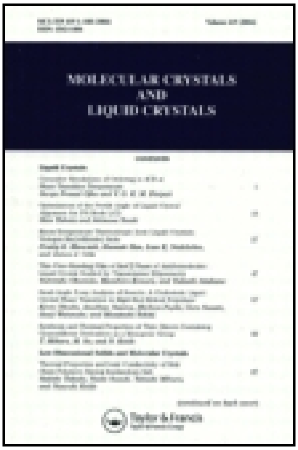

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Experimental Charge Distribution in Polyacetylene

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EXPERIMENTAL CHARGE DISTRIBUTION IN POLYACETYLENE

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Abstract The charge distribution (static and dynamic) in polyacetylene(pristine and doped)are derived from infrared spectra.

In another paper[1] of this volume the kind of information which can be derived by infrared spectra of polyacetylene(PA) has been extensively discussed.We focus in this paper only on the interpretation of infrared intensity data within the model of Equilibrium Charges and Charge Fluxes(ECCF).[2-5] The equilibrium charges on atoms, q^o_α,measure the excess($q^o_\alpha<0$)or defect($q^o_\alpha>0$)of electronic charge on atom α created in the formation of the bond. It has been shown that[6] their analogous in Quantum Mechanical calculations are the atomic charges derived by Mulliken Population Analysis(MPA).[7] The charges fluxes, $\partial q_\alpha/\partial R_t$,measure the mobility of the charge during the vibrational displacements.[3]

Even if the derivation of accurate ECCF from IR spectra requires the evaluation of absolute intensities,[8] still a large body of experience in this field[9] allows to derive a sufficiently approximate idea of charge distribution in a molecule even from the relative intensities of the IR bands.[5] Let us observe the spectra of undoped PA trans(FIGURE 1.a)and PA cis(FIGURE 1.b).A detailed analysis of these spectra in terms of ECCF,together with a comparison to shorter polyenes,is reported elsewhere,[10]

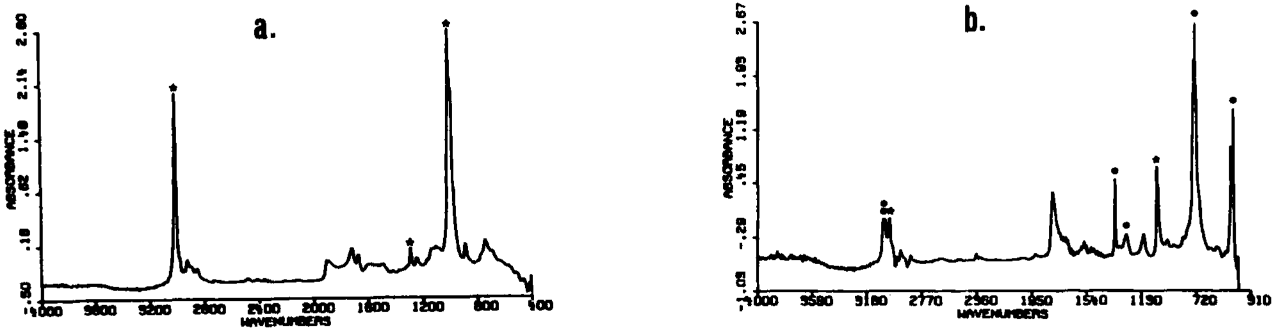

FIGURE 1 Infrared spectrum of highly oriented trans PA (a.) and cis PA (b.). Stars and dots indicate fundamental transitions of trans and cis respectively

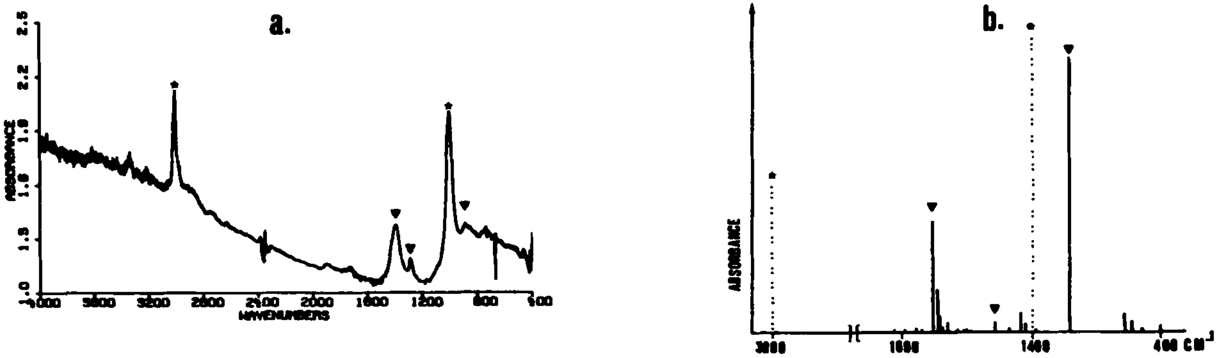

FIGURE 2 Experimental(a.)and calculated(b.)spectrum of doped $(CH(I_3^-)_y)_x$, y= 0.0017 Triangles indicate doping induced bands and stars bands of perfect chain.

but the most relevant results are: i) the ratio $I_{1000}^{trans}/I_{3000}^{trans}=2.5$ (quite similar to the corresponding ratio in shorter trans-polyenes) implies $q_H^o=0.134e$, as in butadiene, while $I_{740}^{cis}/I_{3000}^{cis}=5$ implies $q_H^o=0.160e$; similar trends are suggested by recent MPA data.[11,12] ii) the ratio $I_{1290}^{trans}/I_{1000}^{trans}=0.05$ is not so anomalously small, in the frame of polyenes (butadiene:0.23 and not 1,as claimed by some authors[13]). This ratio is decreasing with increasing conjugation: in PA cis the corresponding ratio is 0.7, suggesting a small conjugation.

When the PA is doped, the interpretation of the spectrum (FIGURE 2.a) in the frame of ECCF is not impossible and seems to have a simple physical meaning. Elsewhere[1,14] it has been shown that the positions in frequency of the peaks (in Fig.2.a) of the doping induced bands can be well represented by localized motions of a centrosymmetrical defect (Fig.1,ref.1). For the calculation of intensities we have superimposed to the distribution of the e-

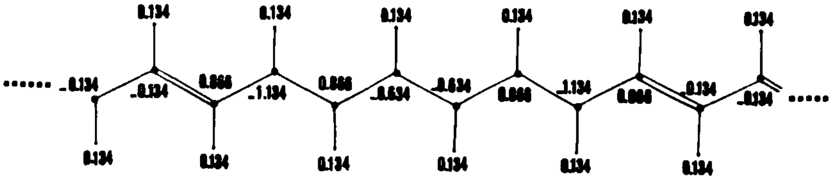

FIGURE 3 Static charge distribution on a p-charged defect.

lectronic charge of pristine PA trans[10], a charge +1e,due to the charge transferred to Iodine (FIGURE 3). This charge is distributed in such a way to make CC bonds polar,at difference from those of perfect chain and in agreement with recent Quantum Mechanical results.[15,16] Polar CC bonds introduce large charge fluxes ($\partial q_C/\partial R_{CC}$) with the stretching of the backbone. $\partial q_C/\partial R_{CC}$ has been fitted on the observed I_{1462}/I_{3000} and has automatically reproduced the other bands (FIGURE 3.b); the values taken by $\partial q_C/\partial R_{CC}$ is $3.5eA^{-1}$, one order of magnitude larger than in undoped molecules containing polar C=C bonds; this may be interpreted as an increase of the mobility of the charge with doping.

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