvent reorientation process of the intramolecular charge-transfer (ICT) process in the excited electronic state of CPDS−$(H_2O)_2$ was investigated by transient IR spectroscopy. It was found that at least two isomers are generated in the ICT process of CPDS−$(H_2O)_2$. One of the isomers exhibits a band of π−hydrogen-bonded OH stretch of the water moiety. This is very clear evidence of the movement of the water molecule from the side position to the top of the phenyl ring. In addition, our results indicate that the water molecules reorientate, holding the dimer structure during the ICT process.

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