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Density Functional Theory Study on the Raman Spectra of Negative Polarons and Negative Bipolarons in Na-Doped Poly(*p*-phenylene)[†]

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Density functional theory with the 6-31G* basis set and the BYLP nonlocal exchange-correlation functional has been used for the normal coordinate calculations of the neutral, radical anion, and dianion species of *p*-terphenyl to *p*-sexiphenyl. The bands attributed to negative polarons and negative bipolarons in the reported Raman spectra of Na-doped poly(*p*-phenylene) have been successfully assigned on the basis of the present calculations. The calculated atomic displacements have indicated that the Raman bands not corresponding to the zone-center modes of neutral poly(*p*-phenylene) are due to negative polarons and negative bipolarons. The Raman bands characteristic of negative polarons and negative bipolarons have been identified. The frequency of the inter-ring CC stretch is sensitive to the structural changes in going from benzenoid to quinoid structure in negative polarons and negative bipolarons.

1. Introduction

Conjugated polymers such as poly(*p*-phenylene) (abbreviated as PPP) show high electrical conductivity upon doping with acceptors or donors.[1] These conjugated polymers are used for the active materials of electronic devices such as light-emitting diodes and field-effect transistors.[2] Recently, Batlogg and coworkers have reported superconductivity at 2.35 K by using a field-effect device fabricated with regioregular poly(3-hexylthiophene).[3] Electrical properties of nondegenerate polymers such as PPP and polythiophene have been interpreted in terms of polarons[4−6] and bipolarons[5−7] that are nonlinear excitations in conjugated polymers. A polaron has charge $+e$ (or $-e$) and spin 1/2, whereas a bipolaron has charge $+2e$ (or $-2e$) but no spin. They are considered to be charge carriers in doped polymers. The formation of polarons or bipolarons are associated with localized electronic states and structural changes over several repeating units. Polarons and bipolarons can therefore be characterized by electron-spin resonance, electronic absorption, and vibrational spectroscopies. It has been demonstrated[8−10] that upon formation of a polaron two sub-gap absorption bands appear, and upon formation of a bipolaron a single sub-gap band appears. Raman spectroscopy is a powerful tool for studying the electronic and molecular structures of polarons and bipolarons in doped polymers.[11−13] Two of the present authors (YF and MT)[14,15] have identified negative polarons and negative bipolarons in Na-doped PPP on the basis of the Raman spectra of the radical anions and dianions of *p*-terphenyl to *p*-sexiphenyl. The results of Raman studies of other doped polymers are summarized in previous reviews.[11−13] Theoretical studies on the Raman spectra of polarons and bipolarons are important for a better understanding of the structures of doped polymers. Normal coordinate calculations have been performed by using empirical force fields[16,17] and scaled quantum mechanical force fields for oligomers.[18] However, the reported Raman spectra of Na-doped poly(*p*-phenylene) have not been fully explained by these calculations. Recently, ab initio molecular orbital methods have been used for computing vibrational spectra. For the purpose of obtaining vibrational frequencies associated with bipolarons, the vibrational frequencies in the Raman and infrared spectra of the dications of α-oligothiophenes up to α-quinquethiophene have been calculated at the ab initio Hartree−Fock level with the 3-21G* basis set.[19,20] The Hartree−Fock method incorporates electron exchange, but does not contain electron correlation explicitly, whereas Shimoi and Abe,[21] Tol,[22] and Irle and Lischka[23] have shown that the effect of electron correlation is significant in the stability of polarons and bipolarons. Thus, ab initio quantum mechanical methods incorporating electron correlation are required. However, it is practically impossible to calculate the vibrational frequencies of the radical ions and divalent ions of long-chain *p*-oligophenyls at post-Hartree−Fock

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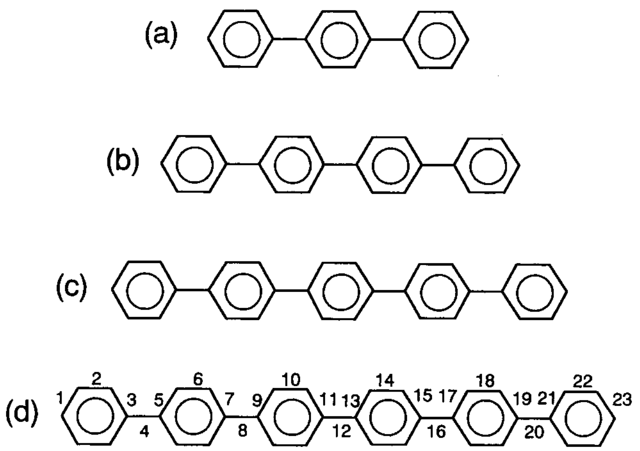


Figure 1. Schematic structures of *p*-oligophenyls: (a) *p*-terphenyl; (b) *p*-quaterphenyl; (c) *p*-quinquephenyl; (d) *p*-sexiphenyl.

