Xth INTERNATIONAL CONFERENCE ON MOLECULAR SPECTROSCOPY

From Molecules to Molecular Materials and Biological Systems

Organized by

Faculty of Materials Science and Ceramics, AGH - University of Science and Technology, Kraków, Poland

Faculty of Chemistry, University of Wrocław, Poland

Institute of Low Temperature and Structure Research of the Polish Academy of Sciences, Wrocław, Poland

Kraków – Białka Tatrzańska
6 - 10 September 2009
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WELCOME

Dear Colleagues,

I wish to welcome all participants to the jubilee Xth Conference on Molecular Spectroscopy which will be held in Białka Tatrzańska, 20 km from Zakopane about 100 km from Kraków in the picturesque Tatra Mountains. The conference is organized by Faculty of Materials Science and Ceramics of AGH-University of Science and Technology – Kraków in cooperation with Faculty of Chemistry, University of Wrocław and Institute of Low Temperature and Structure Research of the Polish Academy of Sciences – Wrocław.

As usual, the conference topics are focused on wide range of molecular spectroscopy but connected with molecular biological system and molecular materials. During the conference will be presented 14 invited lectures, contributions to the conference will be presented as a oral (25 presentation) or as posters (70 presentation). All presented papers are related to applications of spectroscopic and quantum mechanical methods to the study of:

- Structural and physical properties of molecules;
- Molecular materials and materials engineering;
- Molecular biological systems;
- Noncovalent interactions;
- Molecular recognition.

I do hope that you will find the scientific program of Xth International Conference on Molecular Spectroscopy: From Molecules to Molecular Materials and Biological Systems interesting and the contacts with spectroscopists from different country will be fruitful and enjoyable in beautiful Tatra Mountains.

Welcome to Białka Tatrzańska

[Signature]

Professor Miroslaw Handke
Chairman of the Xth ICMS Scientific Committee
History of ICMS

Ist National Conference on Molecular Spectroscopy with International Participation,
Vibrational Spectroscopy and Structure of Molecular Systems
Wrocław, 28 - 30 October 1991
Participants: 81, Lectures: 27, Posters: 62.

IInd National Conference on Molecular Spectroscopy with International Participation
Spectroscopy of the Solid State, Liquid Crystals, Phase Transitions and Related Phenomena
Wrocław, 27 - 30 September 1993
Participants: 84, Lectures: 37, Posters: 55.

IIIrd National Conference on Molecular Spectroscopy with International Participation
Spectroscopy of Molecular Interactions, Molecular Recognition and Related Phenomena
Wrocław – Przesieka, 7 -10 December 1995

IVth National Conference on Molecular Spectroscopy with International Participation
From Molecules to Molecular Materials: The Role of Molecular Interactions and Recognition
Wrocław – Polanica Zdrój, 28 September - 1 October 1997
Participants: 90, Lectures: 28, Posters: 51.

Vth International Conference on Molecular Spectroscopy
From Molecules to Molecular Biological Systems and Molecular Materials:
The Role of Molecular Interactions and Recognition
Wrocław – Łądek Zdrój, 26 - 30 September 1999
Participants: 88, Lectures: 30, Posters: 81.

VIth International Conference on Molecular Spectroscopy
From Molecules to Molecular Biological Systems and Molecular Materials:
The Role of Non-covalent Interactions and Molecular Recognition in Supramolecular Systems
Wrocław – Łądek Zdrój, 29 September – 3 October 2001
Participants: 105, Lectures: 30, Posters: 81.

VIIth International Conference on Molecular Spectroscopy
From Molecules to Molecular Biological Systems and Molecular Materials:
The Role of Molecular Interactions and Recognition
Wrocław – Łądek Zdrój, 11 - 14 September 2003
Participants: 149, Lectures: 38, Posters: 115.

VIIIth International Conference on Molecular Spectroscopy
From Molecules to Molecular Biological Systems and Molecular Materials:
The Role of Molecular Interactions and Recognition
Wrocław – Łądek Zdrój, 13 - 16 September 2005

IXth International Conference on Molecular Spectroscopy
From Molecules to Molecular Biological Systems and Molecular Materials:
The Role of Molecular Interactions and Recognition
Wrocław – Łądek Zdrój, 12 - 16 September 2007
Participants: 110, Lectures: 28, Posters: 98.
CONFERENCE PROGRAMME

Sunday 6.09.2009

1500  Lunch

1800  Opening Ceremony

1815  Henryk Ratajczak (Poland)
      *International Conference on Molecular Spectroscopy - past, present and future*

1900 – 2200  Get Together Party

Monday 7.09.2009

7 30 – 900  Breakfast

900  L-01  Stefan Jurga, Jacek Jenczyk, Monika Makrocka-Rydzyk, Aleksandra Wypych, Stanisław Głowinkowski (Poland)
      *Dynamics and structure of diblock copolymers studied by NMR, Rheology and Broadband Dielectric Spectroscopy*

945  L-02  M. Drozdowski, P. Ziobrowski, K. Łapsa, E. Andrzejewska, A. Marcinkowska (Poland)
      *Polymerizable two-component systems: Brillouin Scattering study*
1030  
L-03  Marek W. Urban (USA)  
*From Heterogeneous Polymer Networks to Self-Repairing Materials*

1115 – 1155  
Coffee break

1200  
O-01  Agnieszka Sozańska  
*New techniques for Raman spectroscopy: fast imaging and nano-chemical analysis*

1220  
O-02  M. Magdalena Szostak, Urszula Okwieka (Poland)  
*Spectroscopic and structural consequences of a methyl group presence in optically nonlinear 2-methyl-4-nitroaniline crystals*

1240  
O-03  Mia Melavuori, Jan Lundell (Finland)  
*Vibrational spectroscopy of formic acid dimers: a computational approach*

1300  
O-04  Adriana Olbert-Majkut, Jussi Ahokas, Mika Pettersson, Jan Lundell (Poland)  
*Formic acid in matrices: Raman studies and photochemistry*

1400  
Lunch

1500  
L-04  S. Bratos, M. Wulff, H. Ihee (France)  
*X-ray filming of the birth of a new molecule*

1545  
L-05  James R. Durig, Arindam Ganguly, Joshua J. Klaassen (USA)  
*Microwave, Infrared and Raman determinations of the ro structural parameters, conformational stability and vibrational assignments of mono-substituted cyclobutanes*

1630 – 1655  
Coffee break
1700 – 1900 Poster session

1900 Dinner

Tuesday 8.09.2009

7 30 – 900 Breakfast

900 L-06 Halina Abramczyk, Jakub Surmacki, Piotr Ciacka, Beata Brozek-Pluska, Joanna Jablonska, Radzislaw Kordek (Poland)
Primary femtosecond events and quantum coherences in biological systems: bacteriorhodopsin, lipid membranes, and human breast cancer tissue.

945 L-07 Giorgio Tosi (Italy)
Microimaging FT-IR of Head and Neck Tissues. Are cysts tumors?

1030 O-05 Piotr Bruździak, Rafał Piątek, Beata Zalewska-Piątek, Janusz Stangret (Poland)
Structure and stability of fimbrial proteins – FT-IR studies

1050 O-06 M.I. Oshtrakh, I.V. Alenkina, O.B. Milder, V.A. Semionkin (Russia)
Mössbauer spectroscopy with high velocity resolution in the study of iron containing proteins and model compounds

1120 – 1155 Coffee break
1200  
**O-07**  F. Partal Urena, J.R. Aviles-Moreno, J. Lopez Gonzales (Spain)  
*Application of vibrational spectroscopies (IR, Raman, VCD) and quantum chemical calculations to the study of the conformational landscape and self association of biological molecules: terpenes*

1220  
**O-08**  T. Peña Ruiz, A. Drzewiecka, M. Fernández Gómez, A. E. Koziol, (Spain)  
*Structural studies on Kv1.3 potassium channel blockers: visnaginone and khellinone*

1240  
**O-09**  N. Kudryasheva, N. Belogurova (Russia)  
*Spectral components in coelenterate bioluminescence and photoluminescence of Ca$^{2+}$ discharged photoproteins*

1300  
**O-10**  M. Szafrań, P. Barczyński A. Katrusiak, Z. Dega-Szafrań, K. Stanek, (Poland)  
*1-carboxyethylpyridinium-4-carboxylate studied by X-ray, FTIR and NMR spectroscopy and DFT calculations*

1400  
**Lunch**

1500  
**L-08**  Zdzisław Latajka (Poland)  
*Modern quantum chemistry methods as powerful tools for materials science*

1545  
**L-09**  Austin Barnes (Great Britain)  
*Strongly hydrogen-bonded systems studied by vibrational spectroscopy*
Perturbation of Hydrogen Bond Network of Hydroquinone Crystal by Xenon Guest Atoms. Is it Prototypic Mechanism for Anesthetic Action of Xenon Gas?

Combined NMR/UV-Vis Spectroscopy of Short OHO and OHN Hydrogen Bonds in Polar Aprotic Solvents

Coffee break

Vibrational spectroscopic studies of DMPU/water system

Photoinduced long-distance intramolecular hydrogen transfer via molecular crane

Analysis of the H-F stretching band profile in absorption spectra of complexes of HF with water, acetone and dimethyl ether in the gas phase. Experiment and theory

Quantum dot-based energy transfer

Dinner
Wednesday 9.09. 2009

7 30 – 900  Breakfast

900  L-10  Augusto Marcelli (Italy)
Synchrotron radiation IR micro-spectroscopy, a unique powerful molecular probe for time resolved imaging experiments at high spatial resolution: status and perspectives

945  L-11  Howell G.M. Edwards (Great Britain)
Raman spectroscopy of extremophiles from terrestrial hot and cold deserts to the exomars mission to Mars

1030  O-17  A. Wesełucha-Birczyńska, Ł. Natkaniec-Nowak, M. Słowakiewicz, L.M. Proniewicz
Raman microspectroscopy of organic inclusions in spodumenes from Nilaw (Nuristan, Afghanistan) (Poland)

1050  O-18  E. Mikuli, M. Liszka-Skoczylas, J. Szklarzewicz (Poland)
FT-IR and differential scanning calorimetry study of the phase transition in [Mn(NH3)6](NO3)2

1110 – 1135  Coffee break

1140  O-19  A. Bródka, Ł. Hawełek, A. Burian, T.W. Zerda (Poland)
Nanodiamonds at elevated temperatures – molecular dynamic simulation study
12:00  **O-20**  Pavel Matejka, M. Vyskovska, H. Korenkova, A. Kokaislova, V. Prokopec, M. Clupek (Czech Republic)
*Surface-enhanced spectroscopic methods on metal nano-surfaces*

12:20  **O-21**  Jens B. Simonsen, Bartosz Handke, Zheshen Li, Preben J. Møller (Denmark)
*A study of the interaction between semi-large organic compounds and the TiO$_2$ (110)(1x1) surface – based on XPS, UPS and NEXAFS measurements and DFT calculations*

12:40  **O-22**  V. Videnova-Adrabińska, M. Wilk, (Poland)
*Crystal engineering and structural modifications of novel inorganic – organic hybrid materials*

13:00  **Lunch**

14:00 – 15:30  **Poster Session**

16:00 – 19:00  **Visit in the Geothermal Complex in Bukowina Tatrzańska**

20:00 – 20:00  **Conference Dinner**

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**Thursday 10.09. 2009**

7:30 – 9:00  **Breakfast**

9:00  **L-12**  Rui Fausto (Portugal)
*Conformational cooling in matrix isolation*

9:45  **L-13**  Zofia Mielke, Barbara Golec, Małgorzata Mucha, Adriana Olbert-Majkut (Poland)
*The effect of molecular complexation on photochemical reactions in cryogenic matrices.*
10:30 - 10:45  **Coffee break**

10:50  **O-23**  Anatoliy Yaremko, V.O. Yukhymchuk, V.M. Dzhagan (Ukraine)
*Spectroscopy study of exciton-phonon interaction in organic and semiconductor quantum dots*

11:20  **O-24**  Piotr Drożdżewski (Poland)
*Selected problems of experimental and theoretical support for vibrational band assignment*

12:00  **O25**  M. Biczysko, J. Bloino, V. Barone (Italy)
*Noncovalent interactions in the gas phase: new insights from experimental and computational spectroscopy*

12:30  **Closing Ceremony**

13:00  **Lunch**

15:00  **Departure to Kraków**
INVITED LECTURES
Xth ICMS – Kraków – Biały Tatrzański, 6-10 September 2009
L-01

DYNAMICS AND STRUCTURE OF DIBLOCK COPOLYMERS STUDIED BY NMR, RHEOLOGY AND BROADBAND DIELECTRIC SPECTROSCOPY

Jurga Stefan, Jenczyk Jacek, Makrocka-Rydzyn Monika, Wypych Aleksandra, Glowinkowski Stanislaw

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Block copolymers are under intense experimental and theoretical studies due to their current and potential applications. Properties of these systems depend on individual blocks characteristics and on the interaction between the components [1]. The immiscible polystyrene (PS) and polyisoprene (PI) systems exhibit the ability to self-organize by microphase separation. The investigated PS-b-PI diblock copolymers (SI) nearly symmetric in composition, consist of polystyrene and polyisoprene chain blocks having molecular weight of 11500 and 10500 g/mol (SI1), and of 45000 and 46000 g/mol (SI2), respectively.

NMR, Rheology and BDS studies were applied to characterize molecular motions in copolymers and their neat components. We have observed various motions in a wide frequency range, namely: (i) segmental motions which correspond to the glass transition processes for both PI and for PS parts of copolymer, (ii) normal mode motions of PI chains, which involve the fluctuations of the end-to-end vector and (iii) rotation of methyl groups.

Flexible (PI) and stiff (PS) domains in copolymer influence mutually their molecular dynamics. As a result the increase of the glass transition temperatures (T_g) for PI chains and decrease of T_g for PS chains for both copolymers was observed [2]. Moreover, the distribution of relaxation times connected with the glass transition process was broader than for neat components and more pronounced for the copolymer of higher molecular weight. It is assumed that these changes result from mutual interactions of tethered chains, since PS blocks make spatial confinement for PI chains motion, whereas the moving PI chains act as plasticizer for PS blocks. The sizes of PS domains of 9 nm and 19 nm for SI1 and SI2 copolymers, respectively, were determined by NMR spin diffusion experiment [3]. These values compare well with other measurements [4, 5].

Acknowledgements

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References

POLYMERIZABLE TWO-COMPONENT SYSTEMS:
BRILLOUIN SCATTERING STUDY

M. Drozdowski,¹ P. Ziobrowski,¹ K. Łapsa,¹ E. Andrzejewska², A. Marcinkowska²

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Recently, many attention has been paid to the study of the photocurable compositions, which can be widely used in industrial applications. The physical properties of two-component systems, such as: monomer/monomer, monomer/polymer, and monomer/ionic liquid and their curing process are the subject of many investigations, since their knowledge allows to design conditions for industrial processes.

This contribution reviews the results obtained by us for such two-component systems using differential scanning calorimetry (DSC) and Brillouin scattering method.

The monomers can be polymerized, either as individual compounds or as the mixture of two or more components. The polymerization course of the mixture of two monomers highly depends on the feed composition. It may result from changes in the system viscosity as well as from intermolecular interactions between monomers which, in turn, depend on their molar ratio.

The mechanism of the processes occurring during the polymerization process and their kinetic parameters can be deduced from kinetic curves obtained at various experimental conditions.

One of the methods used also successfully in the investigations of the monomers and their polymerization process is Brillouin scattering.

The physical parameters characteristic for the systems composition being under study, such as velocity $V$, attenuation coefficient $\alpha$ of acoustic waves, adiabatic compressibility $\beta$, real $M'$ and imaginary $M''$ parts of elastic modulus can be estimated from Brillouin spectra.

The obtained results can be discussed in terms of the influence of the system composition and viscosity on its elastic properties before and during the polymerization process.

Using Brillouin spectroscopy, the study of the influence of the system viscosity on the molecular dynamics of the mixtures, such as relaxation processes taking place on the picoseconds time scale can be also realized.

