

Two-photon-absorption spectrum of poly(di-*n*-hexylsilane) films

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Two-photon-absorption (TPA) spectra of poly(di-*n*-hexylsilane) (PDHS) films are obtained from 605 to 410 nm at 295 and 11 K, where the intensity is an order of magnitude higher. A strong TPA band is found above 5 eV and interpreted in terms of interacting σ electrons in a Pariser-Parr-Pople (PPP) model. PPP models for $(\text{Si})_n$ chains relate the excitonic (one-photon) absorption at $E_g = 3.4$ eV in PDHS to the 4.2-eV TPA at the alternation gap and the high-energy TPA derived from two-electron excitations at E_g . The smaller alternation gap in π -conjugated polymers and their intense TPA above E_g also indicate correlated states and differ qualitatively from single-particle descriptions.

I. INTRODUCTION

Large nonlinear-optical (NLO) coefficients^{1,2} in conjugated polymers are generally associated with delocalized electronic states and are expressed³ as sums over virtual excited states. Third-order NLO processes in polymers with centrosymmetric backbones depend strongly on even-parity states probed in two-photon absorption (TPA). Interacting π electrons lead to qualitatively new features^{4,5} in the TPA spectra of conjugated polymers, as shown for Pariser-Parr-Pople (PPP) models with long-range Coulomb interactions. The TPA spectrum⁶ of a polydiacetylene (PDA) waveguide supports a correlated model, as do⁵ previous measurements of even-parity states in PDA crystals, films, solutions, and oligomers.

We present here the TPA spectrum of poly(di-*n*-hexylsilane), or PDHS, a thoroughly studied^{7,8} polysilane (PS), and interpret it in terms of correlated electronic states. The connection between σ conjugation along $(\text{Si})_n$ and π conjugation has long been recognized,⁹ and Hückel theory becomes the Sandorfy C model.¹⁰ We have extended¹¹ the PPP model to σ -conjugated PS chains, to fit the optical gap E_g in permethylsilane oligomers and the lowest TPA of PDHS reported by Thorne *et al.*¹² The model predicts additional TPA at energies well above the one-photon gap E_g .

TPA and NLO processes in Hückel models of conjugated polymers were analyzed in general in the pioneering study of Agrawal, Cojan, and Flytzanis.¹³ Polyacetylene (PA), PDA's, and PS all have filled valence bands, a gap $E_g = 4t\delta$ to the conduction band, and alternating transfer integrals $t(1 \pm \delta)$ along the backbone. These polymers have centrosymmetric backbones in their idealized extended conformation. The TPA spectrum peaks a few percent above E_g and is essentially independent⁵ of δ in the reduced units $\hbar\omega/E_g$, while selection rules exclude TPA at E_g . The TPA spectrum reflects the accumulation of states of both symmetries at the band edge. Similar

conclusions hold in any single-particle or mean-field description of the valence and conduction bands.

Correlated models for weakly alternating infinite chains, by contrast, have two TPA bands,^{4,5} a weak band associated with alternation $t(1 \pm \delta)$ along the chain and an intense band above E_g derived from two-electron excitations. The hypothetical regular ($\delta=0$) Hubbard chain has finite E_g for $U > 0$, but a vanishing two-photon gap. Finite δ leads to an alternation gap in the TPA spectrum that exceeds E_g for $U \ll t$ and vanishes in the spin-wave limit $U \gg t$. The alternation dependence is illustrated by finite polyenes ($\delta=0.07$), where the two-photon gap $E(2^1A_g)$ is well below¹⁴ E_g ; by $E(2^1A_g)$ slightly below¹⁵ E_g in PDA ($\delta \sim 0.15$); and by $E(2^1A_g)$ almost an eV above¹² E_g in PS ($\delta \sim 0.33$).

The two-photon cross section diverges at $2E_g$ due to one-photon resonances in either correlated or single-particle descriptions. Both one- and two-photon transitions occur in this regime, however. The PDHS spectrum is limited to $< 1.8E_g$ by excitation into the fluorescence band. Even-parity states derived from exciting two electrons across E_g , on the other hand, may shift below $2E_g$ in correlated systems and thus be accessible experimentally. Their TPA cross sections are still large, though not divergent. TPA in Hubbard or PPP dimers⁴ provides simple, analytical results for the two-electron excitation.

