

Systematic Analysis of Bandgap Evolution of Conjugated Polymers

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A systematic method is presented to analyze the bandgaps of conjugated polymers in terms of geometrical relaxations and electronic effect of moieties using the equation of $E_g = \Delta E^{\delta r} + \Delta E^{1-4} + \Delta E^d$. The relationship between $\Delta E^{\delta r}$ and δr is derived from trans-PA and is transferred to other conjugated polymeric systems. By applying this method to heterocyclic polymers, very useful information is obtained to understand the evolution of bandgaps of PT, PPy and PF in connection with the chemical structures and electronic effect of the heteroatoms. We believe that this method is very helpful to understand the evolution of bandgaps of various conjugated polymers in connection with the chemical structures and electronic effect of moieties. Also, the method is expected to provide valuable information to design a small bandgap polymers.

Introduction

During the last several decades, conjugated polymers have attracted great attention as organic conductors due to their unique electrical properties. A lot of theoretical work has been devoted to understanding the relationship between chemical structures and electronic properties of the conjugated polymers. It is well-known that the bandgap of trans-polyacetylene (PA) arises from the so-called Peierls distortion,¹ viz. bond-length alternation.²⁻⁴ Lowe and Kafafi clarified the effects of chemical substitution on bandgaps of trans-PA type polymers.⁵ Polymers based on *cis*-PA backbone such as poly(*p*-phenylene), polythiophene (PT) and polypyrrole (PPy) are nondegenerate in their ground states and their bandgaps decrease as the structures of the polymers are transfigured toward quinoid forms.^{6,7} The role of heteroatom on the electronic properties of those polymers has been investigated.⁸⁻¹¹ Also, the effects of pendant substituents such as alkyl and alkoxy groups on the bandgaps of the polymers were theoretically explained in parallel with experimental observations.^{11,12} Bredas demonstrated that ring-fused heterocyclic polymers show small bond-length alternation and may possess small bandgaps.¹³ With the help of such theoretical work, new conjugated polymers such as polyisothianaphthene¹⁴ and poly(5,5'-bithiophenemethine)¹⁵ emerged. Of course, a lot of theoretical work followed to understand the geometrical and electronic structures of those polymers and the similar polymeric systems.^{10,12,16-22}

Recently, many experimental²³⁻²⁷ and theoretical^{20,21,28-34} efforts have been focused on the design of new conjugated polymers with very small bandgaps ($E_g < 1$ eV) that exhibit intrinsic conductivities or at least semiconductive properties even in the ground states. To be successful in designing such polymers, it is essential to understand the evolution of the bandgaps of conjugated polymers in connection with their chemical structures. However, one of the major difficulties encountered in elucidating the bandgap evolution lies in the fact that the bandgap arises from the strong coupling of geometrical relaxation along the conjugated carbon backbone and electronic perturbation by other moieties like heteroatoms in heterocyclic polymers. Recently, we have successfully decoupled those effects for various conjugated five-

membered ring polymers using the following equation.³²⁻³⁴

$$E_g = \Delta E^{\delta r} + \Delta E^{1-4} + \Delta E^d \quad (1)$$

Here E_g is the bandgap of a conjugated polymer. $\Delta E^{\delta r}$ is the contribution arising from bond-length alternations (δr) along the conjugated carbon backbone and ΔE^{1-4} from the interaction between the C1 and C4 atoms of *cis*-PA type backbone. ΔE^d corresponds to the pure electronic effect of the bridging atom or group.

In this study, we present in detail how to systematically decompose the bandgap of a conjugated polymer into three terms in eqn. (1) by applying the equation to polyacetylenes and heterocyclic polymeric systems since the method has been only introduced briefly in our previous work.

Methodology

Semiempirical band calculations with AM1 Hamiltonian³⁵ were performed to obtain the geometrical parameters for the polymers. The most stable structures in the ground states were obtained through full optimization of the geometrical parameters with the assumption of the anti-coplanarity of the heterocyclic polymers. To examine the potential energy change of the polymers with the inter-ring distances, we carried out total energy calculations at various inter-ring distances. The inter-ring distance was stepwise varied by 0.02 Å from the optimized one. The other geometrical parameters were optimized at each inter-ring distance.

