### Electronic Excitations in Polysilane: σ-Conjugation, Excitons, and Nonlinear Optical Response

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Effects of Coulomb interactions in electronic excited states of polysilane are discussed theoretically. It is demonstrated that the addition of Coulomb interactions to the Sandorfy C one-electron model drastically alters the energy dispersions of nonlinear optical susceptibility  $\chi^{(3)}$ . The comparison of calculated spectra with experiments on third-harmonic generation, two-photon absorption and electroabsorption allows us to conclude that the Coulomb interactions are of primary importance in the one-dimensional Si polymer in contrast to bulk Si crystal.

KEYWORDS: polysilane, one-dimensional semiconductor, Sandorfy C model, Pariser-Parr-Pople model, exciton, nonlinear optical response

### **§1. Introduction**

For more than a decade, various forms of polysilane have been synthesized and investigated extensively by chemists<sup>1</sup>), while interests in this material among the physics community were originally rather limited. One of a few papers that attracted much attention among physicists is a theoretical work by Rice and Phillpot<sup>2)</sup>, who discussed the possible existence of polarons and bipolarons. Although these nonlinear excitations are well known in organic conjugated polymers such as poly $acetylene,^{3}$  there have been to date no indication of their existence in polysilane. Presumably, the electron-lattice coupling for  $\sigma$ electrons in polysilane is much weaker than that for  $\pi$  electrons in polyacetylene. Yet the two systems are similar to each other in the sense that electrons are delocalized along the onedimensional polymer backbone. This is why polysilane is sometimes called a  $\sigma$ -conjugated polymer.

It has long been recognized that the

delocalization of electrons enhances optical nonlinearity.<sup>4)</sup> Based on this idea, many experimental and theoretical studies have been conducted on the nonlinear optical properties of conjugated polymers. Fairly large values of third-order nonlinear susceptibility  $\chi^{(3)} \sim 10^{-10}$  to 10<sup>-9</sup> esu have been observed for third-harmonic generation (THG) in polydiacetylene<sup>5</sup>) and polyacetylene<sup>6</sup>). The first experimental study of  $\chi^{(3)}$  in polysilane was performed by Kajzar et al.,7) who reported  $\chi^{(3)}$  of about 10<sup>-12</sup> esu. Although this is smaller than the values in conjugated polymers, an interesting feature was reported by Thorne and coworkers,<sup>8)</sup> who found a two-photon absorption (TPA) peak at an energy much higher than the peak energy of the linear (or one-photon) absorption (LA) spectrum. This was confirmed by electroabsorption and TPA measurements,9,10) where electroabsorption (EA) implies modulation of an absorption spectrum by a static electric field. The large energy difference between the peaks of LA and TPA cannot be explained by oneelectron models, as we see in the next section, suggesting the importance of electron correlation<sup>11</sup>) or exciton effects<sup>12</sup>). From a general theoretical point of view, 13, 14) one-

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dimensional excitons possess various unusual properties and play important roles for optical properties. In fact, an exciton model<sup>12</sup>) for polysilane has been quite successful in describing not only the LA and TPA peaks but also the energy dispersion of THG<sup>15</sup>). The theoretical aspect of these developments are surveyed in the present paper.

# §2. A Simple Model of $\sigma$ -Conjugation: the Sandorfy C Model

Polysilane in a narrow sense is a saturated Si polymer  $(SiH_2)_n$ , while most of experiments have been done in its derivatives such as poly(alkylsilane), where hydrogen atoms are substituted by alkyl groups.1) Different substituents often lead to different conformations.<sup>1)</sup> The first question that one might ask for such polysilane derivatives would be whether the  $\sigma$ -conjugation on the polymer backbone is decoupled from the substitution groups. In the case of  $\pi$ -conjugation, the decoupling from side chains can be clearly defined by the absence of  $\pi$ -bonding between the backbone and side chains. However, in the case of  $\sigma$ -conjugation, there are always connections to side chains with  $\sigma$  bonding, and there is no a priori reason why the backbone  $\sigma$ electrons can be decoupled from side chain  $\sigma$ electrons. In spite of this, such decoupling has often been assumed, leading to a simple model of saturated homopolymers introduced by Sandorfy as "model C".<sup>16</sup>)