II. TWO-PHOTON SPECTRUM OF PDHS FILMS

The strong fluorescence⁸ of PDHS and other polysilanes differs sharply from π -conjugated polymers. A host of PS experiments^{16,17} exploit the frequency dependence of either the absorption or emission, their relative polarization, or the time dependence of the emission. The fluorescence may be excited by either one- or two-photon absorption, and its narrow energy width is understood¹⁸ in terms of energy transfer to the longest $(\text{Si})_n$ segments prior to emission. The longest segments in PDHS are

thought to be around $n \sim 20$, while individual strands have $n \sim 10^4$.

High molecular weight, monodisperse PDHS strands with $n \sim 10^4$ Si atoms were synthesized by Zeigler's method.¹⁹ PDHS films were prepared by casting the polymer from toluene solution on uv fused-silica substrates. During the experiments, the samples were mounted in a vacuum on the cold finger of a closed-cycle refrigerator.

We obtained the TPA spectrum by exciting with wavelengths from 605 to 410 nm and measuring the fluorescence intensity at each λ . The time-integrated emission is independent of λ within the experimental accuracy; it peaks at 382 and 370 nm for $T = 295$ and 11 K, respectively, and the full width at half height decreases from 0.09 to 0.05 eV. We then assumed that the fluorescence quantum efficiency is constant in this range and took the ratio of the fluorescence intensity to the square of the intensity of the excitation pulse.

The experimental setup, shown schematically in Fig. 1, incorporates several controls for reliable intensity measurements. Tunable light from a dye laser, a Spectra Physics PDL-2 pumped by a DCR-2 Nd:YAG (yttrium aluminum garnet) laser, was passed through a monochromator before reaching the sample. This eliminates amplified spontaneous emission, which became troublesome at the extremes of the useful wavelength range of the dyes. A second monochromator, set at the peak of the PDHS fluorescence, selects the fluorescence from the sample. By scanning this monochromator across the PDHS spectrum, we verified that scattered light did not contribute significantly to the signal. A photomultiplier (PM) and a gated integrator were used to measure the fluorescent light passing through the monochromator. The intensity of the incident laser beam was measured by reflecting a fraction into a photodiode (PD), whose output was measured by another gated integrator. The relative TPA intensity at a given wavelength was taken as the ratio of the photomultiplier signal to the square of the photodiode signal for each laser pulse. The average of at least 100 pulses was used at each λ .

The TPA spectrum at 295 K is shown in Fig. 2, with a different symbol for each dye and every point obtained as described above. There are two principal causes for the scatter in the data, particularly near the extreme λ of

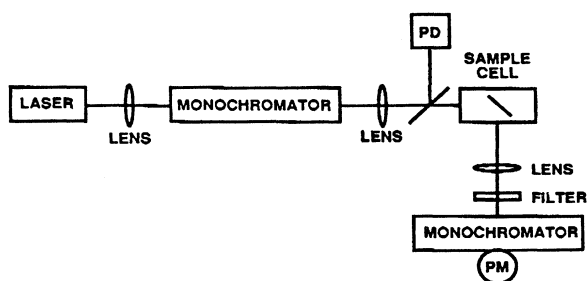


FIG. 1. Schematic of the experimental setup for two-photon absorption.

some dyes; they are changes in the time dependence and spatial distribution of the laser pulse, both of which affect second-order processes. The sharp TPA at 4.18 eV is assigned to the previously reported,^{12,20} 300-K peak at 4.27 eV. The broad TPA above 5 eV is the new feature discussed below.

