

STRUCTURAL CHANGES OBSERVED IN POLYPYRROLE FILMS WITH *IN-SITU* RESONANCE RAMAN TECHNIQUES

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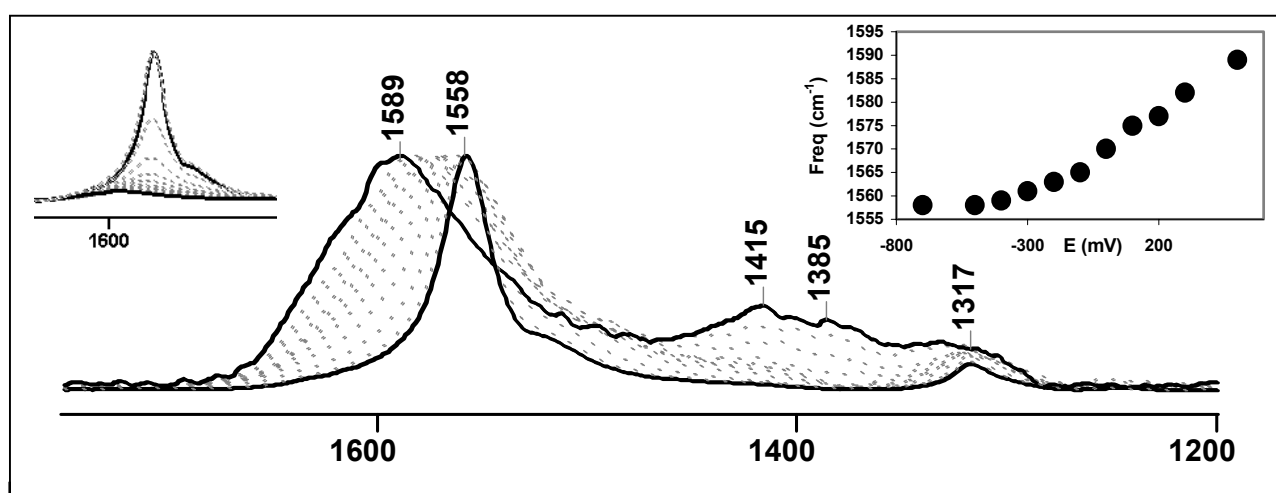
Abstract: The 488 nm *in situ* Raman spectra of electrochemically prepared polypyrrole films permit reliable assessment of oxidation state as a function of doping potential. The more complex 785 nm spectra are analysed to give more detailed information about the nature of the charge carriers in the doped polymer.

The electronic properties of polypyrrole change markedly with the degree of doping or oxidation. Evidence from electronic spectra and solid-state NMR studies suggests that specific structural changes accompany the electronic changes. Undoped or pristine polypyrrole appears to possess an aromatic ground-state, and the process of p-doping or oxidation introduces so-called polarons and bipolarons, being discrete regions in the polymer backbone where the positive charge is concentrated. Significantly, these regions adopt a quinoid ground-state and have characteristic electronic transitions towards the red end of the visible spectrum, rather than the *ca.* 450 nm band-gap of the aromatic polymer. As such, manipulation of the resonance conditions by selecting an appropriate excitation wavelength allows analysis of the structure of either aromatic or quinoid segments of the polymer with minimal interference from the other. To this end we have used 488 nm and 785 nm excitation to study polypyrrole films under electrochemical control, and in the presence of various solution and gas-phase species.