The Sandorfy C model for polysilane is described as follows (see Fig.1). Each Si atom has four  $sp^3$  orbitals, among which two orbitals connected to adjacent Si atoms are taken into account. The remaining two  $sp^3$  orbitals of each Si connected to hydrogens or substituents are neglected. Then the Hamiltonian of this tight binding model reads

$$H_{0} = -t_{g} \sum_{i,\sigma} \left( C_{i,a,\sigma}^{\dagger} C_{i,b,\sigma} + H.c. \right) - t_{v} \sum_{i,\sigma} \left( C_{i,a,\sigma}^{\dagger} C_{i-1,b,\sigma} + H.c. \right), \qquad (1)$$

where  $C_{i,a,\sigma}$  and  $C_{i,b,\sigma}$  annihilate electrons with spin  $\sigma$  at the orbitals of *i*-th atom pointing to (*i*-1)-th and (*i*+1)-th atoms, respectively. The geminal transfer energy  $t_g$  (>0) is smaller than



Fig.1 Sandorfy C model of polysilane.

the vicinal transfer energy  $t_v$  (>0).

In this model, the transfer energy is alternating with  $t_v$  and  $t_g$  along the onedimensional chain. This happens to be similar to bond alternation in polyacetylene. In this sense, the electronic structure of polysilane has some similarity with that of polyacetylene. Note that the bond alternation in polyacetylene originates from the Peierls instability, whereas the alternating transfer in polysilane is an intrinsic property of the tight-binding model.

The Sandorfy C model is considered to be appropriate for describing excitations near the optical gap, if the  $\sigma$  electrons are well delocalized. Band calculations<sup>17,18</sup> indicate that the band dispersion is in fact large for the alltrans form of polysilane. The Sandorfy C model seems to be appropriate in this case. For other forms such as a helix, the band gap becomes larger and the dispersion becomes smaller, so that the applicability of the Sandorfy C model is limited. In spite of this limitation, the Sandorfy C model turned out to be very useful to examine the basic properties of polysilane because of its simplicity.

### §3. Nonlinear Optical Spectra in the Sandorfy-C-Hückel Model

In this section, we consider linear and nonlinear optical spectra of the Sandorfy C model, which is essentially a Hückel model neglecting Coulomb interactions. Throughout the present paper, we assume that the system size is much smaller than the wave length of light. This allows us to use the standard formula<sup>19,20</sup> of nonlinear optical susceptibilities within the uniform-electric-field approximation. We consider systems with inversion symmetry, so that the lowest order nonlinearity is the thirdorder susceptibility  $\chi^{(3)}$ . The formula for the linear susceptibility  $\chi^{(1)}$  and  $\chi^{(3)}$  are: S. Abe

$$\chi_{xx}^{(1)}(\omega) = \sum_{n} \left| d_{gn} \right|^2 \left( \frac{1}{\Omega_n - \omega} + \frac{1}{\Omega_n^* + \omega} \right), \tag{2}$$

$$\begin{split} \chi_{xxxx}^{(3)}(-\omega_{\sigma};\omega_{1},\omega_{2},\omega_{3}) \\ &= \frac{S_{1,2,3}}{3!} \left\{ \sum_{mpn} d_{gm} d_{mp} d_{pn} d_{ng} \left[ \left( \frac{1}{\Omega_{m} - \omega_{\sigma}} + \frac{1}{\Omega_{m}^{*} + \omega_{3}} \right) \frac{1}{(\Omega_{p} - \omega_{1} - \omega_{2})(\Omega_{n} - \omega_{1})} \right. \\ &+ \left( \frac{1}{\Omega_{m}^{*} + \omega_{\sigma}} + \frac{1}{\Omega_{m} - \omega_{3}} \right) \frac{1}{(\Omega_{p}^{*} + \omega_{1} + \omega_{2})(\Omega_{n}^{*} + \omega_{1})} \right] \\ &- \sum_{mn} |d_{gm}|^{2} |d_{gn}|^{2} \left[ \left( \frac{1}{\Omega_{m} - \omega_{\sigma}} + \frac{1}{\Omega_{m}^{*} + \omega_{3}} \right) \frac{1}{(\Omega_{m} - \omega_{2})(\Omega_{n} - \omega_{1})} \right. \\ &+ \left( \frac{1}{\Omega_{m}^{*} + \omega_{\sigma}} + \frac{1}{\Omega_{m} - \omega_{3}} \right) \frac{1}{(\Omega_{m}^{*} + \omega_{2})(\Omega_{n}^{*} + \omega_{1})} \right] \right\}, \end{split}$$
(3)