methods such as Møller-Presset perturbation levels. On the other hand, density functional theory (DFT) can incorporate electron exchange and correlation in treating quite large systems. In our previous papers[24,25] we have demonstrated the usefulness of the DFT approach for evaluating the vibrational frequencies of the radical anion and cation of biphenyl. In particular, unscaled vibrational frequencies calculated with the 6-31G* basis set and Becke-Lee−Yang−Parr exchange-correlation functional (abbreviated as BLYP) have been useful in assigning the observed Raman spectra. Casado et al.[26] have calculated the vibrational frequencies of the radical cations of oligothiophenes up to a pentamer using Becke's three-parameter hybrid method in combination with the LYP correlation functional. In this paper, we have calculated the structures and vibrational frequencies of the radical anion and dianion species of *p*-terphenyl to *p*-sexiphenyl, as models of negative polarons and bipolarons, respectively. On the basis of the results of the DFT calculations, we have assigned the observed Raman spectra of heavily Na-doped PPP and discussed the structures associated with polarons and bipolarons.

2. Calculations

Density functional theory calculations of the structures and vibrational properties (harmonic frequencies and atomic displacements) of the neutral, radical anion, and dianion species of *p*-oligophenyls (*p*-terphenyl to *p*-sexiphenyl) were carried out with the Gaussian 98 program[27] using an HIT Alpha DP264 computer. The schematic structures of *p*-terphenyl to *p*-sexiphenyl are shown in Figure 1. Countercations were not included in the calculations of the radical anions and dianions. The 6-31G* basis set and Becke's exchange functional[28] in combination with the Lee−Yang−Parr correlation functional[29] (BLYP) were used. Full geometry optimization was performed for each species. For neutral *p*-terphenyl, there exist two stable conformers: one with a helical conformation gauche$^+$−gauche$^+$−gauche$^+$ with respect to the three inter-ring CC bonds and the other with a twisted conformation gauche$^+$−gauche$^-$−gauche$^+$. The total energy of the helical structure is nearly equal to that of the twisted one. It is expected that there are several energetically close conformers for each oligomer. However, we did not calculate the energies of all these conformers, because it is not the aim of our present work to determine torsional potentials. The optimized structures of the neutral, radical anion, and dianion species of each oligophenyl assume alternatingly twisted conformation with the exception of the dianion of *p*-terphenyl; the dianion of *p*-terphenyl has a planar structure (D_{2h} symmetry). The twisted structures of *p*-terphenyl and *p*-quinquephenyl have C_{2h} symmetry, and those of *p*-quaterphenyl and *p*-sexiphenyl have D_2 symmetry. Harmonic frequencies and atomic displacements have been calculated for these twisted structures. No imaginary frequency was calculated for any species treated. Atomic displacements in the calculated vibrational modes were depicted with the BLXVIEW program.[30]

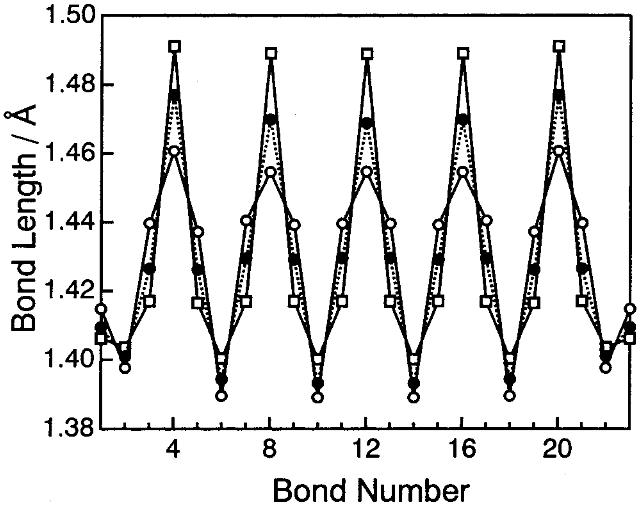


Figure 2. Lengths of the intra- and inter-ring CC bonds of the neutral (open squares), radical anion (closed circles), and dianion (open circles) species of *p*-sexiphenyl.

3. Molecular Structures

The large size of oligophenyls studied in the present work makes it impossible to report all their structural parameters, vibrational frequencies, and atomic displacements in full detail. We will restrict our discussion to the most important structural parameters and vibrational frequencies, their chain-length dependencies, and the substantial differences between the neutral species and the corresponding charged species.

