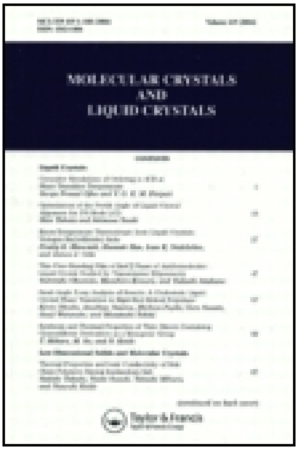

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Infrared Absorption Puzzles in Polyacetylene and Poly(Pyrrole)

Dejan Raković [a] , Ivan Božovič [b] , Seda A. Stepanyan [c] & Lev A. Gribov [c]

[a] Faculty of Electrical Engineering, PO Box 816, 11001, Belgrade, Yugoslavia

[b] Institute of Physics, PO Box 57, 11001, Belgrade, Yugoslavia

[c] Department of Physics, Timiryazev Academy, 125008, Moscow, U.S.S.R.

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INFRARED ABSORPTION PUZZLES IN POLYACETYLENE AND POLY(PYRROLE)

DEJAN RAKOVIĆ
Faculty of Electrical Engineering PO Box 816,
11001 Belgrade, Yugoslavia

IVAN BOŽOVIĆ
Institute of Physics PO Box 57, 11001 Belgrade, Yugoslavia

SEDA A. STEPANYAN and LEV A. GRIBOV
Department of Physics, Timiryazev Academy,
125008 Moscow, U.S.S.R.

Abstract Theoretical infrared (IR) absorption spectra have been computed for various models of trans- and cis-polyacetylene, poly(p-phenylene) and poly(pyrrole). Surprisingly, some supposedly strong bands are missing in the observed IR absorption spectra.

Infrared (IR) and Raman spectra of many polymers, including those with extended π-electron conjugation, have been succesfully interpreted[1] on the basis of the following theoretical model: (a) a single chain is considered which is infinite, extended and translationally periodic; (b) the electrons and the nuclei are decoupled adiabatically; (c) anharmonic effects are neglected; (d) the force constants and the electro-optical parameters (i.e. dipole moments of the chemical bonds, and their derivatives with respect to the natural coordinates) are assumed to be fairly local (i.e. independent on the structural details except for the location and the type of the few nearest neighbours), and hence they can be transferred from small molecules of appropriate stereochemical structure.

Along these lines we have computed[2] theoretical vibration spectra for poly(p-phenylene) and cis-polyacetylene (and its fully-deuterated analog). A good agreement with the observed IR and Raman spectra is obtained, as seen in Figures 1 and 2. Hence one can reasonably view such polymers as simple concatenations of many identical structural elements.

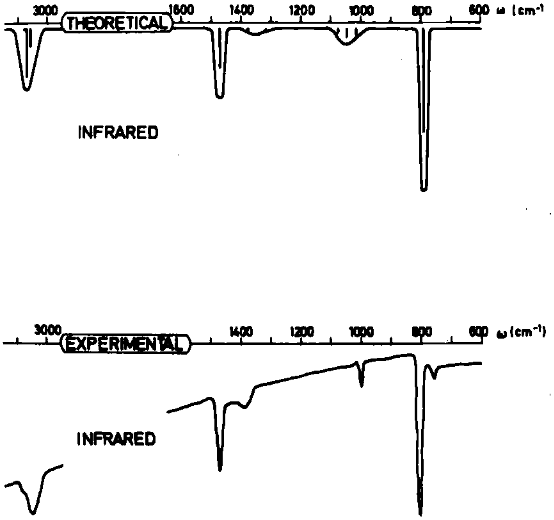

FIGURE 1 IR spectra of poly(p-phenylene).

However, in the case of trans-polyacetylene, two pronounced non-additive effects appear in the (infinite) polymer, in contrast to shorter oligomer: the frequencies of the two strongest resonant Raman bands (corresponding to the two "Peierls" modes) are lowered for ∼10-15%[3,4], and the intensity of the supposedly strongest IR absorption band (corresponding to the in-plane C-H bending mode) is dramatically reduced[4], see Fig. 3. Strong electron-phonon coupling is believed to cause both effects (In support of the latter conclusion, let us remark that (i) we have utilized the force and electrooptical fields obtained with extreme care, by solving the generalized inverse spectral problem for trans- and cis-hexa-1,3,5-trienes and their 2,3,4,5-tetra-deutero analo-

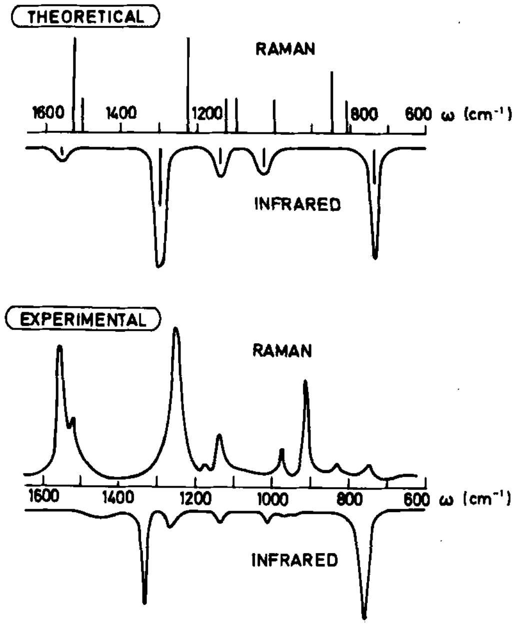

FIGURE 2 Vibrational spectra of cis-polyacetylene

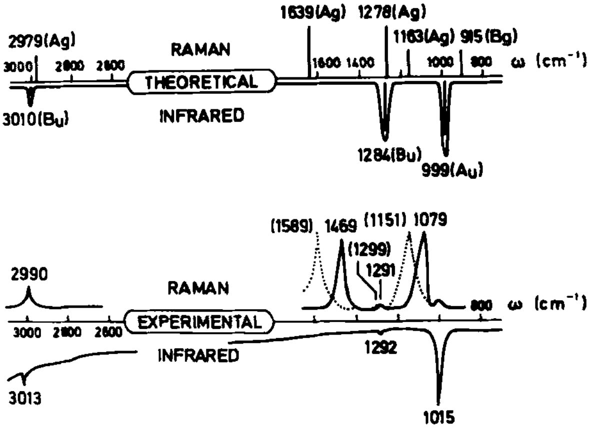

FIGURE 3 Vibrational spectra of trans-polyacetylene

gues[5], and (ii) experimentally, the in-plane C-H bending vibrations are indeed strongly IR active in trans-hexatriene.[5]).

To acquire some additional information, we have studied the IR absorption spectra of poly(pyrrole), but some surprises came out again. The in-plane C-H bending is strongly IR-active, as predicted; however, the supposedly strong band at ∿1700 cm^{-1}, due to the in-plane N-H bending, is not observed in poly(pyrrole) while it is seen in poly(N-methyl pyrrole)[6].

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