Acknowledgements:

This work was supported in part by Research Projects of Poznan University of Technology: BW 64-032/2009 and DS 32 – 061/2009.
Considerable challenges and recent interests are the developments of heterogeneous polymeric solid materials that maintain useful functions and, at the same time, are capable of self-repairing under various conditions. The presence of heterogeneous regions at nano- and microscales facilitates localized structural variations enabling favorable spatial and energetic conditions for macromolecular segments to respond to external stimuli. While Brownian molecular motions can be easily overcome in solutions, energetic and spatial restrictions are significantly more severe on materials surfaces and in the bulk. To achieve stimuli-responsive properties in solids it is necessary to design networks that are heterogeneous, but contain long-range organized structural features along a polymer backbone (M.W.Urban, Prog. Polym. Sci., 2009). These generalized concepts were utilized to synthesize heterogeneous colloidal dispersions that upon coalescence form polymeric films that exhibit simultaneous response to temperature, pH, light, or mechanical deformations. Along the same lines, a new generation of thermosetting polymer networks containing energetically favorable substitute pending groups was designed and developed to provide self-healing and repairing characteristics. One example
are reactions of hexamethylene diisocyanate (HDI) and polyethylene glycol (PEG) in the presence of oxetene-modified chitosan which maintain useful polyurethane properties, but upon mechanical damage and exposure of the damaged area to UV light, result in self-healing (B. Ghosh and M.W. Urban, Science, 2009, 323(5920), 1458). This is the first example of polymer networks where the exposure to the sunlight may repair mechanical and other damages in polymeric coatings.
X - RAY FILMING OF THE BIRTH OF A NEW MOLECULE

S. Bratos\(^{(1)}\), M. Wulff\(^{(2)}\), H. Ihee\(^{(3)}\)

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One of the most powerful methods of monitoring atomic motions during a chemical reaction is time-resolved x-ray diffraction. We recently applied this technique to study the recombination of laser dissociated iodine atoms in liquid CCl\(_4\). These motions were followed up to times of the order of 200 ps, and many details concerning dynamics of this process were detected. Unfortunately, this research did not permit to visualize the birth of the new I\(_2\) molecule. In fact, the ultimate contact between the two atoms takes place in times of the order of 10 ps, and we did not dispose of x-ray pulses shorter than 200 ps. A considerable effort was thus necessary to realize our project. The pulse duration was reduced from 200 to 100 ps, and techniques of spectral deconvolution were used; the latter were transferred from optical spectroscopy to time-resolve x-ray diffraction. Moreover, a special procedure was invented to separate the scattering from the iodine atoms from that due to the solvent atoms. Fruit of all these efforts, we were finally able to “see” the birth of a new I\(_2\) in CCl\(_4\) in real time. The resulting films are presented, interpreted and are discussed in some detail.
The cyclobutane molecule is puckered in the ground vibrational state which results from the steric forces being larger than the ring strain forces. The structural parameters of cyclobutane have been determined from a microwave investigation of four different deuterated isotopomers and the puckering angle was determined [1] to be 28.58(9)°. Prior to this study only the structural parameters of the equatorial chlorocyclobutane had been reported [2] from a microwave study but the reported A rotational constants were found to differ significantly from those obtained from adjusted parameters from \textit{ab initio} predicted values [3]. However from a more recent microwave investigation of both the equatorial and axial conformers of chlorocyclobutane [4] it has been possible to obtain the complete structural parameters [5] from the revised rotational constants of the equatorial conformer along with those for axial conformer combined with those obtained from the \textit{ab initio} MP2(full)/6-311+G(d,p) calculations. By utilizing the \textit{ab initio} predicted parameters in combination with previously reported microwave rotational constants for a number of mono-substituted cyclobutanes it has been possible to obtain complete r\textsubscript{0} structural parameters for bromocyclobutane, fluorocyclobutane, cyclobutylamine and cyanocyclobutane. All of these molecules have at least two conformers present at ambient temperature. By variable temperature infrared investigations of rare gas solutions [6] the enthalpy differences have been determined after confident vibrational assignment have been made by using \textit{ab initio} predicted frequencies, infrared band contours and intensities, along with Raman activities and depolarization values. By using far infrared and low frequency Raman spectra of the gases it has been possible to obtain the potential function governing the conformational interchange for many of these molecules. A comparison of the different values of the heavy atom structural parameters and the barrier to inversion and enthalpy differences about these molecules will be provided. These values will be also compared to those predicted from various quantum chemical calculations. The other substituted cyclobutane where structural information was reported [7] from a microwave study was cyclobutanol where the parameters obtained for chlorocyclobutane and methanol were transferred. By utilizing the six reported rotational constants from the normal and O-d isotopomers it was possible to obtain [8] complete structural parameters since the carbon-hydrogen distances could be transferred from the \textit{ab initio} MP2(full)/6-311+G(d,p) predicted values [9]. These initial parameters were later shown [10] to be within experimental errors of those obtained from a more extensive structural determination of O-d, α-13C, β-13C, γ-13C and 18O isotopomers of cyclobutanol.
References


†Taken in part from the thesis of Arindam Ganguly, which will be submitted to UMKC in partial fulfillment of the Ph.D. degree.
Ultrafast spectroscopy has played an important role in the study of a number of biological processes and has provided unique information about primary events and the role of quantum coherences. Biological activity of molecules is frequently initiated by elementary chemical reactions such as energy and electron transfer, cis-trans isomerizations, and proton transfer. The nature of these reactions generally makes them very fast and efficient, occurring on picosecond and femtosecond timescales.

First, we review the current understanding of light-energy collection and the primary light-initiated reactions of the biological photoreceptors and the role of long-lasting quantum coherences. As an example illustrating the ultrafast dynamics we present our recent results on primary events upon light excitation in bacteriorhodopsine (BR) and its retinal modified analogs 1-2. Recently we proposed the theoretical model 1 to explain the primary events in BR immediately upon light excitation up to the K species formation. The model is based on the linear and nonlinear formalism. We have applied the model of vibrational coupling which simply means that the electronic and nuclear vibrational degrees of freedom cannot be separated. Using the formalism for the hole burning case (as opposite to the homogeneous bleaching) we calculated the hole burning profiles for the coupling with the most important retinal vibrations. The vibrational coupling shifts the maximum of absorption from near IR to VIS depending on the frequency of the vibrational mode. The primary accepting mode is the high frequency C=C stretching mode and is responsible for the stimulated emission observed in near IR and excited state absorption (ESA) at 460 nm. The coupling with the HOOP vibration is responsible for the J-625 absorption whereas the coupling with the torsional motion is responsible for the equilibrium electronic absorption spectrum of BR. According to the proposed mechanism the H, I, J and K intermediates do not represent different electronic species or different structures. They simply represent the same electronic transition coupled to the different vibrations.

We then briefly describe recent advances in the elucidation of the dynamics of energy dissipation in lipid membranes. We will present energy dynamics at the water/lipid interface by femtosecond infrared (IR) two-color and bleaching pump-probe experiments investigating vibrational relaxation dynamics of C-H stretch modes in the lipid alkyl chains of 2,3-Dipalmitoyl-snglycero-1-phosphocholine (DPPC) and O-H stretch mode of water for a controlled humidity of the sample.
Finally, we will focus on the role of carotenoid molecules in photostability of the biological human tissue. We will illustrate the mechanism with our recent results on the normal and malignant breast human tissue by Raman spectroscopy\textsuperscript{3-6}.

Acknowledgement

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References


L-07

MICROIMAGING FT-IR OF HEAD AND NECK TISSUES
ARE CYSTS TUMORS?

Giorgio Tosi

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Recent advances in technology have brought a near-revolution in the application of vibration-al spectroscopy in the biomedical field. At this regard, infrared spectroscopy, based on characteristic molecular vibrational spectra of cells, may have the potentiality to detect early transformations before morphological changes can be visualized by light microscope.

In particular, spectroscopic imaging in combination with multivariate data analysis, results in high biochemical and adequate spatial information giving an objective analysis which could coadivuate classical histopathological and immuno-histochemical screening. The identification of molecular markers can be helpful to define those neoplasms responsible for an aggressive clinical behaviour.

From the mid 90’s by means of infrared spectroscopy, we have been exploring breast, colon and mainly, head and neck specimens, for highlighting possible links between cells and in vi tro/ex vivo human tissues pathological states[1-3].

This lecture will deal with the application of infrared spectroscopy in the study of the following head and neck pathologies:
- oral cavity carcinomas of tongue, gingiva, floor, cheek mucosa (squamous cell carcinoma, mainly)[1];
- in the case of squamous cell carcinoma of the tongue, a spectroscopic comparison between cultured cells, inoculated and excised tissues[2];
- benign and malignant tumour of salivary glands [3];
- odontogenic cysts lesions with the aim to add insights on their potential tumorigenic character[4].

References
Nowadays the advanced quantum chemical methods are very widely applied in study and design of new materials. First-principle methods enable one to study the electronic and geometrical structure of molecular systems as accurately as possible with modern computational effort. Moreover, using \textit{ab initio} molecular dynamics methods, which calculate the forces exerted on atoms at each time step of simulation, one can calculate the evolution of atomic and electronic motions without assuming empirical parameters.

In order to design new chemicals with desired properties it is important to understand the nature of chemical bonds for some model systems. In recent years very powerful tool for theoretical analysis and interpretation of chemical bonds is an approach called generally as Quantum Chemical Topology (QCT). In the framework of QCT, which contain several theoretical formalisms, two methods are especially popular among chemist: theory named as Atoms in Molecules (AIM) and topological analysis of Electron Localization Function (ELF). Not going into details, the ELF is a relative measure of electron localization associated with the spherically averaged conditional same-spin pair probability density and therefore is very interesting theoretical tool for study of nature of chemical bonds. In recent years very attracting approach to study the nature of chemical bond is topological analysis of the Electron Localizability Indicator (ELI).

In the lecture, analysis of the nature of chemical bonds for MONO (where M = Li, Na, K) molecules using the topological analysis of ELF and ELI methods will be presented. Studied molecules although very simple are important in materials science because e.g. NaNO$_2$ is one of the well known ferroelectrics. Moreover, some examples of recently discovered protocovalent bond will be discussed, which constitute a new class bond family distinct from the covalent and ionic bonds.

One of the most famous nanometerscale materials are fullerenes. Although the number of papers devoted to fullerenes is large and growing rapidly, only a small proportion concerns fullerene oxides. Unlike the C$_{60}$ molecule, C$_{70}$ has five non-equivalent carbon atom types, which leads to eight non-equivalent C-C bonds. There are therefore at least eight \textit{a priori} possible isomers of C$_{70}$O. A series of \textit{ab initio} calculations have been carried out to determine the stability of different isomers of mono-oxides and mono-ozonides of C$_{70}$. On the basis of density functional theory method calculations and Born-Oppenheimer molecular dynamics we will present a mechanism for the thermally induced dissociation of C$_{70}$O$_3$. It is interesting to note that the first two steps of studied process is identical with the general mechanism for ozonolysis of alkenes proposed by Criegee.
STRONGLY HYDROGEN-BONDED SYSTEMS STUDIED
BY VIBRATIONAL SPECTROSCOPY

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The well known shift of the XH stretch to lower frequency and the increase of its infrared intensity in hydrogen-bonded systems are of electronic origin and are related to the change of electronic structure of the hydrogen-bonded system. However, the band shape represents a particularly complex problem and should be related to the dynamics of the X–H···Y system. A great deal of effort has been made over the past 60 years to understand the complex infrared absorption profiles of hydrogen-bonded stretching bands in gas, liquid and solid phases with many theories being proposed. In recent years it has been recognised, both theoretically and experimentally, that the shape of the XH stretching absorption is generated mainly by mechanical anharmonic coupling between the high frequency, \( \nu(XH) \), and low frequency, \( \nu_s(XHY) \) and \( \delta(XHY) / \gamma(XHY) \), vibrational modes of the hydrogen bond X–H···Y. In condensed phases, the system is further coupled to the thermal bath.

However, for medium-strong and strong hydrogen bonds, one must take into account an additional mechanism in the generation of the complex shape of the XH stretching band profile, namely Fermi resonances between the \( \nu(XH) \) stretching mode and some other internal modes. Recently it has been shown that in strongly coupled systems Fermi resonances generate complicated shapes with sub-structure. In principle, on the basis of these approaches, it is possible to understand the origin of the complex shapes of the XH stretching bands and to reproduce them semi-quantitatively.

The influence of these various factors on profiles of XH stretching absorptions of strongly hydrogen-bonded systems will be illustrated with examples drawn both from isolated complexes (trapped in low-temperature inert matrices) and solid state systems (such as the potassium hydrogen maleate crystal).
SYNCHROTRON RADIATION IR MICRO-SPECTROSCOPY, A UNIQUE POWERFUL MOLECULAR PROBE FOR TIME RESOLVED IMAGING EXPERIMENTS AT HIGH SPATIAL RESOLUTION: STATUS AND PERSPECTIVES

A. Marcelli

Fourier-transform infrared (FTIR) synchrotron radiation (SR) micro-spectroscopy is a powerful molecular probe of samples at high temporal and spatial resolution that probes the rotations and the vibrations of molecules, the low-energy excitations of solids and many other phenomena occurring in condensed matter physics, chemistry, biophysics and materials science.

The incredible performances of non-thermal SR sources are witnessed by the results obtained in different research areas and the continuously increasing number of users in the existing facilities all around the world. Since the brilliance of a SR source is 100-1000 times higher than conventional sources also in the IR region of the SR emission we observed in the last three decades a continuous increase of beamlines and users. The high source brilliance of SR (defined as the photon flux or power emitted per source area and solid angle) enables FTIR microscopy and imaging to be performed within a few minutes at the resolution of a few microns so that SR may provide much better performances than any conventional source. Because also of the lack of thermal noise the superior signal-to-noise ratio achievable combined with its high brilliance, SR guarantees the achievement of spatial resolution down to the diffraction limit, or to allow working on thick samples while maintaining the ultimate spatial resolution. FTIR micro-spectroscopy experiments are non-destructive methods that can be applied to metallic, semiconductor or insulator systems and to biological samples returning accurate information on vibrational and phonon spectra as a function of external parameters such as temperature or pressure. For all these reasons FTIR microscopes are now available in almost all advanced SR facilities where samples can be now investigated on the scale of minutes.

I will present examples of experiments that may experience a great advantage by using IR SR sources in particular and unique applications of IR SR such as time-resolved spectroscopy and imaging. Indeed SR has a time structure that ranges from hundreds of ps to ns, e.g., comparable with the time of molecular vibrations and several times faster than conformational changes or protein folding phenomena. With new array detectors the possibility to investigate protein processes in real time and in their native environments is now possible both in the mid- and far-IR regions. I will show how with the use of a high current (>1.2 A) low energy storage ring, a dedicated detector set up and a slight defocusing of the IR source, it is possible to collect IR images of individual cells at high sensitivity and high spatial resolution within a few minutes. Actually, an optimal coupling between a SR-IR source and a FTIR imaging instrumentation equipped with a small FPA detector may really push the existing limits towards a “real time” imaging of single-cell phenomena and to the opportunity to perform time-resolved experiments of many other chemical-physical processes.
L-11

RAMAN SPECTROSCOPY OF EXTREMOPHILES FROM TERRESTRIAL HOT AND COLD DESERTS TO THE EXOMARS MISSION TO MARS

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The survival strategies of extremophilic organisms such as lichens and cyanobacterial colonies in terrestrially stressed locations and habitats are critically dependent upon the production of protective chemicals in response to desiccation, low wavelength radiation insolation, temperature and the availability of nutrients [1]. The adaptation of life to these harsh prevailing conditions involves the control of substratal geology; the interaction between rock and the organisms is critical and the biological modification of the geological matrix plays a very significant role in the overall survival strategy [2,3]. The identification of these biological and biogeological chemical molecular species in the geological record is necessary for the recognition of the presence of extinct or extant life in terrestrial and extraterrestrial scenarios.

The Raman spectroscopic technique has been identified as valuable instrumentation for the detection of life extraterrestrially because of its use of non-destructive laser-based excitation of organic and inorganic molecules with a high discriminatory capability. The interactions effected between biological organisms and their environments are detectable through the molecular entities produced at the interfaces for which the vibrational “fingerprints” are unique. A very important attribute of Raman spectroscopy is the lack of sample preparation required in order to interrogate the specimen; this has been a major factor in the proposal for the adoption of Raman instrumentation on robotic landers and rovers for planetary exploration, particularly in the forthcoming ESA ExoMars mission [4].

In this paper, the merits of using Raman spectroscopy for the recognition of key molecular biosignatures from several terrestrial extremophile specimens will be illustrated. The data and specimens used in this presentation have been acquired from the Arctic and Antarctic cold deserts, a meteorite crater, ancient stromatolites and from a hot desert saltpan evaporite location. From these examples, novel information can be acquired about several survival strategies that are adopted by terrestrial extremophiles using Raman spectroscopy and the potential of the technique for the detection of extraterrestrial biosignatures as part of instrumentation aboard a remote robotic lander or planetary rover vehicle can be assessed.

References

CONFORMATIONAL COOLING IN MATRIX ISOLATION

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For matrix-isolated compounds, accessible thermal processes are in principle restricted to low energy barrier reactions (a few kJ mol\(^{-1}\)) since the work temperature is very low. However, conformational changes are frequently observed thermal processes in matrices. Three different basic situations are possible: (i) the conformational barriers are high enough to prevent any reaction, the gas-phase conformational distribution is preserved in a deposited matrix and no reactions are observed upon annealing the matrix at higher temperatures; (ii) there are very low (below 1 kJ mol\(^{-1}\)) energy barriers that can be easily surmounted even at the matrix temperature. This leads to establishment of a true equilibrium between conformers in the matrix and the trapped conformational distribution strongly differs from the gas phase. Annealing the matrix produces reversible conversion, and higher temperatures increase the population of higher energy conformers; (iii) the energy barriers are intermediate (a few kJ mol\(^{-1}\)) and partial conformational conversion can take place during deposition; hence the matrix population of the conformers differ from the gas phase with the increased population of the more stable conformers. Annealing the matrix to a higher temperature leads to conversion of higher energy conformers to lower-energy forms.

The complexity is even greater because the matrix environment can perturb the potential energy landscape, change the relative energy of the conformers and the barriers, or even create or destroy specific conformational states, so that the knowledge of the gas phase potential energy surface may not be enough to predict the experimental results in a solid matrix.

In this talk I will discuss some notorious examples of molecular systems where conformational cooling is of fundamental importance in a matrix isolation experiment, from cases where the most abundant conformers in the gas phase could not be observed in the low temperature matrices, to cases where conformational cooling selects a single conformer among several dozens existing with significant populations in the gas phase at room temperature. Media effects on conformational cooling will also be addressed.

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THE EFFECT OF MOLECULAR COMPLEXATION ON PHOTOCHEMICAL REACTIONS IN CRYOGENIC MATRICES

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FTIR spectroscopy combined with matrix isolation technique provides a unique experimental methodology for studying reaction mechanisms in solid materials. The low temperature inert host environment stabilizes intermediates and traps the products. However, the reactions in matrices often proceed along photochemical pathways that are not observed in liberated gas phase or in solutions. This effect occurs most often in the case of bimolecular photoreactions when the reactants form molecular complexes or aggregates. The formation of hydrogen bonded complexes particularly affects the photochemistry of the system.

We have studied the photochemistry of a number of hydrogen bonded complexes of atmospheric relevance by help of FTIR matrix isolation spectroscopy. The reactions photoproducts were identified by isotopic studies and by comparison of the experimental IR spectra with the MP2/6-311++G(2d,2p) calculated ones for the possible reactions photoproducts.