The calculated torsional angles around the inter-ring CC bonds in the twisted structures of neutral *p*-terphenyl to *p*-sexiphenyl are in the range from 34.5 to 36.0°. The calculated CC bond lengths associated with phenylene and phenyl rings are in the range between 1.400 and 1.417 Å; neutral species of *p*-oligophenyls take benzenoid structures. The calculated lengths of the inter-ring CC bonds are in the range between 1.489 and 1.491 Å. The inter-ring CC bonds are thus regarded as single bonds. As a typical example, the calculated intra- and inter-ring CC bond lengths of *p*-sexiphenyl are shown in Figure 2 with open squares. The numbering of bonds in *p*-sexiphenyl is shown in Figure 1d. The structures of neutral *p*-oligophenyls have been calculated by the ab initio Hartree−Fock method.[31−33] These calculations also show that neutral *p*-oligophenyls take benzenoid structures.

The calculated torsional angles around the inter-ring CC bonds in the radical anions of *p*-terphenyl to *p*-sexiphenyl are in the range between 16.8 and 26.2 °. Each torsional angle is smaller than that of the parent neutral species. The intra- and inter-ring CC bond lengths of each radical anion are different from those of the neutral species. The calculated intra- and inter-ring CC bond lengths of the radical anion of *p*-sexiphenyl are plotted in Figure 2 with closed circles. In the terminal rings, the calculated lengths of bonds 1, 2, and 3 are 1.409, 1.401, and 1.426 Å, respectively. In the inner rings, the lengths of bonds 5, 6, 7, 9, 10, and 11 are 1.426, 1.394, 1.429, 1.429, 1.393, and 1.430 Å, respectively. The lengths of inter-ring CC bonds 4, 8,

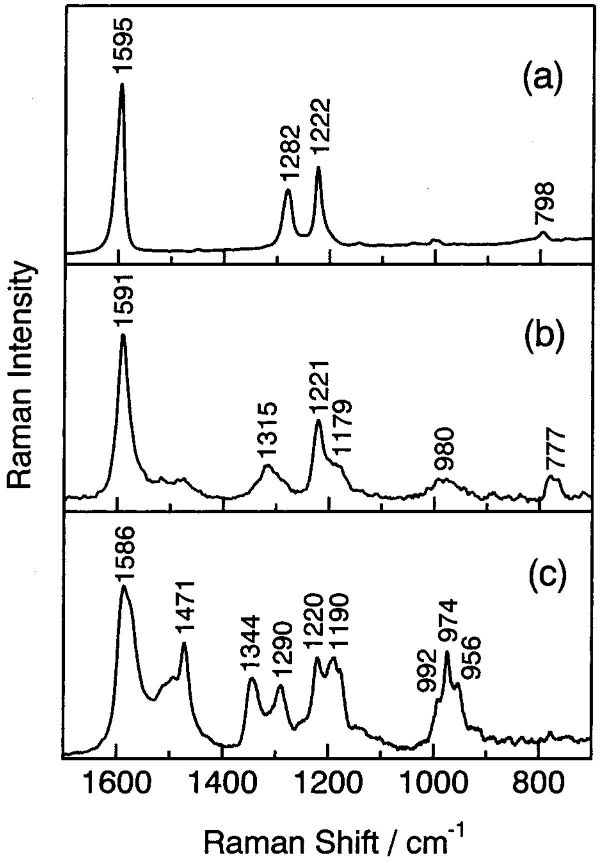


Figure 3. Raman spectra of (a) neutral and (b and c) heavily Na-doped PPP. Excitation wavelengths are 1064, 514.5, and 1064 nm for (a), (b), and (c), respectively.

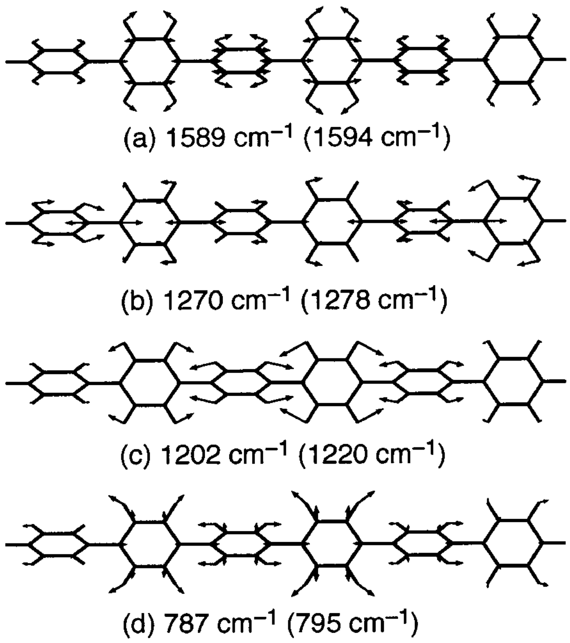
and 12 are 1.477, 1.470, and 1.467 Å, respectively. The inter-ring CC bond lengths are shortened in going from the neutral species to the radical anion. These results indicate that the changes of the bond lengths in going from the neutral species to the radical anion occur in the direction from benzenoid to quinoid.

