

Conjugated polymers and carbon materials with low defect content for ultra efficient generation, transmission and conversion of energy.

Сопряженные полимеры и углеродные материалы с низким содержанием дефектов для высоко эффективной генерации, передачи и преобразования энергии.

Valerii Kobryanskii

*Lebedev Physical Institute*

*119 991, Moscow, Leninsky prospekt 53, Russia*

*E-mail: kobryan@mail.ru*

# Preface to problem.

- Crystal silicon with very low concentration of defects was created about half a century ago. Advances in inorganic semiconductors determined the course of scientific and technical advance for many years ahead.
- In 1964, Little suggested (Phys. Rev 134, A1416) that it might be possible to synthesize a room temperature superconductor using organic materials in which the electrons traveled along certain kinds of chains, effectively confined to one dimension.
- Above enumerated discoveries led to changes in the general concept of future scientific and technical progress.
- Unprecedented search of new materials disposing of unique electro-physical and optoelectronic properties began. The ion-radical salts, conjugated polymers, ceramic superconductors and carbon materials were discovered. Scores of thousand articles were published, thousand patents were issued and obtained, several hundred start-up companies were set up. According to the expert estimation, total expenses for research in this area amounted to hundred billion dollars for the last 50 years.
- **However, none of the above-stated materials have found any wide application in the Hi-Tech industry.**
- The published results reveal that a structural disorder and defects are a primary cause preventing the application of the above-stated materials in electro-physics and optoelectronics. They result in low stability, low conductivity in conductors, low critical current in superconductors, low mobility of charges and excitations in semiconductors and, consequently, lead to low efficiency displayed by the devices made.

# Nature and Structure of defects in conjugated materials.

- There can be a very large variety of chemical, conformation and supra-molecular defects in solid matter. Defects are formed in the processes of chemical synthesis and solid phase formation. The most highly ordered and low-defect solid state specimens are inorganic mono-crystals. While using special methods for chemical cleaning of the initial substances/compounds and due to controlled crystal growth inorganic mono-crystals can acquire less than  $10^{-7}$  (<sup>-9</sup>) molar percent of admixtures (defects).
- Conjugated materials as a rule amorphous and nanostructured with 1D, 2D and 3D structures. They contain considerably more defects than inorganic mono-crystals. Besides, the important feature about these materials is that they differ from inorganic mono-crystals by a larger variety of defects inherent in them. For this reason research workers can hardly succeed in their efforts to establish not only the concentration, but also the structure of defects in these materials. Long-term efforts experienced by thousand research workers reveal that standard methods of chemical synthesis and solid state formation can hardly be used to manufacture highly ordered and low-defect amorphous, ceramic, conjugated polymeric and carbon materials for applications in electro-physics and optoelectronics.
- Thus: The problem of creating the highly ordered and low-defect conjugated materials for electro-physics and optoelectronics is part of a general issue. Throughout the ages the scientists have been able to create perfect crystals, but they are making only the first steps in creating the highly ordered and low-defect amorphous, conjugated polymeric, ceramic and carbon materials that meet the requirements of electro-physics, and optoelectronics. It is not a problem of chemical technology, but rather, a general problem of finding the ways and means under which natural science can develop and reveals itself.

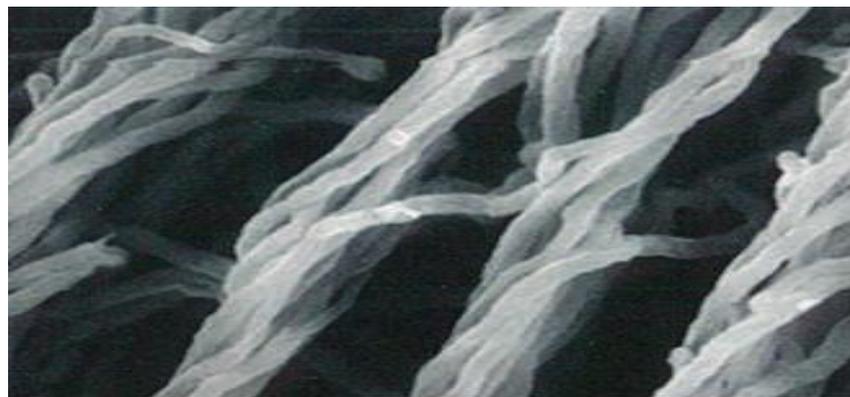
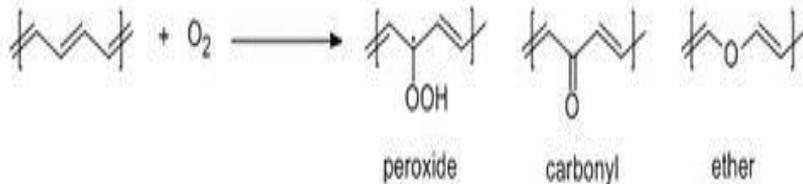
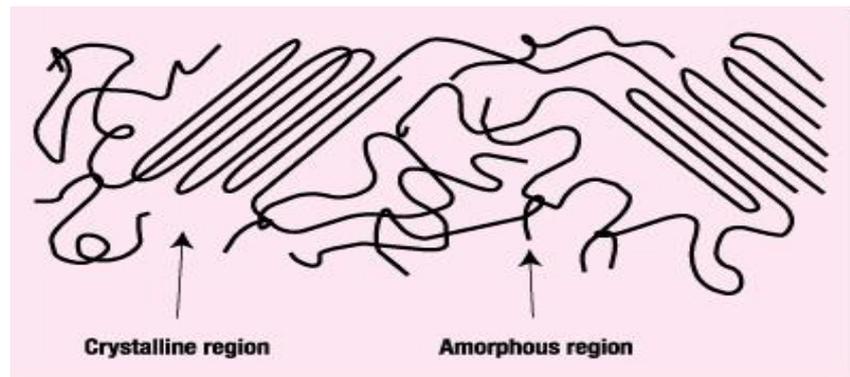
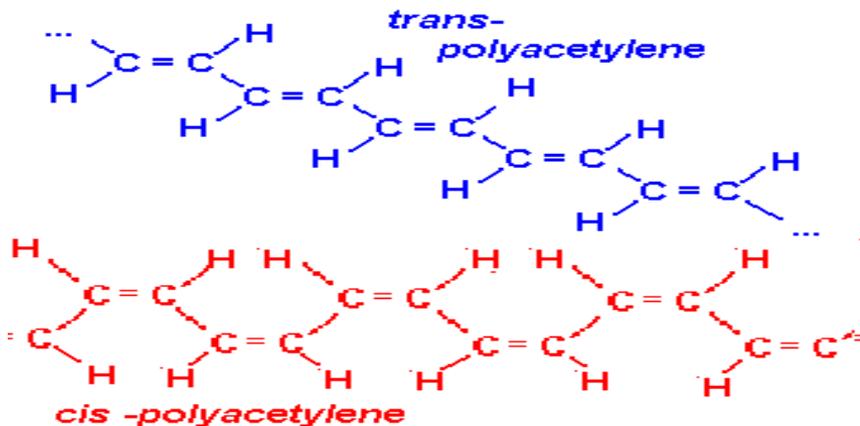
# Methods for development of highly ordered and low-defect conjugated materials

- Structural disorder and defects in conjugated polymers, carbon materials and other conjugated materials are formed in the processes of chemical synthesis and solid phase formation. As a rule the chemical and conformational defects are produced mainly in the process of chemical synthesis, while supra-molecular defects and structural disorder are formed during a solid phase formation.
- In our projects chemical synthesis combined with the stereo-specific catalysis, self-organization and matrix synthesis are used to produce organic, polymeric, carbon and nano-structured materials with a small amount of defects. The essence of developing procedures consists in high mobility of chemical groups and matrix identification of fragments of chemical structure throughout all the stages of synthesis and solid phase formation. Stereo-specific catalysis allows manufacturing conjugate systems with a low level of chemical and conformational defects. Their high mobility can affect the structure and amount of defects in materials by altering conditions of self-organization and thus manufacturing items of desired structure with a small amount of defects. Matrix recognition is an extra boundary condition, which allows combination of solid phase formation with a "push-out" effect from the ordered structure of alien and / or defective molecules.

# The essence of the defect control methods

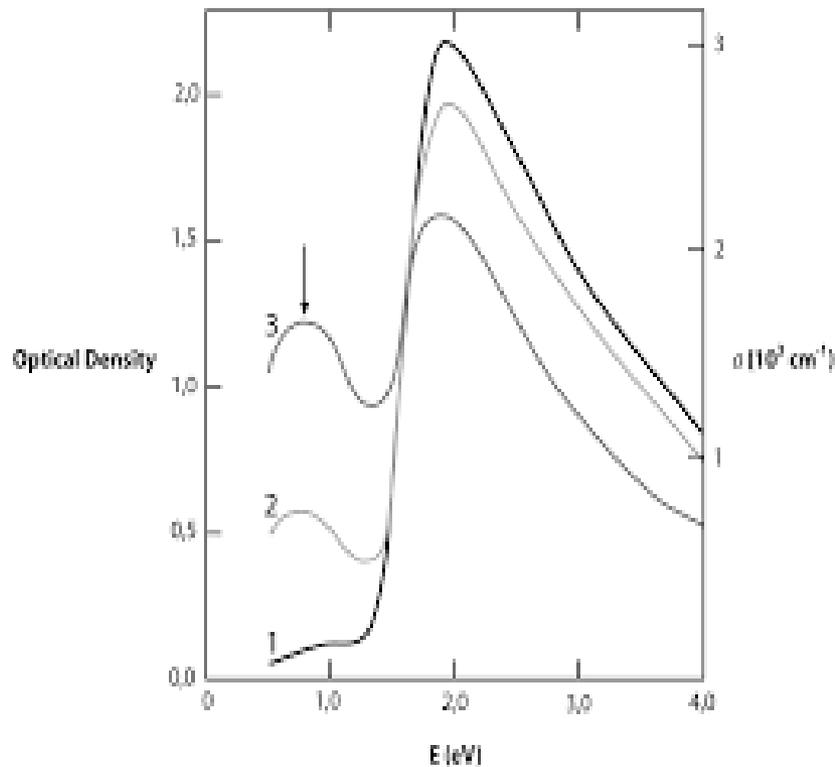
- Chemical defects and structural disorder result in the formation of conjugated systems fragments displaying different conjugation efficiency, various band-gap width and various types of static and dynamic defects of electronic structure. Depending on the amount of defects electro-physical and optoelectronic properties of conjugated materials can vary over a very wide range.
- Taking this into account the standard spectroscopy and physicochemical analysis are used to determine the amount of defects in conjugated systems with sufficiently high amount of defects.
- The nonlinear and pulse spectroscopy enabling to evaluate the lifetime and mobility of charges and excitations is applied to determine the amount of defects in highly ordered and low-defect conjugated systems with small amount of defects.
- Finally, in the case of conjugated systems with very low content of defects the ultra short pulse (5 – 10 fs) pump-probe spectroscopy is used evaluating the area of coherent oscillations and lifetime of coherent states.
- A short description is given below to report some examples of highly ordered conjugated polymeric materials with a low amount of defects developed by the authors of our projects.