The photochemical behaviour of the following complexes trapped in argon or nitrogen matrices is overviewed:

- HONO\(\cdots\)C\(_2\)H\(_2\)Cl\(_2\), HONO\(\cdots\)CH\(_2\)NOH
- CHOCHO\(\cdots\)CH\(_3\)OH, CHOCHO\(\cdots\)H\(_2\)O\(_2\), CHOCHO\(\cdots\)NH\(_2\)OH.

The photochemistry of the above systems involves different types of reactions: addition (HONO\(\cdots\)C\(_2\)H\(_2\)Cl\(_2\), CHOCHO\(\cdots\)H\(_2\)O\(_2\), CHOCHO\(\cdots\)NH\(_2\)OH), hydrogen abstraction (HONO\(\cdots\)CH\(_2\)NOH) and rearrangement (CHOCHO\(\cdots\)CH\(_3\)OH, CHOCHO\(\cdots\)NH\(_2\)OH).

The opening of new photoreaction paths in matrices allowed us to obtain the unique products like hydroxyketene.
ORAL PRESENTATIONS
NEW TECHNIQUES FOR RAMAN SPECTROSCOPY: FAST IMAGING AND NANO-CHEMICAL ANALYSIS

Agnieszka Sozańska

Raman spectroscopy has become an important tool for material science, forensic, gemology, pharmacy, medicine etc. providing crucial information to experimentalists working in the fields of semiconductor, ceramics, composite materials, polymers, biomolecules. The unique confocal and spatial resolution of micro-Raman systems enables optical far field resolution to be pushed to its limits with often sub-micron resolution achievable for chemical imaging of small structures.

Conventional Raman spectroscopy is limited to a spatial resolution on the micron scale. The next step is to break diffraction limit using a combination of Raman spectroscopic analysis with near field optics and Atomic Force Microscopy (AFM). The combination of both techniques enables nanometric topographical information to be coupled to chemical information. The unique design of this instrumentation enable researcher to explore a new and evolving techniques such as nanoRaman spectroscopy based on the TERS (tip enhanced Raman spectroscopy) and SERS (surface enhanced raman spectroscopy).

The ability to create chemical and compositional images by acquiring Raman spectra from an array of positions and then processing them to reveal the parameters of interest is a powerful technique. New approaches to Raman imaging have been developed that enhance the capabilities of modern Raman instruments.

In comparison to other techniques like fluorescence imaging or NIR, Raman imaging was seen as rather slow method. A new method ‘Streamline’ (patent pending) let us obtaining high quality Raman images with unprecedented acquisition speeds. Spectra are collected in parallel, rather than in series using the traditional methods. Shorter total acquisition times result, with high quality individual spectra recorded in the order of fifty milliseconds. The method also benefits from ‘on the fly’ data analysis resulting in real time image creation. Geological, pharmaceutical, biological and materials examples will be shown to illustrate the benefits of this method.
O-02

SPECTROSCOPIC AND STRUCTURAL CONSEQUENCES
OF A METHYL GROUP PRESENCE IN OPTICALLY NONLINEAR 2-METHYL-4-NITROANILINE
CRYSTALS

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The low-temperature (5K) emission spectra of the 2-methyl-4-nitroaniline (MNA) crystals have been quite different from those of the parent 4-nitroaniline (p-NA) compound. As the reason, the planar conformation of the MNA molecule in the excited state in contrast with the non-planar one of p-NA has been proposed [1]. The room temperature X-ray structure redetermination as well as the UV-Vis-NIR, FT-IR, IINS and Raman spectra analysis have revealed other differences between MNA and p-NA crystals: numerous CH..O, CH..C and CH..HC short contacts and the intermolecular charge transfer. The paramagnetic species detected by the EPR method have been the cause of the large bands in the NIR region of the MNA spectra [2]. The variable temperature FT-IR spectra and the solid state 1H-NMR relaxation T1 time and second moment of line records have evidenced the dynamical disorder in the MNA crystals above 100K.

The findings from the quoted papers [1-3] and the information about chirality induced by crystallization of achiral organic compounds [4] inspired us to measure the circular dichroism spectra of the MNA solution in CHCl3 and of the solid MNA. The results of the measurements and of the previous data will be discussed in terms of the role of the methyl group substituent towards intra and intermolecular charge transfers and optically nonlinear properties of the MNA crystal.

O-03

VIBRATIONAL SPECTROSCOPY OF FORMIC ACID DIMERS:
A COMPUTATIONAL APPROACH

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Formic acid (HCOOH) is the simplest organic acid exhibiting rotational isomerism, and it exists in two planar structures: the trans and cis conformers with H-C-O-H dihedral angles 180° and 0°, respectively. The trans-form is the most stable and the predominant one in the gas phase, while the higher-energy cis-form has been hard to characterise spectroscopically due to its fast tunneling relaxation into the more stable form. 1 Formic acid is also found to readily engage into intermolecular interactions that act as small models for many processes including the science of life.

We have applied quantum chemical calculations to study the structural, energetical and vibrational properties of trans-trans, trans-cis and cis-cis formic acid dimers. Especially, we are interested to provide adequate predictions of the vibrational spectra of dimer species that could be realised in solid noble gas matrices based on the previous knowledge of the trans-trans dimers in solid argon, laser activation of the higher-energy cis-form of formic acid monomer 2 and the very recent observation of the first trans-cis dimer in solid argon. 3

In this work, we will present computational results for the infrared and Raman spectra of formic acid dimers, as well as discuss the predicted anharmonic effects.

References

Formic acid (FA) is the smallest carboxylic acid that is of considerable interest in atmospheric chemistry and in biological context. It is one also of the simplest models for rotational isomerism as FA exhibit in two planar structures. The trans-form is the most stable and predominant one in the gas phase. The higher-energy cis-form has been recently characterized by means of IR matrix isolation technique as a product of fundamental, combination or first overtone IR-pumping of the trans-FA isomer. In turn, cis-FA converts to trans-FA via dissipative proton tunneling through the torsional barrier, which limits its lifetime.

Five dissociation pathways are possible in the photolysis of formic acid. Three of them proceed via radical- and two via molecular channels. However, in an Ar matrix environment only CO + H2O and CO2 + H2 elimination channels have been observed and the respective molecular complexes have been identified by IR spectroscopy.

Formic acid is also found to readily engage into intermolecular interactions. It can and has been found to form a variety of hydrogen bonded structures including self-association. The most stable trans-trans FA dimer is a cyclic structure of C2h symmetry that consists of an eight-membered ring with two equivalent C=O…H-O hydrogen bonds. Recently, the family of trans-trans formic acid dimers have been added with the first mixed trans-cis FA dimer.

Here, we present new insight into the spectroscopy, photochemistry and molecular interactions of formic acid. For the first time the Raman spectroscopy has been used to study formic acid and its dimers isolated in a low temperature matrix. This approach reveals new information on the centrosymmetric FA dimer, for which especially new spectroscopic observations in the intermolecular spectral region is acquired.

It is also demonstrated that in matrix isolation conditions, the unstable cis-form can be efficiently produced by excitation of high overtone states (6←0) of the trans-FA by visible radiation. The experimental arrangement applied allows us to use the same laser source for simultaneous overtone-pumping and Raman excitation. Simultaneously, Raman spectroscopy can be applied on the photoproducts. Here, particular interest is awakened when the photoproducts of the decarboxylation channel CO2+H2 are probed.

References

STRUCTURE AND STABILITY OF FIMBRIAL PROTEINS – FT-IR STUDIES

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The \textit{dra} operon is responsible for Dr fimbriae expression on the cell surface of uropathogenic \textit{Escherichia coli} causing pyelonephritis. One of its elements is a \textit{draE} gene encoding structural component of fimbriae – DraE protein. The \textit{draD} gene encodes DraD invasin, protein responsible for internalization into the epithelial cells. Both proteins share similar structural topology that enables to classify them as Ig-like proteins superfamily members. Although the sequence similarity of those proteins is low, the 3D-structure is surprisingly similar.

This presentation is focused on spectroscopic aspects of our collaboration. The Fourier Transform Infrared Spectroscopy (FT-IR) is powerful technique, widely used to study the secondary structure of proteins. The use of FT-IR allowed to draw many conclusions concerning structure and stability of examined proteins. High structural similarity between these proteins let us verify some assignments of characteristic bands of particular structures. The use of second derivative spectra allowed us to observe changes in the amide I’ band during temperature increase. In this way, structure and thermal stability of DraE protein monomer with structure and stability of native Dr fimbriae and DraD invasin were compared.

The main band most often used to analyze the FT-IR data is the so called amide I, corresponding almost entirely to the C=O stretching vibrations of polypeptide backbone (1600 – 1700 cm\textsuperscript{-1}). Due to structural constrains the vibration at frequencies of individual secondary structures are slightly different, making it possible to determine the structural composition of particular protein. The main problem of protein FT-IR spectroscopy consists in water subtraction from the measured spectrum of a sample. Even if D\textsubscript{2}O is used as a solvent there is sometimes a necessity of isolation of pure protein spectrum. The presented routine shows how to isolate it from the series of spectra and how to obtain valuable information without water subtraction, especially in the case of relatively low concentration samples.
MÖSSBAUER SPECTROSCOPY WITH HIGH VELOCITY RESOLUTION IN THE STUDY OF IRON–CONTAINING PROTEINS AND MODEL COMPOUNDS

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Iron-containing proteins are vitally important in the living systems. They realize oxygen, electron and iron transport, oxygen and iron storage, enzyme functions, etc. Therefore, the knowledge about structure-function relationship in these proteins is very important for understanding the features of its variations in normal and pathological cases. The presence of iron in these proteins permits to apply Mössbauer spectroscopy for analysis of iron electronic structure role in functional features of proteins. There is a long experience of the applications of Mössbauer spectroscopy in biophysical [1–5] and biomedical [6–9] research. These studies used Mössbauer spectroscopy with low velocity resolution (measurements in 512 channels or less). However, improving of velocity resolution may be very useful to increase the quality and accuracy of measurements. An increase of velocity resolution leads to less experimental error in determination of hyperfine parameters (this allows to distinguish small variations of parameters) as well as to more reliable fitting of complicated spectra. In this work we demonstrate the results of the study of hemoglobins, ferritin and its pharmaceutically important models as well as ferritin in tissues, etc. in normal and some pathological cases using Mössbauer spectroscopy with high velocity resolution (measurement in 4096 channels with further spectra presentation in 1024, 2048 and 4096 channels). The obtained results demonstrated new possibilities to reveal small variations of iron electronic structure in iron-containing proteins due to natural variety and pathological changes.

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APPLICATION OF VIBRATIONAL SPECTROSCOPES (IR-RAMAN-VCD) AND QUANTUM CHEMICAL CALCULATIONS TO THE STUDY OF THE CONFORMATIONAL LANDSCAPE AND SELF-ASSOCIATION OF BIOLOGICAL MOLECULES: TERPENES

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Terpenes are one of the main groups of secondary metabolites in nature and show a great diversity in structure and activity. In particular, Monoterpenes are components of citrus fruits, olive oil, etc. They show antitumor, antimicrobial and antioxidant activities [1,2,3]. In addition, they are atmospheric pollutants [4]. From this point of view, a deep knowledge of the molecular structure and possible conformers of this type of compounds would be desirable.

In the literature, works dealing with the vibrational study of terpenes are scarce. In the present work, a study of the molecular and possible supramolecular structures of R-(+)-Limonene(1), S-(-)-Perillyl alcohol(2), S-(-)-Limonene oxide(3), S-(-)-Perillaldehyde(4), and (1R,2S,5R)-(-)-Menthol(5) is presented.

For this task, a systematic and detailed study has been carried out starting from a theoretical investigation of the molecular structures, possible conformers and rotamers and the relative abundance of them in the gas phase, according to the Boltzmann’s distribution at the DFT/B3LYP/cc-pVDZ (DFT/B3LYP/6-31+G(d) for H-bonded alcohol oligomers). Later, IR, Raman and VCD spectra were recorded and the interpretation of them was done taking into account the most stable rotamers and using the Scaled Quantum Mechanical Force Field (SQMFF) methodology by Pulay et al. [5] in the vibrational analysis.

STRUCTURAL STUDIES ON Kv1.3 POTASSIUM CHANNEL BLOCKERS: VISNAGINONE AND KHELLINONE

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A large variety of biological and biomedical applications of khellinone and visnaginone has been known for long. Recent studies reveal the usefulness of such chemicals in the treatment of autoimmune diseases due to their ability for blocking the potassium channel kv1.3 of the T-cells that is involved in cells proliferation.

It has been proved by SAR studies that the methoxy groups in positions 4 and 7 for khellinone, and 4 for visnaginone (Figure 1), play a key role for noncovalent linking of those compounds (and their derivatives) to the Kv1.3 potassium channel. Thus, we determined the Total Energy Surface for the rotation of the methoxy groups within the isolated molecule approximation and by simulation of the systems in water solution at human body temperature with the IEFPCM model. Several theoretical approaches involving the density functional and \textit{ab initio} methods along with an assortment of basis sets have been tested vs the experimental solid-state X-ray structural data and the vibrational (IR and Raman) spectrum. On average B3LYP/6-31G* provides the best results.

As a result two possible conformations have been obtained from the theoretical calculations (Figure 2, khellinone); the most stable one is that with the methoxy group on C4 quasi-coplanar to the benzofuran ring. The second conformer exhibits a torsion angle for the methoxy group around 70°. Since the barriers of rotation are just in the limit of free rotation at room temperature (RT), or even lower, only the most stable conformer is observed in the vibrational spectrum.

![Figure 1.](image)

![Figure 2.](image)

Figure 1. Structure of visnaginone and khellinone. Figure 2. TES for rotation of –OCH₃ on C4.
SPECTRAL COMPONENTS IN COELENTERATE BIOLUMINESCENCE AND IN PHOTOLUMINESCENCE OF Ca\(^{2+}\)-DISCHARGED PHOTOPROTEINS

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Ca\(^{2+}\)-regulated photoproteins are responsible for bioluminescence of marine coelenterates. The photoprotein is a stable enzyme-substrate complex consisting of: a single polypeptide chain (near 20 kDa, containing three EF-hand Ca\(^{2+}\)-binding consensus sequences), substrate molecules – coelenterazine (imidazopyrazinone derivative) and oxygen. The addition of calcium ions to Ca\(^{2+}\)-regulated photoproteins results in light emission. This peculiar feature of the photoproteins serves the basis for their analytical application, mainly in monitoring of intracellular biomedical processes in the presence of calcium ions [1-2]. The reaction generates a protein bound product, coelenteramide, in its excited state. The excited coelenteramide relaxes to its ground state producing blue light, with a spectrum maximum being in the range of 465 – 495 nm depending on the photoprotein type. Bioluminescent and photoluminescent spectra of products of the bioluminescent reactions (Ca\(^{2+}\)-discharged photoproteins) are complex, wide, and asymmetric.

In our work, bioluminescence spectra of photoproteins from marine coelenterates – jellyfish Aequorea victoria and hydroid Obelia longissima, and photoluminescence spectra of their Ca\(^{2+}\)-discharged photoproteins were deconvolved into spectral components. Resolution of the spectra was performed in a combined way involving the methods of (1) function increment based on Gauss distribution, (2) secondary derivative, and (3) optimization of spectral components’ parameters and minimization of divergence. Four spectral components were found in original bioluminescent and photoluminescent (excitation and emission) spectra. Spectral maxima and contributions of the spectral components into the original spectra were determined. The spectral components were attributed to four forms of coelenteramide – one unionized and three ionized forms. Contributions of spectral components into the photoluminescence spectra of Ca\(^{2+}\)-discharged obelin were found to depend on calcium concentration, but bioluminescence spectra were not. Dependence of the photoluminescence spectra on excitation (for emission spectra) and registration (for excitation spectra) wavelength have been revealed. Photoluminescence spectra of Ca\(^{2+}\)-discharged photoprotein obelin have been shown to serve as respective colored marker to monitor intracellular processes with a resource for color variation.

The differences in bioluminescence spectra and photoluminescence spectra of Ca\(^{2+}\)-discharged photoproteins is discussed with protonic environment of coelenteramide taking into consideration. Proton transfer in the first singlet electron-excited state of enzyme-bound coelenteramide molecule is considered as a reason for variation of color components in bioluminescence and photoluminescence spectra of the of Ca\(^{2+}\)-discharged photoproteins.

References

1-CARBOXYETHYLPPYRIDINIUM-4-CARBOXYLATE STUDIED BY X-RAY, FTIR, AND NMR SPECTROSCOPY AND DFT CALCULATIONS

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Betaines [≥N(CH2)nCOO−] are zwitterions (inner salts) containing quaternary ammonium or pyridinium moiety and carboxylate group separated by CH2 groups. Pyridine carboxylic acids (picolinic, nicotinic and isonicotinic) on methylation are converted into other betaines (inner salts): homarine (1-methylpyridinium-2-carboxylate), trigonelline (1-methylpyridinium-3-carboxylate) and 1-methylpyridinium-4-carboxylate and their structures have been determined by X-ray diffraction. Other interesting molecules are 1-carboxymethylpyridinium-2-carboxylate [1] and 1-carboxymethylpyridinium-3-carboxylate [2,3] and 1-carboxymethylpyridinium-4-carboxylate [4] inner salts, which are dicarboxylic betaines. In this work, we report the synthesis, crystal structure and spectral data of the 1-carboxyethylpyridinium-4-carboxylate inner salts.

The crystals are monoclinic, space group P2₁/n. The acidic proton residing on the carboxylethyl group forms a strong and asymmetric O-H−⋯O hydrogen bond of the length 2.533(2) Å with the ring of the carboxylate group of an adjacent molecule (head to tail), giving rise to a polymeric chain growing along the crystal direction [010]. There are only C-H−⋯O interactions between the chains.

In 1-carboxymethylpyridinium-4-carboxylate inner salt connection between adjacent molecules are different [4]. Each molecule is engaged in two short and asymmetric O-H−⋯O hydrogen bonds of the lengths 2.449(2) and 2.481(2) Å with two adjacent molecules through head to head and tail to tail connections.