The modified extend Hückel (MEH) method¹¹ was employed to calculate the electronic properties of the polymers. The MEH method was designed to reproduce a bandgap defined as the λ_{max} for the π - π^* transition of conjugated polymers, and not the band edge as is often used to define the gap experimentally. This approach has been shown to yield remarkably accurate bandgaps for a wide variety of conjugated polymers.^{11,36} The relationship between $\Delta E^{\delta r}$ and δr was obtained from the computed E_g and δr for trans-PA. For a given heterocyclic polymer, the bandgap (E_g') arising only from the conjugated carbon backbone was estimated by removing the atomic orbitals of the heteroatom from the Hamiltonian and overlap matrices. Since E_g' for the heterocyclic polymers corresponds to E_g for *cis*-PAs, the ΔE^{1-4} value

Table 1. Valence shell atomic parameters used in the modified extended Hückel band calculations. n and l are the principal and angular momentum quantum numbers, respectively. Ionization Potentials (IP in eV), Slater orbital exponents (ζ in au)

Atom	n	l	IP	ζ	n	l	IP	ζ
C	2	0	21.4	1.625	2	1	11.4	1.625
H	1	0	13.6	1.300				
S	3	0	20.0	2.117	3	1	13.3	2.117
N	2	0	26.0	1.950	2	1	13.4	1.950
O	2	0	32.3	1.975	2	1	14.8	1.975

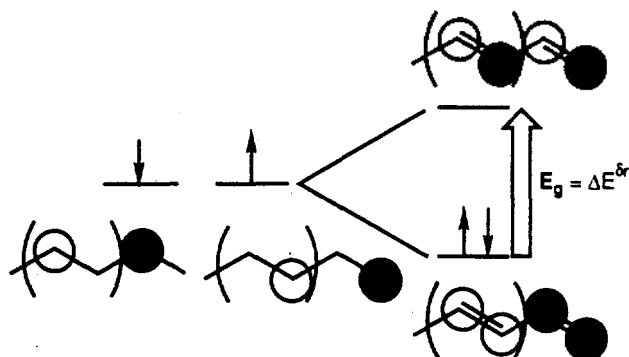


Figure 1. Schematic diagram for the evolution of the bandgap of trans-polyacetylene.

amounts to $E_g - \Delta E^{\delta r}$. $\Delta E^{\delta r}$ was evaluated by applying eqn. (1) and solving for $\Delta E^{\delta r}$. MEH parameters used in the calculations are listed in Table 1.

Polyacetylenes

In polyacetylenes, there exist three isomers: trans-PA, trans-cisoid PA and cis-transoid PA. Among the isomers, trans-PA is the most thermodynamically stable. It is also believed that cis-transoid PA is slightly more stable than trans-cisoid PA as demonstrated by the *ab initio* calculations of Karpfen and Holler.³⁷ Since the bandgaps of PAs emerge only from geometrical relaxation, we examined the geometrical and electronic structures of polyacetylenes. As shown in Table 2, the three isomers have similar bond-length alternation but possess quite different bandgaps. Our calculated values are consistent with the experimental measurements. Obviously, the bandgap of dimerized trans-PA is evolved only from bond-length alternation, that is $E_g = \Delta E^{\delta r}$. This comes from the fact that equidistant trans-PA is predicted to have zero bandgap with the degenerate π and π^* energy levels at the Fermi level and is susceptible to geometrical distortion toward dimerization to stabilize the electronic energy as in Figure 1.²⁵ It is known that E_g of trans-PA is linearly proportional to δr .^{21,42} Therefore, from our calculated values of δr (0.096 Å) and E_g (1.55 eV) for trans-PA, we establish the following relationship between them.

$$\Delta E^{\delta r} = 16.1 \times \delta r \quad (2)$$

In spite of the similar δr values, cis-PAs have bandgaps about 0.2 eV smaller or larger than does trans-PA. The dif-