# Free-standing films of polyacetylene (fs-PA) Shirakawa polyacetylene



J. Am. Chem. Soc., 129, 10, 1021 (2007)

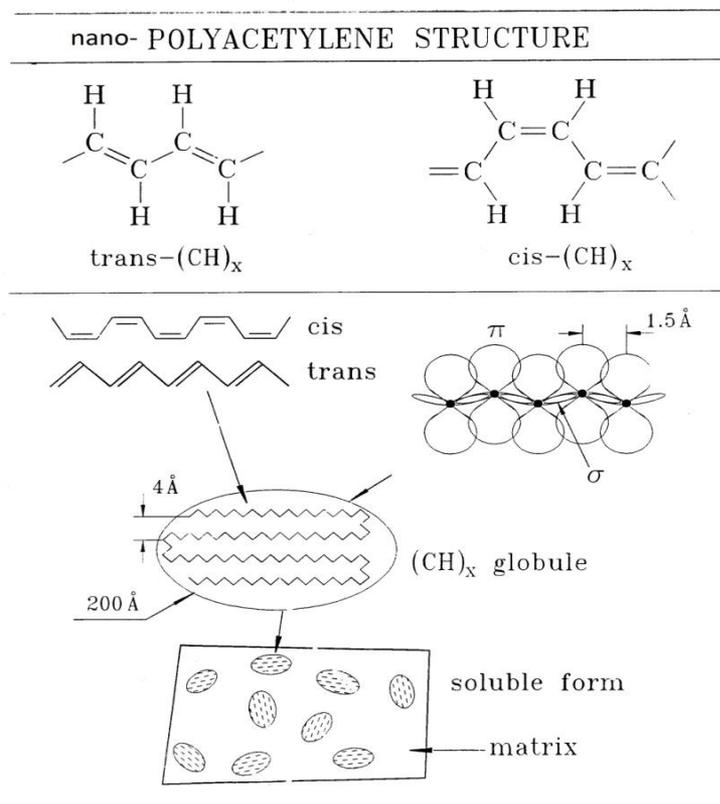
# The Nobel Prize in Chemistry, 2000: Conductive polymers



Optical absorption of undoped polyacetylene (curve 1). Like a classical semiconductor the sample is transparent for light with a photon energy smaller than the band gap (1.7 eV). Curves 2 and 3 show the absorption of polyacetylene with increasing dopant. Note the emergence of a midgap state (arrow at 0.7 eV) upon doping and that the absorption curves cross at an isosbestic point, because midgap states grow at the expense of the others. (Results adapted from Ref 7)

# Polyacetylene and nano-polyacetylene obtained at Lutinger catalysts and new stereo selective catalysts.

## Polyacetylene

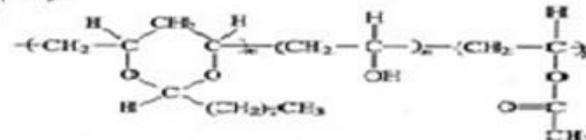


## Polvinylformal (butvral)

ACRONYMS, TRADE NAMES: PVB, Butvar<sup>®</sup> (Montanto), Butacite<sup>®</sup> (Du Pont), Vinylite Xr<sup>®</sup> (Union Carbide), Kuviral<sup>®</sup> B (Rhône-Poulenc), Morital<sup>®</sup> (Isochit), S'Loc<sup>®</sup> (Shelco), Saf-x<sup>®</sup> (Montanto), Trocofol (I'Ilis).

CLASS: Polyvinyl

STRUCTURE



This schematic should not be construed as a block structure.

### New catalysts and new dopants.

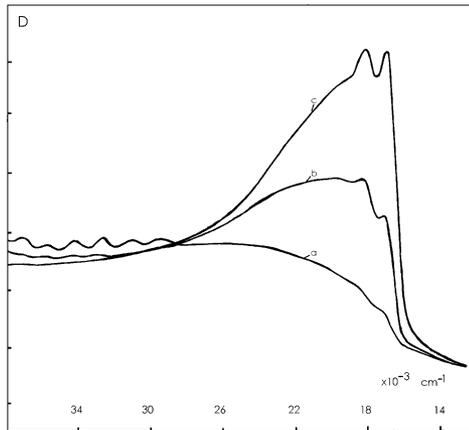
- 1. Shirakava polyacetylene at Ziegler catalyst – 1971.
- 2. Nanopolyacetylene at Re catalyst - 1997.
- 3. Nanopolyacetylene can be prepared as a) high viscous solution; b) gel; c) film; d) plate.

**Complex formation of hydrocarbons conjugated polymers with non-oxidizing protonic acids.**

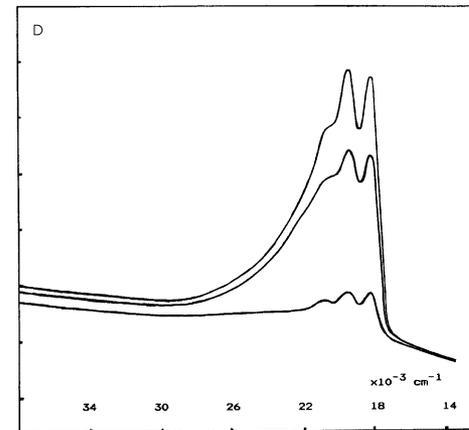
- **H Br ; HCl and so on.**
- **CH<sub>3</sub>COOH; CF<sub>3</sub>COOH and so on.**

**Complex formation of hydrocarbons conjugated polymers with non-oxidizing molecules with high dielectric constants.**

# Acetylene polymerization at Luttinger's catalyst $\text{Co}(\text{NO}_3)_2/\text{NaBH}_4$ in solutions of polyvinylbutiral at $-40\text{ C}$ results in cis-PA.

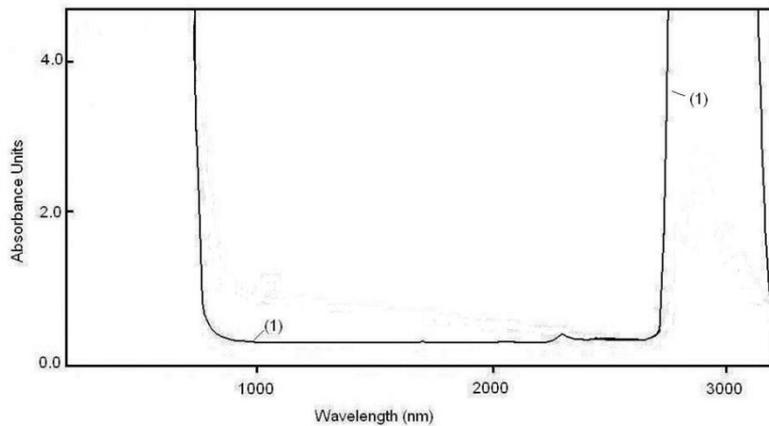
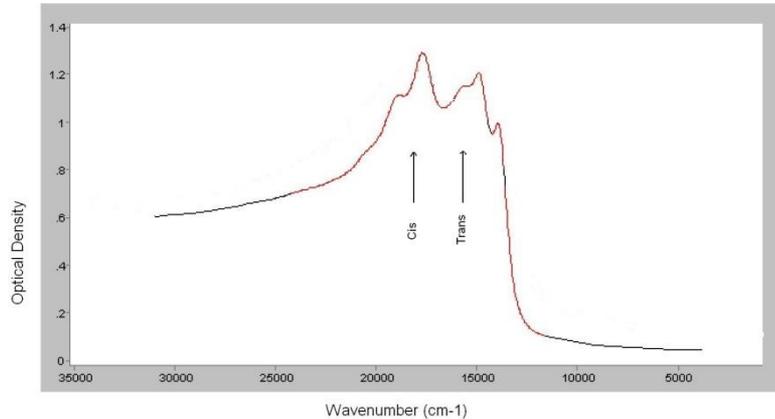


- Acetylene polymerization in middle viscous solution at  $-40\text{ C}$ .
- Optical spectra of reaction mixture. Thickness of optical layer: (a) 2,95 mm, (b) 0,95 mm, (c) 0.2 mm.
- Registration time– 1 min.
- Time interval between spectra – 24 min.



- Acetylene polymerization in high viscous solution at  $-40\text{ C}$ .
- Optical spectra of reaction mixture. Thickness of optical layer: (a) 2,95 mm.
- Registration time– 1 min.
- Time interval between spectra – 8 min.
- 100% cis-nanopolyacetylene.
- Vibrational structure characteristic for individual polyenes.
- **(first example).**

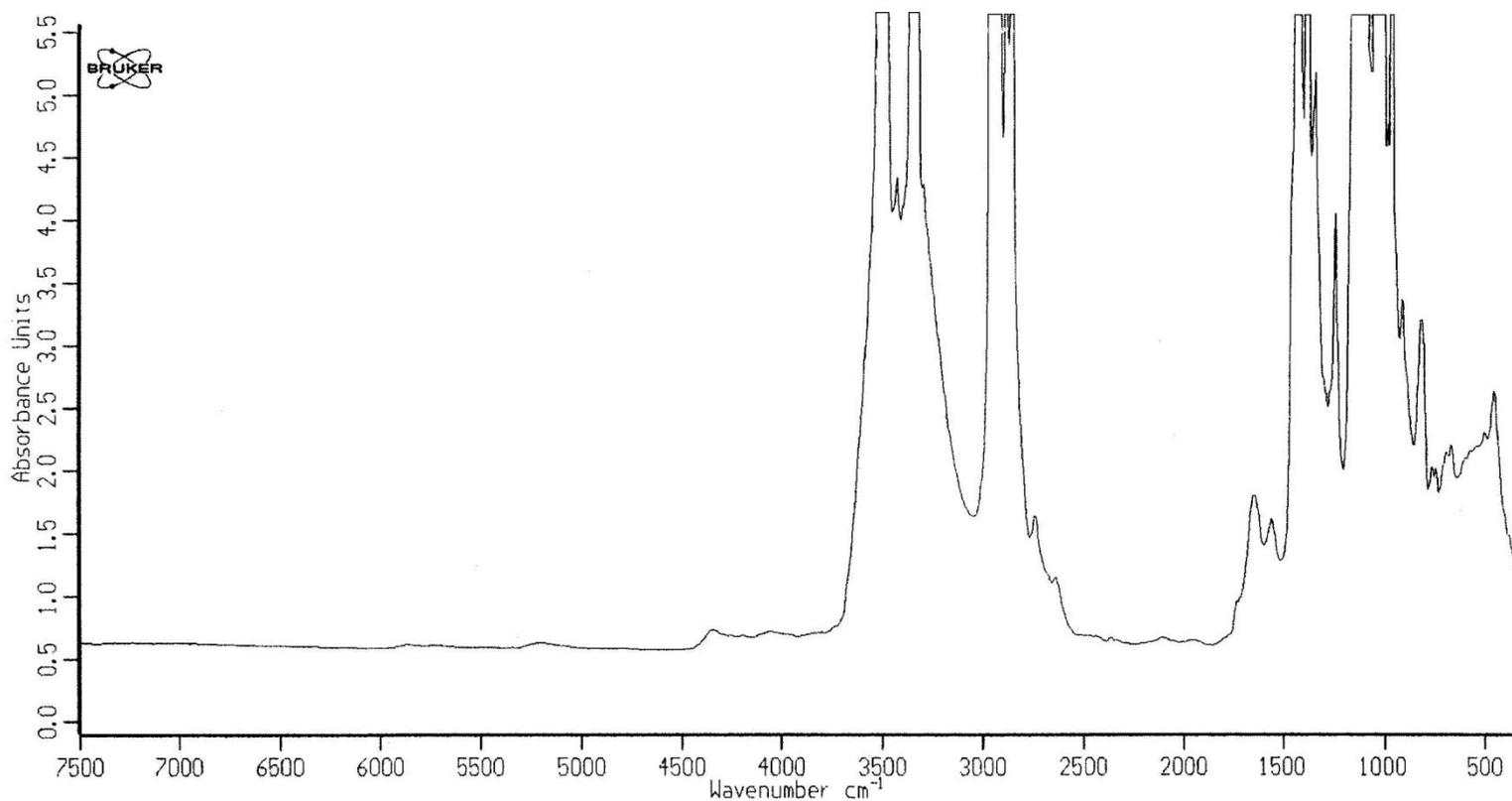
# Nanopolyacetylene at Re catalyst at room temperature.



- Films of 50% cis- 50% trans- nanopolyacetylene with very low content of defects and vibrational structure of cis- and trans- absorption bands were obtained **(first example)**.
- Films were obtained in high viscous solutions at room temperature. Film thickness 5 mk. Polyacetylene nanoparticles content – 4% by weight.
- It is known that low loss optical windows are characteristic for some high quality inorganic semiconductors.
- The low loss optical windows was observed for high quality nanopolyacetylene films.
- UV-Vis spectrum of 250 microns thickness nanopolyacetylene film. One can see from the picture the low-loss optical windows in the field 800 – 2700 nm. **(first example)**.