The FTIR spectrum of 1-carboxyethylpyridinium-4-carboxylate inner salt shows a broad and intense absorption in the 1600-900 cm⁻¹ region, typical of such short hydrogen bonds. Linear
correlations between the experimental $^{13}$C and $^1$H NMR chemical shifts ($\delta_{\text{exp}}$) in D$_2$O and the GIAO/B3LYP calculated isotropic shielding tensors ($\sigma_{\text{cal}}$), $\delta_{\text{exp}} = a + b \sigma_{\text{cal}}$, are analyzed.

In β-hydroquinone – xenon crystal the guest – xenon atoms are placed inside cages pointed out by eighteen hydrogen atoms. Twelve of them, H(O), participate in two parallel hexagonal rings of coupled ⋯O-H⋯O- hydrogen bonds. The remaining six hydrogen atoms belong to the phenyl C-H groups, H(C), and are oriented into six sides of these chambers. Deuteration of the crystal changes isotopic composition of the cages: {1H(O)-12 + 1H(C)-6} → {2H(O)-12 + 1H-6} due to the substitution of the 1H(O) protons only. We treat these clathrates as model systems for monitoring of xenon interactions. Our method is based on recording and analysis of different isotopic effects due to this 1H → 2H replacement: (i) structural variations of the {H(O)-12 + H(C)-6 + Xe} clathrate (results of X-ray diffraction), (ii) variations of its selected vibrations (IR spectra) and (iii) its 129Xe NMR chemical shift (CP MAS spectra). These observations indicate weak interactions between xenon guest and protons of the OHO hydrogen bonds and disappearance of the O–H⋯Xe interactions in deuterated crystal. We discuss nature of the xenon interactions with hydroxyl protons in terms of hydrogen bonds to xenon base1,2. Perturbation of the ⋯O-H⋯O- hydrogen bond network by xenon atom is considered as prototypic mechanism of xenon anesthetic action3.

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**COMBINED NMR/UV-VIS SPECTROSCOPY OF SHORT OHO AND OHN HYDROGEN BONDS IN POLAR APROTIC SOLVENTS**

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The temperature dependencies of the spectroscopic parameters of AHB hydrogen bonds formed in polar aprotic solution are often analyzed assuming either one of the following options. a) A shift of a tautomeric equilibrium between two temperature-independent proton positions (A-H-B ⇔ A-H-B) or b) a continuous displacement of the bridging particle with temperature (A-H-B changes to A-H-B). Distinguishing between these two scenarios is especially challenging on the basis of NMR spectra, where signals could be averaged over the tautomeric states.

In this work we have attempted to go beyond the “tautomeration or continuous shift” dilemma by using the newly developed experimental setup for combined liquid-state NMR/UV-Vis measurements (see Scheme) [1]. Usage of low temperatures (down to 170 K for CD₂Cl₂ and 110 K for CDF₃/CDF₂Cl) allowed us to reach the slow molecular exchange regime, when the NMR signals of different intermolecular complexes are resolved in the NMR spectra allowing one to identify the one of interest. Usage of UV-Vis spectroscopy gave us the information about the presence of fast tautomeric proton motions within these complexes.

As objects for our study we have selected a series of anionic and neutral intermolecular complexes with OHO and OHN hydrogen bonds formed between phenols/phenolates, carboxylic acid/carboxylates and pyridines:

Analysis of the UV-Vis spectra, NMR chemical shifts and H/D isotope effects on them allowed us to separate contributions of “tautomeration” and “continuous proton shift” to the overall temperature dependence. The proton transfer pathway and structures of the complexes’ solvation shells are discussed.

VIBRATIONAL SPECTROSCOPIC STUDIES OF DMPU / WATER SYSTEM

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1,3-dimethylpropylene urea (DMPU) is an N,N’-alkylated cyclic derivative of urea. It differs from the more often encountered tetramethylurea (TMU) only by methyl group closure of the alkyl ring (Fig. 1). In spite of the expected high hydrophobicity of the molecule, DMPU is miscible with water in the whole composition range [1] and is an excellent solvent for electrolytes, often favouring unusual coordination numbers [2].

![Figure 1. Structural formulae of 1,3-dimethylpropyleneurea and tetramethylurea](image)

We have studied the hydration of DMPU in an aqueous solution by two different methods: (1) determination of the DMPU-affected HDO spectrum in an isotopically diluted D₂O/H₂O solution on the basis of FTIR spectra of moderately concentrated DMPU solutions in the OD stretching range; (2) investigation of molecular complexes in the DMPU/H₂O system on the basis of ATR FTIR spectra of solutions in the whole composition range and factor analysis.

DMPU in infinite dilution limit affects water in a manner similar to other N-alkyl substituted ureas, notably its close analogue – TMU [3]. It affects on average 8.3 HDO molecules, with the HDO band position of the affected water only slightly red-shifted from the bulk water case. The affected HDO band is, however, distinctly different in shape from the bulk HDO band, with a significantly red shifted centre of mass. This results in a more symmetric curve of the interatomic oxygen-oxygen distance probability distribution, where the population of weak hydrogen bonds is diminished in respect to the bulk water, whereas the opposite effect is observed for strong hydrogen bonds.

In the DMPU/H₂O system several molecular complexes might be detected by factor analysis techniques. Complementary results are obtained by analysing the entire spectral range covered, as well as by focusing on characteristic regions for water or DMPU. In the low water content solution series, determination of the water-affected DMPU spectrum reveals that the most probable complex in infinite dilution approximation is H₂O(DMPU)₂.

References

PHOTOINDUCED LONG-DISTANCE INTRAMOLECULAR HYDROGEN TRANSFER VIA MOLECULAR CRANE

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For 7-hydroxyquinoline-8-carbaldehyde derivatives isolated in Ar matrices, transfer of hydrogen atom from O(7)H group to the remote N(1) atom was observed to occur upon excitation with UV (λ > 295 nm) light [1]. During this process, the exocyclic carbaldehyde group plays the role of an intramolecular crane which first picks up the hydrogen from OH group and then drops it down to the N atom. Subsequent irradiation with UV of longer wavelength (λ > 360 nm) demonstrated that the photoreaction is partially photoreversible.

The structures of substrate and product of the photoreaction were identified by their IR spectra. The photophysical mechanism of the photoprocesses was modeled by calculating the potential-energy profiles of the ground state and of the lowest excited singlet state along the minimum-energy path connecting the initial and the final tautomeric forms [1,2]. The conical intersection between the ground and the excited state occurs at an approximately perpendicular conformation of the carbaldehyde moiety with respect to the quinoline ring.

This is the first experimental evidence that, in an optically driven process, hydrogen atom can be moved between two remote spots of a molecule [O(7)----N(1) distance is about 4.8 Å], with intermediacy of a functional group playing a role of molecular crane.

O-15

ANALYSIS OF THE H-F STRETCHING BAND PROFILE IN ABSORPTION SPECTRA OF COMPLEXES OF HF WITH WATER, ACETONE, AND DIMETHYL ETHER IN THE GAS PHASE. EXPERIMENT AND THEORY

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Comparative analysis of the $\nu_1$(H-F) band shape in the absorption spectra of complexes of HF with water, dimethyl ether, and acetone and the mechanisms of formation of this band is performed on the basis of experimental spectra and quantum-mechanical calculations. Particular attention is paid to the complex with acetone.

The spectra of these complexes in the region of the $\nu_1$(H-F) band were recorded with Bruker IFS-113v and Bruker IFS-125 HR vacuum Fourier spectrometers at a resolution of 0.1 cm$^{-1}$ in the temperature range 190-293 K. The first three spectral moments of the $\nu_1$(H-F) band were determined. The $\nu_1$(H-F) bands have the complicated structure in all the complexes, which facilitates comparison of the theoretical predictions with experimental data.

The spectra studied were reconstructed theoretically using the ab initio potential energy and dipole moment surfaces. The electro-optical parameters necessary for the reconstruction were obtained from variational solutions of multidimensional anharmonic vibrational problems. The anharmonic coupling of the $\nu_1$(H-F) mode to all low-frequency intermolecular modes and its effect on the $\nu_1$(H-F) band structure are considered explicitly. The spectral manifestations of the intermode coupling depend on the interplay between the H-bond strength, the barrier height for tunneling, the magnitudes of frequencies of intermolecular vibrations and rotational constants of subunits, etc. The relative positions of frequencies of the fundamental and hot transitions, as well as the relative intensities of combination bands at a given temperature can considerably vary from one complex to another. For example, in the complex with water the frequency of a hot transition involving the out-of-plane bending mode can be lower than the fundamental $\nu_1$(H-F) frequency, which is not the case in the complex with ether. The resulting theoretical spectra reconstructed as a superposition of rovibrational bands associated with the fundamental, hot, sum, and difference transitions reproduce the shape and separate spectral features of the experimental spectra. The theoretically predicted values of the $\nu_1$(H-F) fundamental transition are in good agreement with the experimental findings, for example, the $\nu_1$(H-F) frequency of 3432.8 cm$^{-1}$ in the complex (CH$_3$)$_2$CO…HF is close to the frequency of the main maximum. Among the complexes considered the intermode coupling was found to be most strong in the complex with dimethyl ether and acetone. In the latter complex the picture of intermode coupling is more complicated than in the complex with ether because of the difference in the electronic structure of the O atom.

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Here, we demonstrate the fluorescence resonance energy transfer from organic dye to gold NP’s and CdS NP’s to organic dye. A pronounced effect on the PL quenching and shortening the lifetime of the dye indicates the energy transfer. The steady state and time resolved spectroscopic analysis of nanoassemblies confirm the formation of one donor and multiple acceptors.

Förster resonance energy transfer (FRET), which involves the non-radiative transfer of excitation energy from an excited donor fluorophore to a ground state acceptor fluorophore, is a well characterized photophysical tool. Here, we demonstrate the fluorescence resonance energy transfer from organic dye to gold NP’s and CdS NP’s to organic dye. A pronounced effect on the PL quenching and shortening decay time of dye molecules are observed when dye molecules are interacting with the Au nanoparticles. The calculated distance (d) between the donor and acceptor varies from 86.06 to 102.47 Å with changing the concentration of Au and dye. Analysis suggests that the energy transfer from dye to the Au nanoparticles is the dominant by surface energy transfer and follows $1/d^4$ distance dependence. The observed quenching of PL intensities are 78.8% and 63.8% for CdS QD’s and QR’s, respectively in presence of Nile Red dye. The calculated energy transfer efficiencies are 45% and 19% from QD’s and QR’s to dye, respectively. In the present study, the estimated distance ($r$) between one donor and one acceptor are 39.1 and 43.1 Å for QD’s and QR’s, respectively, using the efficiency of FRET which depends on the inverse sixth power of the distance of separations between one nanocrystal and one dye molecule. Considering single donor and multiple acceptors interactions, the calculated average distance ($r_n$) between the donor and acceptor are 47.7 and 53.9 Å for QD’s and QR’s, respectively. The steady state and time resolved spectroscopic analysis of nanoassemblies confirm the formation of one donor and multiple acceptors.

Au nanoparticle based surface energy transfer (SET) process has been used to measure conformational changes in proteins. A significant quenching of PL intensities of tryptophan of bovine serum albumin (BSA) protein is observed in presence of Au nanoparticle, and the measured distances between the donor (tryptophan) and the acceptor (Au nanoparticle) are 27.0, 22.9 and 25.7 Å for E, N and B forms of BSA protein, respectively. Such bioconjugated Au nanoparticles should have great potentials for optical-based molecular rulers and it could pave the way for designing new optical based materials for the application in chemical sensing or biological imaging.

RAMAN MICROSPECTROSCOPY OF ORGANIC INCLUSIONS IN SPODUMENES FROM NILAW (NURISTAN, AFGHANISTAN)

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The colour varieties of spodumene (vert spodumene, kunzite) from Nilaw mine (Nuristan, Afghanistan) have been investigated by the microthermal analyses and Raman spectroscopy. These minerals are rich in primary and secondary fluid inclusions. Measured values of temperature homogenization (Th) and pressure (P) for selected fluid inclusion assemblages VI FIA in vert spodumene and V FIA in kunzite happen in the ranges 370-430°C, 1.16-1.44 kbar and 300-334°C, 0.81-1.12 kbar, respectively. The brine content and concentration varies at 4.3-6.6 wt.% eq. NaCl. Amongst the abundant and diverse mineral phases (i.e. quartz, feldspars, mica, zirconium, apatite, calcite) studied by non-destructive Raman micro-spectroscopy of particular interest are beryl inclusions (324, 397, 686, 1068 and 3610 cm⁻¹), accompanied by fluid inclusions (liquid and gaseous hydrocarbons) with bands at 2350 cm⁻¹ (CO₂, N₂), 2615 cm⁻¹ (H₂S) and 2962 cm⁻¹ (C₂H₆ - CH₃). Some inclusions contain carbonaceous matter (ca 1320 cm⁻¹) and/or graphite (ca 1600 cm⁻¹). Micro-Raman spectra of selected inclusions as well as line or rectangular maps of interesting parts in spodumenes and also depth profiles were collected to study the size and contents of it. As an example, figure below shows a complex inclusion found in vert spodumene (c - calcite, b – beryl, cb - carbonaceous matter, hc – hydrocarbons, w – OH, water).
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FT-IR AND DIFFERENTIAL SCANNING CALORIMETRY STUDY
OF THE PHASE TRANSITIONS IN [M(NH₃)₆](NO₃)₂

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Among quite big family of coordination ionic compounds of the type: [M(NH₃)₆]X₂, these of them which have X = NO₃ posses somewhat different physical properties. Up to now, we have investigated the [M(NH₃)₆](NO₃)₂ compounds with M(II) = Ni, Mg, Cd and Co [1-4]. Actually we have synthesized and investigated compound with M = Mn.

X-ray powder diffraction (XRPD) measurements indicated that [Mn(NH₃)₆](NO₃)₂ at room temperature possesses regular structure of the crystal lattice (space group Fm3m) with the lattice parameter \( a = 11.0056 \) Å and with 4 molecules in the unit cell.

Two phase transitions between 93 and 297 K, namely: at \( T_{C1}^{h} = 207.2 \) K and at \( T_{C1}^{c} = 207.8 \) K and \( T_{C2}^{h} = 160.8 \) K and \( T_{C2}^{c} = 184.4 \) K (where \( h \) denotes heating and \( c \) cooling), were detected by differential scanning calorimetry (DSC). The presence of 0.6 K hysteresis of \( T_{C1} \) and of 23.6 K hysteresis of \( T_{C2} \) suggests that the detected phase transitions are of the first-order type. Large thermal hysteresis of the phase transition at \( T_{C2} \) is just very typical for the hexaaminemetal(II) nitrates(II).

Fourier transform middle infrared spectroscopy (FT-MIR) measurements in the temperature range of 20-300 K were performed. Splitting of the infrared band connected with \( v_4(\text{NO}_3^-)E \) mode near the phase transition at \( T_{C1}^{c} \) suggests lowering of symmetry of the crystal lattice. Sudden changes in temperature dependence of the full width at half maximum of the band connected with \( \rho_\text{NH}_3(\text{NH}_3)\nu_{1u} \) mode at \( T_{C1}^{c} \) and \( T_{C2}^{c} \) suggest that these phase transitions are associated with an essential changes of the speed of the NH₃ reorientational motions.

References
NANODIAMONDS AT ELEVATED TEMPERATURES - MOLECULAR DYNAMICS SIMULATION STUDY

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The reactive empirical bond order (REBO) potential for carbon-carbon interaction [1] was used in molecular dynamics (MD) simulations of nanodiamond (nD) in the shape of a truncated octahedron (TONd) and a sphere (SnD) with diameter ranging from 3 to 9 nm. In the MD simulation we used the Evans-Hoover thermostat, which contrary to earlier applied Berendsen thermostat [2] does not generate rotations of the nanodiamond, and gives possibility to control internal temperature of the nanodiamond.

Initial calculations performed at 300 K show rebuilding of the nD surface, whereas structure of the nD interior remains almost unchanged. Additionally, MD simulations were performed at 340 K. From atom positions obtained for temperatures 300 and 340 K we calculated structure factors and then reduced radial distribution functions that were used to estimate values of the thermal expansion coefficient. The obtained results show the decrease of the coefficient with the nD size, and for larger nD the coefficient is close to the value obtained from simulation of bulk diamond [3].

To study graphitization process of the nDs with diameter of 3 nm we performed MD simulations at elevated temperatures: up to 1800 K for SnD and 1200 K for TOnD. All simulations were carried out through 7.5 ns for SnD and 5 ns for TOnD. An onion structure was observed at 1500 K for SnD and about 84% of carbon atoms had trivalent co-ordination. The process started at the surface, where fragments of quasi-spherical shells were formed, and evolved into the centre. Graphitization of TOnD appeared at 1200 K and 92% of atoms had trivalent co-ordination. In this case, bonds between [111] planes are broken easily, almost in the whole nanodiamond. For both nDs the process became faster and more effective with increasing temperature. It must be noted that structure of the graphitized nDs are irregular and separations between layers ranged from 2 to 3 Å, and they are smaller then the experimentally observed distanced.

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SURFACE-ENHANCED SPECTROSCOPIC METHODS
ON METAL NANO-SURFACES

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Surface-enhanced Raman scattering (SERS) and surface-enhanced infrared absorption (SEIRA) spectroscopies are vibrational spectroscopic methods allowing detection and identification of molecular species on nanostructured surfaces of several metals, especially coin metals (Au, Ag and Cu). To achieve required enhancement of the spectral signal a proper preparation procedure has to be tailored. This study is aimed at comparison of series of Au, Ag and Cu nanostructured materials used for either SERS or SEIRA spectroscopy.