The one-photon spectrum of PDHS films is dominated⁸ by an exciton around $E_g = 3.4$ eV, with a full width at half height of ~ 0.2 eV at 295 K, that shifts ~ 0.1 eV to the blue at 77 K. The upper scale in Fig. 2 shows the 4.18-eV feature to be at $1.22E_g$. The blue shift of E_g on cooling is paralleled by the TPA spectrum at 11 K in Fig. 3, where the peak occurs at 4.25 eV. Although the 11- and 295-K spectra are identical up to 4.18 eV, the 11-K spectrum is ~ 12 times more intense at higher energy. This remarkable temperature dependence is absent²¹ in poly(methyl-phenylsilane). Blue shifts of spectral features¹⁸ on cooling are opposite from changes for increasing conjugation lengths, and it has been suggested that they involve density effects.¹⁸

The linear spectrum at 295 K has another peak at 3.9 eV, whose height depends on the sample's history. It is generally assigned⁸ to remnants of a high-temperature phase from the 315-K transition. The 3.9-eV feature may exist as a shoulder to the main exciton peak at 77 K, but

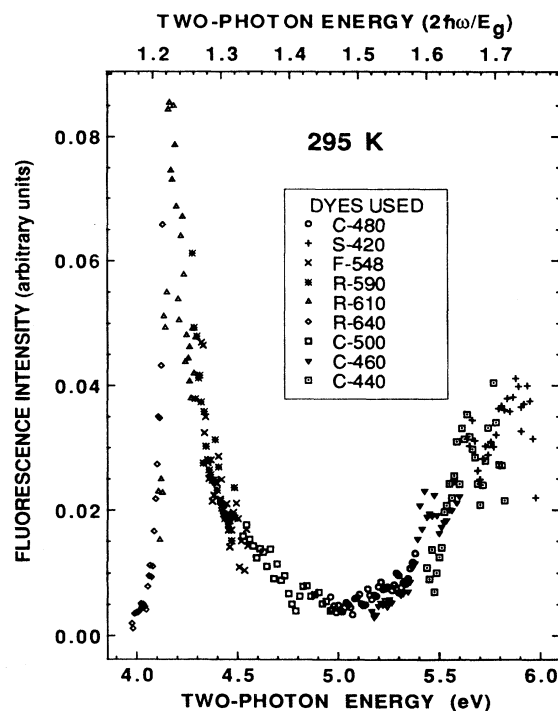


FIG. 2. TPA spectrum of poly(di-*n*-hexylsilane) films at 295 K; the symbols identify the dyes used (C, coumarin; S, stilbene; F, fluorescein; and R, rhodamine) and each point is the average of at least 100 shots. The upper scale is in units of the one-photon gap, $E_g = 3.4$ eV.

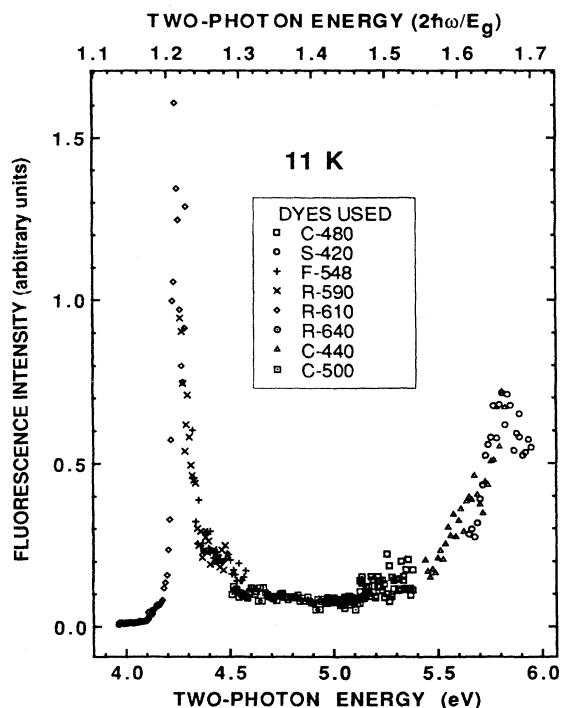


FIG. 3. TPA spectrum of PDHS films at 11 K, with different symbols for each dye. Note the increased intensity compared to Fig. 2. The upper scale is $2\hbar\omega/E_g$, with $E_g = 3.5$ eV at low temperature.

tends to disappear at low temperature. We have no evidence for this phase in the TPA spectrum, at either 295 or 11 K, in several PDHS samples that were repeatedly cycled between 295 and 11 K.

