Raman spectra and electron-phonon coupling in poly(*p*-phenylene)

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We have computed the vibrational spectrum of poly(*p*-phenylene) (PPP), transferring the force and electro-optical fields from toluene. The results are in good agreement with the observed infrared and Raman spectra of PPP. No signatures of strong electron-phonon coupling are seen and in this respect PPP is similar to *cis*-polyacetylene while it is qualitatively different from *trans*-polyacetylene.

Poly(*p*-phenylene) (PPP) is a rather interesting material: its conductivity can be tuned by doping over almost 20 orders of magnitude, from $\sim 10^{-17}$ S/cm in very pure samples[1] to ~ 500 S/cm in heavily doped ones;[2] the transport mechanism is unusual and it involves spinless charge carriers (bipolarons).[3,4] To understand the underlying physics, one of the key questions is how strong is the electron-phonon interaction in the polymer. We have adressed that question by studying[5–7] vibrational spectra of PPP and other conducting polymers [*trans*- and *cis*-polyacetylene and their deuterated analogs, and poly(pyrrole)]. Our approach is to consider a single periodic chain and adiabatic nuclear motion in a harmonic potential; the covalent bonds in polymers are rather local so we assume the force constants and electro-optical parameters [needed to compute the infrared (ir) absorption intensities] to be of short range and hence, transferrable from small molecules of appropriate geometry.[8] For example, utilizing the force and electro-optical fields transferred from hexatrienes a good agreement between the calculated and the observed ir and Raman spectra was achieved[7] in the case of *cis*-$(CH)_x$ and *cis*-$(CD)_x$; thus one can view such polymers as simple concatenations of the corresponding small molecular fragments. However, two substantial nonadditive effects are seen[6] in *trans*-$(CH)_x$ and *trans*-$(CD)_x$: (i) the in-plane CH bending mode shows unexpectedly a very weak ir absorption, and (ii) the resonant Raman bands are observed at frequenceis lower by 10–15% than the calculated values. Both effects are considered as signatures of strong coupling of the LO phonons involved to the delocalized π-electron system; a quantitative account of (ii) can be made if long-range—up to 5th or 6th neighbors, at least—force constants are included.[9] The origin of this major difference between the two isomers is believed to be electronic: *trans*-polyacetylene has two degenerate ground-state configurations, while in *cis*-polyacetylene there is a significant difference in energy (~ 0.14 eV per monomer) between the *cis-transoid* (ground-state) and the *trans-cisoid* (metastable) configuration.[10] PPP is analogous to *cis*-polyacetylene: The metastable quinoid configuration is substantially higher in energy than the ground-state benzenoid configuration,[4,10] and from this analogy one might expect a relatively weak electron-phonon coupling and absence of effects (i) and (ii) in PPP.

As for (i), the above expectation was confirmed by an elaborate computation of the ir absroption spectrum of PPP.[5] Both the in-plane and the out-of-plane degrees of freedom were considered in Ref. 5 and the ir absorption intensities were evaluated. The force and electro-optical fields were transferred from toluene; the computations did not include any adjustable parameters. Since the Raman spectrum of PPP was not known at that time (the Raman signal is covered in PPP by strong luminescence), in Ref. 5 we assignated and analyzed only the ir-active vibration modes. A good agreement was found with the experimental ir absorption data; the effect (i) is not seen in PPP.

It is now possible to complete this analysis, since Krichene *et al.* have succeeded in obtaining good quality Raman spectra of PPP recently.[11] The calculated and the experimental Raman frequencies are compared in Table I, to test our theoretical predictions and also to offer an assignation of the observed spectral features. Notice that the Raman bands shift somewhat with the excitation wavelength and with the degree of polymerization; for consistency, we reproduce in Table I the approximate values corresponding to very long chains.

The principal Raman bands are seen at ~ 1220 cm^{-1}, 1280 cm^{-1}, and 1600 cm^{-1}, i.e., within a few percent of the predicted values, despite the limitations of the model. Hence we conclude that the effect (ii) is also absent in PPP.

The weaker features (observed in dedoped samples at low temperature) are also well accounted for by the theory. The only exception is the very weak feature at ~ 1250 cm^{-1}; an overtone or a combination band is ruled out by the temperature dependence and there is no nearby ir mode to be Raman activated by disorder. A possible explanation is that, as in shorter oligomers,[12] phenyl rings are tilted out of plane in alternation in PPP at low temperature. In this case, the $L2/mmm$ line group of the planar PPP reduces onto the $L2/mcc$ line group, with the translational period twice the original value. Consequently, one has to fold the phonon dispersion curves in Fig. 1 of Ref. 5 around the $q=\pi/2a$ vertical axis[13] and all the modes originally situated at the $q=\pi/a$ zone edge would become fundamentals. Some of them—and in particular, the ${}_{\pi}A_1^-$ mode at ~ 1280 cm^{-1}, which becomes a ${}_0B_1^-$ mode in the $L2/mcc$ nonplanar configuration—would be (weakly) Raman activated in this way. However, to clarify further this point and to check other assignations in Table I, additional experimental data are needed, on ^2D and ^{13}C isotope-substituted PPP and on oriented PPP samples (however, the latter could prove tedious to prepare).