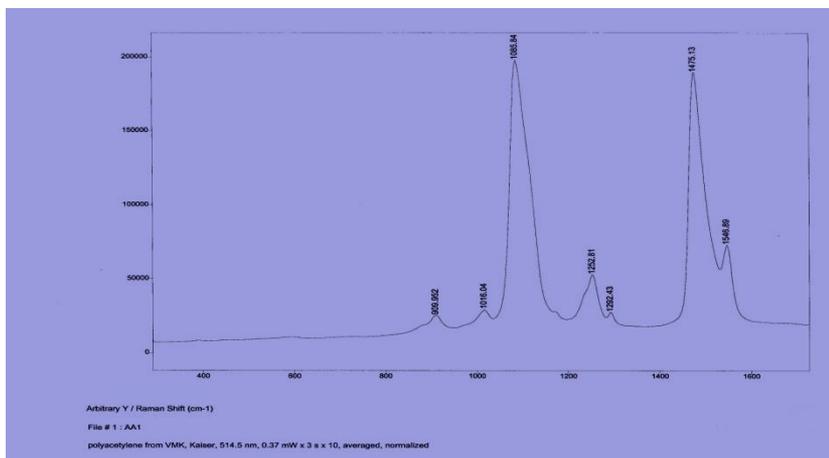
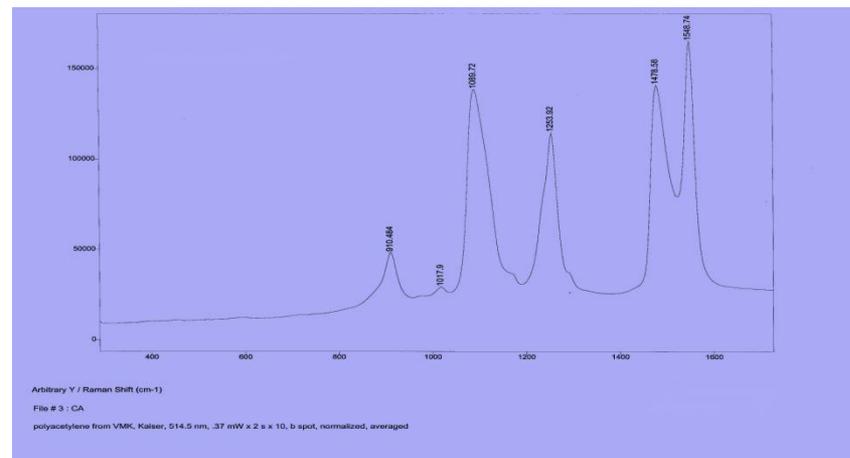
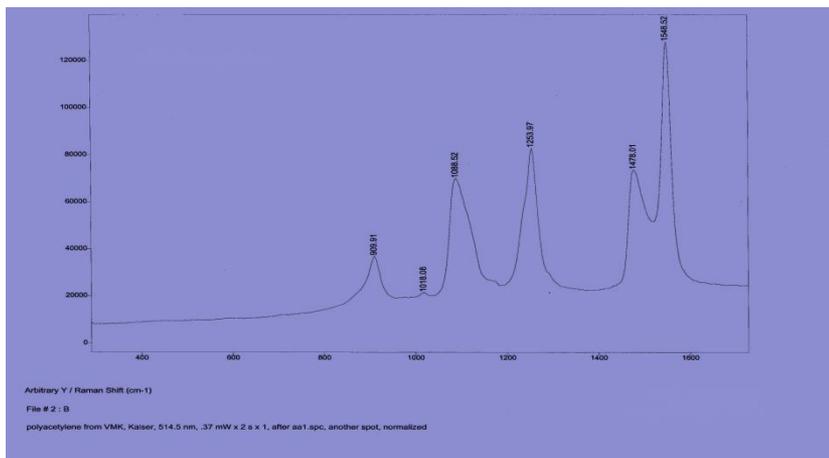
NIR+IR spectrum of 400 microns thickness nanopolyacetylene film (Re catalyst).  
One can see from the picture “low-loss” optical windows without Rayleigh scattering in the field 7500 -3700  $\text{cm}^{-1}$  with optical density = 0.7

**IFS28**



# Raman scattering spectra of 55% cis- 45% trans- nanopolyacetylene film (Re catalyst).

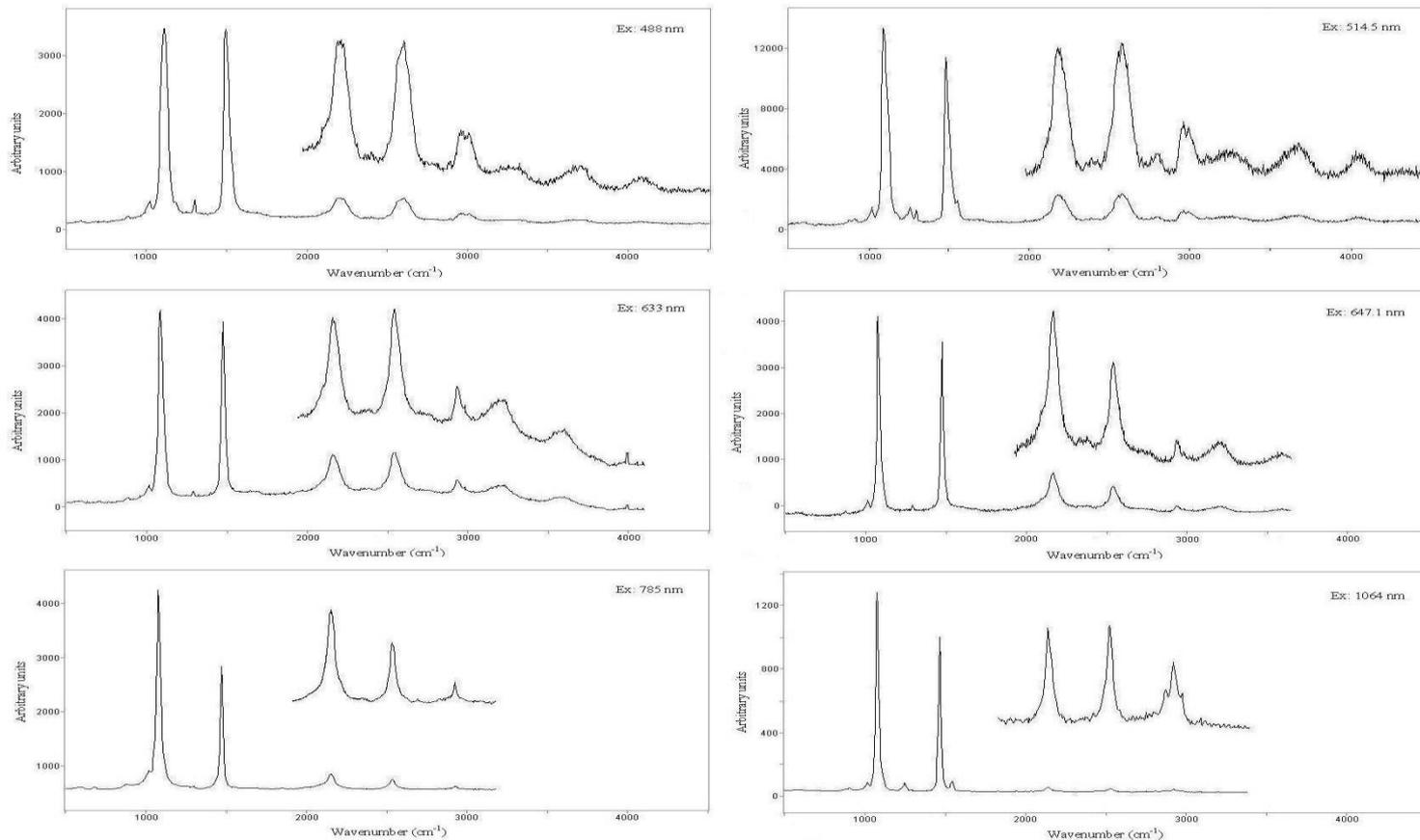
The excitation wavelength - 514, 5 nm. It coincides with a band cis- NPA in the optical absorption spectra of 55% cis- 45% trans- nanopolyacetylene. (previous slide)



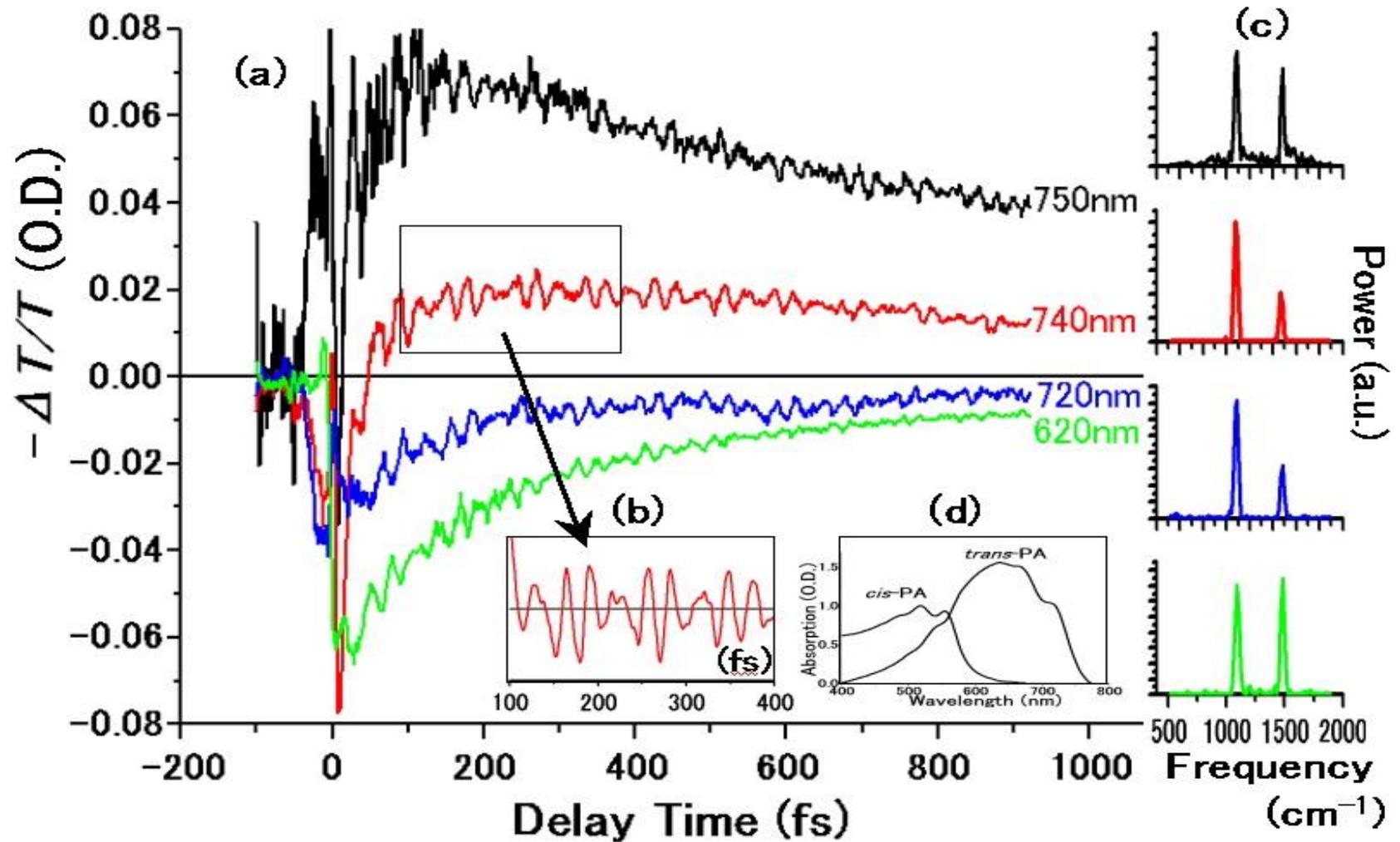
- **(first example).**
- It was demonstrated the abnormally high efficacy of cis - trans isomerization of 60% cis-40% trans- nano-polyacetylene with formation of 100% trans- nano-polyacetylene. The power of radiation is 370 microwatts. The isomerization time is about 2 minutes.
- Prof. Richard L. McCreery, OHIO STATE University

Raman scattering spectra of trans- nano-polyacetylene taken at excitation 488, 514.5, 533, 672, 785 and 1064 nm. For all excitation wavelengths there are two fundamental vibrational bands of single (C-C) and double (C = C) bonds of the chain and their overtones.