III. PPP MODEL FOR TWO-PHOTON ABSORPTION

In the Sandorfy C model,¹⁰ each Si provides two sp^3 orbitals and two valence electrons, except at chain ends. Si—Si bonds are assigned transfer integrals $t(1+\delta)$, and sp^3-sp^3 transfer at one Si is $t(1-\delta)$. In contrast to partial single and multiple bonds in hydrocarbons, alternation is intrinsic and large^{9,22} ($\delta \sim 0.3-0.6$) even in idealized, regular *all-trans* $(Si)_n$ arrays. Interactions between the σ electrons are introduced in PPP models, with on-site repulsion²² $V(0)=U=9.04$ eV taken from atomic data for two electrons in the same sp^3 orbital. The form of $V(R)$ is e/R for distant sites, as given by the Ohno interpolation.²³ We retain¹¹ a typical $t = -2.40$ eV for hydrocarbons (bandwidth $4|t| \sim 10$ eV), the atomic value of $V(0)$, alternation $\delta = \frac{1}{3}$ and an *all-trans* geometry that reflects experiment and Hartree-Fock results²² for the charge centroids of the sp^3 orbitals.

The proper description of conformational degrees of freedom has been a major thrust in PS models.¹⁷ Since one- and two-photon spectra for a given sample clearly probe the same conformations, however, TPA in units of $\hbar\omega/E_g$ is less sensitive to defects, side groups, or the environment. The strong n dependence of $(Si)_n$ segments is

also minimized. The simulated TPA spectrum in Fig. 4 has $n=6$ and the previous PPP parameters. The $n=4$ and 5 curves are virtually identical, in units of E_g , with shifts of $<1\%$ in the low-energy feature. PDHS may consequently be modeled qualitatively in the reduced units of Fig. 4. The actual TPA spectrum in Fig. 4 is given for $E_g = 3.4$ eV at 295 K, while $E_g = 3.5$ eV is appropriate at 11 K.

The strongest dipole transitions of linear chains involve electric fields polarized along the chain. The two-photon transition moment $M(Y)$ to an even-parity state at $E(Y) = 2\hbar\omega_Y$ is⁵

$$M(Y) = \langle Y | \mu | \phi(-\omega_Y) \rangle \\ = \sum_R \langle Y | \mu | R \rangle \langle R | \mu | G \rangle / [E(R) - \hbar\omega_Y], \quad (1)$$

where $|R\rangle$ is an odd-parity state, principally the $|1^1B_u\rangle$ state at E_g , and $\phi(-\omega_Y)$ is a response function whose direct evaluation²⁴ bypasses the difficult sum over states in Eq. (1). Near $\omega \sim \omega_Y$, the TPA spectrum goes as

$$I(\omega \sim \omega_Y) \propto |M(Y)|^2 / \{ [E(Y) - 2\hbar\omega]^2 + \Gamma^2(Y) \}, \quad (2)$$

and depends on the excited-state lifetime Γ .

The complete expression³ for the TPA spectrum, as $|\text{Im}\chi^{(3)}(-\omega, \omega, -\omega, \omega)|$, contains additional lifetime parameters. For polarization along the chain, the first few odd- and even-parity states account for most of the one- and two-photon intensity.⁵ The spectra in Fig. 4 are based on exact PPP energies and transition moments for the lowest ten states in the $^1A_g^+$ and $^1B_u^-$ manifolds. They deviate by at most a few percent from the exact re-

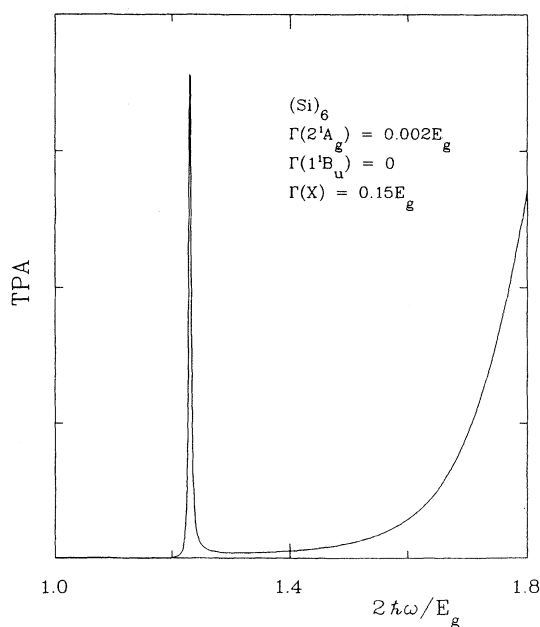


FIG. 4. Simulated TPA spectrum of $(Si)_6$ chains for exact solutions of PPP models with parameters from Ref. 11 and excited-state lifetimes given in the text.

sult, which can readily be found²⁴ at some given ω 's but is too time consuming to derive for an entire spectrum.

