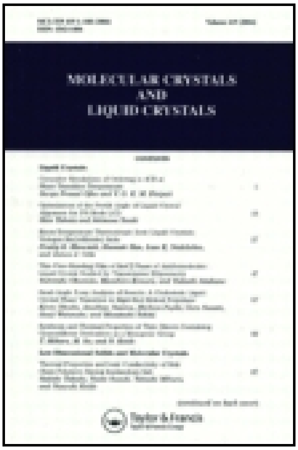

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Vibrational Spectra of Doped Polypyrrole Studied by Means of Raman and Infrared Optical Absorption Measurements

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VIBRATIONAL SPECTRA OF DOPED POLYPYRROLE STUDIED BY MEANS OF RAMAN AND INFRARED OPTICAL ABSORPTION MEASUREMENTS

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Abstract Optical absorption spectra in the range $5x10^4$- 400 cm^{-1} and Raman spectra are studied in polypyrrole, as function 1) of the sample preparation; 2) of the temperature (10-300 K) and 3) of the nature of dopant counterions (BF_4, SO_4, ClO_4, NO_3).

INTRODUCTION

Combined optical absorption and Raman spectroscopies have already proved to be effective tools for investigating the structural and chemical properties of organic conductors. With this aim we started a preliminary study of optical absorption and Raman spectra on polypyrrole (PP) films, with a variety of dopant counterions.

EXPERIMENTAL DETAILS

The samples were obtained by electrochemical polymerisation at RT either as free standing films deposited on a Pt electrode or on a transparent conducting substrate. The thicknesses ranged between .1-5 μ. The supporting electrolytes were acids or tetrabutilammonium salts which gave as acceptor-type counterions SO_4,ClO_4,NO_3,BF_4.

The optical absorption spectra were measured in the range $5x10^4$-400 cm^{-1} by means of Varian 2390 and Jasco 704G recording spectrophotometers. For low temperature spectra (∿10 K) a model 21SC Cryodine Cryocooler of CTI-Cryogenics was used.

Raman spectra were excited by Argon-and Krypton lasers at 15454, 19432 and 20492 cm^{-1} and analyzed through a Spex 1401 double monochromator.

RESULTS AND DISCUSSION

Optical absorption spectra - The optical absorption spectra in the i.r. (4000-400 cm^{-1}) were measured and compared for different sample preparations, i.e. free standing film, film deposited on a transparent substrate and KBr pellets: the essential features of the spectra were the same independently of the preparation procedure. However the films deposited on transparent substrates offered us the attractive opportunity to measure the PP absorption spectra in a much wider spectral range ($400-5x10^4$ cm^{-1}) and at temperatures as low as 10 K on the same sample. Fig. 1 shows the spectra obtained for different dopant counterions, such as BF_4, SO_4, ClO_4.

By comparing curves c) and d) it turns out that, by lowering the temperature, the spectral resolution is significantly improved chiefly in the i.r. range.

The role of different counterions on the absorption spectra can be summarized as follows:

1) it is not possible to detect in the i.r. lines directly related to a specific dopant counterion, in agreement with the suggestion of Street et al.[1] and at variance with what argued by Tanaka et al.[2];
2) the same i.r. spectral components are present, independently of the nature of the counterions;
3) the components, however, exhibit different statistical weights for different counterions;
4) the position and the relative intensity of the broad bands which appear in the n.i.r., vis. and u.v. range are more sensitive to the nature of the dopant.

From points 2) and 3) it turns out that some vibrational modes of PP are selectively inhibited by the counterions, but their characteristic vibrational frequencies are not significantly affected.

The considerations of point 4) are consistent with the results by Yakushi et al.[3] who showed that the absorption spectrum, induced by transitions within the gap, is dependent on the counterion concentration.

Raman Spectra - The detected radiation was backscattered from the shiny side of the PP free standing films. The probed region depth was $>10^3$ Å, as estimated from the absorption measurements: hence we were concerned mainly with bulk effects.

In order to avoid photoeffects and hence degradation of the material (strongly absorbing in the excitation range) the beam power density was minimized by spreading the laser image over a 5-10 mm length, by using a suitable cylindrical lens.