Two groups of substrates were prepared and tested. The first group is a series of massive Pt targets with electrochemically deposited nanostructured layers of Au, Ag and Cu [1 – 3]. The individual metal layers were prepared under different current densities with the aim to test their surface morphology and SERS-activity at different excitation wavelengths varying from 488 nm to 1064 nm. Several aliphatic and aromatic thiol derivatives were used as model analytes. The results demonstrate that not only the type of metal and parameters of surface preparation procedures, but also the types of analytes affect the dependence of spectral quality on excitation wavelength.

The second group of substrates is represented by gold, silver and copper nanoparticles prepared by various chemical reduction procedures with two different reduction agents used, i.e. borohydride and citrate. The colloidal systems of nanoparticles were modified with a set of compounds either in the course of preparation procedure or immediately after preparation of nanoparticles. Not only ATR spectra were studied to detect and identify the species deposited; furthermore, the UV-visible and NIR absorption spectra were evaluated considering the optical properties of individual metal nanoparticles, the repeatability of their preparation and the stability of the systems obtained.

In both cases the repeatability of data was evaluated as a key parameter for an analytical usage of both SERS and SEIRA techniques.


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A study of the interaction between semi-large organic compounds and the TiO$_2$(110)-(1x1) surface - based on XPS, UPS and NEXAFS measurements and DFT calculations

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The presented work focuses on the interaction between the semi-large organic compounds perylene, 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP), 1,10-phenanthroline-5,6-dione (phendione) and the TiO$_2$(110)-(1x1) surface. The interaction and orientations of the organic molecules adsorbed to the TiO$_2$(110)-(1x1) surface have primarily been studied by means of ultra high vacuum (UHV) based methods such as synchrotron based photoemission spectroscopy (PES) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. A novel analysis of the valence band data of a monolayer of perylene adsorbed to the TiO$_2$ surface has been employed to show that no strong chemical interaction takes place between perylene and the TiO$_2$(110)-(1x1) surface. Furthermore, angle-dependent NEXAFS measurements and the growth curve results suggest that the perylene molecules are oriented flat down onto the TiO$_2$ substrate due to weak van der Waals interactions between perylene and the TiO$_2$ surface. In the case of the di-ortho carbonyl (phendione) and di-ortho hydroxyl (HHTP) compounds, the oxygen functionalities enable the compounds in both cases to align along the [001]-direction of the TiO$_2$(110) surface most likely due to bidentate-like coordination of the oxygens toward the Ti(5f)$^{4+}$ surface ions. This trend was elucidated from PES and NEXAFS measurements. Additionally, scanning tunneling microscopy (STM) measurements and density functional theory (DFT) calculations support the bidentate coordination fashion in the case of the phendione compound.
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CRYSTAL ENGINEERING AND STRUCTURAL MODIFICATIONS OF NOVEL INORGANIC-ORGANIC HYBRID MATERIALS

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The hybrid inorganic-organic compounds are of great interest for their potential application in chemical separation, gas sorption, sensing and catalysis [1]. For that reason numerous metal-organic carboxylates, sulfonates and phosphonates have been synthesized and studied during the last decade [2]. However, the search for new materials is not just a synthetic problem, but an engineering problem, purpose-directed at design of coordination polymers with functionalized porous or layered structures. In particular, the question of fine-tuning the material properties comes across. Therefore, finding approaches for reliable control and modification of extended metal-organic frameworks MOF is of prime importance for crystal engineers.

Here we report the recent accomplishments of our research group in a material design project based on the 3-pyridyl phosphonic acid and its 5-functionalized analogues. We discuss the synthesis and the structural arrangement of several Co(II) and Zn(II) hybrid compounds. The ligands themselves are novel, originally designed for the purposes of the project and are topologically predisposed for hydrogen-bond controlled self-recognition and self-organization in non-centrosymmetric (chiral) crystal structures.

\[ R = \text{H, COOH, PO}_3\text{H} \]

The Zn(II) compounds display extended MOFs (1D ladder or 2D layer). The overall three-dimensional organization is layered and/or porous, dependent upon the chemical nature of the R-group in 5-position on the aromatic ring and the preferences of the metal ion for a coordination geometry. On the other hand the coordination frameworks of the cobalt compounds are 0-dimensional, but the supramolecular networks are three-dimensional. The Co(II) coordination units are arranged in monolayer structures via hydrogen-bond interactions, but the organization and the connectivity patterns inside the layers are different and depend upon the chemical nature of the auxiliary R-group. It is worth to note that one of the cobalt structures appeared to be also chiral.


SPECTROSCOPY STUDY OF EXCITON-PHONON INTERACTION IN ORGANIC AND SEMICONDUCTOR QUANTUM DOTS

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Optical and structural properties of crystal nanostructures (organic and semiconductor types) are intensively studied during last two decades. It is caused both the practical aim in developing of new elements of devices and fundamental physical reasons. In such structures the space confinement influence significantly on their properties, in particular on optical ones. The important characteristic for solids and nanostructures is the electron (exciton) – phonon interaction (EPI) which describes the response of electron system of crystal on the incident electromagnetic field.

Effect of space confinement on the value of EPI in QD’s was investigated both the experimentally and theoretically. Obtained results concern to change of EPI constant are non-simple (contradictory) and there is no clear understanding of this problem. In the present communication we look on this problem once more and study it theoretically and experimentally for number of nano-dots with different size.

Response of system on EM field depends on the EPI which can be considered as week ($\beta_s < 1$) or strong ($\beta_s \geq 1$) coupling depending on the parameter $\beta_s = \chi_s / \Omega_s$, which is the ratio of the EPI constant, $\chi_s$, to the corresponding phonon frequency, $\Omega_s$. For organic type crystals and crystal with hydrogen bonds, in which the Frenkel type exciton are realized, $\beta_s \geq 1$ as usual, and many phonon replicas are observed experimentally in this case. The similar many phonon features are observed in Raman spectra of number semiconductors CdS, ZnO etc. Therefore in present work the problem of EPI we study in the framework of identical approach for organic and semiconductor structures. The idea of approach is to describe the spectrum (using developed in our works theory) by varying the coupling constant, $\chi_s$. After fitting theoretical spectrum one can make the conclusion concern to constant EPI, $\beta_s$. Such method is especially convenient if several phonons, having frequency $\Omega_s$, take part in formation of spectrum. The corresponding analysis was made for number of quantum nanostructures. The numerical calculations showed that constants EPI depend strongly on the size and concentration of QD’s. Beside take place the intermixing of vibrations in such structures.
The proper assignment of bands observed in the vibrational spectra of complex molecules is always a challenge. Commonly used attempt, based on “characteristic vibrations”, provides a rough characterization of a very limited number of bands and can frequently be misleading if the wavenumber region specific for particular vibration is covered by more than one band. On that account, the special experimental techniques and theoretical methods have been developed. Among the former, the stable isotope substitution, especially the deuteration, is the most popular. That method points out the bands related to the vibrations of altered fragments of the molecule, but still do not provide the full description of normal vibration generating the given band. The last information can be obtained from the theoretical attempts, currently based on quantum methods. However, when applying these methods, the crucial point is the correlation between computed normal vibrations and observed bands. Since the number of bands is usually smaller than the number of computed frequencies, the additional criteria, as relative intensities should be taken into account. For this purpose, a computation of the simulated IR or Raman spectra based on calculated intensities (or activities) and predefined half-band-width, are recommend. Such spectra reflect the frequent phenomenon, when the intensities of several vibrations contribute in the intensity of the observed band.

The correlation between theoretically simulated and observed spectra should be done with the special care when the calculations are carried out for the isolated molecule, but the spectra are collected for the solid or liquid sample. Several intermolecular interactions influence then the spectra, altering the band positions, including the band order. In such cases, the additional experimental support, as selective deuteration or metal isotope labeling, may be helpful. Such experiments can also be simulated in calculations and computed band shifts compared with the observed ones. In case of deuteration, the computation of the deuterated molecule spectrum may by used not only for the vibrational characterization of the deuterated groups, but also for the neighbor fragments of the molecule, which vibrations are frequently sensitive to the H-D substitution, but in lesser extend.

The quantitative and the most complete band characterization is usually expressed in terms of the potential (or total) energy distribution. This procedure requires the prior definition of the symmetrized internal coordinates. The proper labeling of some of these coordinates will also be discussed.
NONCOVALENT INTERACTIONS IN THE GAS PHASE: NEW INSIGHTS FROM EXPERIMENTAL AND COMPUTATIONAL SPECTROSCOPY

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Recently, many gas phase spectroscopic studies have been focused on the understanding of the nature of weak interactions in model biological systems and on the microsolvation phenomena. However, only few of them have been performed under high resolution conditions. Among the aromatic molecules, anisole is particularly interesting due to the possibility of different solvent-molecule interaction schemes: hydrogen bonding, van der Waals forces, dipole-dipole interactions. Moreover, in many cases none of these mechanisms is clearly dominant and a delicate balance of different terms is likely to be expected as highlighted by recent studies of the anisole complexes with ammonia [1] and water [2].

The study of the noncovalent interactions in dimers of anisole took full advantage of the general method we developed to compute vibrationally resolved electronic spectra from first principles[3]. The integrated procedure has first been exploited to simulate the gas phase optical spectra of the \(S_1 \leftrightarrow S_0\) electronic transitions of anisole monomer. On the whole, a remarkable agreement between computed and experimental vibrationally resolved REMPI spectrum has been achieved [4], allowing revision of some assignments of fundamental vibrations in the \(S_1\) state of anisole. Next, the results from high resolution spectroscopic observations combined with computational studies led to unequivocal determination of the ground and excited state stacking equilibrium structure of the anisole dimer. Moreover, the direct comparison between theoretical vibrationally resolved electronic spectra and experimental REMPI spectra of clusters with different isotopic composition revealed the local excitation character for the \(S_1 \leftrightarrow S_0\) electronic transition. The overall combined experimental/theoretical study allowed a detailed description of the stacking interaction in the anisole dimer.
References


Posters
THE FTIR STUDIES OF GELS AND THIN FILMS OF Al₂O₃-TiO₂ AND Al₂O₃-TiO₂-SiO₂ SYSTEMS

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In this work, samples in form of bulk ones and thin films were obtained using the sol-gel method. The bulk samples were heated at different temperatures (500°C, 850°C and 1100°C) corresponding to the annealing process of coatings, deposited on different substrates by dipping and pulling out samples from the proper sol with the stable speed. Thin films of both Al₂O₃-TiO₂ and Al₂O₃-TiO₂-SiO₂ systems were deposited on carbon, steel and titanium substrates in two different ways: as single layers obtained from Al₂O₃ sol, TiO₂ sol and Al₂O₃ sol or deposited as mixed coatings from Al₂O₃-TiO₂ sol as well as Al₂O₃-TiO₂-SiO₂ one.

All bulk samples were studied by the FTIR spectroscopy and the X-ray diffractometry while thin films were also investigated by the electron microscopy together with the EDS method.

In all spectra measured, the bands assigned to the stretching vibrations of OH groups (at about 3432-3672 cm⁻¹) together with the bending vibrations in H₂O molecules (at about 1630 cm⁻¹) are observed, what is connected with the sol-gel synthesis. The intensity of all those bands decreases during an annealing process.

In the IR spectra of Al₂O₃-TiO₂ samples, as well gels as coatings, bands due to the stretching vibrations of Al-O bonds of the octahedrally coordinated aluminium were observed in the range of 500-750 cm⁻¹, whereas in the range of 750-900 cm⁻¹ bands due to vibrations of Al-O bond in Al₂O₃ units are present.

The IR spectra of samples of Al₂O₃-TiO₂-SiO₂ system differ from that of Al₂O₃-TiO₂ one in presence of bands assigned to the Si-O bond vibrations and in positions of bands due to Al-O bond vibrations. The band at 450 cm⁻¹ is connected with the bending vibrations of O-Si-O linkage whereas the band at 790 cm⁻¹ one can assign to the symmetric stretching vibrations of Si-O-Si bridge. In the range of 1034-1051 cm⁻¹, bands due to the asymmetric stretching vibrations of Si-O-Si and Si-O-Al bridges are observed (Al is present in tetrahedral coordination in this case). There is one more additional band in spectra described, at about 1220 cm⁻¹ which can be assigned to the double Si=O bond. The bands assigned to the stretching vibrations of OH groups and the bending vibrations in H₂O molecules are observed in all spectra at the same position as in Al₂O₃-TiO₂ ones.

In all spectra of bulk samples and coatings, the positions of Ti-O bond vibrations were ascribed basing on the IR spectra of the pure anatase and rutile.
P-02

INFLUENCE OF THE SOLVENT IN TERPENES: IR-RAMAN-VCD STUDY OF R-(+)-PULEGONE

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In the literature, works dealing with the vibrational study of terpenes are scarce, our research team being one among others which are devoted to this task [1].

In the present work, a study of the molecular structure and spectroscopic signatures in solution of the R-(+)-pulegone molecule is presented. A systematic and detailed study has been carried out starting from a theoretical investigation of the molecular structure and vibrational features for the neat title compound at the DFT/B3LYP/cc-pVQZ level. Solvent effects have been predicted using the IEF-PCM methodology [2] as implemented in GAUSSIAN03 package [3].

Later, IR, Raman and VCD spectra were recorded and compared with the theoretical ones. In the vibrational analysis the Scaled Quantum Mechanical Force Field (SQMFF) methodology by Pulay et al. [4] was applied.

P-03

CONFORMATIONAL LANDSCAPE AND HYDROGEN BONDING IN S-(-)-PERILLYC ACID: EXPERIMENTAL VCD, IR, RAMAN AND THEORETICAL DFT STUDIES

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A complete study of the molecular structure and of the IR, Raman and VCD spectra of the S-(-)-Perillyc acid is presented for the first time.

Following previous works by us on terpenoid systems [1], a systematic and detailed study has been carried out starting from a theoretical investigation of the conformational landscape of the monomers, dealing 24 stable conformations of S-(-)-Perillyc acid, and vibrational features at the DFT/B3LYP/cc-pVDZ level. Later, the H-bonded dimers are modeled at the DFT/B3LYP/6-31+G(d) level leaving us a total of 18 structures. GAUSSIAN03 package was used for this task [2].

Afterwards, experimental IR, Raman and VCD spectra were recorded and the assignment of them was done taking into account the most stable rotamers for each system. The experimental features are in good agreement with our DFT calculations.


VIBRATIONAL STUDIES OF THE MOLECULAR MECHANISM FOR THE PARA ELECTRIC – FERRO ELECTRIC PHASE TRANSITION IN THE TGS CRYSTAL

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TGS – type crystals (i.e. triglycine sulphate) are the best known ferroelectrics. Their ferroelectrics properties were discovered in the fifties of the 20th century [B.T. Matthias, C.E. Miller and J.P. Remeika, Phys.Rev., 104(1956), 849]. Despite of a great interest in these crystals, their molecular mechanism of the paraelectric-ferroelectric phase transition is not fully understood yet. By the diffraction (X-ray and neutron) methods it was not possible to solve all problems of the crystal structure at paraelectric phase (i.e. above \( T_c = 49^\circ \text{C} \)) [K. Itoh, T. Mitsui, Ferroelectrics 5(1973), 235-251 and papers quoted therein]. The crystals are monoclinic in both phases; space group P2₁ and \( P2_1/m \) for ferroelectric and paraelectric phase, respectively. Formally, the TGS crystal is built of glycinium cations \( (\text{+NH}_3\text{CH}_2\text{COOH}; \text{denoted as GI}) \), other two types of glycine molecules (GII and GIII) joined by strong hydrogen bonds into dimers \( ((\text{+NH}_3\text{CH}_2\text{COO}^-)_2\text{H}) \) and of the sulfate ions \( (\text{SO}_4^{2-}) \). There is still problem related to the structural properties (disordered or of \( \text{Cs} \) symmetry) of the GI cations in the paraelectric phase and to the structural nature of the GII and GIII molecules. These structural problems can be solved by the vibrational spectroscopy, however, applying the most advanced techniques which use the polarized radiation and single crystal samples. In our paper the polarized IR and Raman spectra will be presented and discussed. The polarized IR spectra were measured applying the transmittance and specular reflectance methods. The transmittance polarised IR spectra were measured in the function of temperature. The significant advantage of the transmittance methods over the specular reflectance will be shown. Analysis of the polarized properties of the bands arising from the internal vibrations of the sulfate ions clearly shows that the site symmetry of these ions in the paraelectric phase is \( \text{Cs} \). This allows to suggest that the glycinium cations GI either lay in the mirror plane perpendicular to the \( Y(b) \) axis or exhibit tunneling type disorder in the paraelectric phase. Such conclusion follows from the fact that the sulfate ions and the GI cations lay in the same mirror plane. The glycine molecules GII and GIII are joined by the very strong hydrogen bonds, the asymmetric stretching vibrations \( (\nu_1\text{OHO}) \) of which give rise to a very broad and strong band appearing at ca. 1100±50 cm⁻¹ in the IR spectrum of the (010) sample polarized at ca. 30° with respect to the X optical direction. Neither GII nor GIII molecule appears in the zwitterionic form. Their structures are in between that of the glycinium cation and zwitterionic one.
Morphine studied by vibrational spectroscopy and DFT calculations

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Morphine, the principal alkaloid of Papaver somniferum is a highly potent opiate analgesic drug, and is considered to be the prototypical opioid. It acts directly on the central nervous system and is used as an analgesic (eliminates or relieves pain) and narcotic (induces sleep or drowsiness) in preparations such as laudanum and paregoric. In an attempt to make morphine less addictive Bayer chemists acetylated the hydroxyl groups of morphine to produce diacetylmorphine, but it was recognized to be more addictive than morphine. Other derivatives of morphine have been developed and found use as opiate antagonists or as animal tranquilizers.

