This probably shows that either the deposited Ag functions as a catalyst for the succeeding Ag deposition or very small Ag clusters do not absorb 633 nm monitoring light. A detailed study is now under way.

The I_{OWG} change in Figure 3a was ca. 0.01 in optical density (OD). This means that OD will only be ca. 10^{-4} when the monitoring beam is incident vertically over the OWG. Thus, the OWG method proved to be very effective for monitoring surface photoreactions. We are now also testing OWG's having semiconductor films including conductive SnO_2 and photoactive TiO_2.

Observation of a Local Minimum on the S_1 Surface of *cis*-Stilbene Solvated in Inert Gas Clusters

Hrvoje Petek,[†] Yoshihisa Fujiwara,[‡] Dongho Kim,[§] and Keitaro Yoshihara*

Institute for Molecular Science
Myodaiji, Okazaki 444, Japan

Received May 2, 1988

Contrary to previously accepted view, this work presents strong evidence for a minimum on the S_1 surface of *cis*-stilbene in which the molecule lives on a nanosecond time scale. *Cis*- and *trans*-stilbene have been extensively studied as model systems for photochemical cis–trans isomerization in gas phase under isolated conditions and in solution where solvent viscosity opposes large amplitude geometrical changes.[1-8] In *trans*-stilbene, isomerization is inhibited by a 1200-cm^{-1} barrier.[2] By contrast, at ~300 K in gas[3] and solution,[4,7] *cis*-stilbene is nonemissive presumably because the S_1 state decays by barrierless isomerization on an ~1 ps time scale. In viscous solutions, a marked increase in *cis*-stilbene fluorescence quantum yield has been ascribed to retardation of isomerization by solvent-dependent viscosity barrier.[5,8] In this work, some of these ideas are challenged by observation of the same emission spectrum from inert-gas *cis*-stilbene clusters formed by supersonic expansion. Namely, the macroscopic viscosity of inert gas clusters (e.g., Ar)[9] is more than 10^6 times smaller than in viscous solutions;[5] therefore, viscosity may not be the controlling factor, rather it is proposed that *cis*-stilbene in a cluster vibrationally relaxes into an inherent minimum on the S_1 surface, from where it decays with the observed 20 ns lifetime. Fluorescence excitation and emission spectra of *cis*-stilbene seeded in several gases support these conclusions.

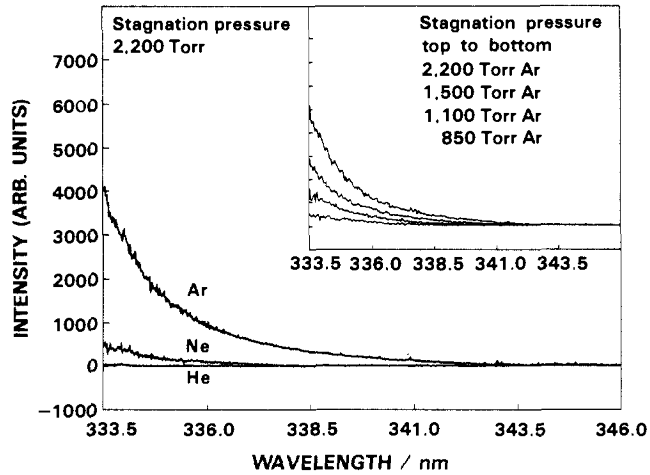


Figure 1. The fluorescence excitation spectra of *cis*-stilbene in He, Ne, and Ar expansions. Argon stagnation pressure dependence of the emission intensity is shown in the insert.

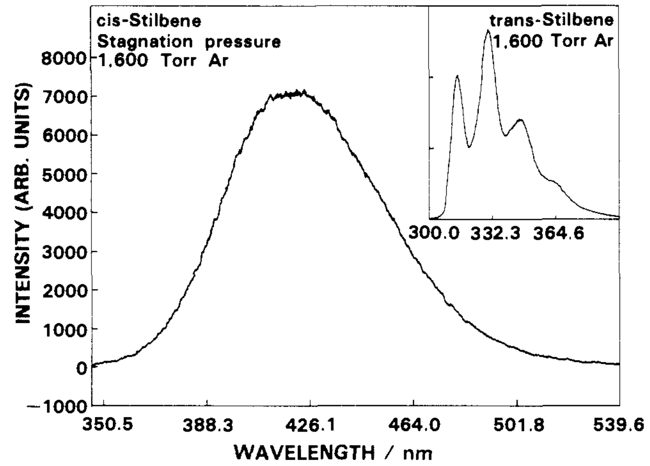


Figure 2. The emission spectra of *cis*- and *trans*-stilbene (insert) in Ar clusters generated by supersonic expansion. Excitation wavelength is 266 nm.