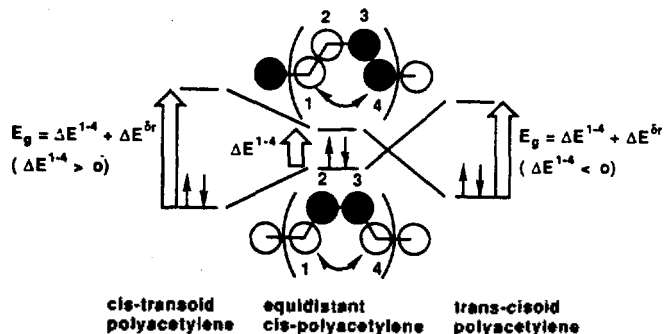


Figure 2. Schematic diagram for the evolution of the bandgaps of cis-polyacetylenes.

ference in bandgaps between cis-PA and trans-PA was also observed experimentally⁴¹ and was explained in terms of the C1-C4 interactions of the carbon backbones from a molecular orbital argument.² Using eqn. (2), the contribution from the given bond-length alternation, δr to the bandgaps of cis-PAs is calculated to be about 1.5 eV. This value is almost the same as that of trans-PA. To figure out the effect of the C1-C4 interactions on bandgaps, we investigated the electronic property of equidistant cis-PA. The bandgap of equidistant cis-PA with the optimized geometrical parameters (C-C bond length = 1.391 Å and C-C-C bond angle = 125.9°) is calculated to be 0.18 eV. Of course, this bandgap is not due to the contribution from δr . It is easily found out by scrutinizing the frontier crystal orbitals near the Fermi level that the bandgap arises from the C1-C4 interactions. As shown in Figure 2, the interaction between C1 and C4 atoms is bonding in the highest occupied crystal orbital (HOCO) while in the lowest unoccupied crystal orbital (LUCO) it is antibonding. The distance between C1 and C4 atoms was calculated to be 3.023 Å. Since the effect of the C1-C4 interaction on the bandgap is additive, the following equation is valid for cis-PAs.

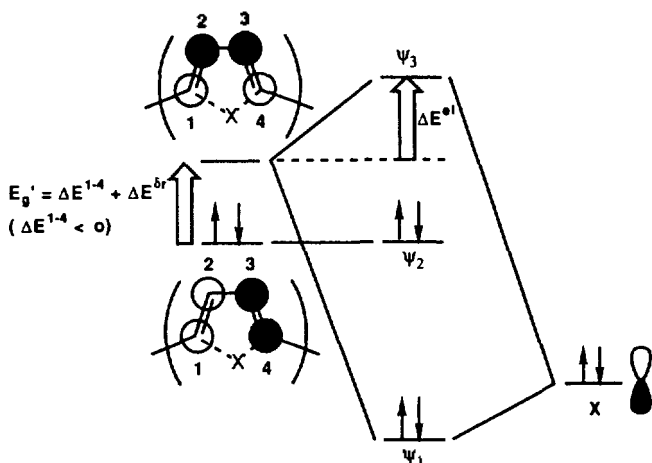
$$E_g = \Delta E^{\delta r} + \Delta E^{1-4} \quad (3)$$

Since the HOCO and LUCO of cis-transoid PA are identical to those of equidistant PA, geometrical distortion toward cis-transoid PA stabilizes the HOCO and destabilizes the LUCO of cis-transoid PA (Figure 2), and consequently the bandgap further increases. Therefore, the contribution (ΔE^{1-4}) due to the C1-C4 interaction to the bandgap is positive for cis-transoid PA. The HOCO and LUCO of trans-cisoid PA are in the reverse order of those of equidistant cis-PA. Therefore, ΔE^{1-4} is negative for trans-cisoid PA. As the geometrical distortion proceeds toward trans-cisoid PA, the bandgap decreases and becomes zero at some δr value (ca. 0.01 Å). The bandgap increases again by further distortion. Using the eqns. (2) and (3), for cis-transoid PA $\Delta E^{\delta r}$ with $\delta r = 0.093$ Å was calculated to be 1.50 eV and ΔE^{1-4} with the C1-C4 distance of 3.045 Å to be 0.17 eV. The $\Delta E^{\delta r}$ and ΔE^{1-4} values for trans-cisoid PA with $\delta r = 0.095$ Å and the C1-C4 distance of 3.010 Å amount to 1.53 and -0.20 eV, respectively. Therefore, it can be understood that the bandgap difference between two cis-PA isomers is due to the opposite interactions between C1 and C4 atoms of the polymers near the Fermi level. The result of bandgap analysis of cis-PAs is summa-