where  $\omega_{\sigma} = \omega_1 + \omega_2 + \omega_3$  and  $\Omega_n = E_n - i\Gamma_n$ with energy  $E_n$  and damping  $\Gamma_n$  of state *n*. A primed summation  $\sum'$  implies that the ground state should be excluded in the summation.  $S_{1,2,3}$  denotes summation over all possible permutations of  $\omega_1$ ,  $\omega_2$ , and  $\omega_3$ .  $d_{nn} = \langle n|d|m \rangle$ is the matrix element of the dipole operator d = -ex with respect to states *n* and *m*, where *e* is the electron charge and *x* is the *x*-coordinate of electron. It should be noted that the states here refers to many-body states of the system. In the case of one-electron models such as the Sandorfy C model, we can use a more convenient expression of  $\chi^{(3)}$  in terms of oneelectron states<sup>21</sup>, although we do not write it down here because it is rather tedious.

When we calculate  $\chi^{(1)}$  and  $\chi^{(3)}$  using eqs. (2) and (3) for a chain of *n* atoms, we obtain the molecular susceptibilities of the chain. To translate them into the bulk susceptibilities, they should be divided by the volume of the polymer chain. If the Si-Si distance along the chain axis is *a*, and the chain density per area is  $\sigma$ , then the volume is given by  $na/\sigma$ . We introduce the characteristic susceptibilities  $\chi_0^{(1)} \equiv \sigma e^2 a/2t$  and  $\chi_0^{(3)} \equiv \sigma e^4 (a/2t)^3$ , where *t* is the average transfer energy  $t = (t_g + t_v)/2$ , and in the following sections we display calculated bulk susceptibilities in units of these quantities.

Optical nonlinearity may be classified into

two categories: resonant and nonresonant nonlinear optical processes. Resonant nonlinearity, examples of which are degenerate four wave mixing and pump-probe absorption, stems from real population of excited states, whereas nonresonant nonlinearity, such as thirdharmonic generation (THG), involves virtual excitations. In the present paper we discuss the latter nonlinearity only. In addition to the THG spectrum  $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ , we also study the two-photon absorption (TPA) spectrum, which can be calculated as the imaginary part of  $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$ , restricting the frequency range to around  $\omega \sim E_g/2$ , where  $E_g$  is the optical gap. We also discuss the electroabsorption (EA), by calculating the imaginary part of  $\chi^{(3)}(-\omega;\omega,0,0)$ , which is the proportionality coefficient in the quadratic term (the lowest order non-zero term) with respect to the static electric field  $E^{23}$ 

As for the parameters of the Sandorfy C model, we fix  $t_v/t_g = 2$  as used in Ref.11, while we use the average transfer energy t as an adjustable parameter. The nonlinear spectra including the linear absorption (LA) spectrum, Im  $\chi(1)$ , calculated for a chain of n = 250 atoms are shown in Fig.2. These spectra actually consist of many contributions corresponding to band-to-band transitions. We immediately notice that the peak energy of the TPA is located very close to that of the LA. This feature is



Fig.2 (a) Linear absorption (LA), (b) twophoton absorption (TPA), (c) electroabsorption (EA), and (d) third-harmonic generation (THG) spectra of the Sandorfy C model for a ring of n = 250 atoms with  $t_g = \frac{2}{3}t$  and  $t_v = \frac{4}{3}t$ .  $\chi_0^{(1)}$ and  $\chi_0^{(3)}$  are the characteristic linear and thirdorder susceptibilities defined in the text. A lifetime broadening  $\Gamma = 0.02t$  is assumed for all the excited states in (a), (b), and (d), while a larger value  $\Gamma = 0.06t$  is used in (c) to weaken the oscillations in the high energy region due to a finite size effect. Broken curves indicate the contribution of the processes involving a double excitation or the ground state as an intermediate state.

essentially the same as obtained for conjugated polymers.<sup>22)</sup> The EA spectrum is approximately proportional to the third derivative of the LA spectrum, being consistent with the analytic result obtained by Aspnes and Rowe.<sup>23)</sup> The oscillations of EA in the high energy region ( $\omega$ >1.5t) are a finite size effect. (The effect is especially severe in the EA spectrum, which is related with the third derivative of the LA. This is the reason why we used a larger  $\Gamma$  for the EA in Fig.2.) The spectrum of THG (absolute value of  $\chi^{(3)}$ ) in Fig.2(d) is dominated by a continuum of three-photon resonances at  $\omega \ge E_g$  in the same manner as for a continuum model of polyacetylene.<sup>24</sup>)

As mentioned in §1, these results disagree with the large energy separation of one-photon and two-photon states observed in the TPA and EA measurements.<sup>8-10</sup>) Also an observed THG spectrum<sup>25</sup>) exhibits three peaks in contrast to Fig.2(d). These facts demonstrate that the Sandorfy C model at the Hückel level is inappropriate to describe optically excited states of polysilane even qualitatively. We will see in the following sections that the effect of Coulomb interactions, especially exciton effects, turns out to be essentially important.