The supersonic beam of *cis*-stilbene (at 80 °C) seeded in He, Ne, Ar, Kr, N_2, or C_2H_4 is formed by expansion through a 0.2 mm diameter pulsed nozzle. *cis*-Stilbene fluorescence is excited by an excimer-pumped dye laser between 354 and 308 nm. Emission spectra are excited by the same laser or by fourth (266 nm) or fifth (213 nm) harmonics of a Nd:YAG laser, dispersed with a 25 cm monochromator, and detected by an OMA. The signal is measured to be linear with laser power.

cis-Stilbene fluorescence excitation spectra in Figure 1 show extraordinary dependence of emission intensity on the seeding gas and its pressure (insert). The spectrum between 308 and 333.5 nm (not shown) is featureless and monotonically rising. The displacement of the Franck–Condon maximum from the origin is due to large changes in the geometry between ground and excited states. Since the density of *cis*-stilbene in the supersonic beam is determined by *cis*-stilbene density before expansion, the observed effects suggest unexpected increase in *cis*-stilbene fluorescence quantum yield for higher stagnation pressures and for heavier noble gases.

The emission spectrum of *cis*-stilbene (Figure 2) closely resembles the previously observed spectra in viscous solutions.[5] The spectral profile is independent of seeding gas, stagnation pressure, excitation wavelength, and laser power. The relative emission intensity with 266-nm excitation and 1600 Torr stagnation pressure has the following dependence on seeding gas: Kr; Ar; N_2; Ne; C_2H_4; He/1.0; 0.5; 0.09; 0.0086; 0.0067; 0.0058. The same

---

[†] Supported by Yamada Science Foundation Fellowship and National Science Foundation Grant INT-8419500.

[‡] Permanent address: Faculty of Pharmaceutical Sciences, Kanazawa University, Takara-machi, Kanazawa 920, Japan.

[§] Permanent address: Optics Laboratory, Korea Standards Research Institute, Taedok Science Town, Chungnam 300-31, Korea.

(1) Saltiel, J.; D'Agostino, J. T.; Megarity, E. D.; Metts, L.; Neuberger, K. R.; Wrighton, M.; Zafiriou, O. C. *Org. Photochem.* **1973**, *3*, 1. Fleming, G. R. *Ann. Rev. Phys. Chem.* **1986**, *37*, 81.

(2) Syage, J. A.; Lambert, Wm. R.; Felker, P. M.; Zewail, A. H. *Chem. Phys. Lett.* **1973**, *88*, 266. Amirav, A.; Jortner, J. *Chem. Phys. Lett.* **1983**, *95*, 295. Syage, J. A.; Felker, P. M.; Zewail, A. H. *J. Chem. Phys.* **1984**, *81*, 4706.

(3) Greene, B. I.; Farrow, R. C. *J. Chem. Phys.* **1983**, *78*, 3336.

(4) Doany, F. E.; Hochstrasser, R. M.; Greene, B. I.; Millard, R. R. *Chem. Phys. Lett.* **1985**, *118*, 1.

(5) Malkin, S.; Fisher, E. *J. Phys. Chem.* **1964**, *68*, 1153. Saltiel, J.; D'Agostino, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 6445. Fischer, G.; Seger, G.; Muzkat, K. A.; Fischer, E. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1569.

(6) Sumitani, M.; Nakashima, N.; Yoshihara, K.; Nagakura, S. *Chem. Phys. Lett.* **1977**, *51*, 183.

(7) Sumitani, M.; Nakashima, N.; Yoshihara, K. *Chem. Phys. Lett.* **1979**, *68*, 255.

(8) Yoshihara, K.; Namiki, A.; Sumitani, M.; Nakashima, N. *J. Chem. Phys.* **1979**, *71*, 2892.

(9) Lowry, B. A.; Rice, S. A.; Grey, P. *J. Chem. Phys.* **1964**, *40*, 3673. The viscosity of Ar at its boiling point is taken as the upper limit for Ar cluster viscosity. The excess excitation energy (up to ~18 000 cm^{-1}) is sufficient to heat a cluster larger than 100 atoms to Ar boiling point assuming no initial energy content.

emission spectrum is observed even when *cis*-stilbene is excited by 212.8 nm light to the second absorption maximum ~18 000 cm^{-1} above the red limit of *cis*-stilbene fluorescence excitation spectrum.