Finally, let us remark that the important issue of chain-

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TABLE I. The Raman bands calculated and observed in poly(*p*-phenylene). For the geometry and the symmetry labels see Ref. 5; *xx*, *yy*, and *zz* polarizations belong to A_0^+, *xz* to A_1^-, *xy* to B_0^+, and *yz* to B_1^-. In the last column, *s* denotes strong.

Symmetry	Theory Type	Theory Frequency (cm^{-1})	Experiment Frequency (cm^{-1})
A_0^+	CH stretch	3065	
A_1^-	CH stretch	3055	
A_0^+	CC stretch	1665	1709
A_1^-	CC stretch	1610	1600, *s*
A_1^-	CH bending (in plane)	1335	1340
A_0^+	CC stretch	1300	1280, *s*
? $_{\pi}A_1^-$	CC stretch + CH bending (in plane)	1280	1250
A_0^+	CH bending (in plane)	1170	1220, *s*
B_1^-	CH bending (out of plane)	950	920
B_0^+	CH bending (out of plane)	850	
A_0^+	CCC deformation (in plane) + CC stretch	805	
B_1^-	CC + CH deformation (out of plane)	740	
A_1^-	CCC deformation (in plane)	605	
B_1^-	CC + CH deformation (out of plane)	415	460
A_1^-	CH bending (in plane)	410	

length distribution in actual PPP samples can be addressed *via* the Raman spectroscopy in principle, since certain bands shift with the excitation wavelength. In addition, Krichene *et al.* have compared the spectra of biphenyl, terphenyl, quaterphenyl, and sexiphenyl oligomers and "Yamamoto" and "Kovacic" polymers, and they have observed that the ratio of intensities of the Raman modes at ~ 1220 cm^{-1} and ~ 1280 cm^{-1} increases when the number of phenyl rings increases.[11] Further study of this issue requires additional computations on oligomers, which are in progress now.

In conclusion, recently reported Raman spectra of PPP are in good agreement with our theoretical predictions, based on a fairly local force field transferred from toluene. The same is true for the ir absorption spectra, and hence in PPP vibrational spectroscopy shows no signature of strong coupling of LO phonons to the π-electron system. In this respect, PPP is similar to *cis*-polyacetylene and qualitatively different from *trans*-polyacetylene.

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[1]F. Maurice, G. Froyer, M. Minier, and M. Gauneau, J. Phys. (Paris) Lett. **42**, 425 (1981).
[2]D. M. Ivory, G. G. Miller, J. M. Sowa, L. W. Shacklette, R. R. Chance, and R. H. Baughman, J. Chem. Phys. **71**, 1506 (1979).
[3]J. C. Scott, P. Pfluger, M. T. Krounbi, and G. B. Street, Phys. Rev. B **28**, 2140 (1983).
[4]J.-L. Brédas, R. R. Chance, and R. Silbey, Phys. Rev. B **26**, 5843 (1982).
[5]D. Raković, I. Božović, S. A. Stepanyan, and L. A. Gribov, Solid State Commun. **43**, 127 (1982).
[6]D. Raković, I. Božović, S. A. Stepanyan, and L. A. Gribov, Phys. Rev. B **28**, 1977 (1983).
[7]D. Raković, I. Božović, L. A. Gribov, S. A. Stepanyan, and V. A. Dementiev, Phys. Rev. B **29**, 3412 (1984).
[8]L. A. Gribov, *Theory of Infrared Spectra of Polymers* (Nauka, Moscow, 1977), in Russian.
[9]E. J. Mele and M. J. Rice, Solid State Commun. **34**, 339 (1980); L. Piseri, R. Tubino, L. Paltinieri, and G. Delepiane, *ibid.* **46**, 183 (1983).
[10]A. Karpfen, Phys. Scr. **T1**, 79 (1982). T. Yamabe, Mol. Cryst. Liq. Cryst. (to be published).
[11]S. Krichene, S. Lefrant, G. Froyer, F. Maurice, and Y. Pelous, J. Phys. (Paris) Colloq. **44**, C3-773 (1983); S. Krichene, J. P. Buisson, S. Lefrant, G. Froyer, F. Maurice, J. Y. Goblot, Y. Pelous, and C. Fabre, Mol. Cryst. Liq. Cryst. (to be published).
[12]J.-L. Baudour and H. Cailleau, Acta Crystallogr. B **33**, 1733 (1977); J.-L. Baudour, Y. Delugeaud, and P. Rivet, *ibid.* **34**, 625 (1978).
[13]I. Božović, Phys. Rev. B **29**, 6586 (1984).