Before proceeding to the topic of excitons, a preparation is necessary concerning the nature of intermediate states that contribute to the nonlinear spectra. The first summation in eq.(3)runs over intermediate states m, p and n, among which m and n are one-photon allowed states and p is a two-photon allowed state. In the case of non-interacting electrons, the one-photon states are single electron-hole (e-h) pair states, while the two-photon states are either single e-h states or double e-h states. The second summation in eq.(3) originates from the processes in which the two-photon intermediate state is the ground state. For nonresonant nonlinearity, the main contributions come from the terms involving only single e-h states. The remaining contributions of the terms involving double e-h excitations and the ground state are small, as indicated by broken curves in Fig.2(bd). The only exception is the resonant region  $(\omega - E_g)$  in the TPA spectrum, where strong absorption saturation occurs due to this kind of contributions.

### §4. One-Dimensional Excitons in the Sandorfy-C–Pariser-Parr-Pople Model

In general, photo-created electron and hole can attract each other by a Coulomb force and form an exciton state. Although the exciton binding energy in bulk Si crystal is quite small (~15 meV), the confinement of an exciton in a one-dimensional geometry of a polymer chain can lead, in principle, to a very large binding energy.<sup>13</sup>) This is associated with the fact that the binding energy of the lowest bound state of an electron in a one-dimensional Coulomb potential is infinitely large.<sup>26</sup>) In real systems there is a cutoff length for the interaction potential, so that the binding energy becomes finite but still can be very large compared with the ordinary effective Rydberg energy. This special character of excitons in one dimension has drastic effects on the optical properties of one-dimensional semiconductors.<sup>13</sup>)

To discuss exciton states in polysilane, an electron-electron interaction Hamiltonian  $H_{e-e}$  should be added to the Sandorfy C model.<sup>11</sup>) We employ the Pariser-Parr-Pople (PPP) model<sup>27,28</sup>) for the interactions:

$$H_{e-e} = U \sum_{i,\mu} \rho_{i,\mu,\uparrow} \rho_{i,\mu,\downarrow} + \frac{1}{2} \sum_{\substack{i,\mu,\sigma \\ (i,\mu)\neq (i,\mu')}} \sum_{j,\mu',\sigma'} V_{i,\mu;j,\mu'} \rho_{i,\mu,\sigma} \rho_{j,\mu',\sigma'}, \quad (4)$$

where  $\rho_{i,\mu,\sigma} = C_{i,\mu,\sigma}^{\dagger}C_{i,\mu,\sigma} - \frac{1}{2}$ . For the longrange part of interactions, we use Pople's potential<sup>28</sup>)  $V_{i,\mu;j,\mu'} = V(R_{i,\mu;j,\mu'}) = e^2/\varepsilon R_{i,\mu;j,\mu'}$  where  $\varepsilon$  denotes the dielectric constant,  $R_{i,\mu;j,\mu'}$  the distance between the centers of the orbitals  $(i,\mu)$  and  $(j,\mu')$ . Although this potential depends on the conformation of each polymer, we use a simple form  $V_{i,\mu;j,\mu} = V/2|i-j|$  ( $\mu = a, b$ ) and  $V_{i,a;j,b} = V/|2(i-j)-1|$  assuming an equally spaced linear array of orbital centers.

Exciton states are calculated with the intermediate exciton approach<sup>29)</sup> or equivalently the single-excitation configuration interaction (single-CI) method, in which the total Hamiltonian  $H = H_0 + H_{e-e}$  is diagonalized within the subspace of single e-h excitations.