The choice of excited-state lifetimes in Eqs. (1) and (2) affects the shape, but not the position, of the TPA spectrum. We set $\Gamma(1^1B_u)=0$, since fluorescence lifetimes⁸ of 10^2 – 10^3 ps imply negligible energy widths for the TPA spectra. Hole-burning experiments²⁵ for PDHS indicates that most of the ~ 0.2 -eV one-photon width is due to disorder and should consequently be modeled by convoluting the spectrum with a Gaussian or other broadening function. The sharp 4.2-eV TPA in Fig. 3 is still dominated by disorder. The choice $\Gamma(2^1A_g)=0.002E_g$ (0.007 eV) in Fig. 4 probably overestimates the homogeneous width at 11 K. The widths of higher excited states are larger and poorly known. The simulation in Fig. 4 has $\Gamma(X)=0.15E_g$ for all states except $1B$ and $2A$. The strong TPA absorption, calculated to be $\sim 1.78E_g$ for PS parameters in the PPP model, then becomes a shoulder on the one-photon divergence at $2E_g$, where $M(Y)$ in Eq. (1) diverges.

Correlated states in PPP models for PS chains thus account for the broad TPA above 5 eV in Figs. 2 and 3 without changing the preliminary Si parameters. The calculated intensities are somewhat length dependent, however, even when normalized to the low-energy feature, and are several times higher than those observed above 5 eV. We speculate that decay channels other than emission from the longest segments may be possible at such high energies. TPA spectra of PS with different side groups may clarify the generality of such processes.

IV. DISCUSSION

The electronic structure of polysilanes presents many open questions. Quantum-chemical calculations²⁶ on linear or cyclic oligomers with H or CH₃ substituents provide information about the ground-state potential surface and the composition of the highest occupied and lowest unoccupied orbitals. Most discussion of polymeric spectra, including energy transfer between segments, has been in terms of phenomenological models for the σ electrons along the Si backbone. Interacting σ electrons in a PPP model are a natural generalization of the Sandorfy C or Hückel model. The TPA spectra in Figs. 2 and 3 differ qualitatively from a single-particle description. Single-particle theory also leads to free-carrier bands, rather than to excitons²⁷ at E_g . In addition to their simplicity and generality, noninteracting σ electrons rationalize the size dependence of the one-photon absorption in oligomers and the insensitivity of E_g to nonconjugated substituents in polymers. These features are retained in PPP theory, which is here also restricted to σ electrons.

The simplest exciton theories⁹ for PS treat the bonding and antibonding Si-Si orbitals separately. Charge-carrying excitations are then excluded. Philpott²⁸ sketched a more general exciton theory for PDA's that has also been applied^{12,11} to PS. Vicinal sp^3 - sp^3 overlaps correspond to multiple bonds, while geminal sp^3 - sp^3 overlaps to single bonds. Charge-transfer (CT) excitons

are derived from electron transfer from one Si—Si bond to another, while bond excitations are still related to σ - σ^* excitation of one Si—Si bond. In both PDA and PS, bond and CT excitons are strongly mixed, however, and require adjustable parameters that are difficult to estimate. In the limit of large alternation, bond and CT excitons are simply related¹¹ to the microscopic parameters t and $V(R)$ in PPP models. Although such relations are approximate for the PS alternation of $\delta \sim \frac{1}{3}$, exciton descriptions may still help to rationalize correlated PPP states.