Table 2. Geometrical parameters (in Å) optimized by AM1 band calculations and bandgaps (in eV) from modified extended Hückel band calculations for polyacetylenes (PA)

	trans-PA		cis-transoid PA		trans-cisoid PA
	calc.	exptl. ^a	calc.	exptl. ^b	calc.
C=C bond length	1.347	1.36	1.348	1.35	1.349
C-C bond length	1.444	1.45	1.441	1.46	1.442
C1-C4 distance	—	—	3.045	3.04	3.010
l'	2.452	2.456	4.393	4.39	4.452
δr^d	0.096	0.09	0.093	0.11	0.095
E_g^e	1.55	1.8-1.9	1.67	2.0	1.33
ΔE^{br}	1.55	—	1.50	—	1.53
ΔE^{1-4}	—	—	0.17	—	-0.20

^aExperimental values for the geometrical parameters from Ref. 38 and E_g from Ref. 39. ^bExperimental values for the geometrical parameters from Ref. 40 and E_g from Ref. 41. ^cRepeating unit length. ^dBond-length alternation. ^eEnergy gap corresponding to the π - π^* λ_{max} value of the optical spectra.

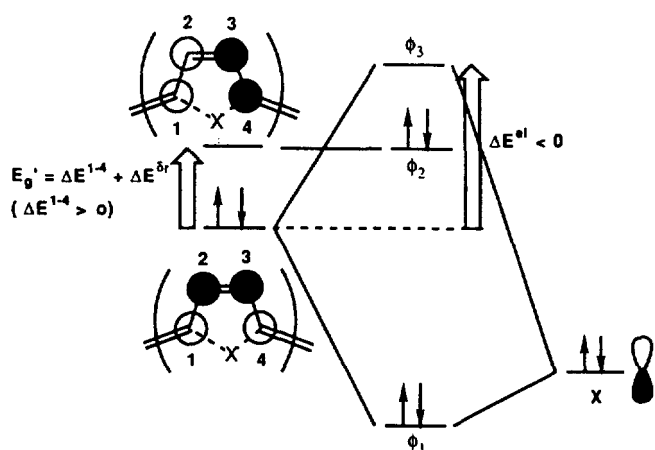
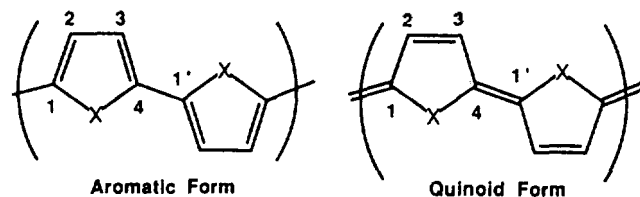
**Figure 3.** Schematic diagram for the evolution of the bandgaps for aromatic forms of heterocyclic polymers.

rized in Table 2.

Heterocyclic Polymers

Heterocyclic polymers such as PT, PPy and PF consist of five-membered rings, which have heteroatoms bridging C1-C4 atoms of *cis*-PA type backbone. Since the heterocyclic polymers are based on *cis*-PA backbone, they are nondegenerate in their ground states and possess two types of possible isomers (aromatic and quinoid forms). A lot of theoretical work has demonstrated that the aromatic forms are more stable than the quinoid forms.^{7,10,19} Vibrational analysis of PT and PPy confirmed that both of them are aromatic in their ground states.¹⁸

It was pointed out that the heteroatoms play an important role in determining the bandgaps of the polymers and are responsible for the higher stability of the aromatic forms compared

**Figure 4.** Schematic diagram for the evolution of the bandgaps for quinoid forms of heterocyclic polymers.

to the quinoid forms.⁸ Lee and Kertesz argued that δr for the aromatic forms decreases compared to δr of PA because the crystal orbital (Ψ_1 of Figure 3) with antibonding character in the double bond region and bonding character in the single bond region is occupied by electrons due to the interaction of the heteroatomic p orbital with the LUCO of trans-cisoid PA backbone.¹⁰ Also, heteroatoms shorten the C1-C4 distance by bridging the two atoms and perturb the π electronic system of the polymeric backbone.¹¹ Therefore, bandgaps of the heterocyclic polymers can be affected by the three factors as implanted in eqn. (1). Schematic diagrams for the evolution of the bandgaps of the heterocyclic polymers are presented in Figure 3 for the aromatic forms and in Figure 4 for the quinoid forms. The position of the ϕ_3 energy level in Figure 4 relative to that of the ϕ_2 energy level depends on the degree of the interaction of the heteroatomic p orbital with the LUCO of *cis*-transoid PA backbone.