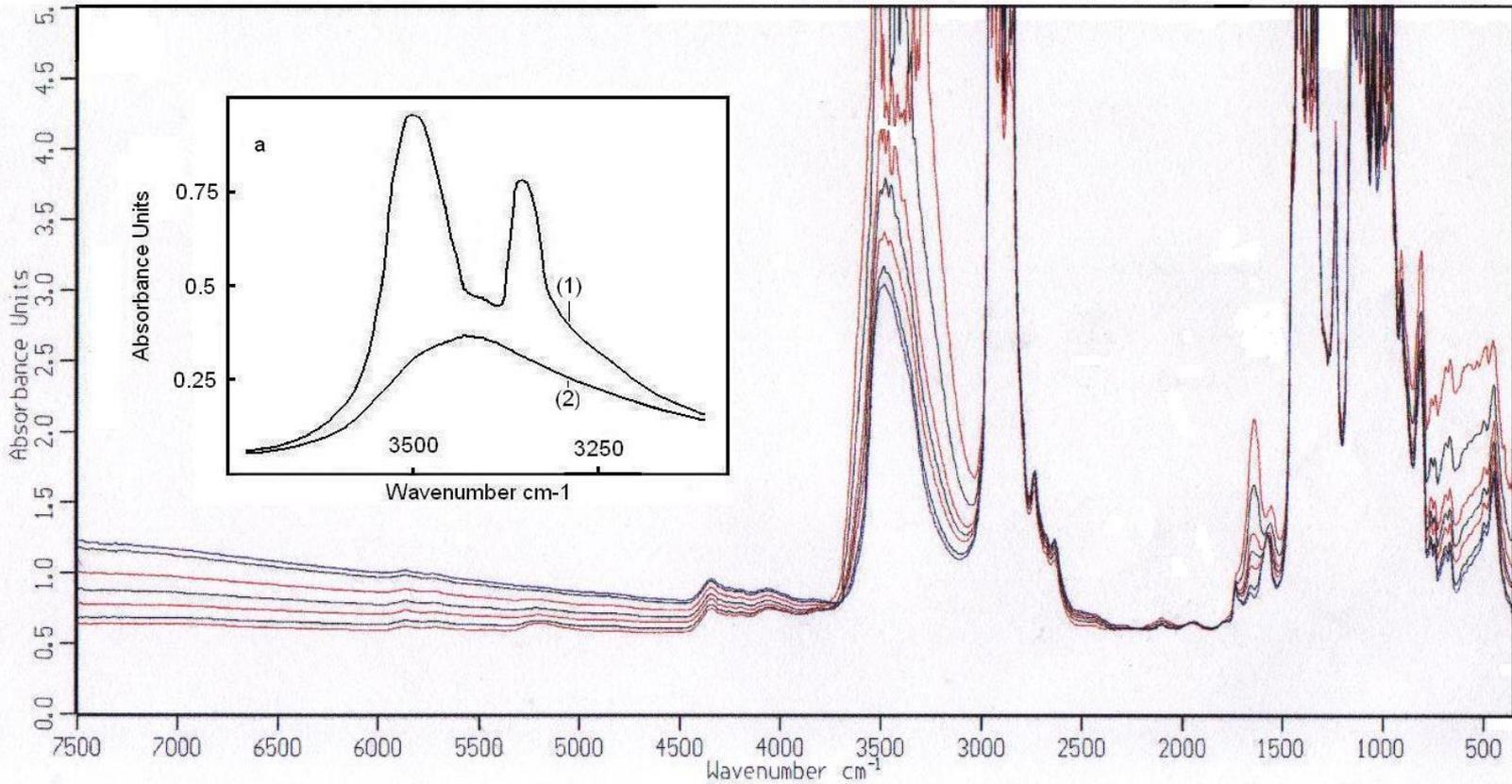
For the **(first time)** there was almost a complete absence of dispersion of fundamentals in the Raman scattering spectra of polyacetylenes with changing the excitation wavelength.



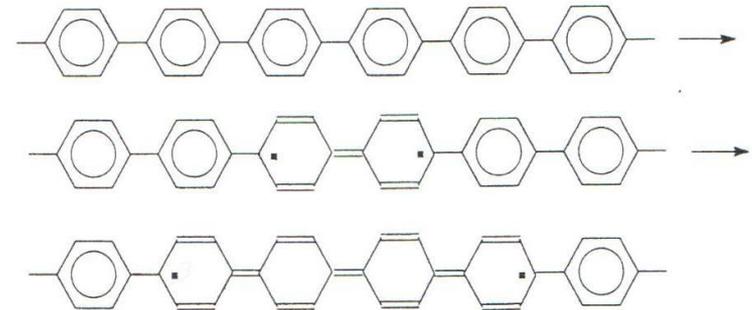
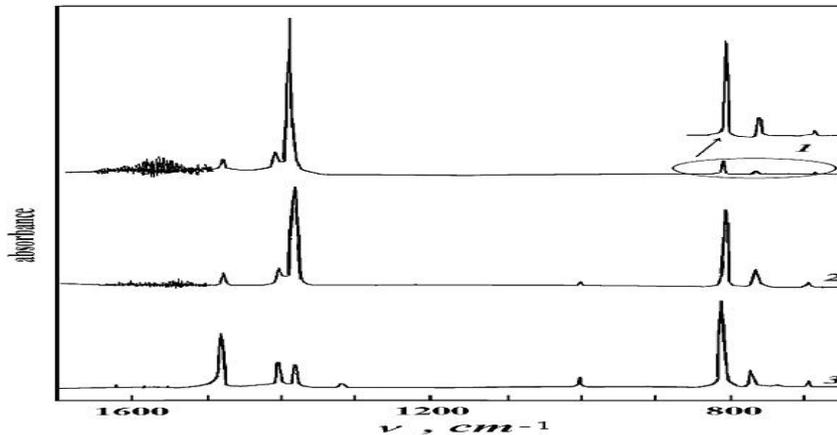
**Time-dependence of pump-probe signals of nanopolyacetylene excited by ultra short laser pulse (4,7 fs).** Fourier transformation of the oscillating components of pump-probe signals at four different wavelength via band-pass filters. For the **(first time in literature)** coherent vibrations of single and double bonds of polyacetylene chain at femtosecond excitation were observed.



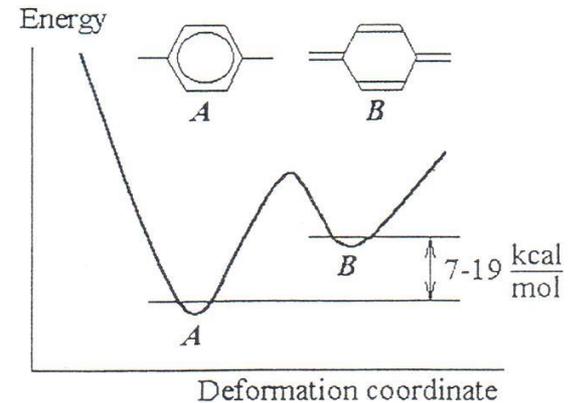
# FTIR spectra of thick (0.5 mm) nano-polyacetylene film in the process of removal of water from IR cuvette.



# Films of 3D ordered, vacuum deposited poly-p-phenylene.

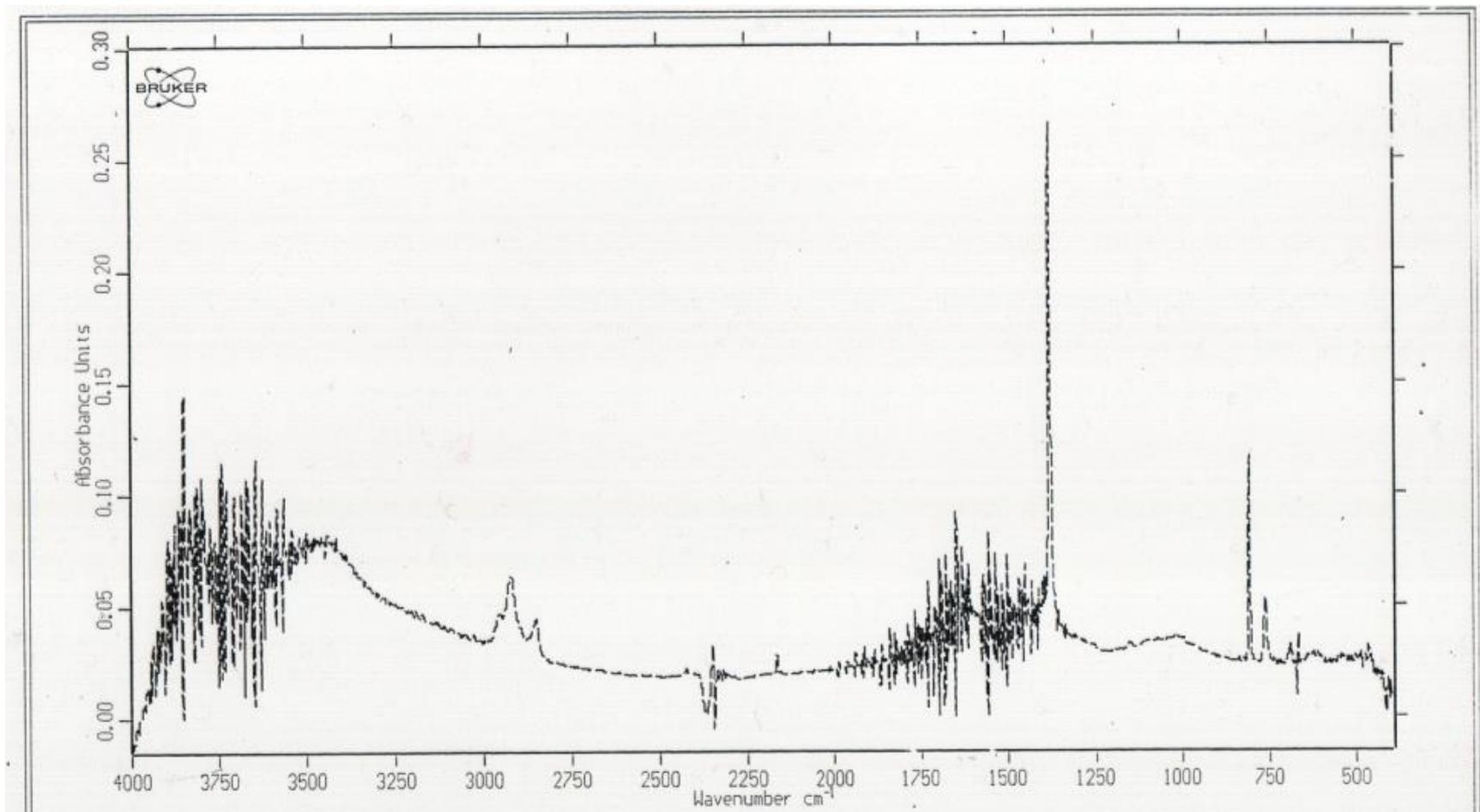


- IR spectrum of vacuum deposited poly-p-phenylene films on KBr support. Conditions of film formation:
- evaporation temperature -680 C;
- substrate temperature: 1-300<sup>0</sup>; 2-200<sup>0</sup>; 3-100<sup>0</sup> C.



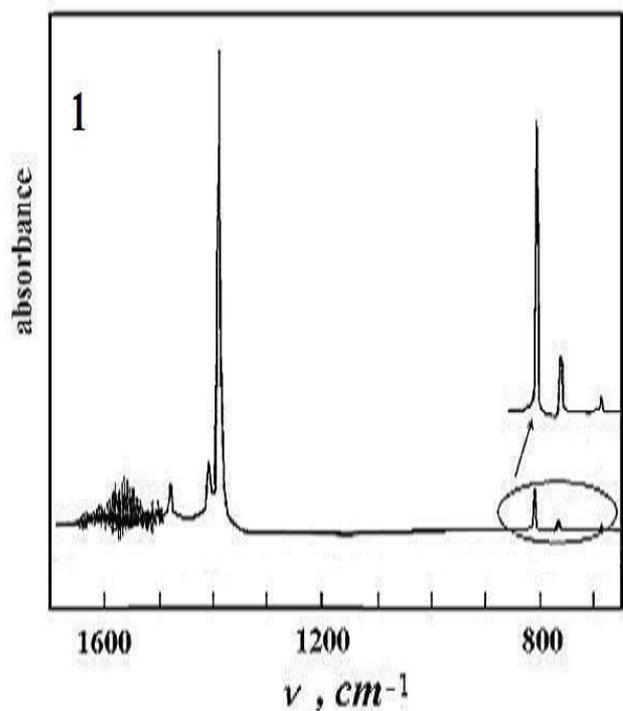
**Figure** . The energies of the benzenoid and quinoid PPP structures.