The calculated torsional angles around the inter-ring CC bonds in the dianions of *p*-terphenyl to *p*-sexiphenyl are in the range between 0.0 and 16.2°, which are smaller than those of the neutral species and the radical anions. The dianion of *p*-terphenyl takes the planar structure, and the other dianions twisted structures. The calculated intra- and inter-ring CC bond lengths of the dianion of *p*-sexiphenyl are shown in Figure 2 with open circles. In the terminal rings, the calculated lengths of bonds 1, 2, and 3 are 1.415, 1.398, and 1.440 Å, respectively. In the inner rings, the lengths of bonds 5, 6, 7, 9, 10, and 11 are 1.437, 1.390, 1.441, 1.439, 1.389, and 1.440 Å, respectively. The calculated lengths of inter-ring CC bonds 4, 8, and 12 are 1.461, 1.455, and 1.455 Å, respectively. The inter-ring CC bond lengths are shortened in going from the radical anion to the dianion. These bond-length changes in going from the neutral species to the dianion occur in the direction from benzenoid to quinoid; these changes are larger than those occurring in the case of the neutral species to the radical anion.

TABLE 1: Calculated and Observed Wavenumbers (cm^{-1}) of the Raman Bands for *p*-Oligophenyls and PPP

	PPP	*p*-sexiphenyl		*p*-quinquephenyl		*p*-quaterphenyl		*p*-terphenyl	
mode	obsd[a]	obsd[b]	calcd	obsd[b]	calcd	obsd[b]	calcd	obsd[b]	calcd
ν_2	1595	1594	1589	1594	1590	1593	1591	1593	1592
ν_3	1282	1278	1270	1277	1270	1275	1269	1275	1268
ν_4	1222	1220	1202	1220	1200	1220	1202	1221	1199
ν_5	798	795	787	791	784	785	779	774	767

[a] Ref 15. [b] Ref 34.


(a) 1589 cm⁻¹ (1594 cm⁻¹)

(b) 1270 cm⁻¹ (1278 cm⁻¹)

(c) 1202 cm⁻¹ (1220 cm⁻¹)

(d) 787 cm⁻¹ (795 cm⁻¹)

Figure 4. Calculated atomic displacements of some of the totally symmetric modes of *p*-sexiphenyl.

4. Mode Assignments of the Raman Bands of Neutral PPP

The Raman spectrum of neutral PPP is shown in Figure 3a. The factor group of a coplanar infinite PPP chain is isomorphous with the point group D_{2h}.[16] It is expected that four Raman-active a_g modes at the zone center ($k = 0$) are observed in the wavenumber region below 1700 cm^{-1}. The Raman bands observed at 1595, 1282, 1222, and 798 cm^{-1} have been attributed to these modes,[15] and are called ν_2, ν_3, ν_4, and ν_5, respectively.[14] Each *p*-oligophenyl has four Raman bands corresponding to these bands of PPP.[34] The calculated and observed[34] wavenumbers of the Raman bands of *p*-oligophenyls are listed in Table 1, together with the wavenumbers of the Raman bands observed for PPP. All of these bands arise from totally symmetric modes. The wavenumbers calculated for *p*-oligophenyls are in good agreement with the observed, as shown in Table 1. We will discuss the assignments of the Raman bands of neutral PPP on the basis of the results for *p*-sexiphenyl. The atomic displacements of the 1589-, 1270-, 1202-, and 787-cm^{-1} modes of *p*-sexiphenyl, which correspond, respectively, to the ν_2, ν_3, ν_4, and ν_5 bands of PPP, are shown in Figure 4. The calculated 1589-cm^{-1} mode is a mode in which the intra-ring CC stretches of type 8a in the Wilson notation[35] of all the rings are combined in phase with each other. Thus the observed 1595-cm^{-1} band (ν_2) of PPP can be assigned to this in-phase intra-ring CC stretch. In this mode, the phenylene rings deform back and forth from benzenoid to quinoid and from quinoid to benzenoid. The calculated 1270-cm^{-1} mode may be called the in-phase inter-ring CC stretch. The observed 1282-cm^{-1} band (ν_3) of PPP can be assigned to this in-phase inter-ring CC stretch. The calculated 1202-cm^{-1} mode is the in-phase CH in-plane bend of type 9a in the Wilson notation. Thus, the observed 1222-cm^{-1} band (ν_4) of PPP is assigned to this in-phase CH in-plane bend. The calculated 787-cm^{-1} mode is assigned to the in-phase in-plane ring deformation of type 6a. The observed 798-cm^{-1}

TABLE 2: Calculated and Observed^a Wavenumbers (cm^{-1}) of the Raman Bands for the Radical Anions of *p*-Oligophenyls and Negative Polarons in Na-Doped PPP

	polaron	*p*-sexi-phenyl		*p*-quin-quephenyl		*p*-quater-phenyl		*p*-ter-phenyl	
mode	obsd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd
A	1591−1590	1593	1590	1592	1591	1594	1593	1599	1599
B			1481	1482	1482	1484	1483	1486	1485
C	1315−1314	1318	1295	1320	1299	1325	1304	1317	1305
D			1279		1286		1299		
E	1221−1219	1215	1208	1215	1211	1218	1215	1215	1215
F	1179		1197		1194		1182		1178
G	980−974		981	992	982	991	980	997	982
H	783−777	780	774	772	769	768	761	753	746

Ref 14.

band (ν_5) of PPP can be assigned to this in-phase in-plane ring deformation.