These spectroscopic observations are explained by the following mechanism: (i) in a free *cis*-stilbene molecule, fluorescence is quenched by isomerization because the Franck–Condon excitation is much above the barrier to isomerization; (ii) in inert gas clusters, intramolecular vibrational relaxation and interactions with the solvent distribute the initial excitation energy among *cis*-stilbene degrees of freedom; (iii) the energy in low-frequency vibrations such as phenyl torsion[10] efficiently transfers to cluster van der Waals modes; (iv) the cluster evaporatively cools; and (v) the cooling process traps some *cis*-stilbene molecules into a potential minimum from where the molecule emits.

This mechanism is tested by exciting *trans*-stilbene above the barrier of isomerization; emission spectral profile changes with stagnation pressure provide evidence for cluster formation and vibrational relaxation. Below 300 Torr Ar, the spectrum is structureless due to the intramolecular vibrational redistribution, but at higher pressures (Figure 2, insert) it develops typical vibrational structure of *trans*-stilbene solution spectra.[5] High-pressure spectra are from *trans*-stilbene S_1 origin (~310 nm)[11] independent of excess excitation energy indicating that vibrational relaxation occurs within 2.7 ns, the emission lifetime of *trans*-stilbene.[2] The emission quantum yield of clusters is found to be higher than for the free molecule because *trans*-stilbene vibrationally cools, in competition with temperature-activated isomerization. The increase in emission intensity with mass of the noble gas correlates well with clustering efficiency; however, other factors such as vibrational relaxation rates should be important. A detailed investigation of these interesting new observations on *cis*-stilbene isomerization dynamics is in progress.

---

(10) Suzuki, T.; Mikami, N.; Ito, M. *J. Phys. Chem.* **1986**, *90*, 6431.

(11) Syage, J. A.; Felker, P. M.; Zewail, A. H. *J. Chem. Phys.* **1984**, *81*, 4685.

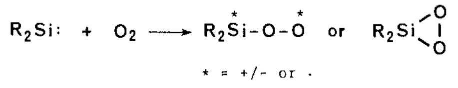
Reaction of Dimesitylsilylene in a Cryogenic Oxygen Matrix: IR Spectroscopic Observation of a Silylene–Oxygen Adduct

Takeshi Akasaka,[1a] Shigeru Nagase,[1b] Akira Yabe,[1c] and Wataru Ando*,[1a]

Department of Chemistry, University of Tsukuba
Tsukuba 305, Japan
Department of Chemistry, Faculty of Education
Yokohama National University, Yokohama 240, Japan
National Chemical Laboratory for Industry
Tsukuba 305, Japan

Received April 18, 1988

The chemistry of silylenes has been the subject of considerable interest in recent years.[2] The isolation of silylenes in an argon or hydrocarbon matrix has contributed greatly to the knowledge of these reactive species.[2c,3] Silylenes are known to react very rapidly with oxygen[2d,4] affording the adducts for which silanone *O*-oxide (**1a**) or siladioxirane (**1b**) structures have been suggested,[2d]



$$R_2Si: + O_2 \longrightarrow R_2\overset{*}{Si}-O-\overset{*}{O} \quad \text{or} \quad R_2Si{<}\begin{smallmatrix}O\\|\\O\end{smallmatrix}$$

$* = +/-$ or $\cdot$

	1a	1b
R = mesityl ;	3a	3b
R = H ;	4a	4b

similar to the case of reaction of carbenes with oxygen giving the corresponding carbonyl oxides and dioxiranes.[5] However, no spectroscopic evidence for such silylene-oxygen adducts has been reported.[2d] Our interest in the reactivities of initially formed peroxidic intermediates in the oxygenation mechanism of divalent atoms, such as carbenes[5a] and sulfides,[6] has led us to initiate low-temperature photolysis studies of silylene precursors.[7] Here, we report the results of recent investigations of silylenes in a cryogenic oxygen matrix, leading to the first spectroscopic observation of a silylene-oxygen adduct. A theoretical study of the

