

First Observation of Intramolecular Charge-Transfer Emission from Jet-Cooled (*p*-Cyanophenyl)pentamethyldisilane in an Isolated Molecular Condition

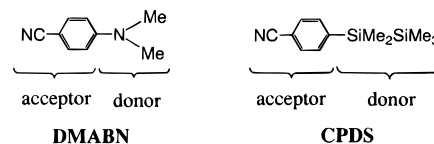
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Since the first report by Lippert on dual fluorescence exhibited by *p*-(dimethylamino)benzonitrile (DMABN),¹ a vast number of studies have been devoted to elucidation of the mechanism of the intramolecular charge transfer (ICT) emission of the molecules in which a donor and an acceptor moiety are linked by a single bond.² The twisted intramolecular CT (TICT) model³ has been widely accepted as the mechanism for the stabilization of the ICT excited state,² where the CT excited state is accompanied by a 90° twist of the dimethylamino group with respect to the aromatic ring, while some other ideas than the TICT model have also been proposed—for example, a quinoid-type structure model for DMABN.^{4a} However, the formation of the ICT excited state via the intramolecular stabilization such as the TICT mechanism is usually accompanied by inevitable solvation of such a highly polarized excited state; it has been difficult to observe the ICT state induced only by the intramolecular origin. Whereas supersonic molecular beam techniques have been applied for spectroscopic studies of ICT molecules under an isolated molecular condition,⁴

no CT emission has been found for isolated jet-cooled molecules without solvation or dimer formation until now.⁵



Among a wide variety of the ICT molecules,² phenyldisilanes, where the disilanyl group and the aryl π system serve as an electron donor and an acceptor, respectively, are quite unique because they show dual fluorescence, one originating from a locally excited (LE) state and the other from an ICT state, even in a nonpolar solvent.^{6,7} We have found that jet-cooled (*p*-cyanophenyl)pentamethyldisilane (CPDS),⁸ which bears a strong electron-accepting substituent at the para position of the phenylpentamethyldisilane (PDS), shows the ICT emission from the isolated molecules without solvation. In addition, the clusters of CPDS with water, CPDS-(H₂O)_n (*n* = 1 and 2), were found to exhibit the enhanced and significantly red-shifted CT emission.

(*p*-Cyanophenyl)pentamethyldisilane (CPDS) was heated to 350 K to gain its vapor pressure. 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. Output of an XeCl excimer laser (Lambda Physik LPX 1051) pumped tunable dye laser (Lambda Physik FL3002) was frequency doubled and used for the excitation of the jet-cooled CPDS. The laser beam irradiated the jet at 10 mm downstream of the pulsed nozzle. Fluorescence was collected by a lens system and detected by a photomultiplier tube (Hamamatsu IP28). For laser-induced fluorescence (LIF) excitation spectra, total emission intensity was monitored as a function of the dye laser frequency. A 25-cm monochromator (Nikon P-250) was used for the dispersed fluorescence (DF) spectra.

Figure 1 shows a LIF excitation spectrum of the LE ($\pi\pi^*$) transition of jet-cooled CPDS and its clusters with H₂O in the vicinity of their 0–0 bands. Identification of the bands of CPDS monomer and CPDS-(H₂O)_n clusters (*n* = 1 and 2) was performed by mass spectrometric analysis with resonance-enhanced two-photon ionization, and by hole burning spectroscopy.⁹ Origins of the LIF excitation spectra of CPDS-(H₂O)_n clusters were found to be red-shifted from that of CPDS monomer (35519 cm⁻¹) by 61 and 121 cm⁻¹ for *n* = 1 and 2, respectively. Short progressions of about 25-cm⁻¹ spacing are

(5) The ICT excited states stabilized by solvation or dimer formation have been investigated by laser spectroscopy combined with mass spectroscopy. For example, it has been observed that the CT state of 9,9'-bianthryl is substantially stabilized by solvation of a few polar molecules such as acetone and that the location of the solvent molecules on the solute molecule is critical for efficient stabilization of the CT state.^{4n,v,w}

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(7) A different nature of the ICT states of aryldisilanes has been proposed by Shizuka et al., where the disilanyl and a π system are assumed to serve as an acceptor and a donor, respectively. (a) Shizuka, H.; Obuchi, H.; Ishikawa, M.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1981**, 405. (b) Shizuka, H.; Sato, Y.; Ishikawa, M.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1982**, 439. (c) Shizuka, H.; Sato, Y.; Ueki, Y.; Ishikawa, M.; Kumada, M. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 341. (d) Shizuka, H.; Obuchi, H.; Ishikawa, M.; Kumada, M. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 383. (e) Shizuka, H.; Okazaki, K.; Tanaka, M.; Ishikawa, M.; Sumitani, M.; Yoshihara, K. *Chem. Phys. Lett.* **1985**, *113*, 89. (f) Hiratsuka, H.; Mori, Y.; Ishikawa, M.; Okazaki, K.; Shizuka, H. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 1665.

(8) We have reported briefly that CPDS shows almost only an intense CT emission even in a nonpolar solvent such as 3-methylpentane.^{6b} The preparation procedure of CPDS is also outlined in ref 6b.

