Fluorescence Spectroscopic and Time-Dependent Density-Functional Theory Studies of Diphenylsilane[†]

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We investigated fluorescence and fluorescence excitation of diphenylsilane (DPS) in a solution and molecular beams in combination with the aid of the DFT method. When the molecule was photoexcited at 250 nm in a cyclohexane solution, normal and excimer fluorescences were observed in the ranges of 260-320 and 330-450 nm, respectively. The fluorescence excitation spectrum indicates that the channel leading to the intramolecular excimer formation is not efficient in comparison with the normal fluorescence. Vibrationally resolved fluorescence excitation spectra were measured for the DPS molecules cooled in pulsed supersonic expansion of He in the range 262.2-271.7 nm, in which we can see several electronic excitation spectra exhibiting the electronic band origins. We found that the simulated absorption spectrum based on the time-dependent density-functional theory calculations accords well with the absorption spectrum.

Key Words : Diphenylsilane, Fluorescence excitation, Time-dependent density-functional theory, Oscillator strength, Molecular beam

Introduction

Diarylalkanes are shown to form excimers having an intramolecular face-to-face arrangement of the two aromatic rings at interchromophore separations of 3-4 Å.[1-6] Boo and co-workers have shown that the substitution of a silicon atom in the insulating carbon atom of bis(9-fluorenyl)-methane makes a great effect on the rate of the intramolecular excimer formation and the stability of the excimer presumably owing to the $p_\pi(C)$-$d_\pi(Si)$-$p_\pi(C)$ hyperconjugation. The extensive hyperconjugation hampers the rotation along the C-Si-C bonds, by which the rate for the excimer formation is expected to be slow.[5] For a detailed understanding of the excited-state dynamics leading to the excimer formation in the singlet excited state, it is essential to elucidate the excited singlet equilibrium conformations and their energies. We presume that diphenylsilane (DPS) is an appropriate molecule for both the theoretical and experimental approaches to the elucidation of the excited structure, dynamics, and stability because the compound is relatively small for quantum mechanical calculations and volatile for molecular beam studies.

Our main research purposes in the present research are: (1) to search for ground-state low-lying conformers and to calculate their energies; (2) to explore how many conformers and the corresponding excited-states are involved in the absorption spectrum in the solution phase and in the fluorescence excitation spectrum in the molecular beam with the aid of the time-dependent (TD) DFT calculations;[7-9] finally (3) to reproduce the absorption spectrum by using the TD DFT method and assign the electronic state relevant to the

electronic absorption. In this work, we present the various spectroscopic and quantum mechanical investigations concerning the fluorescence and the fluorescence excitation in the solution and the beam. We also present ab initio and TD DFT calculation results of the structures and energies of the excited singlet electronic states. Our findings in this work could help to establish the excited-state spectroscopy and dynamics.

Experimental and Theoretical Methodologies

The spectral arrangement contains the light collection optics coupled with a pulsed molecular beam source and tunable dye lasers. The pulsed molecular beam source includes a nozzle assembly, differentially pumped expansion, and collimation chambers. The frequency-doubled tunable dye laser pumped with a Nd/YAG or a XeCl excimer laser is guided into the source chamber in which it intersects a skimmed and collimated supersonic molecular beam. The nozzle assembly and expansion chamber were used with an optical filter and a photomultiplier to record fluorescence. A supersonic molecular beam was formed by expanding the heated DPS molecules at 65 °C in He and with a backing pressure of about 50 kPa through a pulsed valve having a 0.8 mm orifice. The molecular beams were crossed by the laser beams at 1 cm down stream of the nozzle. The DPS compound with a purity of 97% was purchased from Aldrich Advancing Science Co., and was used without purification.
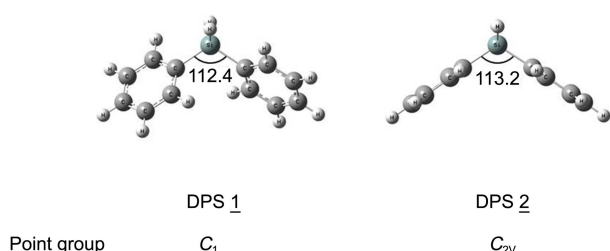
The ground-state equilibrium geometries and the vibrational frequencies were probed by using the Kohn-Sham density-functional theory (DFT).[10] Becke's three-parameter exchange functional[11,12] and the gradient-corrected Lee-Yang-Parr correlational functional (B3LYP)[13] were used with the 6-31G(d) and cc-pVTZ basis sets.[14-17] The time-dependent