The ground-state structures of PT, PPy and PF which were optimized by the AM1 band calculation are all aromatic. Figure 5 shows the energy change of PT, PPy and PF with the inter-ring distance, relative to the formation energy of the corresponding aromatic forms. The energy curves do not show the local minima which would represent the quinoid states. Only the inflection points are shown at the inter-ring distance 0.08 Å shorter ($\Delta r_{inter-ring} = -0.08$ Å) than the optimized one for aromatic PT and at $\Delta r_{inter-ring} = -0.10$ Å for PF. The optimized intra-ring structures at $\Delta r_{inter-ring} = -0.08$ Å for PT, PPy and PF are of all aromatic forms. We performed geometrical optimizations again for the quinoid intra-ring structures. Starting parametric values were selected from the quinoid structures optimized by the MNDO band calculations of Lee and Kertesz.¹⁰ The δr and $\Delta r_{inter-ring}$ values of the reoptimized structures are 0.105 and -0.078 Å for

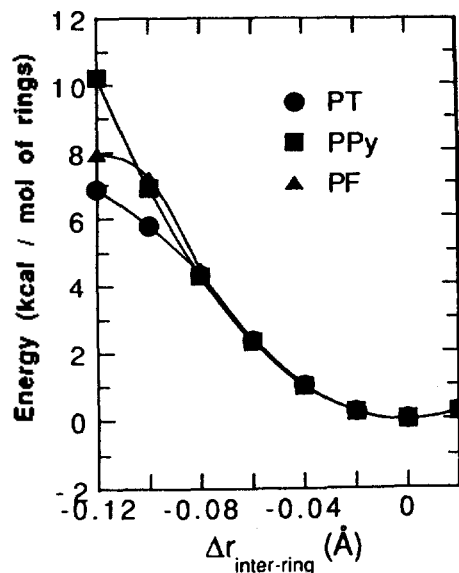


Figure 5. Energetics of polythiophene (PT), polypyrrole (PPy) and polyfuran (PF) with the inter-ring distance. $\Delta r_{\text{inter-ring}}$ represents deviation of the inter-ring distance from the optimized one for the corresponding aromatic form.

Table 3. Geometrical parameters (in Å) optimized by AM1 band calculations for the aromatic and quinoid forms^a of polythiophene (PT), polypyrrole (PPy) and polyfuran (PF)

	PT		PPy		PF	
	Aromatic	Quinoid	Aromatic	Quinoid	Aromatic	Quinoid
C1-C2	1.380	1.456	1.412	1.475	1.388	1.463
C2-C3	1.431	1.356	1.426	1.368	1.438	1.362
C1-X	1.688	1.708	1.396	1.411	1.405	1.419
C4-C1'	1.422	1.344	1.439	1.367	1.424	1.347
δr^b	0.047	0.105	0.021	0.107	0.043	0.108
C1-C4	2.480	2.525	2.269	2.301	2.240	2.266
f^c	7.699	7.663	7.210	7.178	7.023	6.992

^aEach quinoid structure was chosen from the geometry with quinoid intra-rings (see text). ^bAverage bond-length alternation, defined as $\delta r = |[\text{R}(1-2) - \text{R}(2-3) + \text{R}(3-4) - \text{R}(4-1)]|/2$. ^cRepeating unit length.

PT, 0.107 and -0.072 Å for PPy, and 0.108 and -0.077 Å for PF, respectively. Those structures are 1-7.6 kcal/mol of rings less stable than the aromatic intra-ring structures with $\Delta r_{\text{inter-ring}} = -0.08$ Å. However, in this study we chose for the quinoid forms the structures with quinoid intra-rings rather than the more stable ones with aromatic intra-ring structures. Optimized geometrical parameters are given in Table 3. Among them, δr and C1-C4 distance are the crucial parameters which affect the bandgap of the polymer. Those parameters obtained from the X-ray structure of α -terthienyl are $\delta r = 0.049$ Å and C1-C4 distance = 2.505 Å, quite close to ours.⁴³ However, δr value (0.07 Å) from X-ray diffraction powder measurements on neutral PT is larger than our value.⁴⁴ The calculated δr value for the aromatic PT is close