FTIR spectrum of (3D ordered) poly-p-phenylene film vacuum deposited on KBr support. Support temperature – 200 C

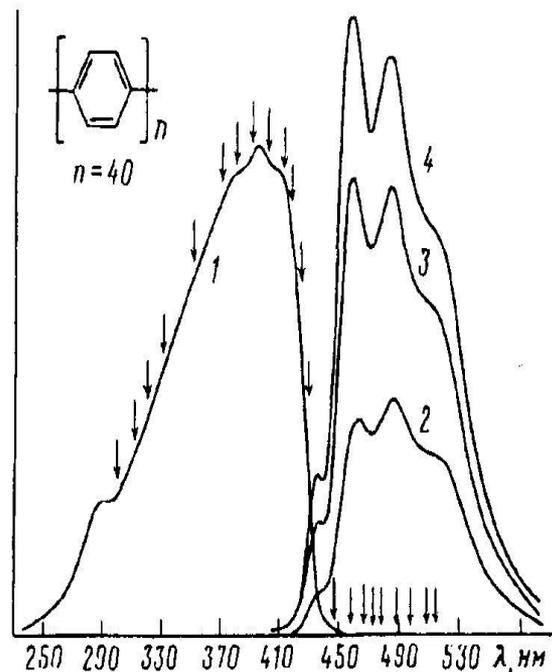


# (3D ordered) vacuum deposited poly-p-phenylene films. Substrate temperature – 300 C.

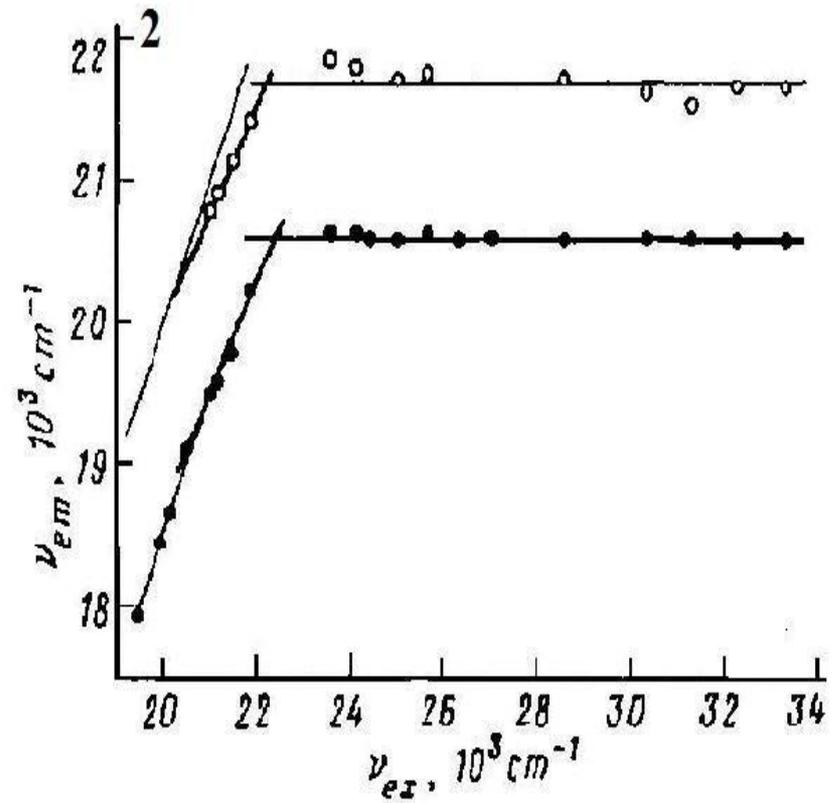
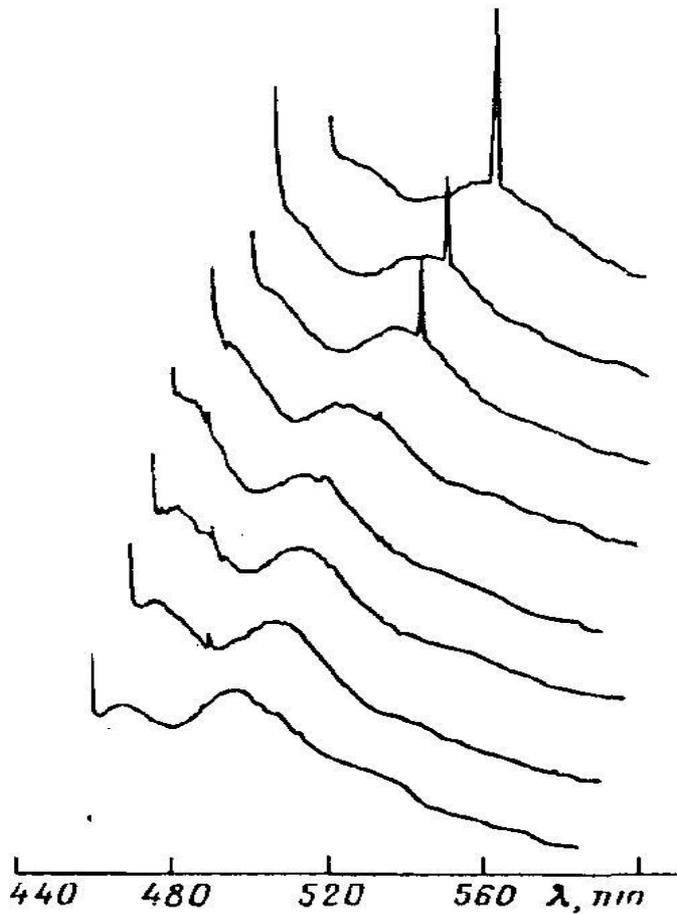
FTIR spectrum of (3D ordered) poly-p-phenylene film vacuum deposited on KBr substrate. Substrate temperature – 300 C.



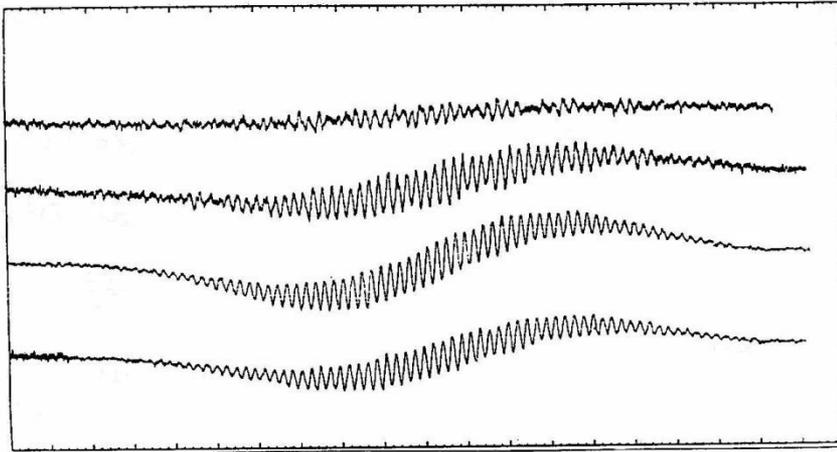
Excitation and luminescence spectra of (3D ordered) poly-p-phenylene film vacuum deposited on quartz substrate. Substrate temperature – 300 C.



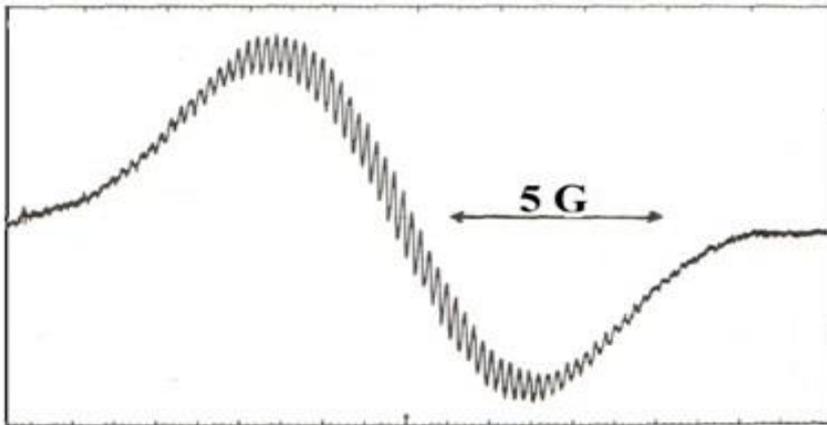
Site selective spectroscopy at room temperature of (3D ordered) vacuum deposited at 300 C poly-p-phenylene films.



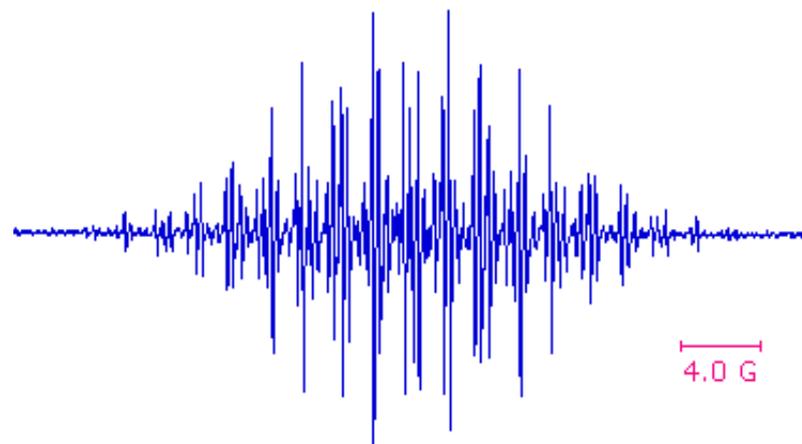
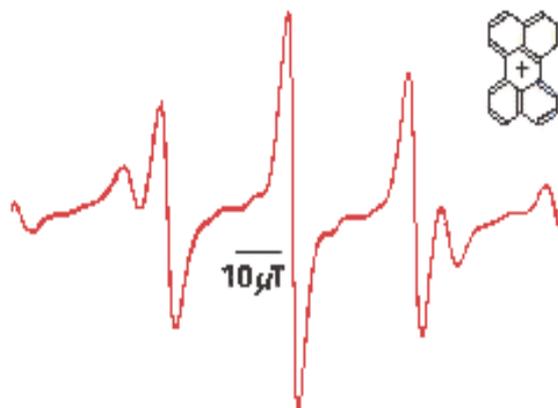
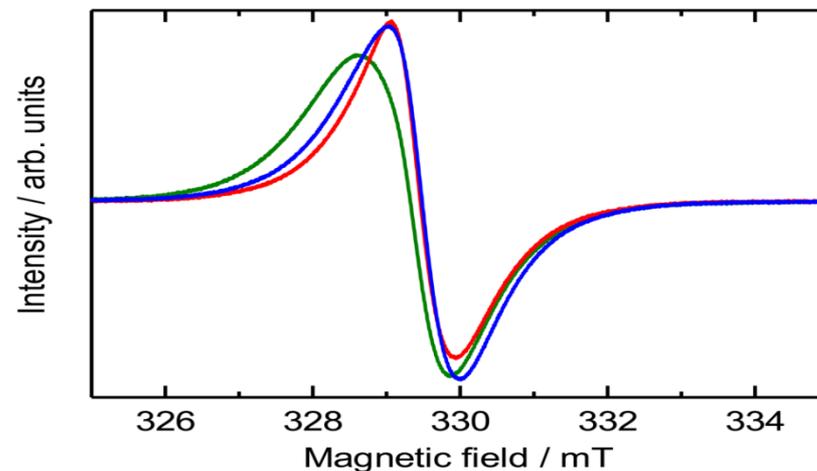
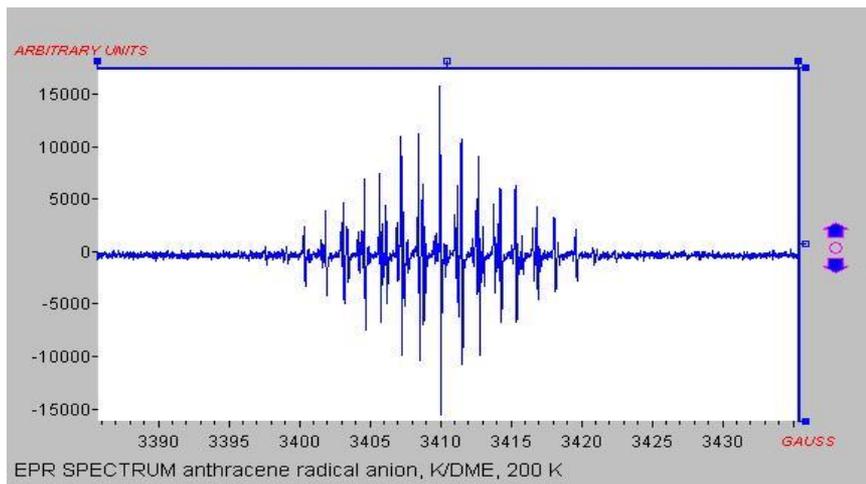
# Example 3. Polyphenylacetylene obtained by anionic polymerization [9]



- It is shown that anionic polymerization of phenylacetylene in hexamethyl phosphorotriamide is followed up by the appearance and growth of ESR signal in the reaction mixture, which consists of a large number of narrow lines.
- An insight into the line shape and hyperfine structure reveals that the EPR signal is appeared due to unpaired electrons delocalized in the system of conjugated double bonds with equivalent protons.
- The hyperfine structure of polymer chain protons in the EPR spectrum of conjugated polymers was observed for the **(first time in literature)**.
- The results obtained are clearly indicates the absence of a) conformational defects and b) macromolecules with different conjugation lengths in conjugated polymers of this type.