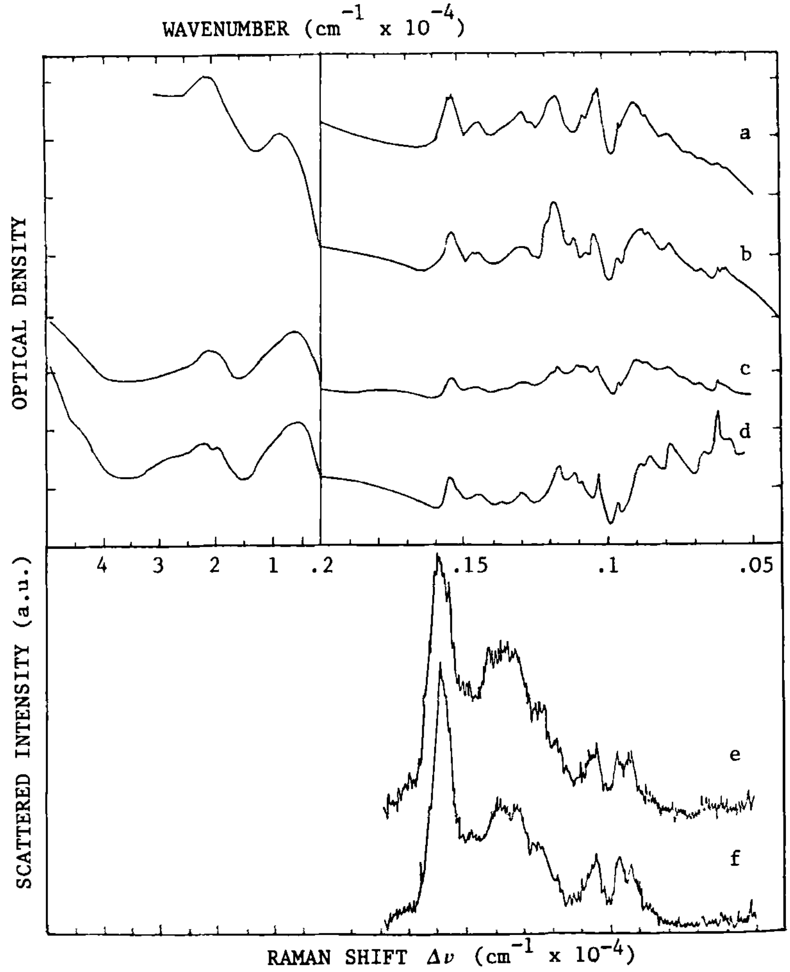

Figure 1. Upper part. Optical absorption spectra in u.v.,vis. i.r. range of polypyrrole deposited on transparent substrate, for different counterion X and observation temperature T: a) $X=BF_4$, T=300 K; b) $X=SO_4$, T=300 K; c) $X=ClO_4$, T=300 K; d) $X=ClO_4$; T=10 K. Lower part: Raman spectra at 300 K of free standing films for different counterions X: e) $X=NO_3$ and f) $X=SO_4$.

As a general feature the intensity of the Raman scattered radiation is very weak for all the excitation wavelengths. Moreover a strong luminescence background overlaps it, as also observed in PPP[4]. The luminescence spectrum is broad peaking in the red independently of the excitation wavelength: its relative weight decreases by decreasing the excitation wavelength, as expected when reaching resonance conditions. The luminescence background 1) decays with a time constant ∿30', and 2) is quenched on increasing the radiation power.

At a fixed Raman shift $\Delta\nu$, the intensity of scattered radiation: 1) is a linear function of the power level up to .4 W, thus ruling out the occurrence of thermochemical effects; 2) is independent of the total radiation dose, hence excluding photochemical effects and 3) decreases with time only due to the overlapping luminescence decay.

The curves e) and f) in fig.1 give the detailed Raman spectra, measured at RT, of free standing films with NO_3 and SO_4 counterions (exc. $\tilde{\nu}$ = 19432 cm^{-1}). Again as for i.r. absorption no appreciable difference can be detected as induced by the counterion change. An additional common feature to Raman and i.r. spectra is the line broadening in comparison with the corresponding monomer spectra [5]: this supports the picture of PP as an amorphous system.

REFERENCES

1. G.B. Street, T.C. Clarke, M. Krounbi, K. Kanazawa, V. Lee, P. Pfluger, J.C. Scott and G. Weiser, Mol.Cryst.Liq.Cryst., 83, 253 (1982).
2. M. Tanaka, A. Watanabe, H. Fujimoto and J. Tanaka, Mol.Cryst. Liq.Cryst., 83, 277 (1982).
3. K. Yakushi, L.J. Lauchlan, T.C. Clarke and G.B. Street, J.Chem. Phys., 79, 4774 (1983).
4. S. Krichen, S. Lefrant, G. Froyer, F. Maurice and Y. Pelous, J.Phys., 44, C3-733 (1983).
5. A. Lautié and A. Novak, J.Chimie Phis., 69, 1333 (1972).