Recently, we studied alkaloid caffeine and its distribution in various pharmaceuticals by using FT-Raman spectroscopy[1]. This prompted us to broaden the research with vibrational methods to other alkaloids. In this paper we have applied FT-IR and Raman spectroscopy to investigate morphine. Experimental spectra were interpreted with the help of quantum-chemical calculation performed at the B3LYP[2]/6-311++G(d,p) level. Additionally, conformational analysis of morphine has been performed. The agreement between experimental and theoretical spectra is good. Detailed assignment of the experimental spectra was performed based on potential energy distribution (PED) analysis of normal vibrations by using Gar2ped program [3].

Fig. FT-IR spectrum of morphine.

References

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RAMAN MAPPING ANALYSIS OF PHARMACEUTICAL PRODUCTS CONTAINING PHOSPHONIC ACID DERIVATIVES

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Numerous phosphonic acid derivatives possess interesting therapeutic applications. Especially, sodium salt of alendronic acid (4-amino-1-hydroxy-1,1-butanediylidiphosphonic acid) is commonly and successfully used in the treatment of various disorders affecting the skeleton, such as osteoporosis, Paget’s disease or hypercalcemia [1-2]. On the Polish pharmaceutical market there are more than ten producers offering the medicines with different trade names and different content of this active compound.

In situ analysis of pharmaceuticals by using special techniques of FT-Raman spectroscopy allows to identify non-destructively and simultaneously various components occurring in tablets. Particularly, point-by-point scanning mapping technique, which requests the using of horizontal xy stage directly connected with the Raman spectrometer, enables the presentation of the results as 2-dimensional spectroscopic maps. Selective maps of the sample depicting the distribution of its content can be obtained by using characteristic non-overlapping Raman bands. However, when the bands overlapped multivariate analysis can be used to extract the useful information. The variation between the spectra collected during Raman mapping can be successfully analyzed by Correlation Analysis or Principal Component Analysis [3].

Our study demonstrates potential of FT-Raman technique for the investigation of a mixture of compounds occurring in medicines used to treat osteoporosis disease. An active component i.e. alendronic acid was in situ identified and simultaneously analysed with other components and any special sample preparation was not necessary. The Raman mapping results were analysed with various analytical methods and discussed.

References


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SPECTROSCOPIC ANALYSIS OF ANTICONVULSANT CARBAMAZEPINE

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Carbamazepine (CBZ), 5H-dibenzo[b,f]azepine-5-carboxamide, is an anticonvulsant and mood stabilizing drug used mainly for treatment of simple and complex epileptic seizures, trigeminal neuralgia, and bipolar affective disorder. The mechanism of action of carbamazepine is relatively well understood. It blocks ion channels and inhibits sustained repetitive neuronal excitation. The drug substance is metabolized in liver into 10,11-epoxycarbamazepine by enzyme CYP3A4.

Carbamazepine, like many other pharmaceuticals, exhibits polymorphism. Although this phenomenon is quite common in pharmaceutical solids, it still represents the major problem to the industry because some properties of drug product, i.e. bioavailability and stability are often related with physicochemical properties of existing polymorphs. One polymorphic form can be bioactive whereas another is an ineffective therapeutic agent. Identification and characterization of drug polymorphic forms is crucial in terms of therapeutic properties, drug formulation, and legal implications. Carbamazepine is known to exist in four anhydrous polymorphs and as a dihydrate [1]. Polymorphic forms of carbamazepine have been studied by several authors with respect to crystal packing, solid phase stability and transformations. However, the literature data seems to be inconsistent, particularly in the range of the spectroscopic characterization of CBZ [2, 3]. Therefore the following research was undertaken in order to verify previous approaches and apply the final results in the analysis of tablets formed during the manufacture process. A single molecule of carbamazepine was modeled by using ab initio density functional theory calculations at the B3LYP/6-31G** level. Theoretical IR and Raman spectra were calculated from the assumed geometry. The obtained results were compared with the experimental spectra of carbamazepine and showed good agreement. To assign the bands in details, analysis of the potential energy distributions for the calculated normal mode of CBZ was performed. Detailed analysis of characteristic bands will be employed during the investigation of carbamazepine distribution in tablets by using Raman mapping technique.

References

VIBRATIONAL STRUCTURE OF OLIGOTHIOPHENE-FULLERENE LINKED DYADS

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Recently, the quest for new materials useful in the solar energy conversion leads to the synthesis of many chromophore-fullerene dyads. Fullerene in such system is used as an electron acceptor, while the chromophore part is responsible for the photoinduced electron transfer. We have chosen the set of three oligothiophenes linked with fullerene for our investigations (Scheme 1). Photoinduced charge separation in various oligothiophene-fullerene dyads and triads has been widely investigated. However, most of investigations focus on the spectral properties in the UV/Vis/NIR range region neglecting the vibrational behaviour of the samples. On the other hand, the vibrational spectroscopy is known as a very sensitive tool for characterization of new molecular materials.

Scheme 1: Molecular structure of investigated dyads

In this work, the vibrational properties of selected oligothiophene-fullerene dyads are presented. The infrared absorption and Raman scattering spectra of investigated dyads have been recorded at room temperature. The density functional theory (DFT) calculations with a B3LYP hybrid functional and 6-31G(d,p) basis set have been used for prediction of the equilibrium molecular geometry and normal mode vibrations of oligothiophenes and oligothiophene-fullerene dyads.

The experimental Raman and infrared spectra are in a good agreement with theoretical predictions. It was shown that the position of normal modes calculated for oligothiophenes is slightly perturbed after linking them to fullerene unit. In a few spectral ranges unique and characteristic features for every dyad have been identified.

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P-09

MOLECULAR DYNAMICS SIMULATION OF METHANE IN CARBON NANOTUBE

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Molecular dynamics simulation is used to study structural and dynamic properties of methane molecules in a single wall carbon nanotube (SWNT). The carbon atoms of the nanotube are arranged according to the (15,15) armchair structure. Interactions of carbon atoms in nanotube are described by REBO (reactive empirical bond order) potential [1]. A methane molecule is modelled by one Lennard-Jones (LJ) interaction site [2] or rigid set of five LJ sites [3]. Different loadings of methane molecules and the effect of the flexibility/ rigidity of the SWNT on the diffusivity are considered.

The velocity autocorrelation functions as well as mean-square displacement ones used to calculate diffusion coefficient give almost identical values. The coefficient decreases with the increase of density that was reported in earlier papers [2,4]. For densities considered here motion of carbon atoms of the SWNT has very small influence on behaviour of methane molecules. However, at small pressures the diffusion coefficient of methane in the flexible SWNT are larger than those for the rigid one. This observation is in accordance with results of Jakobtorweihen et al [4]. For the 5-site model of methane molecules results are almost the same as those presented in the figure.

Diffusion coefficient values for 1-site methane molecules in rigid (C0MT) and flexible (CTMT) nanotube.

References

Salol \([\text{phenyl salicylate; (HO)}C_6H_4CO_2C_6H_5]\) show different dynamics above and below a crossover temperature \(T_c \approx 1.2T_g\), where \(T_g\) (223 K) is the glass-transition temperature. Below \(T_c\) supercooled liquid salol has the non-exponential and non-linear behaviour of structural relaxation. Crossover temperature \(T_c\) for salol from the depolarized-light-scattering data was found to be \(\approx 256\) K \([1]\), and from the optical Kerr effect spectroscopy \(T_c \approx 260\) K \([2]\). However the physical process which governs the kinetics and hence \(T_c\) parameter in supercooled liquids below \(T_c\) remains unresolved problem.

To gain understanding in this subject, we have conducted a low-frequency Raman scattering and differential scanning calorimetry (DSC) measurements for salol in supercooled and glassy states. We demonstrate by DSC that generation of the crystal nuclei (a crystal nucleus can be recognized as a kind of cluster with an ordered arrangement of 10-1000 molecules) begins in a supercooled liquid salol at 258 K. This temperature is closed to the values reported in the literature \((256\) K \([1]\) and 260 K \([2]\)). Thus unstable nuclei, which appear and disappear in supercooled liquid below 258 K, are responsible for the non-exponential and non-linear behaviour of structural relaxation. Low-frequency Raman spectra of glassy salol show a broad feature at \(\approx 17\) cm\(^{-1}\); the ‘Boson peak’, which is associated with the intermediate range order \([3, 4]\). The DSC results allow us to interpret Boson peak in terms of its relationship to the formation of ordered clusters (crystal nuclei). Thereby the ordered clusters in glassy salol can be considered as a measure of the heterogeneous nanostructure in this glass.

P-11

POLYMORPHISM AND STRUCTURE-PROPERTY RELATIONSHIPS IN MOLECULAR COMPOUND 2-BIPHENYLMETHANOL

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We report for the first time the luminescence spectra of two polymorphs phases of the hydrogen-bonded 2-biphenylmethanol (2BPM) in the wide temperature region and Raman spectrum of the metastable phase of 2BPM in the spectral range between 100 and 3400 cm\(^{-1}\). The fluorescence spectrum of the stable phase measured at 4.2 K begins with the band at 294 nm and showed several well defined bands, whose interval corresponds to the stretching frequency of the C-C vibration in the phenyl ring (879 cm\(^{-1}\)). It has been found that the C-C stretching vibration frequency decreases in the excited state on 118 cm\(^{-1}\) in respect to its value in the ground state. The fluorescence spectrum of the metastable phase measured at 4.2 K begins with the well defined band at 282 nm, which is absent in the spectrum of the stable phase. This is the most characteristic difference between these two spectra. It has been shown that the significant differences in the Raman spectra between two polymorphs occur in those frequency regions where the hydrogen-bonding interactions affect vibrations. This concerns the vibrations which described the dynamics of the core of the hydrogen-bonded complex (tetramer or chain of methanol groups). In the spectral region where the stretching vibrations of the C-C bond in the phenyl ring far removed from the methanol group manifest themselves, the frequencies of the corresponding bands practically do not depend on polymorph structure.
THE INCLUSIVE COMPLEX OF BIS(Piperidinium-4-carboxylate) HYDROGEN
Semi-Tartrate Hydrate Methanol Solvate Studied by X-Ray Diffraction, NMR,
FTIR and DFT Methods

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L(+)-Tartaric acid (TA) forms a broad family of hydrogen bonded complexes with amines,
betaines and amino acids. Some of them undergo ferroelectric phase transition and exhibit nonlinear optical properties. In complexes of TA with bases one or two protons can be transferred from the carboxylic groups of TA to the base forming monovalent (semi-tartrate) or divalent (tartrate) anions.

Piperidine-4-carboxylic acid, P4C (isonipecotic acid), can be treated as \( \gamma \)-amino acid. In the solid state and solution it exists as zwitterion, in which the acid hydrogen is transferred to the ring nitrogen atom. P4C has two interacting centers, the proton-donor \( \text{N}^+\text{H}_2 \) group and the proton-acceptor \( \text{COO}^- \) group.

The 2:1 complex of piperidine-4-carboxylic acid with tartaric acid has been synthesized and characterized by X-ray diffraction, \(^1\text{H}, ^{13}\text{C} \) NMR, \(^{13}\text{C} \) CP MAS NMR, FTIR spectra and its structure has been optimized at the B3LYP/6-31G(d,p) level of theory. The title complex is composed of the following units: piperidinium-4-carboxylate (P4C), piperidinium-4-carboxylic acid (P4CH), semi-tartrate anion (TA), water and methanol. The \((\text{P4C})_2\text{H} \cdot \text{TA} \cdot \text{H}_2\text{O} \cdot \text{HOCH}_3\) complex crystallizes in orthorhombic \( \text{P} \quad 2_1 \).2\_1 \) group.

In the crystal, TA anions form infinite chain through the \( \text{COOH} \cdots \text{OOC} \) hydrogen bond of 2.503(5) Å. The zwitterionic P4C molecules are linked by the \( \text{N}^+\text{H} \cdots \text{OOC} \) hydrogen bond of 2.780(5) Å into chain. The P4CH cation is a bridge between the TA and P4C chains. P4CH and P4C form a homoconjugated cation through the \( \text{COOH} \cdots \text{OOC} \) hydrogen bonds of 2.559(5) Å. Water interacts with TA and P4C, while methanol interacts only with water.

Two different piperidinium-4-carboxylate units in the complex investigated are distinguished in the \(^{13}\text{C} \) CP MAS NMR spectrum. The \(^1\text{H} \) and \(^{13}\text{C} \) NMR spectra elucidate the structure of the title complex in the aqueous solution. The magnetic isotropic shielding tensors, determined by the GIAO/B3LYP/6-31G(d,p) method give linear regressions with the experimental chemical shifts in D\(_2\)O. In the optimized molecule of the \((\text{P4C})_2\text{H} \cdot \text{TA} \cdot \text{H}_2\text{O} \cdot \text{HOCH}_3\) complex, the components form a cyclic oligomer through four O-H \cdots O and four N-H \cdots O hydrogen bonds. The FTIR spectrum confirms a very complex structure of the title compound.
SPECTROSCOPIC AND STRUCTURAL STUDIES OF THE 2:3:2 COMPLEX OF DABCO MONO-BETAINE WITH HCL AND H2O

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1,4-Diazabicyclo[2.2.2]octane (triethylenediamine, N(CH2CH2)3N), abbreviated as DABCO, is a globular molecule of high symmetry. DABCO is a strong base, its pKₐ = 8.84 [1]. Recently, we have synthesized and solved the crystal structure of 1-carboxymethyl-1,4-diazabicyclo[2.2.2]octane inner salt (DABCO mono-betaine) [2].

\[
\begin{align*}
&\text{DABCO mono-betaine} \\
&\text{NN C H}_2\text{COO}^+ \\
&\text{N} \quad \text{CH}_2\text{COO}^- \\
\end{align*}
\]

The aim of this work is the synthesis of DABCO mono-betaine hydrochloride (1-carboxymethyl-1,4-diazabicyclo[2.2.2]octane hydrochloride) and its characterization by the spectroscopic methods, X-ray diffraction and DFT calculations.

DABCO mono-betaine forms a complex with HCl of the stoichiometry 2:3 and crystallizes with two water molecules in triclinic P\text{1} space group. Two betaine molecules are joined together by the short COO·H·OOC hydrogen bond of 2.470(3) Å. Both the tertiary nitrogen atoms of DABCO mono-betaines are protonated and interact with the chloride anions by the N-H···Cl hydrogen bonds of 3.049 (3) and 3.027(3) Å. The water molecules are linked themselves and with two chloride anions.

The O-H···O, O-H···Cl, N-H···Cl, O···H···O hydrogen bonds are manifested in the FTIR spectrum as the broad bands in the 3400-3200, 2700-2000 and 1500-400 cm⁻¹ regions. The experimental and calculated IR spectra for the title complex at the B3LYP/6-31G(d,p) level of theory are compared and discussed.

THE INTERPRETATION OF VIBRATIONAL SPECTRA OF ALIZARINE. A COMBINED EXPERIMENTAL AND COMPUTATIONAL STUDY

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Alizarin, 1,2-dihydroxyanthraquinone, is the main natural pigment found in madder root (Rubia tinctorium L., Rubia cordifolia L.) also present in leaves of Polynesian noni tree (Morinda citrifolia L.). Owing to his ability to form complexes with metal ions (Ca2+, Mg2+) it can be used in histoch-chemistry for the in vivo dyeing of growing bone tissues. Alizarin has 5-alpha-reductase inhibitor prop-erties, making madder root functional to stimulate hair growth. It also exhibits an antigenotoxic activity as an inhibitor of the human recombinant cytochrome P450 isozymes.

Recently, we studied alizarin by surface enhanced and FT-Raman spectroscopy [1]. We demon-strated that, for alizarin deposited at the surface of electrode, depending on the excitation line (488, 514.5 and 647.1 nm) either SERS or SERRS spectra was observed. This prompted us to deepen the understanding of the vibrational spectra of alizarin itself. To this aim, we calculated the anharmonic IR and Raman spectra of alizarin at the B3LYP/aug-cc-pVDZ level. The agree-ment between experimental and theoretical spectra is good. To assign the bands in details, the potential energy distribution analysis was performed by using VEDA program [2]. The influence of intermolecular interactions present in crystals was simulated by calculating the vibrational spectra of selected dimers at the B3LYP/6-31G** level.

References
L-ISOSERINE CONFORMATION IN LOW-TEMPERATURE IR MATRIX SPECTRA INTERPRETED BY MEANS OF THE DFT CALCULATIONS

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Izoserine, NH₂CH₂CH(OH)COOH, 3-amino-2-hydroxypropionic acid, is serine isomer in which the NH₂ and OH groups were interchanged. Isoserine is the β-amino acid - an amino acid with the NH₂ placed in the β position. A few β-amino acids have been isolated from plants, bacteria, and invertebrates. Paclitaxel (Taxol), first isolated from the bark of Taxus brevifolia L., is the most important natural compound composed of the isoserine molecule, which is used in chemotherapy of breast, ovarian, and lung cancers. The presence of the additional carbon atom in the backbone of a β-amino acid results in different properties of β-peptides, such that they exhibit higher stability against peptidases, and an enormous potential for secondary structure formation, as documented in numerous comprehensive reviews [1]. Recently, we are studying different aspects of vibrational spectroscopy of small biological molecules of pharmaceutical interest such as halouracils [2], lactic acid [3], cystein [4], and β-alamin [5]. Analysis of literature data devoted to isoserine has shown that knowledge about physicochemistry and spectroscopy of this molecule important to biology and pharmacy is diminutive. This is why this is the first systematic study on conformers and IR spectroscopy of isoserine molecule.

The IR low-temperature Ar matrix spectra of L-isoserine were registered for the first time and interpreted by means of the anharmonic DFT frequencies calculated at the B3LYL/aug-cc-pVTZ level. 54 L-isoserine conformers were calculated to be stable at the B3LYL/aug-cc-pVDZ and MP2/aug-cc-pVDZ levels. The most stable conformer and seven highly populated ones were recalculated by using the two methods and the aug-cc-pVTZ basis set. Inspection into the stretching vibration OH, C=O, and C-O regions of the experimental spectra enables one to detect at least four other L-isoserine conformers. The fact that most stable conformer (1) is dominating and the other are much less populated is visible in the ν(C=O) stretching vibration region of the spectra registered for Ar matrix. The presence of the conformer (2) in the Ar matrix IR spectra of L-isoserine can be proved based on the inspection into the ν(OH) bending vibration region 1500-1200 cm⁻¹. The side bands of the ν(C-O) band of the conformer (1) positioned at 1121 and 1185 cm⁻¹, corresponds the conformer (3).

