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VIBRATIONAL SPECTRA AND STRUCTURE OF UNDOPED AND DOPED POLYPARAPHENYLENE

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Résumé- Nous présentons des résultats par spectroscopie infrarouge et Raman sur du poly(paraphénylène) (PPP) non dopé et dopé avec AsF₅. Les résultats sont interprétés à la lumière des calculs de modes normaux de Rakovic et al. et du modèle par défauts de type bipolaron du polymère dopé proposé par Brédas et al.

Abstract- Infrared and Raman spectroscopic data on undoped and AsF₅-doped polyparaphenylene (PPP), are presented. The results are discussed in terms of the normal mode calculation of Rakovic et al and the bipolaron defect model of the doped polymer proposed by Bredas et al.

Introduction- In recent years a number of conjugated organic polymers have been discovered which undergo a transition to a conductive state on doping with electron acceptors or donors. The most recently discovered member of this group is polyparaphenylene (PPP) /1,2/, which shows a conductivity increase as high as 18 orders of magnitude /3/ on doping. The demonstration that rechargeable batteries based on doped polyacetylene (PA) and PPP are feasible /4,5/, have further stimulated both fundamental and applicative interest in these polymers.

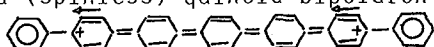
Doped PPP and related polymers show behaviour reminiscent of conventional semiconductors like silicon. However, the presence of highly anisotropic interactions would lead to low dimensionality of electron motion and collective instabilities such as the Peierls transition would occur. In addition disorder initiated during the doping process would give rise to localized electronic states which would affect transport phenomena in these materials. Structurally, topological kinks or so-called solitons are created on doping, and strong evidence has been put forward that in doped all-trans-PA transport occurs via spinless charged solitons /6,7/. In PPP, contrary to trans-PA, the ground state consists of the non-degenerate benzoid and quinoid forms. PPP is, therefore, not expected to accommodate solitons; nevertheless, the transport properties of doped trans-PA and PPP are very similar. A theoretical study of the problem by Bredas, Chance and Silbey /8/ has rationalized this situation by showing that polaron defect formation occurs at low doping levels both in trans-PA and PPP, but at higher doping levels the defects interact to give uncorrelated charged solitons in PA and spinless bipolarons in PPP.

In this paper we present data obtained via infrared and Raman spectro-

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copy, on doped and undoped PPP, and suggest an interpretation which would be relevant to the structural nature of doping in PPP. In what follows, we present first a structural summary and some details regarding the vibrational model of Rakovic et al /9/ for PPP; we then proceed to our experimental results and a discussion and interpretation of the data.

Theoretical and Structural Considerations - PPP consists of benzene rings linked in the para-position. Based on crystallographic data on oligomers, the C-C bond lengths within the rings are 1.4 Å and between the rings 1.50 Å. In the solid two successive rings are tilted with respect to each other by 23° - the result of a compromise among effects associated with conjugation, crystal packing and steric repulsion of orthohydrogen atoms. To a first approximation then, the C-atom network of PPP is isostructural to that of graphite. On doping, it has been shown by Bredas et al /8/ via an adiabatic Hückel calculation that a (spinless) quinoid-bipolaron



with a defect extension of 5 rings, can result. The strong deformation of the rings in the bipolaron pushes the bonding state into the gap and conductivity could arise from the motion of these spinless bipolarons.

The vibrational model of Rakovic et al /9/ for pristine PPP on which we base some of our following interpretations assumes a planar PPP periodic structure and a valence force field transferred from the toluene molecule. In terms of line groups, the symmetry of the PPP model is $L2/mmm$ and modes can be assigned to irreducible one dimensional representations A_0 , B_0 , A_1 and B_1 . Each representation decomposes into a + and a - component, distinguishing those which are even and odd with respect to the plane orthogonal to the benzoid ring. At $k = 0$, the A_0^- , A_1^+ and B_1^+ components are infrared active with eigenvectors parallel to the y (chain direction), x and z (perpendicular to the benzoid plane) axes respectively, while the A_0^+ , B_0 , A_1^- and B_1^- components are Raman active. Thus the Raman and infrared active modes in pristine PPP are expected by symmetry to be mutually exclusive.

Experimental details, results and discussion - PPP used in the present study was prepared at Allied Chemical by the oxidative cationic polymerization of benzene. Acceptor doping was accomplished by exposing PPP pellets to 450 torr AsF_5 , while donor doping was achieved via reaction of PPP with alkali metal naphthalide in tetrahydrofuran. Further details are to be found in refs /1,2/. The infrared spectra were measured with a Perkin Elmer 983 spectrometer which was purged for a minimum of 24 hrs with dry air before each measurement. The sample chamber was in addition flushed with pure N_2 during each measurement. The Raman measurements were made using a Spex double monochromator and photon counting detection. The infrared spectra of pure PPP were measured in the specular reflection geometry using pressed pellets of the polymer. Raman measurements were made on the same samples. Measurements on the doped polymer were made on samples sealed in an inert atmosphere in glass capillaries. For infrared measurements, the sealed capillaries were opened in a glove box, quickly mixed with dried KBr and pelleted in a vacuum of ca. 0.1 torr, and then rapidly transferred to the spectrometer sampling chamber.

The infrared spectra of PPP (in reflection) and AsF_5 and PF_5 doped PPP (in absorption) are shown in Fig. 1 together with the calculated frequencies/9/. The Raman spectrum of AsF_5 doped PPP is displayed in Fig. 2. Sizable fluorescence background was observed from pure PPP samples, precluding a careful study of its Raman spectrum. The peaks which could be separated from the background are listed in Table 1

together with those observed independently by Lefrant (private communication).