Table 4. Analysis of the bandgap evolution of polythiophene (PT), polypyrrole (PPy) and polyfuran (PF) using the equation of $E_g = \Delta E^{\text{ar}} + \Delta E^{1-4} + \Delta E^{\text{het}}$ (in eV)^a

	PT		PPy		PF	
	Aromatic	Quinoid	Aromatic	Quinoid	Aromatic	Quinoid
E_g	2.32	-0.06	3.15	-1.29	3.07	-0.78
E_g^b	0.38	2.02	-0.31	2.25	0.03	2.33
ΔE^{ar}	0.76	1.69	0.34	1.72	0.69	1.74
ΔE^{1-4}	-0.38	0.33	-0.65	0.53	-0.66	0.59
ΔE^{het}	1.94	-2.08	3.46	-3.54	3.04	-3.11
exptl. E_g^c	2.5-2.7		3.2		3.0	

^aBandgaps (E_g) were obtained from the modified extended Hückel band calculations. Negative E_g and E_g' values indicate the reversal of the highest occupied crystal orbital and the lowest unoccupied crystal orbital compared to those of the corresponding *cis*-polyacetylenes. ΔE^{ar} is the contribution from bond-length alternation, ΔE^{1-4} the contribution from C1-C4 interaction and ΔE^{het} the electronic effect of heteroatoms. ^bBandgap of the conjugated carbon backbone of the heterocyclic polymer. ^cExperimental $n \cdot \pi^* \lambda_{\text{max}}$ values of the optical spectra from Ref. 47 for PT, Ref. 48 for PPy and Ref. 49 for PF.

to that for the aromatic PF, but larger than that for the aromatic PPy. Microwave data on thiophene and pyrrole also showed larger C-C bond alternation in thiophene than that in pyrrole.⁴⁵ The C1-C4 distance is increasing in the order of PF < PPy < PT in consistent with the order of heteroatomic size. Though much theoretical work has been done for the determination of the equilibrium geometries of conjugated polymers, the comparison of these geometries is not made here since other semiempirical calculations yield similar results as ours. *Ab initio* calculations with a small basis set are known to overestimate δr values.⁴⁶

Table 4 presents the components of the bandgaps of both aromatic and quinoid forms of PT, PPy and PF. Since bandgaps of heterocyclic polymers were demonstrated to evolve linearly as a function of δr ^{13,16} we believe that eqn. (2) holds for any conjugated carbon backbone systems. ΔE^{ar} values for the aromatic forms were calculated to be very small compared to those for PAs. The effect of C1-C4 interactions on the bandgaps is found to be quite significant compared to that found in *cis*-polyacetylenes. Furthermore, for the aromatic forms this effect almost cancels out the effect of the bond-length alternation. The electronic effect of heteroatoms on the bandgaps is estimated to be larger than the other two effects. Consequently, the bandgaps of the heterocyclic polymers correspond in value to the pure electronic effect of the heteroatoms.

Now, we would like to briefly discuss the stability of the quinoid forms in connection with the electronic effect of heteroatoms. Let us assume that $\Delta E^{\text{ar}} = 1.6$ eV (corresponding to $\delta r = 0.1$ Å) and $\Delta E^{1-4} = 0.3$ eV. Then, if the electronic perturbation is so strong that ΔE^{het} is greater than 1.9 eV, the ϕ_2 energy level (see Figure 4) is occupied by electrons and, thereby, the quinoid-type intra-ring structure would no longer persist due to antibonding character in the C=C region and bonding character in the C-C region of the ϕ_2 orbit-

al. In this case, the quinoid forms are very unstable as found in Figure 5 for PT, PPy and PF. On the other hand, if the electronic perturbation by a heteroatom is weak enough that ΔE^{el} is much less than 1.9 eV, the ϕ_3 energy level is lower than the ϕ_2 energy level and is occupied by electrons. Since the ϕ_3 crystal orbital has bonding character in the C=C region and anti-bonding character in the C-C region, the quinoid forms are relatively stable. Poly(cyclopentadienylene) and polysilole belong to this case.³²⁻³⁴