Thorne *et al.*²⁹ adopt a qualitative exciton description based on a three-silicon, two-bond unit for analyzing photoinduced PDHS spectra in solution, where E_g and the fluorescence are at slightly higher energy. The odd-parity $|1^1B_u\rangle$ state at E_g is an exciton whose one-photon excitations are to higher-energy, even-parity 1A_g states. Thorne *et al.*²⁹ assign the photoinduced ir absorption as the previously reported¹² TPA. The other photoinduced absorption, in the uv, is discussed in terms of a biexciton at $2E_g - V$ with binding energy $V \sim 0.5$ eV. The blue edge of the photoinduced features have short (< 1 ps) lifetimes, and both blue edges shift to the red between 100 fs and 4 ps. This parallels the 0.25-eV red shift between absorption by all segments and emission by the longest segments. The inhomogeneous width²⁹ of the uv feature is almost twice that of the exciton.

The TPA spectra of PDHS in Figs. 2 and 3 are consistent with the photoinduced spectra. The high-energy 1A_g state around $1.8E_g$ in the PPP model with Si parameters¹¹ is close to the biexciton around 1.8 – $1.9E_g$. A segment or disorder model leads to several possibilities for the biexciton. The PPP model for a *single* segment shows a strong TPA below $2E_g$ due to Coulomb interactions. Dispersion forces between excitons on *two* nearby segments, in a $|1^1B_u, 1^1B_u\rangle$ state, also produce an even-parity state below $2E_g$. Either possibility rationalizes the greater width of the photoinduced uv feature. More complete experimental and theoretical characterization is needed for the biexciton and other excitations.

Tachibana *et al.*³⁰ have recently reported electroabsorption spectra on PDHS films. In a static electric field, even- and odd-parity states are mixed, and one-photon transitions to 1A_g states become allowed. In addition to the expected electroabsorption at 4.2 eV, they find a strong, second derivative signal around 5.5–6.0 eV at 77 K. The high-energy TPA peak in Fig. 4 is in the same region, and correlated PPP states are again sufficient. As discussed by Sebastian and Weiser,³¹ electromodulation in conjugated polymers may also selectively enhance one-photon features at E_g or at the gap for charge carriers. In contrast to the TPA selection rules in centrosymmetric systems, electroabsorption probes both even- and odd-parity states.

The importance of conformational effects has been reduced but not eliminated by expressing all two-photon features in terms of the one-photon gap E_g . More quantitative models will have to include both conformational and vibronic contributions. The present model does not address the temperature dependence of the PDHS spectra

in Figs. 2 and 3. Correlated PPP states provide a convenient and general framework for TPA in both PS and PDA polymers, without changing microscopic parameters for hydrocarbons. They account naturally for TPA either above E_g in strongly alternating chains or below E_g for small δ , without invoking special segment lengths. The weak length dependence of the calculated TPA spectra in Fig. 4 strongly support similar n dependences for both the one- and two-photon gaps. Although still phenomenological, PPP models for σ -conjugated $(Si)_n$ chains unify several aspects of their delocalized electronic states

and provide an improved starting point for more detailed modeling.