With 488 nm excitation undoped polypyrrole gives characteristically simple spectra, and the vibrational bands have previously been assigned by Furukawa [1] as the A_g modes expected from all-trans (D_{2h}) polypyrrole. The prominent band in Fig. 1 is assigned to a mode with a large inter-ring C-C stretching component. In the undoped polymer this presents as a very strong band centred at 1558 cm^{-1} . As doping proceeds this band moves to higher wavenumbers, a phenomenon that has been previously observed [2,3] and is satisfactorily accounted for in terms of extent of delocalisation along the aromatic chain [4,5]. Thus, as doping introduces polarons or bipolarons the length of the aromatic segments in-between becomes shorter. The reduced delocalisation that ensues causes the band to shift to higher wavenumbers making it a good indicator of the degree of doping. We believe there are certain pertinent observations with regard to this phenomenon. Although the potential/ frequency dependence is observed in any polypyrrole film, the reproducibility and reversibility improve significantly when the film is cycled after polymerization. The decreased peak width with successive reduction/ oxidation cycles implies that the cycling process tends to produce a more homogeneous film with a more even distribution of doping-induced segments in the polymer. With progressive oxidation we find the frequency shift is reliably observed up to *ca.* 1590 cm^{-1} as illustrated, however caution is warranted when interpreting what appears to be a further shift to *ca.* 1610 cm^{-1} in some films, as has been claimed [2,3,6]. Careful observation of an apparent peak-splitting suggests that at high potentials the peaks at 1600 cm^{-1} and above are in fact non-resonance enhanced bands of the quinoid units, visible because the intensity of the aromatic band is greatly reduced at high potential. We are investigating the use of this method to study the interaction of polypyrrole with a variety of gases.

Raman spectra collected with 785 nm excitation are significantly more complex (see Fig. 2), apparently consisting of multiple sets of overlapping peaks. These have tended to be explained as two sets of peaks due to polarons and bipolarons respectively [1]. Bearing in mind that it has been

more usual to use 632 nm excitation to perform similar experiments, we believe that the near-IR source may show at least three distinct (presumably quinoid) species. The C-C stretching region is difficult to deconvolute, however bands between 900 and 1100 cm^{-1} are less overlapped and may indicate four species, one aromatic and three most likely quinoid in nature. The set of bands due to aromatic polymer (995 and 1045 cm^{-1}) are off-resonance, those due to polarons (965 and 1060 cm^{-1}) are in partial resonance and the bipolaron bands (925 and 1070 cm^{-1}) are most likely in full resonance. All of the above are in good agreement with previous literature [1], but a fourth set of peaks (1085 and 945 cm^{-1}) in our spectra have not been previously noted. These predominantly occur at high doping and apparently occur at the expense of the bipolaron peak intensity, which could suggest that at high potentials a third distinct quinoid species is formed. Whether this represents a change in length or conformation, or perhaps a protonation/ deprotonation effect is purely speculation presently, however it is interesting to note that treatment of a moderately doped film with strong acid yields bands which are qualitatively identical. Subsequent exposure to strong base causes them to disappear once again.



Main figure is not to scale, top-left inset shows largest peak with true relative intensities. Inset graph shows shift vs potential.

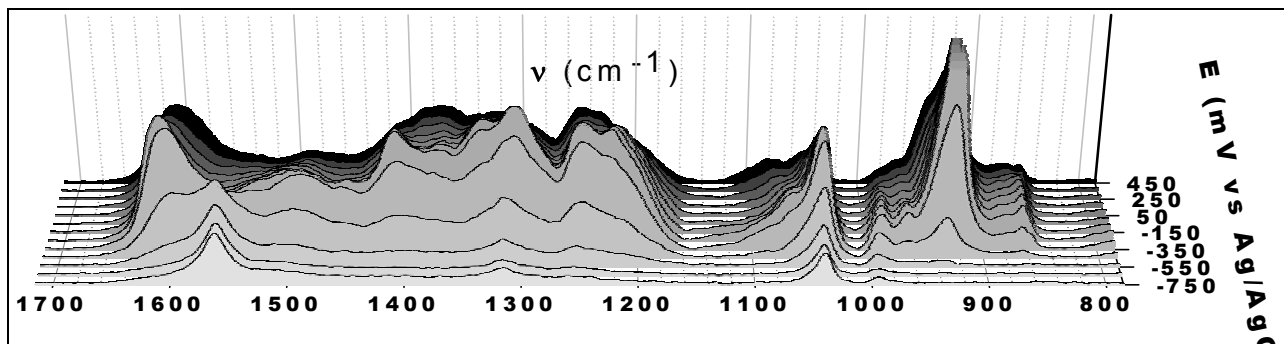


Fig. 2. 785 nm Raman spectra of PPy/Cl under potential control.

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