Conclusions

We have presented a systematic method to analyze the bandgaps of conjugated polymers in terms of geometrical relaxations and electronic effect of moieties using the equation of $E_g = \Delta E^{\text{st}} + \Delta E^{1-4} + \Delta E^{\text{el}}$. The relationship between ΔE^{st} and δr was derived from trans-PA and was successfully transferred to other conjugated polymeric systems. From the analysis of bandgap evolution of PT, PPy and PF using this method, it is found that the electronic effect of heteroatoms is so large to decide the bandgaps of the polymers and affects the relative stabilities of the aromatic vs. quinoid forms. The C1-C4 interaction is quite significant in five-membered ring polymers. This interaction affects the bandgaps of the aromatic forms to decrease ($\Delta E^{1-4} < 0$) and the gaps of the quinoid forms to increase ($\Delta E^{1-4} > 0$). In conclusion, we believe that this method is so useful to understand the evolution of bandgaps of conjugated polymers in connection with the chemical structures and electronic effect of moieties such as heteroatoms in heterocyclic polymers. Also, the method is expected to provide valuable information to design a small bandgap polymers.

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Configuration Interaction Theory and van der Waals Predissociation

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Golden-rule like formulas have been used without theoretical basis to calculate the resonance lifetimes and final state distributions in the predissociation of van der Waals molecules. Here we present their theoretical basis by extending Fano's configuration interaction theory. Such extensions were independently done by Farnoux [*Phys. Rev.* 1985, 25, 287] but his work, unfortunately, was not well known outside some small group of people in the field of Auger spectroscopy. Since my extension is easier to understand than his, it is presented here. Theoretical basis of Golden rule like formulas used in the predissociation of van der Waals molecules was obtained by using such extensions. Factors responsible for several aspects of predissociation dynamics, such as variations of dynamics as functions of resonance lifetimes, or variations in shapes of final quantum state distributions of photofragments around resonances, were identified. Parameters, or dynamical information that could be obtained from the measurement of partial cross section spectra were accordingly determined. The theory was applied to the vibrational predissociation of triatomic van der Waals molecules and its result was compared with those calculated by close-coupling method. An example where Golden-rule like expression fails and branching ratios vary greatly around a resonance was considered.

Introduction

Photofragmentation processes provide a wealth of information on the molecular dissociation dynamics. They could be visualized as half collision processes but their study as a means of obtaining molecular dissociation dynamics have advantages over molecular beam collision experiments. For example, complicated and rich resonance structures are commonly observed in the photofragmentation spectra while not many resonances are identified in the collision experiments. Predissociation spectra of van der Waals molecules with the accompanying final quantum state distributions of photofragments, in particular, have served as the only experimental tool to provide the full features of anisotropic intermolecular potentials, as intermolecular potentials in van der Waals systems are weak and therefore only a few channels are involved in predissociation processes.³ Still, scattering calculations on such predissociation spectra are not easy and Golden-rule like formulas have been used to calculate lifetimes and final quantum state distributions of photofragments.⁴ The Golden-rule like formula provides the detour to the repeated calculations at the finely divided energy mesh points around resonances and directly calculates resonance widths. Though

it has been successfully applied, its theoretical basis is not known yet. It is one of the purposes of this paper to find out in what conditions the Golden-rule like formula could be applied and when it fails by making use of Fano's configuration interaction theory. Another purpose of this paper is to show that analytical solutions for the predissociation processes can be obtained in Fano's configuration interaction theory and many questions on predissociation could be answered in general terms.

Fano showed that the following profile formula parameterizes the photodissociation (including photoionization) spectra:¹²

$$\sigma(\epsilon) = \sigma_0 \frac{(q + \epsilon)^2}{1 + \epsilon^2}, \quad (1)$$

where ϵ is the reduced energy defined by $(E - E_r)/(\Gamma/2)$; E_r and \hbar/Γ represent the resonance energy and the mean life time of the quasi-bound state, respectively; σ_0 represents the photofragmentation cross section to the continuum state that does not interact with the quasibound-bound state; q is an index that characterizes the line profile. This formula shows that measurement of photodissociation spectra provides us with the information on σ_0 , E_r , Γ , and q . It strictly