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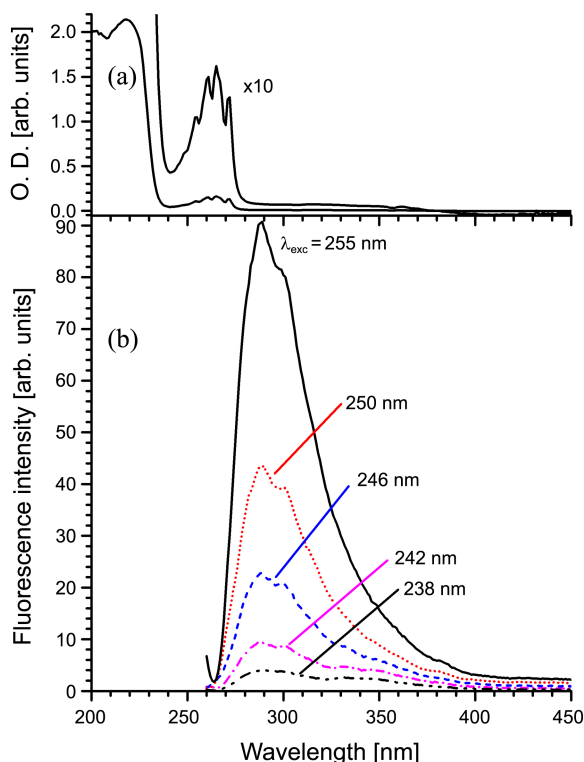[†]This paper is to commemorate Professor Kook Joe Shin's honourable retirement.

(TD) DFT method[14-17] was also applied to compute the vertical excitation energies with the B3LYP/cc-pVTZ// B3LYP/cc-pVTZ method at the various optimized S_0 geometries. All calculations were carried out with the Gaussian 03 suite of program.[18]

Results and Discussion

We searched two conformers which were optimized with the B3LYP/cc-pVTZ method. The molecular models of the two conformers are presented in Figure 1. Our quite recent publication indicates that DPS 1 and DPS 2 are almost thermoneutral.[19] In Figure 2, are compared the fluorescence spectra with the absorption one. Below the excitation wavelength 240 nm, the fluorescence intensities are significantly diminished. We presume that the normal and excimer fluorescences correspond to the peaks observed in the ranges 260-320 and 330-450 nm, respectively.

Figure 3 compares the fluorescence excitation (FE) spectra measured in the solution phase with the absorption one. Here, we observe that the photoexcitation leading to the excimer states occurs in the range above 230 nm. In an effort to analyze the absorption spectrum and to infer the contributions of the two conformers in the absorption spectrum, we performed the TD DFT calculations on the two conformers. Quite recently, our previous study indicates that the TD DFT B3LYP/cc-pVTZ//B3LYP/cc-pVTZ method slightly overestimates the experimental vertical excitation energies of the molecules within 6.83 ± 5.17%. The rms deviation was found to be as low as 0.177 eV.[20] The present study indicates that the TD DFT B3LYP/cc-pVTZ//B3LYP/cc-pVTZ calculations overestimate within 15.3 ± 8.4% the 0-0 bands of four compounds, silicon chloromethylidyne,[21] dodecamethylcyclohexasilane,[22] 2,2-diphenylhexamethyl-trisilane,[23] and diphenylsilane, which contain at least one silicon atom. Table 1 compares the excitation energies calculated with the B3LYP/cc-pVTZ//B3LYP/cc-pVTZ method with the experimental ones of the jet-cooled molecules. The rms deviation was found to be 0.213 eV. The experimental origins in Table 1 were chosen from free jet or molecular beam experiments in which the reliable 0-0 bands of the isolated molecules were appropriately obtained.

In an effort to elucidate the vibration-like structures observed in the absorption spectra as shown in Figures 2 and 3, we measured electronically and vibrationally resolved FE