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- ¹*Nonlinear Optical Properties of Organic Molecules and Crystals*, edited by D. S. Chemla and J. Zyss (Academic, New York, 1987), Vols. 1 and 2; *Nonlinear Optical and Electroactive Polymers*, edited by P. N. Prasad and D. R. Ulrich (Plenum, New York, 1988); *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics, and Molecular Electronics*, Vol. 182 of *NATO Advanced Study Institute Series E*, edited by J. L. Brédas and R. R. Chance (Kluwer, Dordrecht, 1990).
- ²Proceedings of the International Conference of the Science and Technology of Synthetic Metals, Santa Fe, NM, 1988 [*Synth. Met.* **27** (1988); **28** (1989); **29** (1989)].
- ³D. C. Hanna, M. A. Yuratich, and D. Cotter, *Nonlinear Optics of Free Atoms and Molecules* (Springer, Berlin, 1979); Y. R. Shen, *The Principles of Nonlinear Optics* (Wiley, New York, 1984).
- ⁴Z. G. Soos, P. C. M. McWilliams, and G. W. Hayden, *Chem. Phys. Lett.* **171**, 14 (1990).
- ⁵P. C. M. McWilliams, G. W. Hayden, and Z. G. Soos, *Phys. Rev. B* **43**, 9777 (1991).
- ⁶P. D. Townsend, W. Fann, S. Etemad, G. L. Baker, Z. G. Soos, and P. C. M. McWilliams (unpublished).
- ⁷A. J. Lovinger, F. C. Schilling, F. A. Bovey, and J. M. Zeigler, *Macromolecules* **19**, 2657 (1986).
- ⁸R. D. Miller and J. Michl, *Chem. Rev.* **89**, 1359 (1989).
- ⁹C. G. Pitt, in *Homoatomic Rings, Chains, and Macromolecules of Main-Group Elements*, edited by A. L. Reingold (Elsevier, Amsterdam, 1977), p. 203.
- ¹⁰C. Sandorfy, *Can. J. Chem.* **33**, 1337 (1955).
- ¹¹Z. G. Soos and G. W. Hayden, *Chem. Phys.* **143**, 199 (1990).
- ¹²J. R. G. Thorne, Y. Ohsako, R. M. Hochstrasser, and J. M. Zeigler, *Chem. Phys. Lett.* **162**, 455 (1989).
- ¹³G. P. Agrawal, C. Cojan, and C. Flytzanis, *Phys. Rev. B* **17**, 766 (1978).
- ¹⁴B. E. Kohler, C. Spangler, and C. Westerfield, *J. Chem. Phys.* **89**, 5422 (1988).
- ¹⁵B. E. Kohler and D. E. Schilke, *J. Chem. Phys.* **86**, 5214 (1987).
- ¹⁶R. G. Kepler and J. M. Zeigler, *Mol. Cryst. Liq. Cryst.* **175**, 85 (1989); J. R. G. Thorne, R. M. Hochstrasser, and J. M. Zeigler, *J. Phys. Chem.* **92**, 4275 (1988).
- ¹⁷*Silicon-Based Polymer Science: A Comprehensive Resource*, *ACS Symposium Series 381*, edited by J. M. Zeigler and F. W. G. Fearon (American Chemical Society, Washington, D.C., 1990).
- ¹⁸L. A. Harrah and J. M. Zeigler, in *Photophysics of Polymers*, *ACS Symposium Series 358*, edited by C. E. Hoyle and J. M. Torkelson (American Chemical Society, Washington, D.C., 1987), p. 482.
- ¹⁹J. M. Zeigler, *Poly. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **27**, 109 (1987).
- ²⁰F. M. Schellenberg, R. L. Byer, and R. D. Miller, *Chem. Phys. Lett.* **166**, 331 (1990).
- ²¹R. G. Kepler and Z. G. Soos, *Phys. Rev. B* (to be published).
- ²²A. Herman, *Chem. Phys.* **122**, 53 (1988).
- ²³K. Ohno, *Theor. Chim. Acta* **2**, 219 (1964).
- ²⁴Z. G. Soos and S. Ramasesha, *J. Chem. Phys.* **90**, 1067 (1989).
- ²⁵H. P. Trommsdorff, J. M. Zeigler, and R. M. Hochstrasser, *J. Chem. Phys.* **89**, 4440 (1988).
- ²⁶J. V. Ortiz and J. W. Mintmire, *J. Am. Chem. Soc.* **110**, 4522 (1988); K. A. Klingensmith, J. W. Downing, R. D. Miller, and J. Michl, *ibid.* **108**, 7438 (1986); K. Takeda, H. Terame, and N. Matsumoto, *ibid.* **108**, 8186 (1986); R. W. Bigelow and K. M. McGrane, *J. Polym. Sci. Polym. Phys.* **24**, 1233 (1986).
- ²⁷R. G. Kepler, J. M. Zeigler, L. A. Harrah, and S. R. Kurtz, *Phys. Rev. B* **35**, 2818 (1987).
- ²⁸M. R. Philpott, *Chem. Phys. Lett.* **50**, 18 (1977).
- ²⁹J. R. G. Thorne, S. T. Repinec, S. A. Abrash, J. M. Zeigler, and R. M. Hochstrasser, *Chem. Phys.* **146**, 315 (1990).
- ³⁰H. Tachibana, Y. Kawabata, S. Y. Koshihara, and Y. Tokura, *Solid State Commun.* **75**, 5 (1990).
- ³¹L. Sebastian and G. Weiser, *Chem. Phys.* **62**, 447 (1981).