

Excited states of one-dimensional excitons in polysilanes as investigated by two-photon spectroscopy

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Two-photon-absorption spectra have been investigated for solid films of polysilanes with various Si-backbone conformations such as *trans* planar, alternating *trans-gauche*, helical, and disordered forms. In all the polysilanes with ordered backbones, the distinct two-photon-absorption peaks were observed at energies 0.8–1.0 eV above the one-photon-absorption peaks. These one-photon and two-photon transitions are interpreted in terms of the ground and excited states of one-dimensional excitons on the Si backbones.

The polysilanes, σ -bonded silicon polymers with organic substituents, have generated renewed interest because of their unique photoelectronic properties.^{1,2} Unlike silicon crystals, the band structure in the one-dimensional (1D) Si chain of planar zigzag structure is expected to exhibit the direct gap at the $k=0$ (Γ) point.^{3,4} Reflecting the direct gap nature, sharp optical absorption bands (perhaps due to the direct excitons) are observed at 3–4 eV in polysilanes with ordered backbone conformations. Furthermore, a sharp luminescence band is observed with essentially no Stokes shift but with fairly large quantum efficiency (> 0.1), indicating exceptionally small electron (exciton) -lattice interaction among many 1D electronic systems. Therefore the polysilanes provide a good opportunity for the study on prototypical 1D excitonic systems.

Among many interesting photoelectronic properties in polysilanes, particular attention has been devoted to their large nonlinear (third-order) optical response.^{2,5,6} To understand the origin(s) of the large nonlinear optical susceptibilities, accurate information about excited electronic structures including one-photon forbidden (but two-photon allowed) states is necessary. In this Rapid Communication, we report the two-photon-absorption spectra of a number of polysilanes with varying silicon-backbone conformations. The observed two-photon transitions can be interpreted in terms of 1D excitons on the Si backbones. This excited state may play an essential role as an intermediate state in the nonlinear optical process.

The polysilanes selected for the present study are dialkyl ($R_1, R_2 = -C_nH_{2n+1}$) substituted; (a) poly(dihexylsilane) [$n(R_1) = n(R_2) = 6$, abbreviated as PDHS], (b) poly(ditetradecylsilane) [$n(R_1) = n(R_2) = 14$, PDTDS], (c) poly(dibutylsilane) [$n(R_1) = n(R_2) = 4$, PDBS], and (d) poly(methyl-4-methylpentylsilane) [$n(R_1) = 1$ and $n(R_2) = 6$, PMMPS]. At room temperature, the dialkyl-substituted polysilanes (a)–(c) have regular Si-backbone conformations;² (a) *trans* planar, (b) alternating *trans-gauche* (TGTG'), and (c) $\frac{7}{3}$ helical, as

shown schematically in Fig. 1. For the side-chain branched derivative (d) PMMPS, the backbone conformation is a disordered helix even at low temperatures. Such disordered conformations are also present in the high-temperature phases [above a temperature denoted here as the respective critical temperature (T_c)] of the above three polysilanes (a)–(c). A one-photon forbidden but two-photon allowed transition recently has been detected in films of (a) *trans* planar PDHS by excitation spectroscopy for two-photon absorption,⁷ by two-photon-induced birefringence,⁸ and by electroabsorption spectroscopy.⁹ In this study, we have extended the search for two-photon excited states to other polysilanes with different backbone structures.

The polymer samples studied here have been prepared

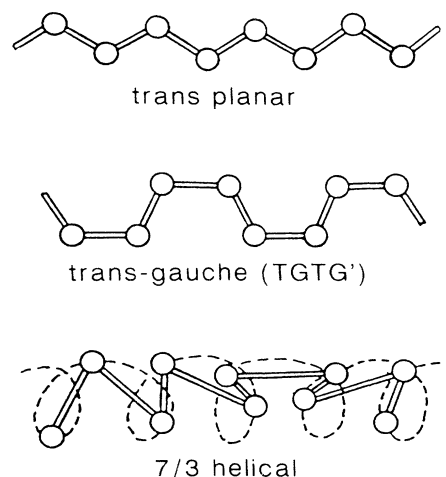


FIG. 1. *Trans* planar, alternating *trans-gauche* (TGTG'), and $\frac{7}{3}$ helical backbones characteristic of PDHS, PDTDS, and PDBS, respectively.