References
SEARCH FOR MATERIALS FOR NONLINEAR OPTICS. NEW COMPLEX OF L-LEUCINE WITH PERCHLORIC ACID. A COMBINATION EXPERIMENTAL AND THEORETICAL STUDIES

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Some complexes of the amino acids with simple organic and inorganic salts appear to be promising materials for optical second harmonic generation (SHG). These crystals display interesting chemical and physical properties, exhibiting phase transitions. There are many examples of perchlorates exhibiting structural phase transitions connected with the ordering of perchlorate anions. Such phenomenon was observed in solid trimethylammonium perchlorate by Stammler et al [1]. Mylrajan and Srinivasan studied molecular motions in tetragonal tetramethylammonium perchlorate with the help of vibrational spectroscopy [2]. Pyridinium perchlorate reveals two structural phase transitions at 233 and 345 K, the second one being of ferroelectric type [3, 4].

The L-leucine*perchlorate acid complex is investigated as potential compound for NLO optics. The X-ray structure was published, previously [5].

The detailed room temperature vibrational studies are reported. The experimental infrared and Raman spectra are compared with theoretical vibrational studies.

The second harmonic generation was found by experimental Kurtz-Perry test (SHG efficiency $d = 0.44d_{KDP}$). These results were compared with theoretical calculation.

Additionally, for the investigated compound the phase transitions were found with DSC method. Differential scanning calorimetric measurements revealed that studied complex undergoes phase transitions at 210, 192 and 183 K.

The DFT theoretical method was used for equilibrium structure and potential energy distribution (PED) with theoretical spectra calculations. The Natural Bond Order (NBO) and hyperpolarizability was calculated, also.

References
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Recently, many attention has been paid to photocurable compositions, widely used in many industrial applications. Usually, such compositions consist of mixtures of two or more monomers. The polymerization behavior of a mixture of two monomers highly depends on their molar ratio, which influences the system viscosity and intermolecular interactions between the monomers.

One of the experimental methods used in investigations of the elastic properties both of solids and liquids is Brillouin light scattering. It can be also used to study molecular dynamics and local structure of monomers and their polymerization process.

In this paper we present results obtained by Brillouin scattering method for two-component systems: (high viscosity monomer)/(low viscosity monomer). The monomers used were crosslinking (divinyl) or linear (monovinyl) ones. The investigated systems were: divinyl/divinyl – bis-GMA/TEGDM; divinyl/monovinyl – bis-GMA/PM; monovinyl/divinyl – bis-MGMA/TEGDM and monovinyl/monovinyl – bis-MGMA/PM, for various molar ratios. The measurements have been performed in temperature range 293-353 K.

The following physical parameters characterizing the investigated systems were estimated: ultrasonic velocity $V$, attenuation coefficient $\alpha$, adiabatic compressibility $\beta$, real $M'$ and imaginary $M''$ parts of elastic modulus, all as a function of temperature and molar monomers ratios.

The obtained results have been discussed in terms of the influence of the system composition and viscosity on their elastic properties. Speed of changes of these parameters as derivative have been also discussed in terms both of temperature as well the component molar ratio in the monomer mixture. Discussion involved also molecular structures and interactions.

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STRUCTURAL STUDIES OF 7-ACETYL-6-METHOXY-3-METHYL-2-BENZOFURANCARBOXYLIC ACID AND ITS SODIUM COMPLEX

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The crystal structure of 7-acetyl-6-methoxy-3-methyl-2-benzofurancarboxylic acid (1) has been solved (Fig. 1). The compound crystallizes in the monoclinic space group \(\text{C}2/c\). The methyl, methoxy and carboxylic groups are essentially coplanar to the benzofuran moiety. The relative orientation of the acetyl group at C7 to the aromatic ring can be described by the torsion angle \(\tau_1\) (O2-C8-C7-C7A) = 134\(^\circ\). The inter-molecular O-H…O hydrogen bonds form centrosymmetric dimers.

Searching for stable conformers the Total Energy Surfaces (TES) for internal rotation about the C7-C8 and C2-C11 bonds have been calculated by using density functional B3LYP with 6-31G* basis set (Figs 2-3). The rotation of the acetyl group yields two conformers for which the O2-C8-C7-C7A torsion angle is 30\(^\circ\) and 150\(^\circ\), respectively. The second one is more stable, showing good agreement with the conformer present in solid phase. As a result of second rotation (Fig. 3) two conformers have been obtained with the more stable one in gas phase with torsion angle equal 0\(^\circ\).

Surprisingly, both calculated conformers can be observed in the asymmetric unit of sodium complex of 1 (Fig. 4). Three molecules of 1 present in this crystal structure adopt different conformations. Moreover, unit 1a is deprotonated while unit 1c is not included in the coordination sphere of Na\(^+\).
The results of X-ray diffraction (XRD), scanning electron microscopy (SEM) and dielectric measurements performed for the polycrystalline solid solutions (Ba_{1-x}Sr_x)TiO_3 (BSxT) samples are presented. The results show weak correlation of average temperatures of the structural phase transitions T_x (from the cubic to the tetragonal structure) with the average temperatures of the para-ferroelectric phase transitions T_m obtained in dielectric investigations (T_m - the temperature of maximum value of real component of the electric permittivity \( \varepsilon_m \)). The increase of diffuseness of ferroelectric phase transition and the decrease of the temperature T_m with increase of Sr concentration in the sublattice A was observed. Measured, in broad region of temperatures, value of the phase angle (approximate to -90°) suggest the occurrence of the polar regions (clusters) in temperature region of para-ferroelectric (PF) phase transition (PT). The evolution of these clusters leads to PF PT, that not always corresponds with structural phase transition.
P-20

STRUCTURE AND TEXTURE OF GLASSES BELONGING TO NaXPO₄-SiO₂ AND NaXPO₄-SiO₂-AlPO₄ (X = Ca²⁺ or/and Mg²⁺) SYSTEMS

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The studies concern silico-phosphate glasses belonging to NaXPO₄-SiO₂ and NaXPO₄-SiO₂-AlPO₄ (X = Ca²⁺ or/and Mg²⁺) systems of systematically changed [SiO₄]⁴⁻/[PO₄]³⁻ proportion. ²⁷Al MAS NMR investigations have shown that aluminum occurs exclusively in the tetrahedral position, i.e. it is a framework-forming cation. Hence, Na⁺, Mg²⁺ and/or Ca²⁺ are the only modifying cations.

Based on detailed microscopic investigations, distinct occurrence of liquation has been established in all the materials obtained. The aluminium has a homogenising effect on the texture of glasses obtained. Addition of a small amount of aluminium (5 mol. % of AlPO₄) already causes the inversion of the compositions of the matrix and the inclusions. Change in the framework modifying cations (Mg²⁺ instead of Ca²⁺) has caused the shift in the matrix and inclusion phase inversion threshold value. In the glasses of NaCaPO₄-SiO₂-AlPO₄ system this inversion occurs when NaCaPO₄ content exceeds 25%, whereas in the glasses of NaMgPO₄-SiO₂-AlPO₄ and Na(Ca,Mg)PO₄-SiO₂-AlPO₄ systems – when NaXPO₄ amount exceeds 35%.

Structural investigations (MIR, NMR) of the obtained glasses as well as of the corresponding crystalline materials have shown that the glasses studied exhibit domain composition. Structure of the domains is close to that of the corresponding crystalline phases.

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P-21

INFLUENCE OF B^{3+} CATIONS ON THE STRUCTURE AND TEXTURE OF SILICO-PHOSPHATE GLASSES

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The studies concern silico-phosphate glasses belonging to NaCaPO₄-SiO₂-BPO₄ system of systematically changed [SiO₄]⁴⁻/[PO₄]³⁻ proportion.

¹¹B MAS NMR investigations have shown that boron occurs in the three and four coordination i.e. it is a framework-forming cation and modifying cation simultaneously.

Microscopic and EDX investigations have made it possible to find out that, (such as in the glasses from NaCaPO₄-SiO₂ system), in all the glasses studied liquation takes place. It has been established that addition of boron changes the number and dimension of inclusions in the silico-phosphate glasses.

Fourier transform infrared spectroscopy (FTIR) measurements as well as computer decomposition of the obtained spectra into component bands were performed. The decomposition made it possible to connect bands with the groups of phospho-oxygen, silico-oxygen, boro-oxygen.

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The nanosystem composed of only as few as seven fullerenols \( \text{C}_{60} \text{(OH)}_{24} \) molecules was studied using the molecular dynamics (MD) technique. The interaction was taken to be the full site-pairwise additive Lennard-Jones (LJ) potential, which generates both translational and anisotropic rotational motions of each fullerene. The radial distribution function, the mean square displacement, the Lindemann index, the translational and angular velocity correlation functions of fullerenol have been calculated for several energies of the nanosystem. We provide also the in-depth evidence of the solid-liquid phase transition in the investigated cluster. The comparison with the properties of pure fullerene cluster \( \text{C}_{60} \) is provided. The study are motivated by the expected diverse biological applications of water-soluble fullerenols.
P-23

MOLECULAR DYNAMICS OF 4-CYANO-4-N-PENTYLBIHENYL (5CB) MESOGEN MOLECULES CONFINED BETWEEN GRAPHENE WALLS – COMPUTER SIMULATION

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The ultrathin film of mesogenic molecules 5CB confined between graphene walls has been investigated by molecular dynamics (MD) technique. The dynamical observables of 4-cyano-4-n-pentylbiphenyl (5CB) were calculated for several temperatures: the mean square displacement, translational and angular velocity autocorrelation function, second rank order parameter.
The influence of fullerensols on the dynamics of nitric oxide molecules in water – computer simulation

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The nitric oxide-scavenging activity of polyhydroxylated derivative of fullerene, fullerensol C_{60}(OH)_{24}, has been investigated using the molecular dynamics (MD) simulation method. The impact of water soluble fullerensol on the dynamics of nitric oxide NO molecules solute in water has been observed by calculating several molecular observables of NO at the physiological temperature.
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THE STRUCTURAL PROPERTIES OF THE O-HYDROXY ACETOPHENON AZINE

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Aromatic azines and their derivatives have become recently the subject of growing interest due to their interesting structural and optical properties. The compounds exhibit thermal and photochemical isomerization about the C=N and N-N bonds 1,2. They were found to exhibit aggregation-induced emission enhancement characteristics. This property is a promise of their potential applications in optical sensors, light emitting diodes and photoemitters 3,4.

This work presents the results of the conformational studies of orto-hydroxy acetophenon azine. The study was performed by the matrix-isolation IR spectroscopy and density functional theory (DFT) calculations. The FTIR spectra evidenced the presence of a few conformers of the studied compound in an argon matrix. The geometries of the low-energy conformers of o-hydroxy acetophenon azine were optimized using the DFT method with the B3LYP parametrization and the 6-311++G(2d,2p) basis set. The harmonic frequencies and IR intensities were calculated for all optimized structures. These data were used to separate and assign the bands of the orto-hydroxy acetophenon azine conformers in the experimental spectra.

References

Sol-gel method of ceramics preparation has been known for many years, but recently it has developed as a method for the synthesis of nanostructural ceramic materials. Hydrolytic polycondensation reaction, leads to formation of xerogels from simple molecules e.g. most widely used tetraethoxysilane (TEOS). The resulting xerogel material can contain macromolecules of distinct random, ladder and cage or partial cage structure. In order to obtain well defined silsesquioxanes it is preferred to start the hydrolytic condensation process with more complex molecules, bringing in a specific structure, that can govern the structure of the product. In the presented work: alkoxy derivatives of cyclosiloxanes and oligosiloxanes as well as hydrides derivatives of octasilsequioxanes (T₈) molecules in the process of hydrolytic polycondensation were applied. Depending on the reaction conditions, polycondensation can result then in the formation of silsesquioxane macromolecules or silica material.

Our approach was to use ethoxy derivatives of cyclosiloxanes with general formula SiₙOₙ(CH₃)ₙ(OEt)ₙ where n = 4, 5 and 6, linear oligosiloxanes with side alkoxy groups and hydrideoctasilsequioxanes (T₈H) as precursors of polysilsesquioxane. Dried polysilsesquioxane were heated at the temperature of 600°C in argon or air atmosphere (pyrolysis or ceramization). In the atmosphere of argon SiCₓOᵧ glass materials were obtained. In the air we have obtained mesoporous organicsilica materials without using any template or surfactant whatsoever. In the case of octasilsequioxanes molecules precursors hydrolytic condensation process gives, directly, mesoporous silica material. The mesopores are created due to the unique structure of initial siloxane or silsequioxane molecules and the specific interactions in the used catalyst solvent system.

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Preceramic polymers constitute an attractive alternative to conventional methods applied for the preparation of ceramic materials. Using these polymers it is possible to obtain ceramics at lower temperatures than in traditional technologies and of various shapes. Additionally, in some cases, polymeric precursors allow to prepare materials unattainable by other methods. Silicon oxycarbides, of general formula SiC_{x}O_{y} (x<2, y>0), belong to such materials. They are formed in the temperature range of 800-1300 °C and at higher temperatures transform first to SiC and SiO_{2}, then to SiC and C [1]. Therefore they cannot be obtained during conventional silica glass fabrication which requires high temperatures.

Silicon oxycarbides can be prepared by thermal decomposition of polyorganosiloxanes, i.e. the polymers containing Si-O linkages as well as organic substituents (usually hydrocarbon) at silicon atoms. Numerous papers have been published in the literature on preceramic polysiloxanes. However, only two types of these polymers have been used as ceramic precursors so far: commercially available products and compounds obtained by the sol-gel method.

In the present work, another route to the preparation of preceramic polysiloxanes is proposed. 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (D_{4}^{Vi})-based networks have been synthesized by its hydrosilylation with various hydrogensiloxanes carried out in the presence of Karstedt catalyst in solvent-free conditions. The following hydrogensiloxanes have been applied in the experiments: 1,1,3,3-tetramethyldisiloxane (HMMH), 1,1,3,3,5,5-hexamethytrisiloxane (HMDMH), 1,1,3,3,5,5,7,7-octamethyltetrasiloxane (HMD2MH) and 2,4,6,8-tetramethylcyclotetrasiloxane (D_{4}^{H}). Two D_{4}^{Vi}: hydrogensiloxane molar ratios equal to 1:1 and 1:3 have been adopted. During the hydrosilylation process, FTIR spectra of the reaction mixtures have been measured. This has enabled us to follow the reaction progress. Morphology of the polysiloxane networks prepared has been investigated by scanning electron microscopy (SEM). Thermogravimetric (TG) investigations have been also performed. Results of the studies show that both, morphology and ceramic yield (defined as the residual mass of the sample in TG experiments) depend on the type of hydrogensiloxane used in the hydrosilylation process. In particular, extremely high ceramic yield (~90 wt. %) observed in the case of D_{4}^{H} should be noted.

VIBRATIONAL STUDIES OF HYDROQUINONE - XENON CRYSTALS

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Hydroquinone (HQ) forms three crystalline modifications denoted as $\alpha$-HQ, $\beta$-HQ and $\gamma$-HQ. Hydroquinone clathrate in the $\beta$-hydroquinone modification ($\beta$-HQ) has approximately spherical cavities in which small molecules (e.g. Ne, Ar, Kr, Xe, N$_2$, O$_2$, NO, CO, HCl) can be trapped. The interaction between enclosed molecule (guest) and surrounding hydroquinone molecules (host) stabilizes the $\beta$-hydroquinone modification structure at room temperature. Theoretical study revealed that the $\beta$-hydroquinone provides an idealized case of the cell model of liquid and solution and the host-guest interaction determines the inclusive phenomena, to which many analogs are thought to exist in biochemistry.

In this contribution the xenon influence on the $\beta$-hydroquinone internal vibrations, particularly on the hydrogen bond network vibrations, has been studied. This main goal has been achieved by recording and consideration of the selected infrared bands on the $\beta$-hydroquinone – xenon crystals changes due to:
1. the substitution of the OHO protons for deuterons;
2. the temperature variation in the very wide range 10K – 458K;
3. the xenon escape from cages of $\beta$-hydroquinone crystal.

Out of the all internal vibrations of the $\beta$-hydroquinone crystal the band due to the $\gamma$OH mode appears to be more useful for such consideration.
QUASI-ONE-DIMENSIONAL ORGANIC METALS BASED ON O-DMTTF AND DMTMTTF DONORS INVESTIGATED BY RAMAN SPECTROSCOPY

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Charge transfer salts with 2:1 stoichiometry formed by the organic donors o-dimethyl-tetra-thiafulvalene (o-DMTTF) with Br or I anions and dimethyltrimethylene-tetra-thiafulvelene (DMtMTTF) with ClO4 or ReO4 anions possess strictly regular organic stacks. Organic conductors with such uniform conducting stacks, which preserve their uniformity down to the lowest temperatures, are very rare. Therefore, our salts offer a unique possibility for investigation of electron-electron correlations in one dimension, i.e. the problem of Mott localization in a one-dimensional 1/4 filled band (in terms of holes). Both o-DMTTF and DMtMTTF salts are isostructural. The salt (o-DMTTF)2Br undergoes a metal-insulator phase transition at TM, = 50 K [1]. In (DMtMTTF)2ClO4 charge localization is observed at about T=150 K [2]. We have performed investigations of these compounds by Raman spectroscopy which is a very good experimental method to study charge distribution in conducting organic stacks and its eventual reorganization due to charge ordering effects.