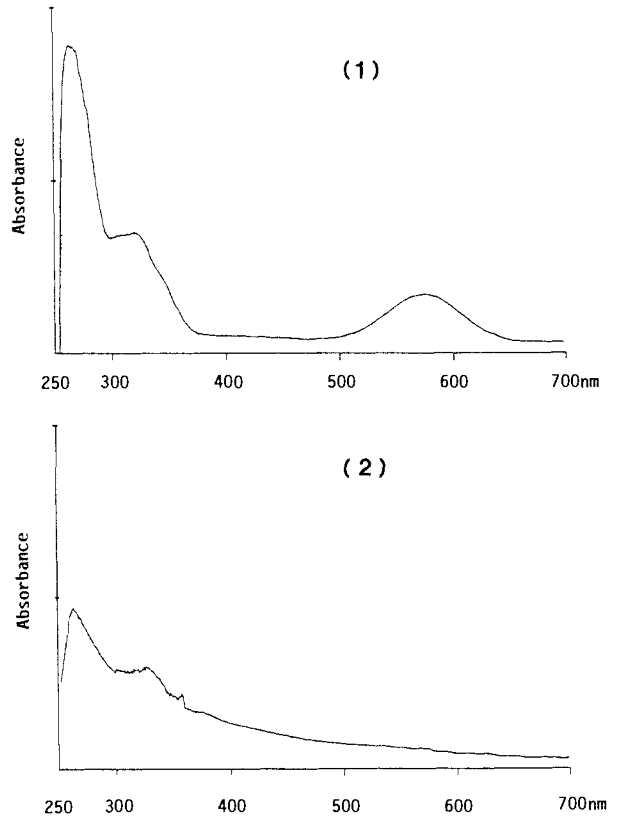


Figure 1. Difference UV spectra, (1) and (2), obtained upon photolysis of trisilane **2** isolated in argon and oxygen matrices at 16 K, respectively.

---

(1) (a) University of Tsukuba. (b) Yokohama National University. (c) National Chemical Laboratory for Industry.

(2) (a) Gaspar, P. P. In *Reactive Intermediates*; Jones, M., Ed.; Wiley: New York, Vol. 1, 1978; p 229. (b) 1981; Vol. 2, p 335. (c) 1985; Vol. 3, p 333. (d) Gaspar, P. P.; Holten, D.; Konieczny, S. *Acc. Chem. Res.* **1987**, *20*, 329. (e) Hawari, J. A.; Lesage, M.; Griller, D.; Weber, W. P. *Organometallics* **1987**, *6*, 880.

(3) (a) Michalczyk, M. J.; Fink, M. J.; De Young, D. J.; Carlson, C. W.; Welsh, K. M.; West, R. *Silicon, Germanium, Tin, Lead Compds.* **1986**, *1*, 75. (b) Sekiguchi, A.; Hagiwara, K.; Ando, W. *Chem. Lett.* **1987**, *209*. (c) Gillette, G. R.; Noren, G. H.; West, R. *Organometallics* **1987**, *6*, 2617. (d) Ando, W.; Sekiguchi, A.; Hagiwara, K.; Sakakibara, A.; Yoshida, H. *Organometallics* **1988**, *7*, 558.

(4) (a) Santon, A. C.; Freedman, J.; Wormhoudt, J.; Gaspar, P. P. *Chem. Phys. Lett.* **1985**, *122*, 190. (b) Gaspar, P. P. In *Proceedings of the 7th International Symposium on Organosilicon Chemistry*; Sakurai, H., Ed.; Horwood: Chichester, 1985; p 87. (c) Eley, C. D.; Rowe, M. C. A.; Walsh, R. *Chem. Phys. Lett.* **1986**, *126*, 153. (d) Sandhu, V.; Jodhan, A.; Safarik, I.; Strausz, O. P.; Bell, T. N. *Chem. Phys. Lett.* **1987**, *135*, 260.

(5) (a) Sugawara, T.; Iwamura, H.; Hayashi, H.; Sekiguchi, A.; Ando, W.; Liu, M. T. H. *Chem. Lett.* **1983**, 1261. (b) Bell, G. A.; Dunkin, I. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1213. (c) Dunkin, I. R.; Bell, G. A. *Tetrahedron* **1985**, *41*, 339. (d) Dunkin, I. R.; Shields, C. J. *J. Chem. Soc., Chem. Commun.* **1986**, *154*. (e) Chapman, O. L.; Hess, T. C. *J. Am. Chem. Soc.* **1984**, *106*, 1842. (f) Werstiuk, N. H.; Casal, H. L.; Scaiano, J. C. *Can. J. Chem.* **1984**, *62*, 2391. (g) Casal, H. L.; Sugamori, S. E.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 7623. (h) Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396. (i) Casal, H. L.; Tanner, M.; Werstiuk, N. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 4616. (j) Ganzer, G. A.; Sheridan, R. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1986**, *108*, 1517. (k) Sander, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 255. (l) Sander, W. *J. Org. Chem.* **1988**, *53*, 121.

(6) Akasaka, T.; Yabe, A.; Ando, W. *J. Am. Chem. Soc.* **1987**, *109*, 8085, references cited therein.

0002-7863/88/1510-6270$01.50/0