by well-established synthetic procedures described in detail elsewhere.^{1,2} Film samples of these polysilanes of thickness $\sim 0.4 \mu\text{m}$ were prepared on fused quartz substrates by casting from hexane solution. The two-photon-absorption spectra were recorded by the measurements of excitation spectra for which the intensity of the luminescence near the one-photon-absorption edge was monitored as a function of twice the exciting photon energy. An excimer laser-driven dye laser was utilized as the excitation source. The wavelength of the laser light, which was continuously scanned using four types of laser dyes, always lay well below the one-photon-absorption edge of the samples, resulting therefore in negligible direct one-photon absorption. For several exciting photon energies, it was confirmed that the observed luminescence intensity due to the two-photon absorption was precisely proportional to the square of the laser intensity. The two-photon-absorption spectra were thus obtained by normalizing the raw-excitation spectra with the square of the excitation-laser intensity. The luminescence spectra generated either by one-photon or two-photon excitations were identical, each showing the sharp band at the energy of the absorption peak due to the recombination of the free (not Stokes-shifted) exciton.

The two-photon-absorption spectra (solid lines) measured at 77 K together with the normal one-photon-absorption spectra (dashed lines) are shown in Fig. 2. Clear two-photon-absorption peaks are obvious for the polymers with ordered backbones (a)–(c), while PMMPS, for which the backbone is disordered, shows a rather broad feature associated with the low-energy threshold. The spectrum for the PDHS films is in good agreement with that recently reported by Thorne *et al.*⁷

The observed resonance energies for both the one-photon and two-photon excitations are listed in Table I. Both peak positions show a strong dependence on the conformation of the Si backbones: The variation of the peak energies may be attributed to the change in the degree of σ -electron delocalization. Intuitively, one would expect that σ -electron delocalization should decrease in going from *trans* planar to helical forms, which is suggested in part by the band calculation.³ In each case, however, the energy separation between the one-photon- and two-photon-absorption peak is nearly constant $\sim 0.9 \text{ eV}$, irrespective of the polymer-backbone conformation. The disordered Si chains in PMMPS show the broad profile of one-photon absorption around 4 eV, which appears to be

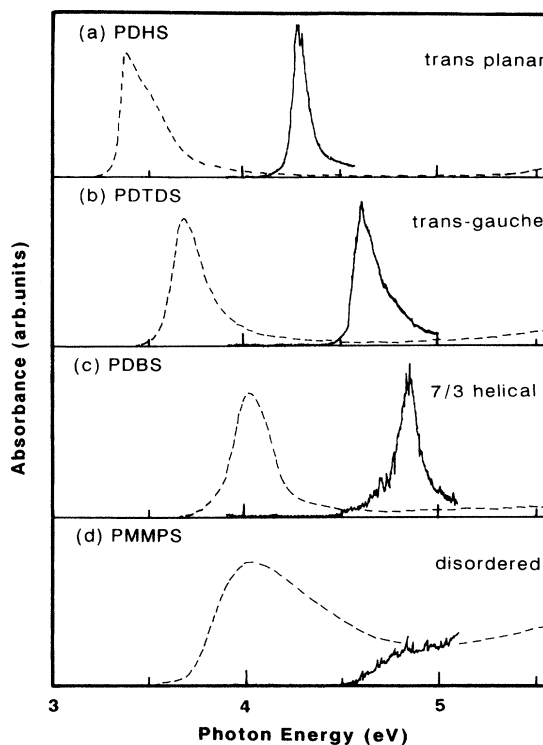


FIG. 2. One-photon- (dashed lines) and two-photon- (solid lines) absorption spectra of polysilane films at 77 K; (a) all-*trans* PDHS, (b) alternating *trans-gauche* (TG TG') PDTDS, (c) $\frac{7}{3}$ helical PDBS, and (d) amorphous PMMPS.

inhomogeneously broadened.

In each case, spectral bandwidth of the two-photon-absorption band is comparable to or even narrower than that of the one-photon-absorption band. Concerning the one-photon-absorption band, in general, the bandwidth decreases at lower temperatures, but this effect tends to saturate around 100 K. The excess width of the absorption band seems to be largely due to inhomogeneous broadening. In this respect, the two-photon state seems to be less affected by local inhomogeneities.

The observed one- and two-photon-absorption bands can be interpreted as the ground and excited states of 1D excitons which are associated with the same interband transitions between the topmost valence (σ_p) band and

TABLE I. Resonance energies of one-photon- and two-photon-absorption bands in polysilanes (at 77 K).