# ESR Spectra of aromatic: radical anion and radical cation, standard conjugated polymers and triphenylmethyl radical.



# Polyacetylene at Luttinger's and Re catalysts. Photoinduced, electroabsorption and Raman scattering spectra.

## Additional information.

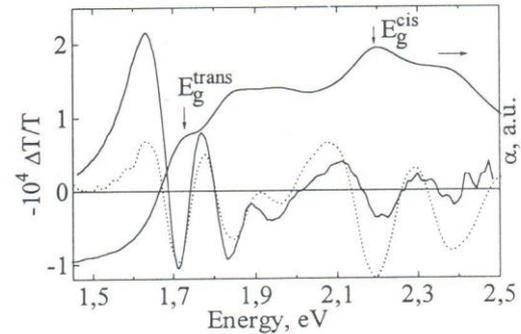
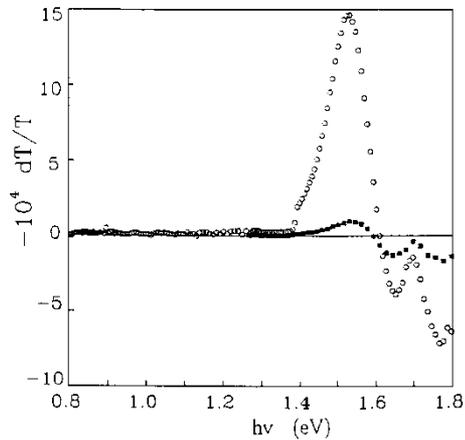
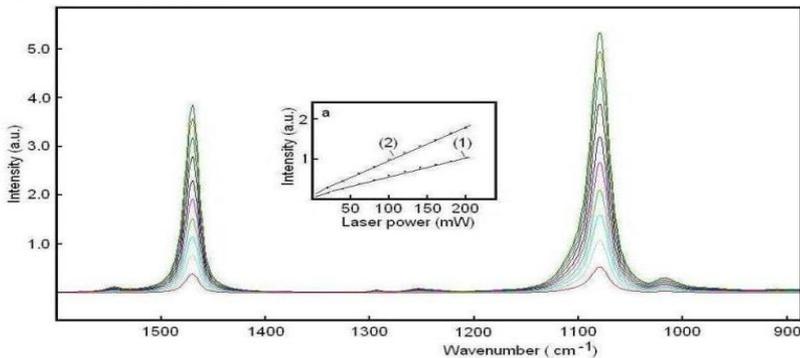
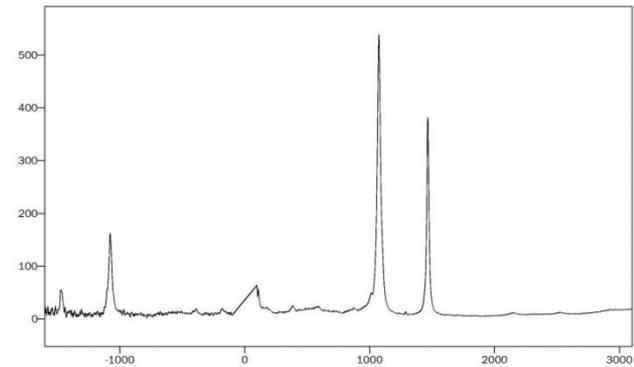


Fig. 1. The electroabsorption and absorption spectra for a *trans-cis* blend film of 'soluble'  $(CH)_x$  at room temperature ( $F \approx 50$  kV/cm,  $\Omega \approx 400$  Hz). The dotted curve shows the second derivative of the absorption spectrum.



Raman scattering spectra of NPA film at excitation power 20 - 200 mW. 2a-Dependence of intensity on excitation power. Stretching vibrations of: - double bond (curve 1); - single bond (curve 2).



Absorbance / Wavenumber (cm<sup>-1</sup>)  
File # 1 = ANTIST2  
SAMPLE NAME

# Literature

- [1] Developments in Polyacetylene - Nanopolyacetylene. Kobryanskii V. M., Rapra review reports, Vol. 10, Number 6, Report 114 (2000).
- [2] Coherent Electron-Lattice Vibrations in Trans-Nanopolyacetylene Probed by Raman Scattering. Paraschuk, D. Yu.; Kobryanskii, V. M. Phys. Rev. Lett., 87(20), 207402/1-207402/4, (2001).
- [3] Excitation of a Breather Mode of Bound Soliton Pairs in Trans-Polyacetylene by Sub-Five-Femtosecond Optical Pulses. Adachi Shunsuke; Valerii M. Kobryanskii Valerii M.; Kobayashi Takayoshi, Phys. Rev. Lett., 89(2), 027401/1-02740/4, (2002).
- [4] 3D ordered composites of nanopolyacetylene: Mechanism of self-organization and properties, V.M.Kobryanskii, arxiv.org/pdf/cond-mat/0607780/ (2007)
- [5] Ultrafast real-time vibronic coupling of a breather soliton in *trans*-polyacetylene using a laser pulse with few cycles, Takahiro Teramoto, Zhuan Wang, Valerii M. Kobryanskii, Takashi Taneichi, and Takayoshi Kobayashi, PHYSICAL REVIEW B 79, 033202, (2009)
- [6] High-pressure Raman spectroscopy of nanoparticle polyacetylene in a poly(vinyl-butyril) matrix, Michael McIntire, Liang Zhao, Valerii Kobryanskii, Eric Chronister, V 42, Issue 6, 1435–1441, (2011)
- [7] Exciton localization in thin polymer films probed by selective fluorescence spectroscopy. Drobizhev, M. A.; Sapozhnikov, M. N.; Kobryanskii, V. M., J. Lumin. (1997), 72-74 490-493.
- [8] Formation of quinoid fragments in vacuum-deposited poly-para-phenylene films: IR spectroscopy evidence. Kobryanskii, V. M.; Kotova, S. L. J. Polym. Sci., Part A: Polym. Chem. (1998), 36(7), 1043-1052.
- [9] Mechanism of anionic polymerization of phenylacetylene. Kobryanskii, V. M. J. Polym. Sci., Part A: Polym. Chem. (1992), 30(9), 1935-9.

## Literature. New theory and new models.

### Superconductivity in diamond, electron–phonon interaction and the zero-point renormalization of semiconducting gaps.

**Manuel Cardona** *Science and Technology of Advanced Materials 7 (2006) S60–S66*

- The superconductivity observed in boron-doped diamond is discussed from the point of view of the phonon-driven BCS theory. It is shown that electron–phonon interaction is particularly strong in diamond. Other semiconductors possibly exhibiting superconductivity are brought to the fore. Related evidence for strong electron–phonon interaction in semiconductors containing carbon, nitrogen and oxygen is presented.
- **Conclusions**
- The appearance of superconductivity in heavily borondoped diamond was firmly established at the time of the Tsukuba Workshop (December 2005). Most theoretical and experimental evidence points to a phonon-induced BCS mechanism. However, isotope effect measurements on  $T_c$ , the smoking gun, are still missing. In this paper, we dissect the components of the BCS mechanism and suggest other materials in which superconductivity may (or may not) be present. Optical experiments which reveal the large electron–phonon interaction present in diamond ((and also in GaN and ZnO) are discussed.

## Literature. New theory and new models.

### Characterization of zero-point vibration in one-component crystals

*Yong Yang and Yoshiyuki Kawazoe, Europhysics Letters, Volume 98 Number 6, EPL 98 66007 (2012)*

- In this work, we attempt to provide a generalized approach for characterizing the magnitude of zero-point vibration in one-component crystals (consisting of one type of atoms) as a function of temperature. Given that the bonding geometry of each atom is identical, we can show the existence of a characteristic temperature,  $T_0$ , at which the atomic zero-point vibration and the excited vibrations are of the same magnitude. Below  $T_0$ , zero-point vibration plays a dominant role. Within the Debye model, we are able to establish a simple relation that  $T_0 \sim 1/3 \theta_D$ , with  $\theta_D$  being the Debye temperature. Calculations based on first-principles show that, for the materials with a high Debye temperature, the zero-point vibration is important not only at low temperatures, but also at the room temperature.

## Literature. New theory and new models.

1. Zero point motion effect on the electronic properties of diamond, trans-polyacetylene and polyethylene.
2. Ab-initio study of the effects induced by the electron–phonon scattering in carbon based nanostructures.

- *1. E. Cannuccia, A. Marini, European Physical Journal B 85, 320 (2012)*

It has been recently shown, using ab-initio methods, that bulk diamond is characterized by a giant band–gap renormalization induced by the electron–phonon interaction. This result casts doubt on the accuracy of purely electronic calculations. In this work we show that in polymers, compared to bulk materials, due to the larger amplitude of the atomic vibrations the real excitations of the system are composed by entangled electron–phonon states. We prove as the charge carriers are fragmented in a multitude of polaronic states leading, inevitably, to the failure of the electronic picture. The presented results lead to a critical revision of the state–of–the–art description of carbon–based nanostructures, opening a wealth of potential implications.

- *2. E. Cannuccia, A. Marini, <http://arxiv.org/abs/1304.0072> (2013)*

In this paper we investigate from first principles the effect of the electron-phonon interaction in two paradigmatic nanostructures: trans-polyacetylene and polyethylene. We found that the strong electron-phonon interaction leads to the appearance of complex structures in the frequency dependent electronic self-energy. Those structures rule out any quasi-particle picture, and make the adiabatic and static approximations commonly used in the well-established Heine Allen Cardona (HAC) approach inadequate. We propose, instead, a fully ab-initio dynamical formulation of the problem within the Many Body Perturbation Theory framework. The present dynamical theory reveals that the structures appearing in the electronic self-energy are connected to the existence of packets of correlated electron/phonon states. **These states appear in the spectral functions even at  $T=0K$ , revealing the key role played by the zero point motion effect.** We give a physical interpretation of these states by disclosing their internal composition by mapping the Many Body problem to the solution of an eigenvalue problem.

## Literature. New theory and new models.

### Mechanically induced metal–insulator transition in carbyne

Vasilii I. Artyukhov, Mingjie Liu, Boris I. Yakobson, *arXiv: 1302.7250v2, 1 Nano Lett.*, **14**, 4224–4229, DOI: 10.1021/nl5017317 (2014).

- First-principles calculations for carbyne under strain predict that the Peierls transition from symmetric cumulene to broken-symmetry polyynes structure is enhanced as the material is stretched. Interpretation within a simple and instructive analytical model suggests that this behavior is valid for arbitrary 1D metals. Further, numerical calculations of the anharmonic quantum vibrational structure of carbyne show that zero-point atomic vibrations alone eliminate the Peierls distortion in a mechanically free chain, preserving the cumulene symmetry. The emergence and increase of Peierls dimerization under tension then implies a qualitative transition between the two forms, which our computations place around 3% strain. Thus, zero-point vibrations and mechanical strain jointly produce a change in symmetry resulting in the transition from metallic to insulating state. In any practical realization, it is important that the effect is also chemically modulated by the choice of terminating groups. Our findings are promising for applications such as electromechanical switching and band gap tuning via strain, and besides carbyne itself, they directly extend to numerous other systems that show Peierls distortion.