The exciton states depend on the interaction strength V, which is associated with the static dielectric constant  $\varepsilon$  as  $V = 2e^2 / \varepsilon a$ . For example  $\varepsilon \sim 5$  with a = 2 Å corresponds to  $V \sim 2.9$  eV. An example of calculated exciton energies and their wave functions of relative motion for typical parameters is shown in Fig.3. For clarity only three lowest states are displayed. The exciton binding energy is defined as the energy difference between the renormalized one-electron optical gap (or the gap at the Hartree-Fock level) and the excitation energy obtained after performing CI. The most important feature is that the lowest exciton has



Fig.3 Energy levels of the lowest three singlet exciton states (v = 1, 2 and 3) and their wave functions (thick curves) calculated in the Sandorfy-C-PPP model with  $t_g = \frac{2}{3}t$ ,  $t_v = \frac{4}{3}t$ , U = 2.4t, V = 1.2t t = 1.85 eV and assuming the cyclic boundary condition.<sup>15</sup>) The wave functions are plotted against the electron-hole distance r with both carriers on the same kind of orbitals, "a" or "b" (see Fig.1). The broken curve indicate the assumed Ohno potential V(r) with a reversed sign.

an unusually large binding energy with a extremely small exciton size, while the energies and sizes of the other exciton states are normal, i.e., similar to those of ordinary Mott-Wannier excitons in three-dimensional Si crystals.

## §5. Exciton Effects on Nonlinear Optical Spectra

We now consider the effect of these excitons on the LA, TPA, EA, and THG spectra. We consider the e-h excitations including excitons obtained in the single-CI and take into account only these states as intermediate states in calculating  $\chi^{(3)}$  with eq.(2). As mentioned in §3, the remaining contributions associated with double excitations and the ground state are considered to be negligible as long as nonresonant nonlinearity is concerned.

The four kinds of spectra calculated in this way<sup>12,15,30</sup> turned out to give a consistent description of experimental results. In Figs.4 and 5, the calculated spectra for a chain of n = 500 with moderate interaction strength are compared



Fig.4 (a) Linear absorption (LA), (b) twophoton absorption (TPA), and (c) electroabsorption (EA) spectra of the Sandorfy-C-PPP model for a ring of n = 500 atoms with parameters  $t_g = \frac{2}{3}t$ ,  $t_v = \frac{4}{3}t$  U = 2t, V = 1.17tand  $t = 2 \text{ eV}.^{13}$  A life-time broadening of  $\Gamma = 0.025t$  is assumed for the lowest exciton, and  $\Gamma = 0.075t$  is used for the other high-lying states. The abscissas are  $\omega$  in (a) and (c), and  $2\omega$ in (b). The experimental data of Thorne *et al.*<sup>8</sup>), Tachibana *et al.*<sup>9</sup>), and Moritomo *et al.*<sup>10</sup> for poly(dihexylsilane) at 77K are also shown with ordinates scaled arbitrarily.

with respective experiments in poly-(dihexylsilane). Many characteristic features are consistent between the calculated and the observed spectra: (i) the separated peak positions of the LA and TPA; (ii) the sharp line shapes of the LA and TPA; (iii) the red shift of the exciton absorption peak in the EA (the Stark effect); (iv) the oscillating structure of the EA spectrum around the e-h continuum threshold (~4.4 eV); (v) the three-peaked structure of the THG spectrum (Fig.5). An important point is that these many features are consistently explained by the model which contains only few parameters. As for the magnitude of  $\chi^{(3)}$ , the



Fig.5 The theoretical third-harmonic generation spectrum (solid curve) of the Sandorfy-C-PPP model for a ring of n = 500 atoms with parameters  $t_g = \frac{2}{3}t$ ,  $t_v = \frac{4}{3}t$ , U = 2.4t, V = 1.2tand t = 1.85 eV is compared with the experimental data in poly(dihexylsilane) at room temperature.<sup>15</sup>) The ordinate is for the experimental  $\chi^{(3)}$ , while the theoretical curve is scaled using  $\chi_0^{(3)} = 9.3 \times 10^{-13}$  esu. For the fitting, we used damping constants  $\Gamma = 0.12$  eV and 0.06 eV for the lowest and the second lowest excitons, respectively, and  $\Gamma = 0.18$  eV for all the other excited states.

theoretical curve in Fig.5 was obtained by assuming  $\chi_0^{(3)} = 9.3 \times 10^{-13}$  esu, which is reasonable compared with an estimation  $\chi_0^{(3)} \equiv \sigma e^4 (a/2t)^3 = 2.0 \times 10^{-13}$  esu for  $\sigma = 10^{14}$ cm<sup>-2</sup>, a = 2 Å, t = 1.85 eV. The underestimation is ascribed partly to uncertainty in  $\sigma$  and partly to the neglect of local-field enhancement.