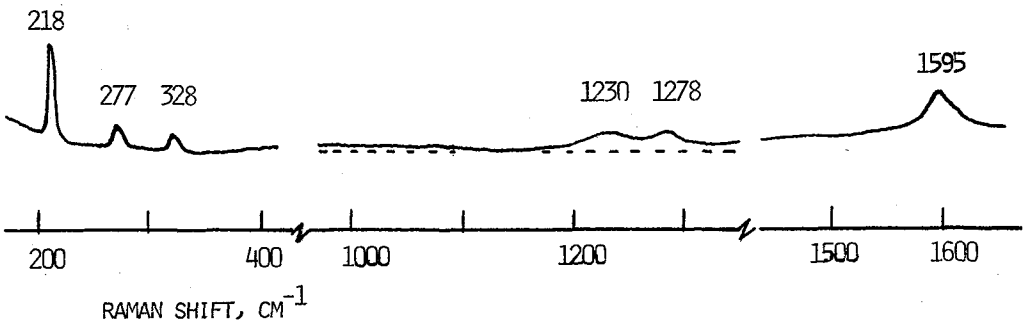
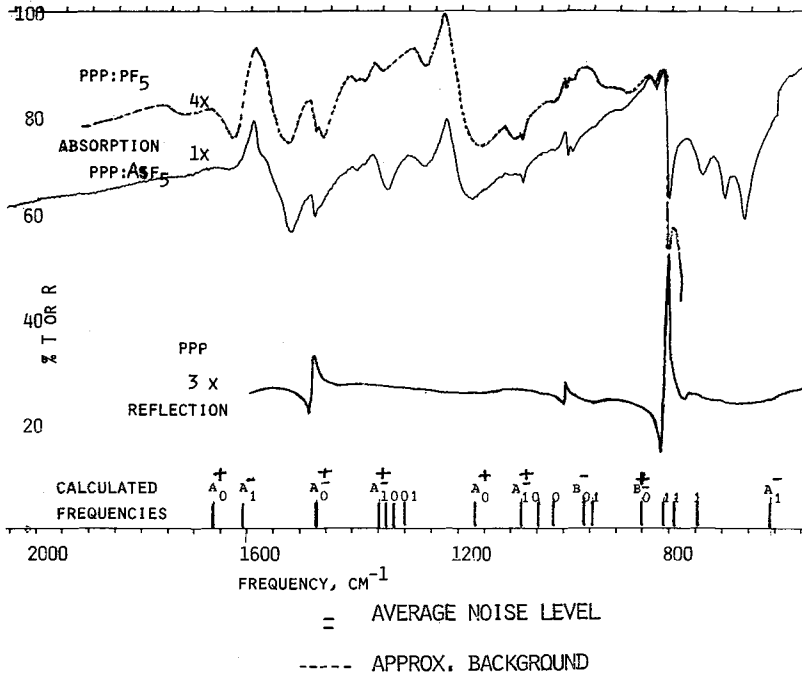
Also listed in Table 1 are the IR and Raman frequencies in AsF₅-doped PPP. Attempts to obtain the Raman spectra of donor doped samples have failed so far, while IR measurements on these samples were not attempted because of their extreme sensitivity to air.

The three main IR lines at 1470, 1000 and 800 cm⁻¹ in pure PPP can be assigned to A_g⁺, A_g⁺ and B_g⁺ modes involving largely

CCC antisymmetric stretching, CCC stretching + CH bend and CCC deformation motions, and are in good agreement with the calculated frequencies. In the Raman spectra lines in the 1600 cm⁻¹ region, and between 1200 and 1350 cm⁻¹ can be assigned to the symmetric stretching (A_g⁺ and A_g⁻) modes of the polymer backbone which distort PPP towards the biradical (1600 cm⁻¹) and quinoid (1300 cm⁻¹) structures. The observed frequencies are again in good agreement with the calculated frequencies. This agreement with the calculation based on a force field transferred from the toluene molecule suggests that the charge density in PPP is largely localized within the benzoid rings.

The IR spectra of AsF₅ and PF₅ doped PPP show a large number of absorptions in the 2000-600 cm⁻¹ region. These are buried under the free-carrier continuum in "over-doped" samples, as has been observed previously [1]. The dominant feature is the appearance of two broad and strong absorptions at 1520 and 1180 cm⁻¹. In addition maxima are observed near 1580, 1270 and 1240 cm⁻¹ both in the IR and Raman spectra of PPP:AsF₅, suggesting a breakdown of the mutual exclusivity of the IR and Raman modes as a result of the statistical nature of defect formation. At the defect site itself localized charge oscillation would make the defect modes strongly infrared-active, consistent with our observations. Also, the downward frequency shifts of the stretching Raman-active modes in the doped samples, suggests increased delocalization of the charge-density probably induced by a quinoid-like deformation of the chain as suggested by the model of Bredas et al [8]. The narrow bands at 1480, 1000 and 800 cm⁻¹ correspond to the undoped polymer regions and those below 700 cm⁻¹ are most likely due to AsF₅⁻ ions. In conclusion then; the results indicate a signature of the defect in doped PPP consistent with a quinoid-like distortion of the chain-the detailed assignments have however to await a calculation of the defect mode frequencies.

PPP frequencies (cm ⁻¹)	IR		Raman	
	IR	Raman	This work	Lefrant
			1643	
			1606	1608
			1570	
				1635
				1580
				1520
				1480
				1470
				1400
				1340
				1270
				1240
				1180
				1085
				1000
				990
				830
				805
				742
				700
				660
				484
				328
				277
				218



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