## Literature. New theory and new models.

**Bond alternation in infinite periodic polyacetylene: Dynamical treatment of the anharmonic potential.** Bruce S. Hudson, Damian G. Allis  
*Journal of Molecular Structure*, 1032 (2013) 78-82

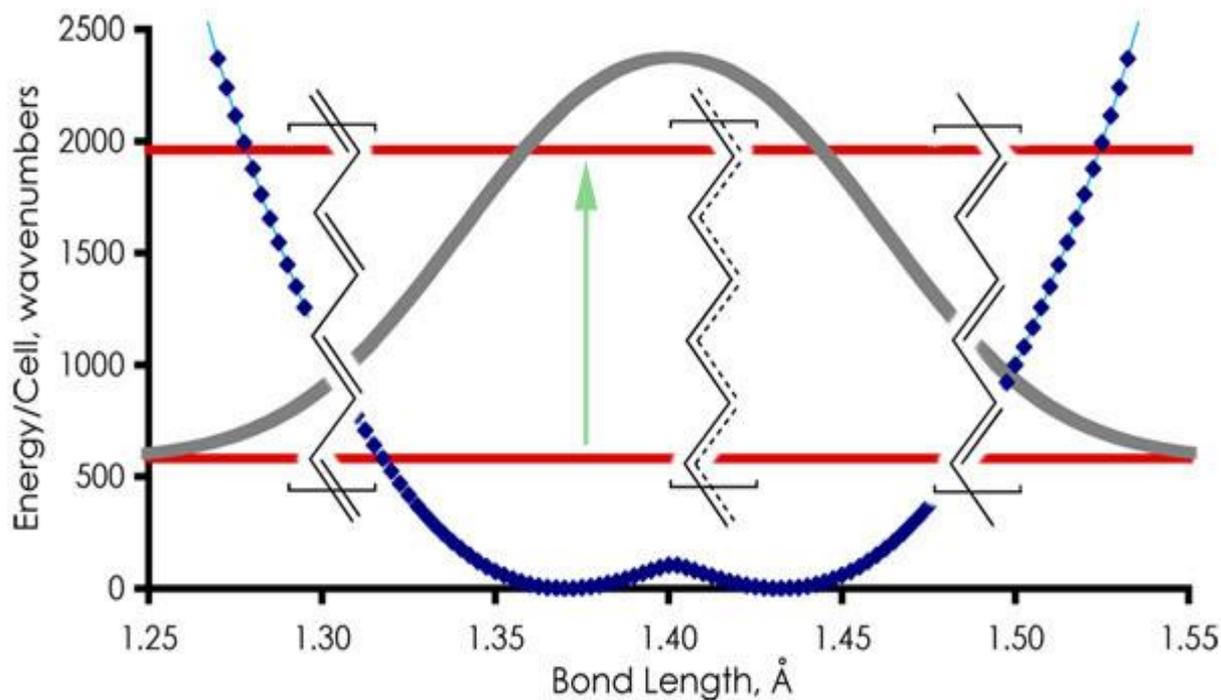
- The potential energy of the infinite periodic chain model of polyacetylene (pPA) is symmetric with two equivalent minima separated by the Peierls' stabilization barrier. In this work it is shown how an energy scale and vibrational energy levels for this highly anharmonic Peierls' degree of freedom can be estimated. Particular attention is given to the potential energy increase for large deformations. Two empirical methods and direct periodic boundary condition (PBC) density functional theory (DFT) calculations are in semi-quantitative agreement with each other. **Each lead to the conclusion that pPA has a zero-point level that is above the Peierls' barrier.** The argument does not depend critically on the barrier height or the other parameters of the model or the computation method. It is concluded that pPA will not exhibit bond alternation since two stable structures are not possible due primarily to the stiffness of the underlying CAC sigma bond system.

## Literature. New theory and new models.

### Bond alternation in infinite periodic polyacetylene: Dynamical treatment of the anharmonic potential. Bruce S. Hudson, Damian G. Allis

*Journal of Molecular Structure, 1032 (2013) 78-82*

May go down in history as a hardest-fought paper acceptance. In a similar line of research as the [\[18\]-annulene study](#), but exploring the infinite limit of geometry and bond length alternation energy barrier for this infinite case. If the numbers are correct, the infinite polyene chains ([polyacetylene](#)) do not exhibit bond length alternation because the [Peierls' barrier](#) between the single-double and double-single bond alternate minima is below the vibrational zero-point level. Plenty of ramifications.



## Literature. New theory and new models.

Superconductivity, Superfluidity, and Zero-point Oscillations

(Russian Edition) April 20, 2015, Amazon by [B. V. Vasilev](#)

- Superfluidity and superconductivity, which can be regarded as superfluidity of the electron gas, are related phenomena. Looking at these phenomena as a consequence of ordering zero-point can construct theoretical mechanisms which distinctive feature obtain estimates for the critical parameters of the systems in question, are in satisfactory agreement with the measured data. As a result, the first manages to show that the basis of two related phenomena, such as superconductivity and superfluidity is a single physical mechanism - regulation of zero-point oscillations. This book, although it contains many formulas, written, as it seems to the author, in plain language and is focused on a fairly wide range of readers-from high school students to professional scientists who are interested in these phenomena.

## Literature. New theory and new models.

Superradiant control of  $\gamma$ -ray propagation by vibrating nuclear arrays

Xiwen Zhang and Anatoly A. Svidzinsky

arXiv:1310.0087v1 30 Sep 2013

- The collective nature of light interactions with atomic and nuclear ensembles yields the fascinating phenomena of superradiance and radiation trapping. We study the interaction of  $\gamma$  rays with a coherently vibrating periodic array of two-level nuclei. Such nuclear motion can be generated, e.g., in ionic crystals illuminated by a strong driving optical laser field. We find that deflection of the incident beam into the Bragg angle can be switched on and off by nuclear vibrations on a superradiant time scale determined by the collective nuclear frequency  $\Omega a$ , which is of the order of terahertz. Namely, if the incident  $\gamma$  wave is detuned from the nuclear transition by frequency  $\Delta \gg \Omega a$  it passes through the static nuclear array. However, if the nuclei vibrate with frequency  $\Delta$  then parametric resonance can yield energy transfer into the Bragg deflected beam on the superradiant time scale, which can be used for fast control of  $\gamma$  rays.

## Literature. New theory and new models.

Ultrafast band-gap oscillations in iron pyrite

Brian Kolb and Alexie M. Kolpak

PHYSICAL REVIEW B 88, 235208 (2013)

Herein we use fully self-consistent *GW calculations coupled* to density functional theory (DFT) to examine the effect of phonons on the band gap of pyrite. We find that the sulfur-sulfur distance plays a pivotal role in determining the band gap of the material and that phonons that change this distance create an oscillating band gap on an ultrafast timescale. The magnitude of the effect depends on temperature and other environmental conditions but it is predicted to create deviations of up to  $\pm 0.27$  eV from the average band gap at room temperature. We stress that this is an effect at a given temperature, distinct from the ubiquitous alteration of the band gap with changing temperature that is well known in semiconductor physics. The effect establishes a significant oscillation of the band gap at room temperature which persists, **through zero point motion, even at 0 K.**

# Literature. New theory and new models. Quantum effect on thermally activated glide of dislocations

Laurent Proville, David Rodney and Mihai-Cosmin Marinica

Nature Materials Letters, PUBLISHED ONLINE: 12 AUGUST 2012 | DOI: 10.1038/NMAT3401

- Crystal plasticity involves the motion of dislocations under stress. So far, atomistic simulations of this process have predicted Peierls stresses<sup>1</sup>, the stress needed to overcome the crystal resistance in the absence of thermal fluctuations, of more than twice the experimental values, a discrepancy best-known in body-centred cubic crystals 2–4. Here we show that a large contribution arises from the crystal zero-point vibrations, which ease dislocation motion below typically half the Debye temperature. Using Wigner's quantum transition state theory 5,6 in atomistic models of crystals, we found a large decrease of the kink-pair formation enthalpy due to the quantization of the crystal vibrational modes. Consequently, the flow stress predicted by Orowan's law 7 is strongly reduced when compared with its classical approximation and in much closer agreement with experiments. This work advocates that quantum mechanics should be accounted for in simulations of materials and not only at very low temperatures or in light-atom systems.

# Conclusion.

## Approximation for materials scientists.

Approximation Born and Oppenheimer, Peierls theorem for 1D materials and Peierls model of crystal plasticity are the three parts of old fundament for theoretical description electronic structure and properties of conjugated materials. Calculations from the first principles are the first part of new fundament.

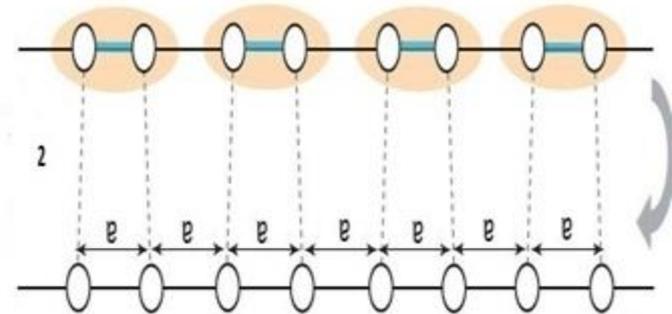
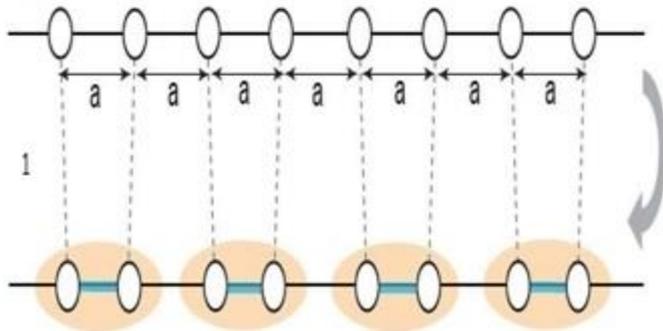
Calculation from the first principles for single-component crystals and conjugated polymers such as polyacetylene and carbyne showed that zero-point energy for defect-free systems can withstand thermal fluctuations and Peierls instability of these systems at temperatures below  $1/3$  of the Debye temperature and leads to the inverse Peierls transition in one-dimensional and quasi-one-dimensional systems.

The calculations of electronic structure of one-dimensional systems by methods of molecular orbitals which do not take into account the motion of the nuclei.

The one-dimensional chain with aligned bonds is unstable. Peierls transition - metal - semiconductor - insulator.

The calculations of electronic structure of one-dimensional systems by methods from the first principles.

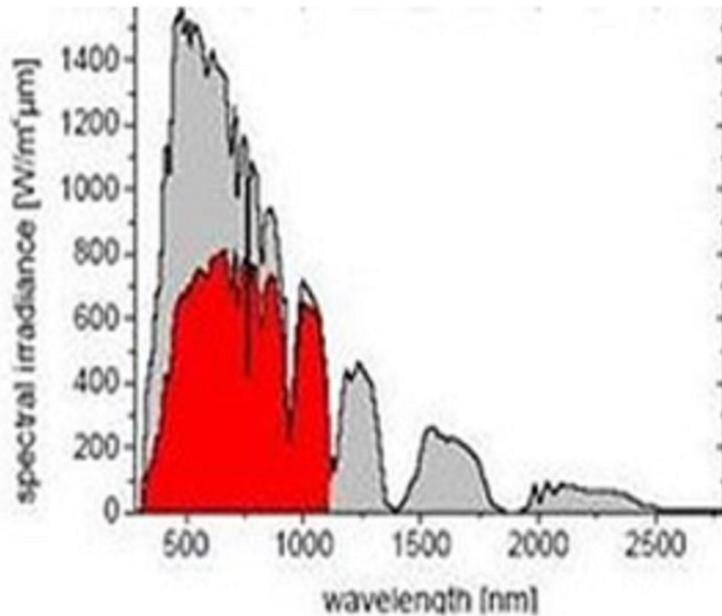
The one-dimensional chain with aligned bonds is stable (in the absence of stable defects). Peierls transition - insulator - semiconductor - metal - Bose condensate.