	$-(R_1R_2Si)_n-$	Backbone conformation	One-photon absorption (eV)	Two-photon absorption (eV)	ΔE (eV)
PDS	$R_1 = R_2 = n\text{-hexyl}$	<i>trans</i> planar	3.36	4.24	0.88
PDTDS	$R_1 = R_2 = n\text{-tetradecyl}$	<i>trans-gauche</i> (TG TG')	3.60	4.57	0.97
PDBS	$R_1 = R_2 = n\text{-butyl}$	$\frac{7}{3}$ helical	3.97	4.83	0.86
PMMPS	$R_1 = \text{methyl}$ $R_2 = 4\text{-methylpentyl}$	disordered	4.00	> 4.5 (threshold)	

lowest unoccupied conduction (σ_p^*) band. An alternative interpretation would be that the one-photon- and two-photon-absorption bands are directly related to singularities of interband transitions. In the latter case, the sharp profiles should be intrinsic to the divergent anomalies of the joint density of states characteristic of the 1D system. However, we propose that the observed absorptions for both the one-photon and two-photon transitions are predominantly due to the excitonic states and much less to the two-particle (electron-hole) scattering continuum.

There are several reasons for the proposed excitonic interpretation: First, it is difficult to rationalize two interband transitions with different symmetries separated by 0.8–1.0 eV from the calculated band structures.^{3,4} Second, we must consider the increasing effect of Coulombic final-state interactions between excited electrons and holes in lower dimensions. In a 1D system, the binding energy of the exciton should become large, giving rise to an intense absorption band relative to the electron-hole scattering absorption continuum.¹⁰ For example, the excitonic absorption in various polydiacetylenes, which show similarities to the present system, has been shown to overwhelm the interband absorption.¹¹ Third, the observed one-photon-absorption peak shows a clear Stark shift of the resonance energy (obviously not a Franz-Keldysh-type signal) in an external electric field applied parallel to the backbone.^{9,12} This suggests the proposed excitonic nature of the state and defines the extension of its internal wave function along the backbone direction.

In consideration of the microscopic nature of the two-photon-transition band, we first consider the following general features of excitons in one dimension: The internal freedom of electron-hole pair is restricted on the Si chains and hence the electronic states may be considered to be in close analogy with the problem of one-dimensional (1D) hydrogen.¹³ The exciton envelope function, which describes the internal motion of electron-hole pair as a function of electron-hole distance ($r_e - r_h$), should appear as an alternating series of symmetric and antisymmetric functions in one-dimensional systems.^{10,13,14} This is in marked contrast to the case in three dimensions in which the exciton states and their envelope function are characterized by quantum numbers and wave functions analogous to atomic hydrogen. According to such a picture, the lowest exciton has a symmetric envelope function with the peak amplitude at the origin ($r_e - r_h = 0$) and is in general assigned to the dipole-allowed *ungerade* state. (For example, in the linear polymers like PDHS with D_{2h} symmetry, such a lowest dipole-allowed state is assigned to the $^1B_{1u}$ exciton.) On the other hand, the first excited state, i.e., the 1A_g exciton

state, has an antisymmetric envelope with a node at the origin ($r_e - r_h = 0$).

When the exciton binding energy is large or equivalently the extent of the envelope function is small, the lowest exciton state is analogous to molecular excitons or Frenkel excitons. By similar analogy in molecular solids, the 1A_g exciton state has a character of the charge-transfer (CT) excitation,^{15,16} because the envelope function has no on-site ($r_e - r_h = 0$) component. This simplified picture (the CT exciton model) was proposed by Thorne *et al.*⁷ to explain the two-photon-absorption peak in PDHS. Recently, a more elaborate calculation has been reported by Soos and Hayden¹⁷ based on the Pariser-Parr-Pople model. We have likewise assigned the observed two-photon-absorption band to the 1A_g exciton with the strong CT character.

As supporting evidence for this interpretation based on the model of 1D hydrogenlike exciton states, we emphasize the very good correspondence between the two-photon-absorption spectra and electroabsorption spectra.^{9,12} The CT exciton state as observed by two-photon-absorption spectroscopy (Fig. 2) appears also in the electroabsorption (EA) spectrum which is recorded as a differential absorption with and without an external electric field. In the EA spectra of these particular polysilane samples, the field-activated absorption bands are detected at energies corresponding to the observed two-photon-absorption peaks. In the EA study on PDHS films⁹ it has been noted that the Stark shift of the lowest $^1B_{1u}$ exciton state as well as the field-activated intensity of the 1A_g exciton can be interpreted in terms of the field-induced mixing of these two 1D exciton states.

In conclusion, we have detected the two-photon-absorption bands in polysilanes of varying backbone conformations. The two-photon excited state is consistently located ~ 0.9 eV above the one-photon-absorption band and these characteristic photoexcitations are attributed to the ground and excited states of one-dimensional excitons on the silicon-polymer backbone. In particular, the observed two-photon allowed (1A_g) exciton has the character of the charge-transfer excitation, which is also likely to play an important role in the resonance process of third-order nonlinear optical response^{18,19} as well as in the photochemical process of two-photon-induced chain scission.⁸

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