Figure 1. Low-lying conformers of diphenylsilane, with numbers indicating the order of Gibb free energy and with point groups. The molecular structures were optimized with the B3LYP/cc-pVTZ method constraining the corresponding symmetries.
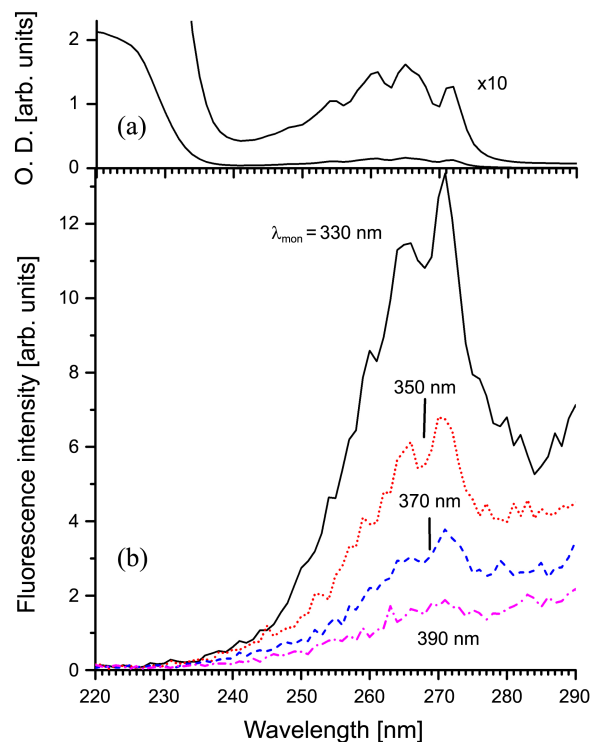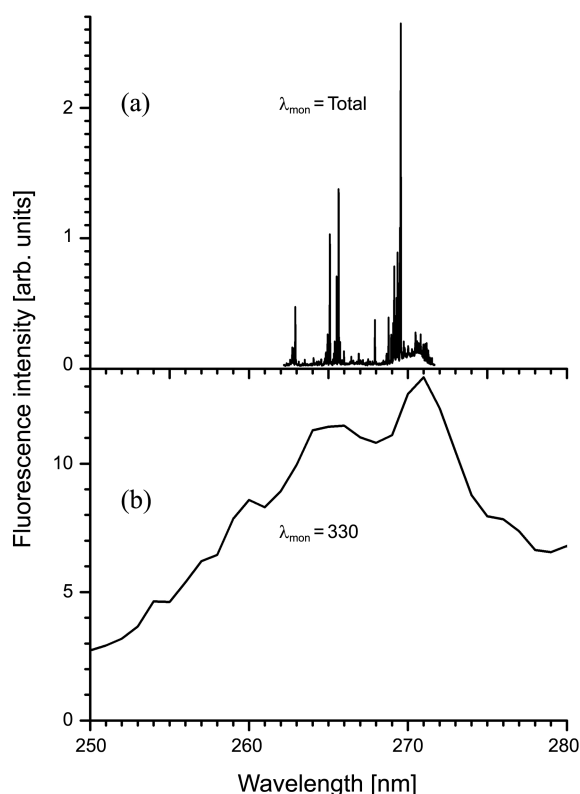

Figure 2. (a) Absorption spectrum of a 1.30×10^{-4} *M* diphenyl-silane solution in cyclohexane. (b) Fluorescence spectra of 0.30 $\times 10^{-4}$ *M* diphenylsilane solution in cyclohexane. The excitation wavelengths λ_{exc} are indicated in the individual fluorescence spectra.

Figure 3. (a) Absorption spectrum of a 1.30×10^{-4} *M* diphenylsilane solution in cyclohexane. (b) Fluorescence excitation spectra of a 1.30×10^{-4} *M* diphenylsilane solution in cyclohexane.
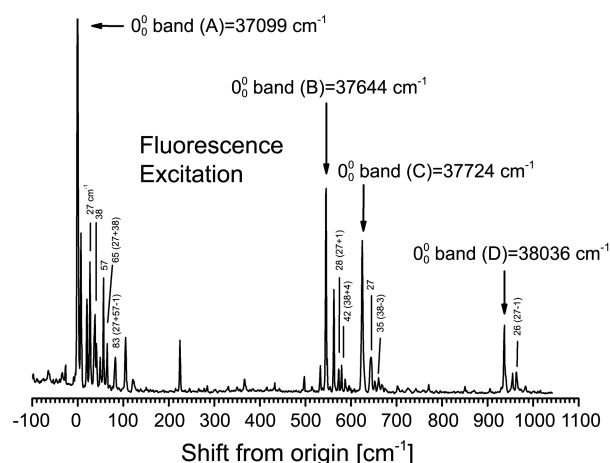
Table 1. Vertical excitation energies (eV) and oscillator strengths for $S_1 \leftarrow S_0$ transition in various molecules containing at least one silicon atom calculated with the TD DFT B3LYP/cc-pVTZ//B3LYP/cc-pVTZ method

Species	Point group	Excited state	Excitation energy (eV)	Oscillator strength	Exptl (eV)
Silicon chloromethylidyne (SiCCl)	C_s	$^1A'$	2.3644	0.0040	1.88984[a]
Dodecamethylcyclohexasilane	D_{3d}	^1E_u	5.2148	0.0289	4.587[b]
2,2-Diphenylhexamethyltrisilane	C_2	^1B	4.7369	0.0312	4.5153[c]
Diphenylsilane	C_{2v}	$^1B_2$	5.4076	0.2123	4.5996[d]