5. Mode Assignments of the Raman Bands Due to Negative Polarons and Negative Bipolarons

In the previous paper,[14] the Raman bands of heavily Na-doped PPP observed with the 488.0- and 514.5-nm laser lines have been attributed to negative polarons, and the Raman bands observed with the 632.8-, 720-, and 1064-nm laser lines to negative bipolarons, on the basis of the Raman spectra of the radical anions and the dianions of *p*-terphenyl to *p*-sexiphenyl. The radical anion and dianion species correspond to a negative polaron and a negative bipolaron, respectively. The Raman spectrum[14] of heavily Na-doped PPP taken with the 514.5- and 1064-nm lines are shown in Figure 3b and 3c, respectively. The Raman bands observed in the 1595−1570, 1480−1470, 1355−1310, 1300−1290, 1225−1215, 1190−1175, 995−950, and 785−775 cm^{-1} ranges are called bands A−H, respectively.

First, we will discuss the assignments of the Raman bands attributed to negative polarons on the basis of the results of the radical anions of *p*-terphenyl to *p*-sexiphenyl. The calculated and observed[14] Raman wavenumbers of the radical anions of *p*-terphenyl to *p*-sexiphenyls are shown in Table 2, with the observed[14] wavenumbers of negative polarons in Na-doped PPP. The calculated wavenumbers of the radical anions are in good agreement with the observed. The calculated atomic displacements of some of totally symmetric modes for the radical anion of *p*-sexiphenyl are shown in Figure 5. The calculated 1590-cm^{-1} mode of the radical anion of *p*-sexiphenyl is the in-phase intra-ring CC stretch of type 8a. In this mode, the phenylene and phenyl rings deform back and forth from benzenoid to quinoid. The observed 1591−1590 cm^{-1} bands due to negative polarons (band A) are assignable to this mode. The calculated 1295-cm^{-1} mode of the radical anion of *p*-sexiphenyl is the in-phase inter-ring CC stretch. The observed 1315−1314 cm^{-1} bands (band C) can be assigned to this mode. The differences between the observed and calculated wavenumbers of this mode for the radical anions are larger in comparison with the other bands and becomes larger with increasing number of phenylene rings: 12, 21, 21, and 23 cm^{-1} for the radical anions of *p*-terphenyl, *p*-quaterphenyl, *p*-quinquephenyl, and *p*-sexiphenyl, respectively. These discrepancies may indicate that the inter-ring CC bond lengths obtained by means of the DFT calculations at the BLYP/6-31G* level are longer than the true values. The calculated 1208-cm^{-1} mode is the in-phase CH in-plane bend of type 9a, while the calculated 1197-cm^{-1} mode to an out-of-phase combination of the same 9a mode. The observed 1221−1219 cm^{-1} bands (band E) can be assigned to the in-phase CH in-plane bend, and the observed 1179-cm^{-1} band (band F) to the out-of-phase mode. The calculated 981-cm^{-1} mode is an out-of-phase in-plane ring deformation. The observed 980−974 cm^{-1} bands (band G) can be assigned to this mode. The calculated 774-cm^{-1} mode is the in-phase in-plane ring deformation of type 6a. The observed 783−777 cm^{-1} bands (band H) can be assigned to this mode.

