The Raman Spectra of *trans*-Stilbene Radical Cations in Boric Acid Matrices

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Photoionization of *trans*-stilbene to radical cation in boric acid matrices was performed at room temperature. We report the Raman spectra of monomer and dimer radical cations of *trans*-stilbene.

Photoinduced electron transfer (PET) reactions have been intensely investigated[1]. Radical ions, the lifetimes of which are less than milliseconds, are considered a key intermediate in these reactions.[2] Indeed, by means of laser flash photolysis, we have observed the behavior of stilbene radical cations in cis-to-trans isomerization,[3] dimerization[4] and oxygenation[5]. Specifically, we have proposed that dimer radical cation is a key intermediate for cis-to-trans isomerization of stilbene radical cation. For further study of these reaction mechanisms, it is important to measure vibrational spectra such as IR and Raman, because structural information ensures the identification of transient species. There are, however, a few papers reporting Raman spectra of radical ions.[6] Hub et al. have reported the resonance Raman spectra of radical ions of *trans*-stilbene.[7] But, when we noticed the high concentrations of *trans*-stilbene that they employed,[3] we suspected that they might have measured the resonance Raman spectra of dimer radical cation instead of monomer radical cation. In this paper, we report the Raman spectra of monomer and dimer radical cations of *trans*-stilbene in boric acid matrices.

Mixtures of *trans*-stilbene (5 mg or 100 mg) and 5 g of boric acid were heated at 220°C to melt, and cast to make boric acid glass of one mm in thickness.[8] When the mixtures were irradiated with the fourth harmonic (266 nm, 7 ns of pulse width) of a Q-switched Nd:YAG laser (DCR-11, Quanta- Ray, 3 mJ / pulse with 10 Hz repetition) or 254 nm light from a low-pressure mercury lamp, the mixtures turned to a greenish yellow and the color was sustained for a few months at ambient conditions. Fig. 1 shows an absorption spectrum for a sample of low concentration of *trans*-stilbene, namely, 5 mg of *trans*-stilbene of 5 g of boric acid (we denote this hereafter as **1** and the glass containing 100 mg of *trans*-stilbene as **2**). Two peaks at λ_{max} = 480 nm and 780 nm are characteristic of *trans*-stilbene radical cation.[2,8,9] Irradiation of **1** containing 9, 10-dicyanoanthracene gave spectra identical with Fig. 1, indicating that we observed *trans*-stilbene radical cation, not anion. ESR signals from **1** also confirm the photochemical generation of *trans*-stilbene radical cation. The signals disappeared with fading of the color at 70 °C. The ESR spectra were similar to that in the literature, measured with γ-irradiation in frozen matrices at 100K.[10]

Irradiation of sample **2** gave almost identical absorptions compared with **1** in the visible region, but in the near-IR region, there was a charge resonance band at 1500 nm, characteristic of dimer radical cations of *trans*-stilbene.[4] This suggested an equilibrium between monomer and dimer radical cations. In the case of **2**, the high concentration of *trans*-stilbene pushed the equilibrium to the right.

$$S^{+\bullet} + S \rightleftharpoons S_2^{+\bullet}$$

Figure 2 depicts the Raman spectrum of **2** after 1 minute irradiation with a 266 nm laser pulse. This is a differential spectrum between the spectra before and after irradiation. As shown in Fig. 3,

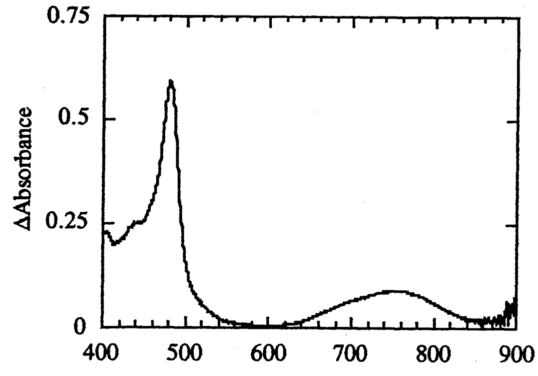

Figure 1. Absorption spectrum of **1** in boric acid matrix after 15 min, irradiation with a low pressure mercury lamp.

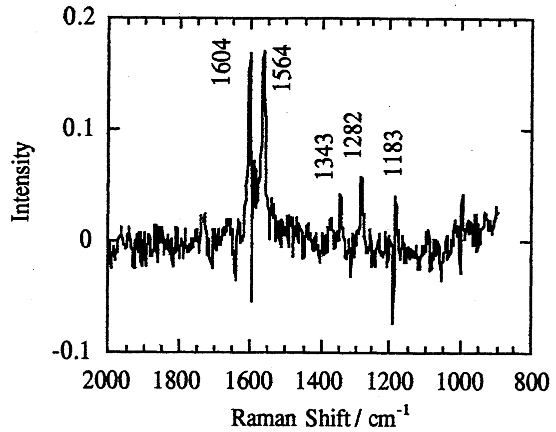

Figure 2. NIR FT-Raman spectrum of **2** after 1 minute irradiation with a 266 nm laser pulse.