In addition, the phase dispersion of  $\chi^{(3)}$  measured by Hasegawa *et al.*<sup>15</sup>) is also in good agreement with the present theory. The exciton model can also be applied to other poly-(alkylsilane)s with different conformations,<sup>30</sup>) although there is a limitation due to the use of the Sandorfy C model as mentioned before.

What has not been properly described in our calculations is the TPA in the case of photon energy  $\omega$  close to the one-photon resonance to the lowest exciton. A pump-and-probe absorption study<sup>31</sup> and a TPA study<sup>32</sup> have revealed the existence of a two-photon state below twice the exciton energy. This state can be interpreted as a biexciton state. We are currently studying the nature of biexciton states by taking configuration interaction among double excitations into account.<sup>33</sup>

#### §6. Dependence on Conjugation Length

In the previous section, we demonstrated that the optical spectra calculated for a fairly long chain (n>100) are consistent with experiments. However, the conjugation length of polysilane has not yet been well characterized experimentally. It is natural to ask whether such a long conjugation length is in fact necessary or not to explain experiments. To answer this question, we examine the size dependence of the optical spectra in this section. Since we are interested only in an overall tendency, we keep the cyclic boundary condition even for small chains for theoretical uniformity. That is, the results presented below are for polysilane rings. However, we have carried out calculations also for the case of a linear chain without the cyclic boundary condition and checked that the qualitative behavior is similar if the boundary condition is properly chosen such that there is no dangling bonds at the chain ends.

We first examine the LA spectrum. Figure 6(a) displays the calculated LA spectra for various sizes n. The effect of decreasing n (from bottom to top in the figure) appears, first of all, as a blue shift of the main exciton peak. This is consistent with the experimental data by Kanemitsu *et al.*<sup>34)</sup> Also weak absorption peaks due to quantized levels appear at high energies. The level separation increases with decreasing n as expected. The experimental absorption spectra<sup>31</sup>) of small oligomers exhibit stronger absorption peaks at energies higher than the lowest exciton energy. This is not reproduced in Fig.6(a), presumably because we have neglected the effects of the chain ends.

The calculated THG spectra for various *n* are shown in Fig.6(b). The discreteness of the continuum states, which appear above  $\omega \sim 0.7t$  as three-photon resonances, becomes more evident for smaller *n*. The two-photon resonance feature at  $\omega \sim t$  can be seen for n = 64 and larger, but is not distinguishable for n = 32 and smaller. The experimental data shown in Fig.5, which are characterized by the three peaks, may be fitted by the cases of n = 128 or 64 if we use a larger broadening  $\Gamma$ , but cannot be fitted by the results of n = 32 or smaller. We conclude that the conjugation length of the polymers used in those THG experiments must be longer than about 50



Fig.6 (a) Linear absorption and (b) thirdharmonic generation spectra calculated for various system size *n* (number of Si atoms) using the Sandorfy-C-PPP model with the cyclic boundary condition and parameters  $t_g = \frac{2}{3}t$ ,  $t_y = \frac{4}{3}t$ , U = 2t, V = t and  $\Gamma = 0.02t$ .

atoms.

In general, a strong size dependence is expected for the magnitude of  $\chi^{(3)}$  in onedimensional conjugated systems.<sup>4,21,22,35</sup>) In the present case, however, such a dependence seems to be limited to very small *n*, while  $\chi^{(3)}$  (per atom) tends to saturate in increasing *n* already at about n = 16 as seen in Fig.6(b). This is associated with the fact that the characteristic delocalization length<sup>22</sup>) of polysilane is fairly small compared with that of a  $\pi$ -conjugated polymer.

#### §7. Conclusions

We have demonstrated that the inclusion of Coulomb interactions in the Sandorfy C model at the level of the PPP model with the single CI allows us to describe the linear and nonlinear optical properties of polysilane quite well. Exciton effects turned out to be of primary importance. The binding energy of the lowest exciton is extremely large, about 1 eV, in remarkable contrast to the case of bulk Si crystal. The difference originates from the confinement of excitons on the one-dimensional polymer backbone. A polymer conjugation length of at least about 50 atoms is necessary to explain the observed nonlinear optical properties of poly(dihexylsilane).

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