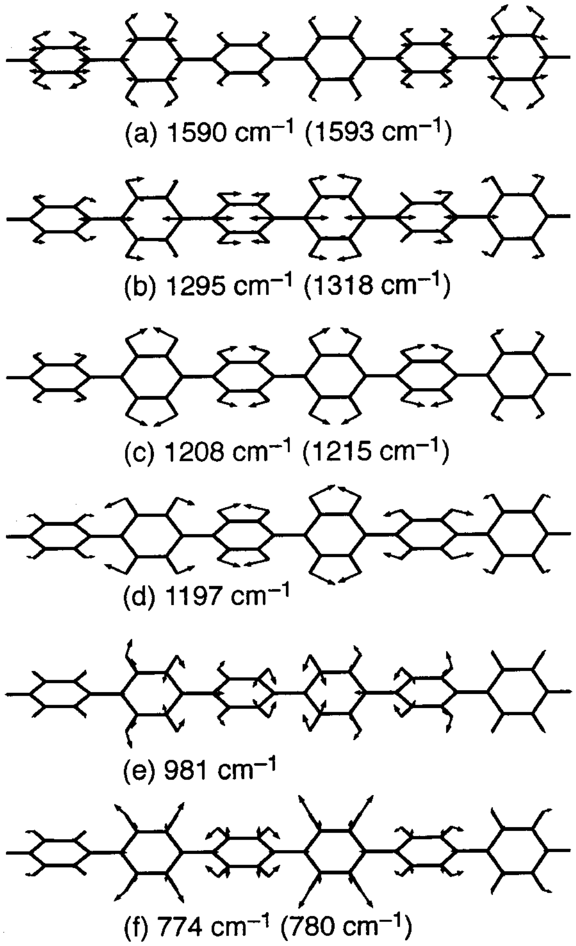


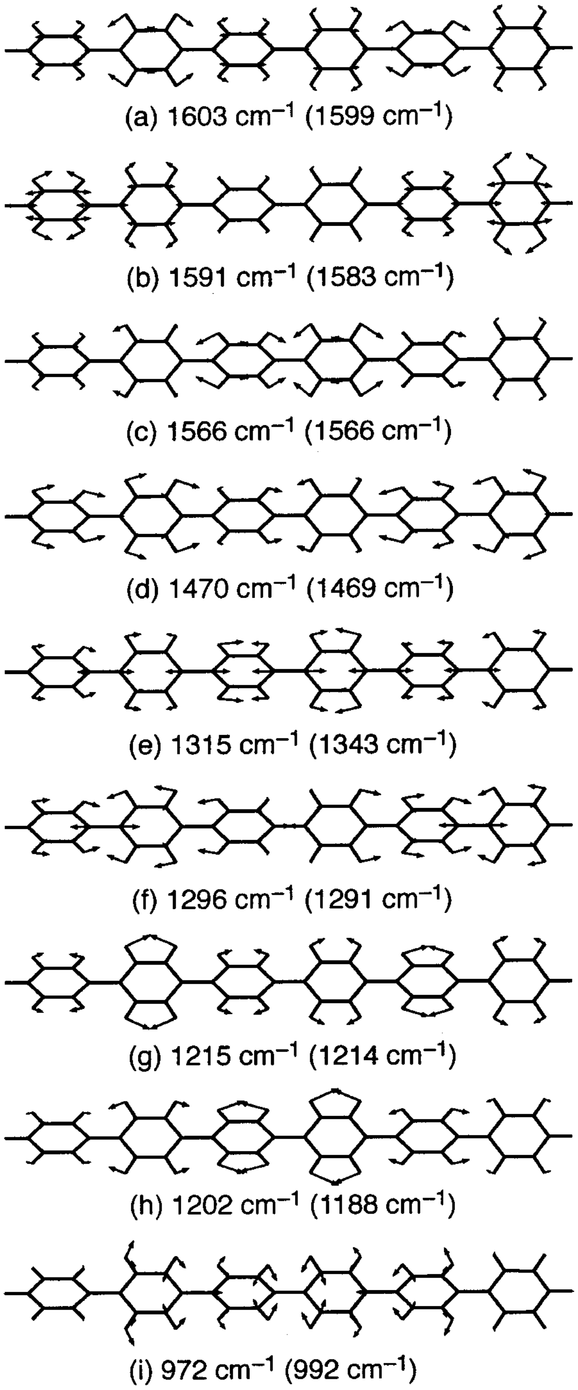
Figure 5. Calculated atomic displacements for some of the totally symmetric modes of the radical anion of *p*-sexiphenyl.

TABLE 3: Calculated and Observed^a Wavenumbers (cm^{-1}) of the Raman Bands for the Dianions of *p*-Oligophenyls and Negative Bipolarons in Na-Doped PPP

	bi-polaron	*p*-sexi-phenyl		*p*-quin-quephenyl		*p*-quater-phenyl		*p*-ter-phenyl	
mode	obsd	obsd	calcd	obsd	Calcd	obsd	calcd	obsd	calcd
A	1594−1573	1599	1603	1601	1611	1592	1598	1592	1604
		1583	1591	1583	1594	1584	1585	1581	1599
		1566	1566	1571	1574				
B	1477−1471	1469	1470	1468	1469	1472	1469	1479	1472
C	1352−1344	1343	1315	1346	1323	1357	1334	1347	1339
D	1297−1290	1291	1296		1308	1325	1327		
E	1222−1219	1214	1215	1214	1219	1219	1225	1213	1224
F	1190−1179	1188	1202	1184	1199	1175	1181	1162	1174
G	992−952	992	972	974	970	951	963	985	966
				951	965				
H			770		759	745	745	729	722

[a] Ref 14.