[a]ref 21, [b]ref 22, [c]ref 23, [d]ref this work

Figure 4. (a) Fluorescence excitation spectrum of the jet-cooled diphenylsilane. (b) Fluorescence excitation spectrum of a 1.30×10^{-4} *M* diphenylsilane solution in cyclohexane, which was measured by monitoring the 330-nm fluorescence.
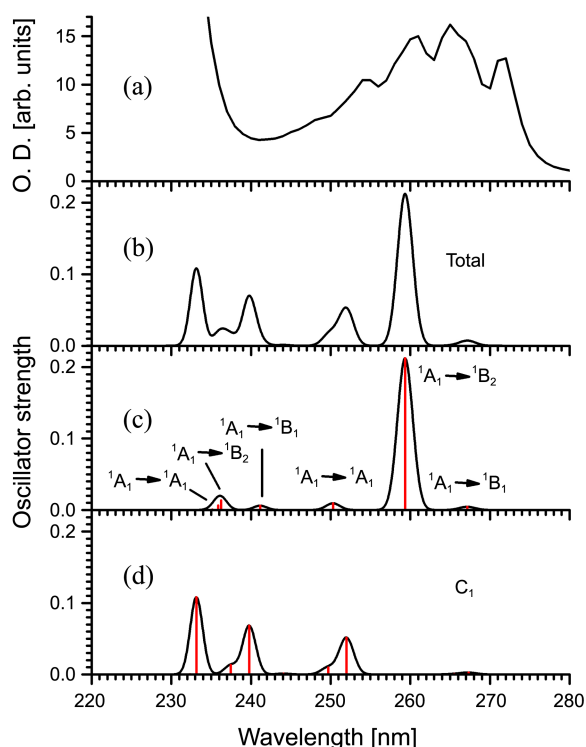
spectrum of the ultracold DPS molecules generated in the supersonic expansion. Figure 4 compares the FE spectrum of the jet-cooled molecules with that of the solution. Note that the FE spectrum of the jet-cooled molecules was measured by monitoring the total fluorescence while the spectrum of the solution was measured by monitoring the 330-nm fluorescence. The solution spectrum is shown to mimic the molecular beam spectrum.

Figure 5 depicts the scale-expanded FE spectrum corresponding to Figure 4(a). At least, we can see four electronic spectra consisting of the corresponding electronic origin bands and their vibronic bands. The four electronic spectra include the common vibrational bands denoted as 27, 38 and 57 cm^{-1} and their combination bands such 65 and 83 cm^{-1}. This implies that the four electronic bands correspond the individual electronic states. The presence of the relatively

Figure 5. Scale-expanded fluorescence excitation spectrum of the jet-cooled diphenylsilane. Various 0-0 bands are indicated in the A, B, C, D spectra.

dense electronic states are presumably attributed to existence of a silicon atom in a DPS molecule. The slightly different vibronic frequencies in the four electronic spectra denoted in Figure 5 may reflect the slightly different electronic environments in which the four electronic states of a DPS molecule are determined.

Figures 6(c) and 6(d) present the Gaussian spread of the oscillator strengths determined in terms of the scaled vertical excitation energies derived with the TD B3LYP/cc-pVTZ//B3LYP/cc-pVTZ method. Note that the scaled vertical excitation energies were evaluated with a uniform scaling factor of 0.884, the factor derived on the basis of the data listed in Table 1. Also note that the symmetries of the excited states of the C_{2v} conformers are denoted in the graph. The theoretically derived oscillator strengths as functions of the scaled excitation wavelengths were broadened by using Gaussian line shape functions having a uniform full width at half maximum (fwhm) of 0.02 eV. The total spread oscillator strengths shown in Figure 6(b) are found to have the similar pattern as that shown in Figure 6(a), however, still blue-shifted with respect to the experimental absorption spectrum. Here, we realized that many excited states are involved in the absorption spectrum. The vibration-like peaks observed in the absorption spectra seen in Figures 2(a), 3(a), 3(b), 4(b), and 6(a) turned out to be actually electronic excitation peaks through the analysis of the well-resolved vibronic excitation spectrum (Figure 5) measured in the molecular beams.

Figure 6. (a) Absorption spectrum of a 1.30×10^{-4} *M* diphenyl-silane solution in cyclohexane. (b) The total oscillator strengths of the conformers DPS 1 and DPS 2. (c) Oscillator strengths of DPS 2. (d) Oscillator strengths of DPS 1.

Conclusions

We have investigated fluorescence and fluorescence excitation (FE) of diphenylsilane (DPS) in a solution and in molecular beams. When the molecule was photoexcited at 250 nm in a cyclohexane solution, the normal and excimer fluorescences were observed in the ranges 260-320 and 330-450 nm, respectively. The fluorescence excitation spectra measured in a solution and in molecular beams indicate that the channel leading to the intramolecular excimer formation was found to be not efficient in comparison with the normal fluorescence. We found that the simulated absorption spectrum based on the time-dependent (TD) DFT calculations accords well with the absorption spectrum.

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