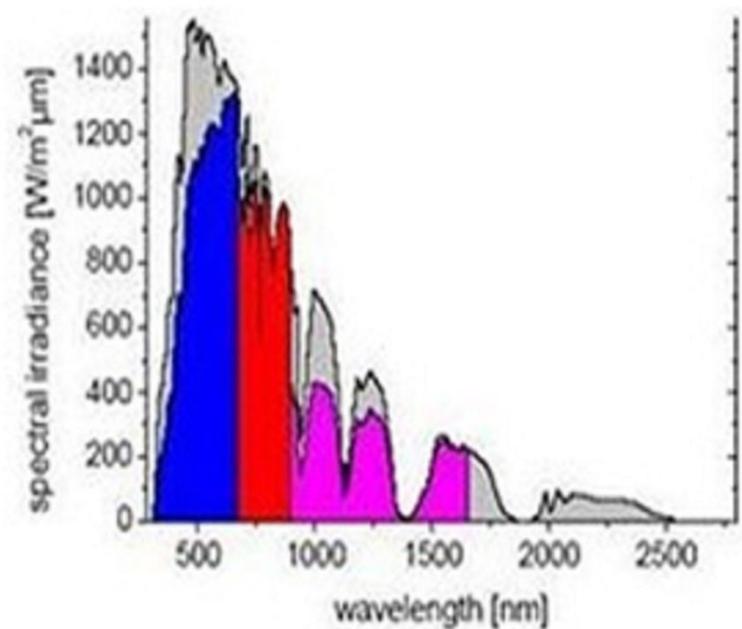
# Applications of conjugated polymers and carbon materials with low concentration of defects.

- High efficiency ( $> 40\%$ ) organic solar cells.
- High efficiency and high performance OLEDs.
- High efficiency FETs.
- Highly stable flexible transparent electrodes.
- High capacity ionic capacitors.
- High efficiency piezo transducers.
- High sensitivity sensors.
- Solid-state lasers based on coherent medium.

# Standard inorganic solar cells based on **Si** structure and **Ga** Geterostructures

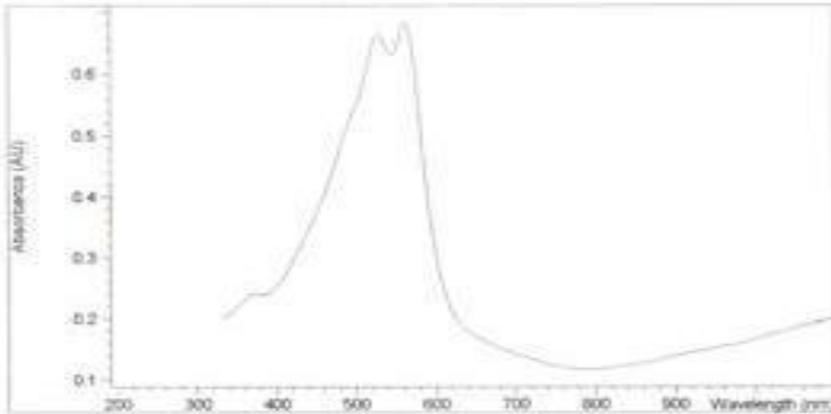


The part of solar spectrum converted by: Si.

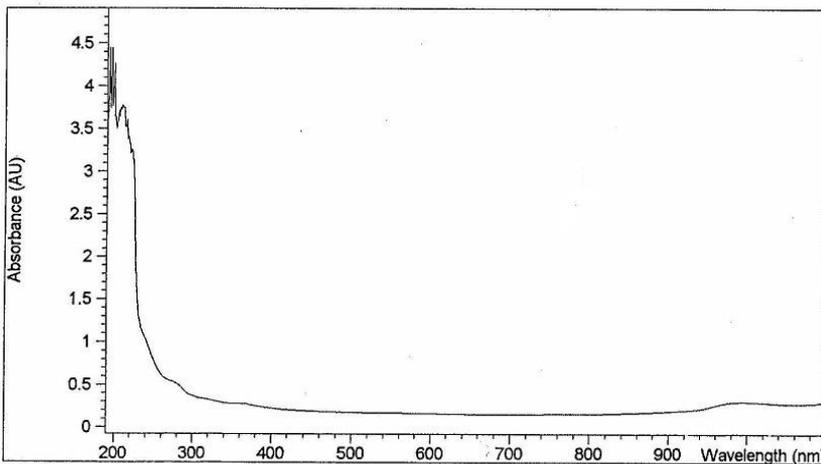


The parts of solar spectrum converted by three different heterostructures: GaInP, GaInAs, Ga.

# New type of (organic-inorganic) heterostructure solar cells. UV-Vis-NIR Spectra of nanopolyacetylene doped with non-oxidizing protonic acids.

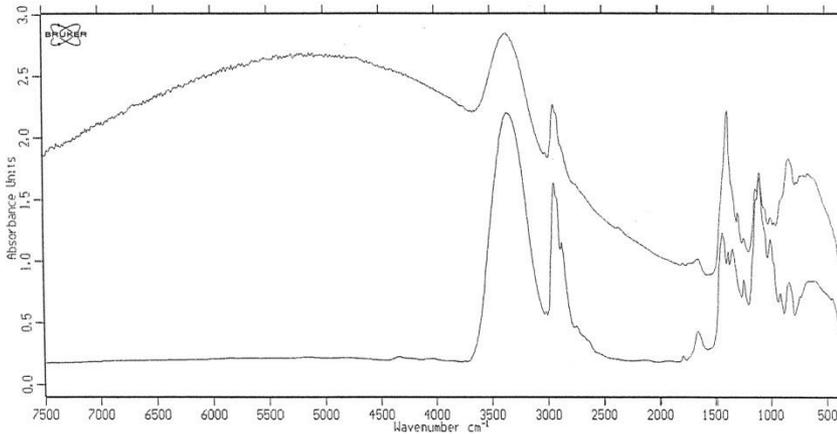


The HCl doped 50% cis- 50% trans-nanopolyacetylene gel (viscous solution). Concentration of HCl in gel - 0.1%. Interaction time 6 second. One can see from the picture, that interaction lead to disappearance of absorption band of trans-nanopolyacetylene and appearance of absorption in near IR field. **(first example).**

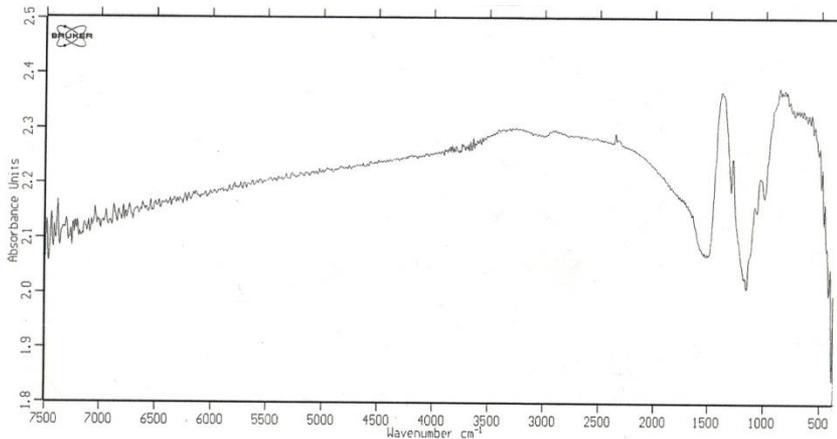


Optical absorption spectra of HCl doped 100% trans- nanopolyacetylene film. The film thickness - 150 mkm. Experiment: 10 mkl of 20% HCl is applied to the film surface area of 2 square centimeters. After 24 hours doping films are characterized by transparency window in the field 300 – 800 nm. Films can be used as chemical sensors and flexible plastic electrodes.

# New type of (organic-inorganic) heterostructure solar cells. FTIR spectra of nanopolyacetylene doped with non-oxidizing protonic acids.



FTIR spectrum of 100 microns thickness nanopolyacetylene film doped by 10% solution of hydrochloric acid. Time of doping is 24 hours. One can see from the spectrum, that doping of nano-polyacetylene film lead to appearance of absorption band in NIR field with maximum 5000  $\text{cm}^{-1}$ .

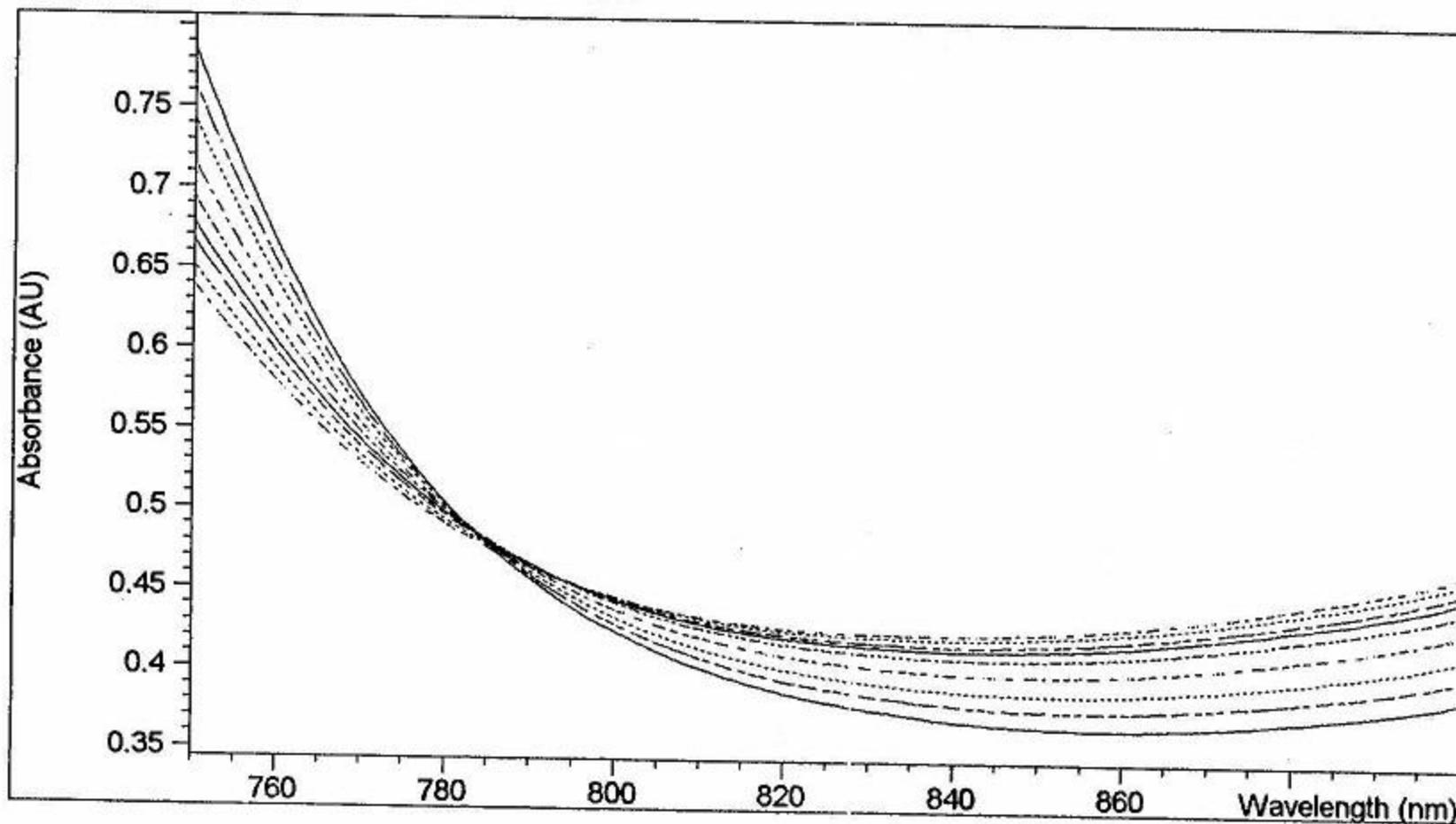


FTIR spectrum of 100 microns thickness nanopolyacetylene film doped by mixture of 10% solution of hydrochloric acid + 10% solution of three fluoroacetic acids.

**Spectrum is characteristic for materials with metallic conductivity. The film is stable in air and retains the optical characteristics for many months. (first example).**

# Doping of 100% trans- nano- polyacetylene by 10% hydrochloric acid in solution.

## Isosbestic point.



## New application (new future) of conjugated polymers and carbon materials with very low concentration of defects.

It is shown today that some of the 1D conjugated materials and carbon materials with very low concentration of defects can demonstrate inverse Peierls transition “semiconductor – metal”. I can demonstrate effect of inverse Peierls transition in any laboratory with standard optical equipment. The only we should sign protocol about intentions.

I believe that inverse Peierls transition of 1D conjugated system is accompanied by a coherent high-frequency oscillation of band gap, which induced by giant zero-point coherent oscillations. Application of 1D conjugated materials with very low concentration of defects is associated with:

- 1) high temperature superconductivity,
  - 2) high temperature super diamagnetism,
- and with "giant" long-range interactions in:
- a) effects of quantum tunneling;
  - b) effects of quantum entanglement;
  - c) Josephson effect;
  - d) Casimir effect;