The calculated and observed[14] Raman wavenumbers of the dianions of *p*-terphenyl to *p*-sexiphenyl are shown in Table 3, together with the observed[14] wavenumbers of negative bipolarons in Na-doped PPP. The calculated wavenumbers are in good agreement with the observed. The calculated atomic displacements of some of totally symmetric modes for the



(a) 1603 cm^{-1} (1599 cm^{-1})

(b) 1591 cm^{-1} (1583 cm^{-1})

(c) 1566 cm^{-1} (1566 cm^{-1})

(d) 1470 cm^{-1} (1469 cm^{-1})

(e) 1315 cm^{-1} (1343 cm^{-1})

(f) 1296 cm^{-1} (1291 cm^{-1})

(g) 1215 cm^{-1} (1214 cm^{-1})

(h) 1202 cm^{-1} (1188 cm^{-1})

(i) 972 cm^{-1} (992 cm^{-1})

Figure 6. Calculated atomic displacements for some of the totally symmetric modes of the dianion of *p*-sexiphenyl.

dianion of *p*-sexiphenyl are shown in Figure 6. The calculated 1603-, 1591-, and 1566-cm^{-1} modes consist of the intra-ring stretch of type 8a. The 1566-cm^{-1} mode is the one close to the in-phase mode, although the contributions from the terminal phenyl rings are not truly in-phase, due to end effects. This is in contrast with the cases of the neutral and radical anion species of *p*-sexiphenyl. The corresponding bands (band A) due to negative bipolarons are observed in the region between 1594 and 1573 cm^{-1}. The width of the 1586-cm^{-1} band (Figure 3c) is broader than that of the corresponding 1591-cm^{-1} band (Figure 3b) of negative polarons. This is probably because this band due to negative bipolarons consists of contributions from modes having various phase sequences. The calculated 1470-cm^{-1} mode is an out-of-phase ring stretch of type 19a. The observed 1477−1471 cm^{-1} bands (band B) can be assigned to this mode. The calculated 1315-cm^{-1} mode is the in-phase inter-ring CC stretch, while the calculated 1296-cm^{-1} mode is an out-of-phase mode. The observed 1352−1344 cm^{-1} bands (band C) can be assigned to the in-phase mode, and the observed 1297−1290 cm^{-1} bands (band D) to the out-of-phase mode. The difference between the observed and calculated wavenumbers for the in-phase inter-ring CC stretch becomes larger with increasing number of benzene rings: 8, 23, 23, and 28 cm^{-1} for the dianions of *p*-terphenyl, *p*-quaterphenyl, *p*-quinquephenyl, and *p*-sexiphenyl, respectively. The calculated 1215-cm^{-1} mode is the in-phase CH in-plane bend of type 9a, while the calculated 1202-cm^{-1} mode is an out-of-phase mode. The observed 1222−1219 cm^{-1} bands (band E) can be assigned to the in-phase CH in-plane bend, and the observed 1190−1179 cm^{-1} bands (band F) to the out-of-phase mode. The calculated 972-cm^{-1} mode is an out-of-phase ring deformation. The observed 992−952 cm^{-1} bands (band G) are assignable to this mode.

We will compare the Raman spectra of the neutral and charged species of PPP. Bands A, C, E, and H of negative polarons and negative bipolarons correspond to the ν_2, ν_3, ν_4, and ν_5 of neutral PPP, respectively. In addition, bands F and G are weakly observed for negative polarons. The observed Raman bands attributed to negative bipolarons are larger in number than those of neutral PPP and negative polarons. The bands that do not correspond to Raman-active zone-center modes of neutral PPP are observed for both negative polarons and negative bipolarons. The appearance of these modes can be understood by considering that the observed Raman bands arise from vibrations over several rings in which structural changes occur upon the formation of negative polarons and bipolarons. The formation of negative polarons or negative bipolarons breaks translational symmetry of a PPP chain. Bands due to the in-phase inter-ring CC stretches are observed at 1282 cm^{-1} for neutral PPP, 1315−1314 cm^{-1} for negative polarons, and 1352−1344 cm^{-1} for negative bipolarons. The upshift of the in-phase inter-ring CC stretch reflects the increasing bond order of the inter-ring CC bonds, i.e., structural changes from benzenoid to quinoid. The inter-ring CC stretch band is a marker for discerning the neutral polymer, negative polarons, and negative bipolarons.

6. Summary

The structures and vibrational frequencies of the radical anion and dianion species of *p*-terphenyl to *p*-sexiphenyl, which are regarded as models of negative polarons and negative bipolarons, respectively, have been calculated by using density functional theory at the BLYP/6-31G* level. On the basis of the present calculations, the observed Raman bands attributed to negative polarons and bipolarons in the literature have been successfully assigned. Some of the observed Raman bands due to negative polarons and bipolarons have been assigned to the modes that do not correspond to the zone center ($k = 0$) modes. The appearance of these Raman bands have been explained by the local structural changes associated with the formation of polarons or bipolarons. The wavenumber shift of the inter-ring CC stretch in going from the neutral polymer to the doped one is the largest among the similar shifts of the observed Raman bands. It has been confirmed that the position of the inter-ring CC stretch band is a marker for characterizing polarons and bipolarons. It has been demonstrated that DFT calculations are very useful for studying the Raman bands arising from polarons and bipolarons in conducting polymers.