(9) Details of their assignments will be published in a forthcoming paper.

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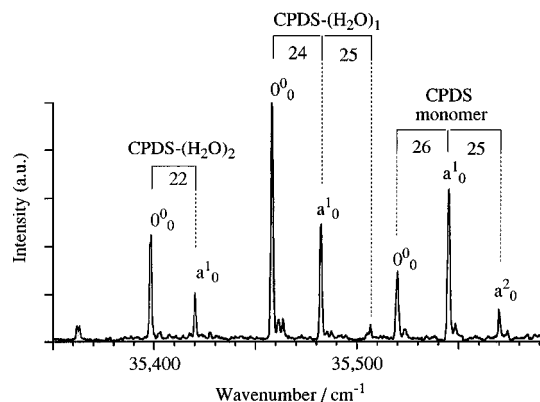


Figure 1. LIF excitation spectrum of jet-cooled CPDS.

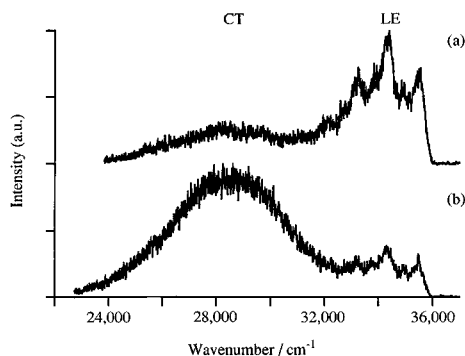


Figure 2. DF spectra of jet-cooled CPDS monomer obtained by the excitation of (a) the 0^0_0 and (b) the a^1_0 bands.

seen for all species. A similar low-frequency vibrational mode also has been observed in the case of PDS (35 cm^{-1}),¹⁰ so that this mode may be due to a torsional motion of the Si–Si group with respect to the phenyl ring. Since definitive assignment of this mode has not yet been made, we denote this mode as “a”.

Dispersed fluorescence (DF) spectra from the 0^0 and a^1 levels of CPDS monomer are shown in Figure 2. In the DF spectrum from the 0^0 level, an intense emission with distinct vibrational structures starting from the level of the laser excitation and a broad and red-shifted emission were observed. The former is assigned to the LE emission from the laser pumped $\pi\pi^*$ level. The peak maximum of the latter is located at $28\,500\text{ cm}^{-1}$ and red shifted by about 7000 cm^{-1} from the excitation level. This feature is very similar to that of the CT emission of CPDS in a nonpolar solvent ($\nu_{\text{max}} = 26\,300\text{ cm}^{-1}$).^{6b} To confirm that this emission is not due to phosphorescence, we measured its

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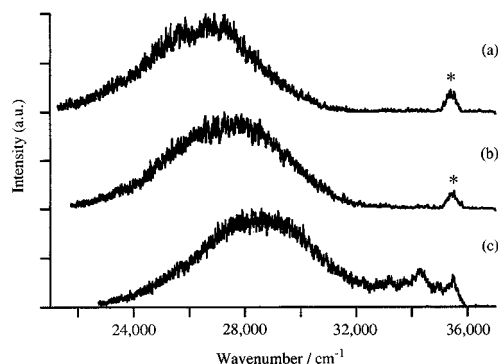


Figure 3. DF spectra of jet-cooled CPDS–(H_2O) $_n$ clusters obtained by the excitation of (a) 0^0_0 ($n = 2$), (b) 0^0_0 ($n = 1$), and (c) a^1_0 ($n = 0$) bands. Peaks indicated with asterisks are due to scattering of the laser light.

lifetime and found that it decayed faster than 20 ns. Such a fast decay cannot be originated from its phosphorescence but is due to a fluorescence-like emission. Thus, we assigned the broad emission as a CT emission. Moreover, it is noted that intensity of the CT emission is substantially enhanced in the DF spectrum from the a^1 level compared with that from the 0^0 level, while the excitation energy increases by only 26 cm^{-1} . The result represents that the excitation of this mode “a” is quite effective for the intramolecular CT process.

In Figure 3, the DF spectra from the 0^0 levels of the CPDS– H_2O clusters are shown together with that from the a^1 level of CPDS monomer. It is apparent that the LE emission is totally quenched and only the CT emission appears in the CPDS– H_2O clusters. The feature is also quite similar to the emission of PDS in solution of a polar solvent. The peak maxima of the CT emission of the CPDS–(H_2O) $_n$ clusters for $n = 1$ and 2 are red shifted by 1000 and 2000 cm^{-1} compared with that of CPDS monomer, respectively. This behavior caused by solvent clustering also supports that the broad emission comes from the CT state.

In conclusion, we have found for the first time that jet-cooled CPDS exhibits the dual emission from the 0^0 level even in an isolated molecular condition, while at present, it remains open whether the stabilization of the ICT state is achieved by twisting around the C(Ar)–Si bond or other molecular deformations. The stabilization of the ICT state and the enhancement of the CT emission are induced by cluster formation of CPDS with one or two H_2O molecules.

Further works are in progress to elucidate the stabilization mechanism for the ICT states of aryldisilanes and their clusters with various small molecules.

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