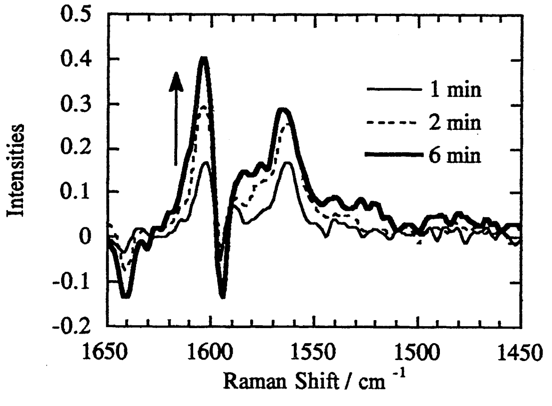

Figure 3. Irradiation time dependence of Raman spectra of **2** with 266 nm laser pulse for 1, 2 and 6 min.

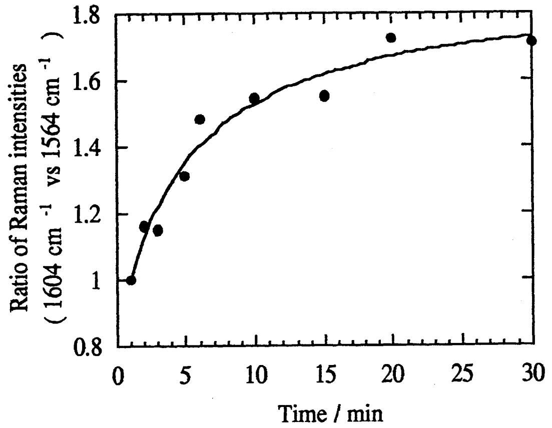

Figure 4. Irradiation time dependence of Raman Intensities at 1604 cm^{-1} and 1564 cm^{-1} of **2** with 266 nm laser pulse.

intensities of 1604 cm^{-1} and 1564 cm^{-1} bands increase with increasing time of irradiation. However, the band at 1604 cm^{-1} grows faster than the band at 1564 cm^{-1} does. Actually, the ratio of intensities for these bands changed with time as depicted in Fig 4. In the case of **1**, the same spectrum as Fig. 2 could be obtained but the time-course was different from the case of **2**. Both peaks at 1604 and 1564 cm^{-1} grew at the same rate, namely, the ratio of intensities at 1604 and 1564 cm^{-1} were constant with time. This observation could be reproduced for the sample **1** containing DCA. In light of the equilibrium between monomer and dimer radical cation, these results indicate that the Raman band at 1564 cm^{-1} is originated from the monomer radical cation and the band at 1604 cm^{-1} is due to both monomer and dimer radical cations. Hub et al. reported time-resolved resonance Raman experiments for *trans*-stilbene radical cation.[6, 7a] The peaks in Fig. 2 are identical with those spectra , except the band at 1564 cm^{-1}. They produced radical cations by electron transfer to an excited DCA from *trans*-stilbene, the concentration of which was 0.05 M in acetonitrile. As we have already reported, in such a high concentration of *trans*-stilbene, a radical cation interacts with a neutral *trans*-stilbene to make a dimer radical cation .[4] Therefore we deduce that their spectra are due to dimer radical cation instead of monomer radical cation. Indeed, Fig. 2 was similar to their spectrum with accumulating dimer radical cation, namely, the relative intensity of 1564 cm^{-1} band to 1604 cm^{-1} band decreased. They calculated force constants of *trans*-stilbene radical cations[7b] and assigned the 1604 cm^{-1} band as Ph-C_e stretching and 1564 cm^{-1} band as C_e=C_e stretching. However,they failed to observe the 1564 cm^{-1} band in their experiments. This was because they produced only dimer radical cation. Both bands at 1604 and 1564 cm^{-1} could be observed in the case of **1** and the change of relative intensity of the bands in the case of **2** could be explained rationally by the equilibrium between monomer and dimer radical cation. Now we are continuing our efforts to calculate the spectrum for a dimer radical cation and to study of cyclobutane radical cations as a model compound for the dimer radical cation of stilbene.

We report for the first time the Raman spectra of monomer and dimer radical cations of trans-stilbene in a boric acid matrix by photoionization.

References and Notes

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