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References and Notes

(1) Kiess, H., Ed. *Conjugated Conducting Polymers*; Springer-Verlag: Berlin, 1992.

(2) Greenham, N. C.; Friend, R. H. *Solid State Physics: Advances in Research and Applications*; Ehrenreich, H., Spaepen, F., Eds.; Academic Press: San Diego, 1995; Vol. 49, pp 1−149.

(3) Schön, J. H.; Dodabalapur, A.; Bao, Z.; Kloc, Ch.; Schenker, O.; Batlogg, B. *Nature* **2001**, *410*, 189.

(4) Su, W. P.; Schrieffer, J. R. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 5625.

(5) Brazovskií, S. A.; Kirova, N. N. *Sov. Phys. JETP Lett.* **1981**, *33*, 4.

(6) Bishop, A. R.; Campbell, D. K.; Fesser, K. *Mol. Cryst. Liq. Cryst.* **1981**, *77*, 253.

(7) Brédas, J. L.; Chance, R. R.; Silbey, R. *Mol. Cryst. Liq. Cryst.* **1981**, *77*, 319.

(8) Furukawa, Y. *Synth. Met.* **1995**, *69*, 629.

(9) Shimoi, Y.; Abe, S.; Harigaya, K. *Mol. Cryst. Liq. Cryst.* **1995**, *267*, 329.

(10) Lane, P. A.; Wei, X.; Vardeny, Z. V. *Phys. Rev. Lett.* **1996**, *77*, 1544.

(11) Furukawa, Y. *J. Phys. Chem.* **1996**, *100*, 15644.

(12) Furukawa, Y.; Tasumi, M. In *Modern Polymer Spectroscopy*; Zerbi, G., Ed.; Wiley-VCH: Weinheim, 1999; Chapter 4.

(13) Furukawa, Y. In *Handbook of Vibrational Spectroscopy*, Vol. 4; Chalmers, J. M., Griffiths, P. R., Eds.; John, Wiley & Sons: New York, in press.

(14) Furukawa, Y.; Ohtsuka, H.; Tasumi, M. *Synth. Met.* **1993**, *55*, 516.

(15) Furukawa, Y.; Ohtsuka, H.; Tasumi, M.; Wataru, I.; Kanbara, T.; Yamamoto, T. *J. Raman Spectrosc.* **1993**, *24*, 551.

(16) Zannoni, G.; Zerbi, G. *J. Chem. Phys.* **1985**, *82*, 31.

(17) Lefrant, S.; Buisson, J. P.; Eckhardt, H. *Synth. Met.* **1990**, *37*, 91.

(18) Cuff, L.; Cui, C.; Kertesz, M. *J. Am. Chem. Soc.* **1994**, *116*, 9269.

(19) Ehrendorfer, Ch.; Karpfen, A. *Vib. Spectrosc.* **1995**, *8*, 293.

(20) Ehrendorfer, Ch.; Karpfen, A. *J. Phys. Chem.* **1995**, *99*, 5341.

(21) Shimoi, Y.; Abe, S. *Phys. Rev. B* **1994**, *50*, 14781.

(22) Tol, A. J. W. *Chem. Phys.* **1996**, *208*, 73.

(23) Irle, S.; Lischka, H. *J. Chem. Phys*. **1997**, *107*, 3021.

(24) Furuya, K.; Torii, H.; Furukawa, Y.; Tasumi, M. *Chem. Lett.* **1996**, 913.

(25) Furuya, K.; Torii, H.; Furukawa, Y.; Tasumi, M. *J. Mol. Struct. (THEOCHEM)* **1998**, *424*, 225.

(26) Casado, J.; Hemández, Hotta, S.; Navarrete, J. T. L. *J. Chem. Phys.* **1998**, *109*, 10419.

(27) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98 (Revision A.9)*; Gaussian Inc.: Pittsburgh, PA, 1998.

(28) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(29) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(30) Yamakita, Y.; Tasumi, M. *J. Phys. Chem.* **1995**, *99*, 8524.

(31) Brédas, J. L.; Thémans, B.; Fripiat, J. G.; André, J. M.; Chance, R. R. *Phys. Rev. B* **1984**, *29*, 6761.

(32) Cuff, L.; Kertesz, M. *Macromolecules* **1994**, *27*, 762.

(33) Ehrendorfer, Ch.; Karpfen, A. *J. Phys. Chem.* **1995**, *99*, 10196.

(34) Ohtsuka, H.; Furukawa, Y.; Tasumi, M. *Spectrochim. Acta* **1993**, *49A*, 731.

(35) Wilson, E. B., Jr. *Phys. Rev.* **1934**, *45*, 706.