Temperature dependence of single crystal Raman spectra of the salts (o-DMTTF)2X (X = Br, I) and (DMtMTTF)2Y (Y = ClO4, ReO4) Br was investigated (T = 4 – 300 K). The spectra were excited with a He-Ne laser (λ=632.8 nm); the exciting beam was polarized but the polarization of scattered radiation was not studied. Additionally, Raman and infrared spectra of neutral o-DMTTF and DMtMTTF molecules were measured at room temperature. The normal vibrational modes of neutral molecules were calculated by DFT method.

In room temperature Raman spectra of o-DMTTF salts three strong lines related to the C=C stretching modes are observed at about 1480, 1509, 1600 cm⁻¹; analogous C=C lines for DMtMTTF salts were found at about 1471, 1551, 1601 cm⁻¹. Temperature dependence of these Raman bands shows that the charge distribution in conducting stacks is uniform in the whole temperature range, i.e. there is no charge ordering in (o-DMTTF)2Br salt below TM, = 50 K as well as in (DMtMTTF)2ClO4 salt below T=150 K. The spectra o-DMTTF and DMtMTTF salts were compared and some differences discussed. Temperature dependence of Raman lines was analyzed. Additionally, the theoretical and experimental vibrational spectra obtained for o-DMTTF and DMtMTTF molecules were compared and discussed in relation with analogous spectral data for TTF and TMTTF molecules.

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INFRARED SPECTROSCOPIC STUDIES OF SOME PHOSPHATES STRUCTURES

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Infrared spectroscopic studies of over 50 mineral and synthetic phosphates have been presented. The interpretation of the spectra has been preceded by the isolated [PO$_4$]$_3^-$ tetrahedron spectra analyse. The K$_3$PO$_4$ saturated aqueous solution was measured in the special cell for liquids. The obtained IR results have been compared with the theoretical number of IR active modes. The number and positions of the bands due to P-O vibrations have been established.

The phase composition of the phosphates has been determined using XRD and IR spectroscopy methods. Some samples have contained different admixtures – mainly carbonates and quartz. In these cases the spectra have been converted using arithmetic functions of WIN-IR BIO-Rad program. The influence of non-tetrahedral cations on the shape of the spectra and the positions of bands has been analysed and the crystalline field splitting effect has been discussed.

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P-31

SPECTROSCOPIC STUDY OF 4-4-1 ZEOLITE STRUCTURAL UNITS

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Calculated vibrational spectra of different terminated zeolite 4-4-1 structural units has been derived using ab initio methods. This unit constitute secondary building unit (SBU) one of the most important natural zeolite structural group. In the calculations the model of pseudomolecules have been constructed with some additional tetrahedrons to restrain its stiffness. As a result of calculations, vibrational spectra and visualizations of individual normal vibrations of the units were obtained. Visualizations of the obtained normal vibrations permitted to identify vibrations characteristic for individual units (especially, the ring vibrations) and to assign them to appropriate bands in the spectra. The effect of terminating cation substitution (Na→K) on the spectra has been also analyzed.

The results of the model studies were used to describe experimental vibrational spectra of natural aluminosilicates (HEU, STI and BRE zeolites) containing the units analogous to the model pseudomolecules in their spatial framework.

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INTERFACE DOPING OF CONJUGATED ORGANIC FILMS UPON INTERACTION WITH METAL OXIDE AND SEMICONDUCTING UNDERLAYERS

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Controlled modification of compositional and electronic properties of conjugated organic films by means of interface doping attracts scientific interest in respect of design of the interfacial layers in organic and hybrid nanoscale structures. The atoms transferred over the interface provide significant modification of the interface potential barrier, which would affect the performance of the nanoelectronic devices.

This presentation reports the results on the interface formation of 5-10 nm thick conjugated layers of Cu-phthalocyanine (CuPc), perylene tetracarboxylic acid dianhydride (PTCDA) and of the phenylene-vinylene oligomer (OPV) with a number of solid surfaces (SiO$_2$)$_n$-Si, ZnO(0001), TiO$_2$(110), Si(100), Ge(111), CdS(000-1) and GaAs(100) [1,2]. These results were obtained using a number of spectroscopy techniques such as Auger electron spectroscopy, low-energy target electron spectroscopy and desorption mass-spectrometry. The island-like organic deposits were excluded from the analysis so that only uniform organic deposits were considered. The peaks corresponding to the atomic components of the substrates were seen in the Auger spectra and in the desorption mass-spectra. The relative concentration of the substrate atomic components diffused in the film was different from their relative concentration in the pure substrate surface. The possibility of doping by Zn, Cd, Ga, O and S substrate atoms was registered in the case of the CuPc films on the corresponding substrates and the concentration of the dopant atoms in the organic was estimated as one atom per one organic molecule. Doping of the OPV films and of the PTCDA films interfacing the CdS and GaAs surfaces was also observed. Using both the target electron spectroscopy and the \textit{ab initio} Density functional theory calculations, it was shown that the substrate atoms admixed in the organic film account for the appearance of a new peak in the density of electronic states. The work is supported by the Russian foundation for basic research 0803-00270.

References


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CONFORMATION-SELECTIVE PHOTOCHEMISTRY:
THE CASE OF ANISALDEHYDE ISOLATED IN ARGON MATRIX

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Molecular conformation is a central concept in molecular physics, chemistry and biochemistry. The conformational structure of a molecule determines not only its physical properties (e.g., dipole moment), but also its chemical and photochemical reactivity. Although these principles are generally accepted, experimental observations of significantly different rates of photochemical transformations in different conformers of the same compound are still very scarce. In the present study, we investigated photochemical transformations for two conformers of anisaldehyde.

Figure 1. Optimized structures of O-trans (left) and O-cis (right) conformers of anisaldehyde

The molecule of anisaldehyde can adopt two conformational structures (Figure 1). These forms are nearly isoenergetic (ΔE = 0.25 kJ mol⁻¹). Hence, both conformers are populated in the gas phase and can be trapped in low-temperature matrices. The experimental investigation of anisaldehyde monomers isolated in an Ar matrix at 12 K demonstrated that two conformers of the compound are indeed populated in a low-temperature solid Ar environment. Infrared spectra of the two forms are very similar. The infrared bands belonging to the spectrum of one of the forms are shifted by several cm⁻¹, with respect to the corresponding bands in the spectrum of the other form. Hence, in the infrared spectrum of matrix isolated anisaldehyde a number of bands appears as doublets.

The presence of two conformers of anisaldehyde in an Ar matrix was confirmed by the results of UV-induced transformations observed for this compound. Upon UV (λ > 305 nm) irradiation, the population of only one conformer decreased significantly. This process was experimentally observed as decrease of intensity of one of the components (due to the O-cis form) of doublet bands, whereas the other component (due to the O-trans form) remained much less affected. Upon irradiation with UV light of shorter wavelengths (λ > 245 nm) both conformers were consumed in a photoreaction leading to a ketene photoproduct. The most intense band in the spectrum of the photoproduct was observed at 2126 cm⁻¹ that is at a frequency characteristic for the “antisymmetric” stretching vibration of the ketene group.

The interpretation of the experimental data received support from theoretical calculations carried out at the DFT(B3LYP) level of approximation, with the 6-311++G(d,p) basis set.

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FLEXIBILITY OF PARAMAGNETIC (D^1) ORGANOMETALLIC DITHIOLENE COMPLEX
[Cp2Mo(DMIT)]^+ STUDIED BY RAMAN SPECTROSCOPY

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In the large family of dithiolene complexes, the non-planar mixed-ligand complexes of general formula Cp2M(dt) (M = Mo, Nb, W, Ti), in which dithiolene (dt) and cyclopentadienyl (Cp) ligands are simultaneously incorporated, deserve a special attention. A striking property of these Cp2M(dt) complexes is their conformational flexibility in the solid state, i.e. the MS2C2 metallacycle is often folded along the S···S axis. Recently, the radical cation salts of the same Cp2Mo(dmit) complex have been synthesized with a variety of anions such as monoatomic Br^−, tetrahedral BF4^−, octahedral PF6^−, AsF6^− and SbF6^−, and more complex anions TCNQF4^− and [ReO(dmit)2]^−. The crystallographic investigations of these salts show that the folding angle of the d^1 [Cp2Mo(dmit)]^+ cation is strongly dependent on the counter ion and the crystal structure with: θ = 0° for PF6^−, AsF6^− and SbF6^−; θ = 5.6° for ReO(dmit)2^−; θ = 10.2° for TCNQF4^−; θ = 23.2° for BF4^− and θ = 30.45° for Br^−. In this work, we studied an influence of the folding of the MoS2C2 metallacycle in [Cp2Mo(dmit)]^+ cation on the spectral properties. The correlation between the folding angle and the frequency of characteristic Raman bands can be very useful in investigations of eventual metallacycle distortions for such type of salts where structural data are unavailable.

Raman spectra of charge-transfer salts formed by the organometallic complex Cp2Mo(dmit) with various anions (Br−, BF4^−, PF6^−, SbF6^−, ReO(dmit)2^−, TCNQF4^−) were recorded at room temperature using red (632.8 nm) and NIR (780 nm) excitations. Moreover, for neutral and ionized complex with various folding angles, using DFT methods, we calculated the bond length, charge distribution, HOMO and LUMO energies, and dipole moments. The normal vibrational modes were also calculated by DFT methods and then used for assignment of bands in Raman spectra. We have shown that the folding of [Cp2Mo(dmit)]^+ cations is related to a low-frequency shift (0.5 – 0.6 cm^−1/deg) of Raman bands assigned to the C=C and some C–S stretching vibrations. The analogous investigations were also performed for other normal modes: C=S stretching (nearly independent on folding) and in-plane C–H bending in the Cp ring (low-frequency shift comparable with that of C=C). The frequency of normal modes assigned to the Mo–S stretching and in-plane Mo(dmit) ring deformation are nearly independent of the folding angle.

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PHOTOPOLYMERIZATION AND BRILLOUIN SPECTROSCOPY STUDIES OF BZMA/BIS-GMA LIQUID MIXTURES

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Photocurable compositions based on mixtures of mono- and multimethacrylate monomers are widely used in many industrial applications such as coatings, adhesives, inks, printing plates, optical waveguides, microelectronics, information storage systems, dental restorative materials and many others. Substantial effort has been devoted to understand how varying structure of methacrylate monomers and photopolymerization conditions impact the polymerization kinetics.

The polymerization rate depends both on the reactivity of the monomers as well as on physical properties of the polymerizing medium which determine the mobility of the reacting species. Additional effect may arise from intermolecular interaction between the monomers used in a formulation.

The aim of the work was to investigate the influence of the system viscosity on the photopolymerization kinetics (by isothermal differential scanning calorimetry) and molecular dynamics (by Brillouin scattering) in a two-monomer system. The investigated system was a mixture of highly viscous 2,2-bis[4-(2-hydroxymethacryloxypropoxy)phenyl]propane (bis-GMA, η²₀=1420 Pa·s) and a monomer of low viscosity – benzyl methacrylate (BzMA, η²₀=0,0026 Pa·s). The viscosity of the system was regulated by molar ratios of monomers being used (bis-GMA/BzMA: 0/100, 10/90, 20/80, 40/60, 60/40, 80/20, 100/0 mol-%).

In the frame of kinetic investigations the photopolymerization of the bis-GMA/BzMA system in a temperature range 20 – 50 °C in 10 °C intervals was studied. The reaction was carried out in Ar and was initiated by 2,2dimethoxy-2-phenylacetophenone and 366 nm light (1 mW/cm²).

Using Brillouin scattering method, the hypersonic wave velocity and attenuation coefficient were investigated in wide temperature range. The acoustic wave velocity in the measured mixtures changes anomaly (S-type curve) with decreasing of the temperature. The temperature dependencies of the attenuation coefficient show characteristic maxima. For some mixtures being under study, the glass transition was observed.

The temperature dependencies of the acoustic wave velocity and attenuation coefficient for the investigated mixtures clearly show that the some relaxation process is taking place on the picoseconds time scale. The character of changes displays the typical features characteristic for the case when a liquid is supercooled from a fluid liquid to the „frozen” state. The increase of mixture viscosity slows down the relaxation process and shifts it to higher temperatures.

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VIBRATIONAL SPECTROSCOPY AS A TOOL FOR ANALYSIS OF WILLOW LEAVES

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Various techniques of vibrational spectroscopy can be used for non-destructive analysis of biological samples. Previously, we demonstrated the potential of FT Raman and ATR spectroscopy for monitoring of Norway spruce needles [1 – 3]. In this study we develop a methodology of fresh willow leaves analysis using attenuated total reflection (ATR) FT-IR, FT-Raman scattering and FT-NIR transmission spectroscopy. The freshly taken leaves were stored at the most several days with water supply, packed in PE bags in brash-ice.

ATR technique provides us with information on the surface layers of the leaves, allows to distinguish both sides of the leaves and to study cuticular waxes and surface humidity. Various classification methods (e.g. cluster analysis, linear discriminant analysis - LDA) enable to classify groups of spectra considering various experimental parameters (e.g. group of trees, ageing of leaves, and sampled side of leaves). The spectral parts contributing to such classification can be found out and they are tentatively assigned to characteristic bands of several leaf constituents.

FT-NIR transmission spectra are dominated by characteristic bands of water and they are not affected by the sides of the leave irradiated. The overall leaf humidity can be monitored, some other components are identified using principal component analysis and inspecting the loadings graphs of second and third principal components.

FT Raman spectra exhibit characteristic features of plant pigments, predominantly carotenoids. The Raman spectral data can be classified mainly with respect to age of leaves. To elucidate the other key factors affecting spectral data the principal component analysis was applied.

Summarily, the set of molecular spectroscopic methods provide us with a complex set of information on physiological state of leaves prior their harvesting.


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SPECTROSCOPIC INVESTIGATION OF ALKALINE IONS INFLUENCE ON THE COMPLEXATION IN THE INTERCALATED LIGAND – DNA SYSTEMS

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Numerous studies of interactions between ligands and DNA consider this process by formation of one type of complexes. However, recent investigations showed that intercalating drugs can form several types of complexes on the polyelectrolyte matrix in broad range of both ligands and DNA concentrations. Undoubtedly, the formation of different complexes simultaneously in the ligand – DNA system complicates determination of their thermodynamical and spectral binding parameters. Moreover, the salt presence can influence on contribution of each different type of complexes into concentration dependences and also lead to complication determination of binding parameters.

We used spectrophotometric titration method to study the processes of complexation in a system of actinomycin derivatives (ActII*, analogue of the known antitumor agent actinomycin D) and native and denatured calf thymus DNA (ctDNA) at different concentrations of monovalent ions. In contrast to some simple methods which usually used only one wavelength for the Scatchard plot construction, we treat whole set of obtained in large range of concentrations and wavelengths data fitting calculated spectra to experimental.

Using different models, which consider ligands interaction with polynucleotide by the set of McGhee and von Hippel equations, the equilibrium composition was calculated in approximation of multimodal binding. As it was shown earlier [1] for actinocin derivatives ActII* can form more than one type of complex with different optical parameters on the both native and denatured DNA forms. The thermodynamic parameters (constants, biding site sizes, cooperativity factor) were calculated on the basis of spectrophotoscopic titration data via DALSMOD optimization programs at multimodal binding of ActII* to ctDNA.

Alkaline ions (Na⁺, K⁺ and NH₄⁺) were considered as competitors to ligand binding to the ctDNA in each model. Contribution of different types of complexes in observable optical absorption were found for different concentration of added ions. Obtained values of ions binding constants are discussed

PERFORMANCE OF NOVEL M05-2X DENSITY FUNCTIONAL METHOD IN CALCULATIONS OF MOLECULAR STRUCTURES AND VIBRATIONAL SPECTRA OF VITAMIN B13 COMPLEXES WITH METAL IONS

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Comprehensive studies of the molecular structures and vibrational spectra of the vitamin B13 complexes with the Cu(II), Ni(II) and Pt(II) ions have been performed by means of the experimental techniques (single crystal X-ray diffraction, FT-IR and Raman spectroscopy) and various theoretical methods including the newly developed M05-2X density functional1. It is shown that M05-2X performs very well in calculations of geometrical parameters of the supramolecular complex formed by the Cu$^{2+}$···π noncovalent interactions2. Both the M05-2X and ab initio MP2 methods predicted the structure of this complex in good agreement with experiment, whereas the B3LYP method failed in geometry optimization. However, the M05-2X’s performance in calculating vibrational frequencies of all the studied complexes is inferior to B3LYP. Moreover, the M05-2X functional considerably overestimates the strength of the interligand N-H···O and O-H···O hydrogen bonds, which are formed in the molecular plane of metal complexes. Thus, the new M05-2X density functional method is recommended for predicting the molecular structures and binding energies of weak dispersion-dominated stacked complexes, but it is less suitable for systems containing medium or strong hydrogen bonds.

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THE SPECTROSCOPIC STUDY OF BUILDING COMPOSITES CONTAINING NATURAL SORBENTS

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This work presents the results of FT-IR and AAS spectroscopic studies of heavy metal cations (Pb^{2+}, Zn^{2+}, Cd^{2+}, Ag^{+} and Cr^{3+}) their immobilization from aqueous solutions on natural sorbents. The sorption has been conducted on sodium forms of zeolite (clinoptilolite) and clay minerals (mixtures containing mainly montmorillonite and kaolinite) which have been separated from natural Polish deposit. In the next part of the work both sorbents were used to obtain new building composites.

It was proven that heavy metal cations’ sorption causes changes in IR spectra of the zeolite and clay minerals. These alterations are dependent on the way the cations were sorbed and their amount. In the case of zeolite, variations in intensities and positions of the bands corresponding to the characteristic ring vibrations have been observed. These rings occur in pseudomolecular complexes $4\cdot4=1$ (built of alumino- and silicoxygen tetrahedra) which constitute the secondary building units (SBU) and form spatial framework of the zeolite. The most significant changes have been determined in the region of pseudolattice vibrations (650÷700 cm$^{-1}$). In the instance of clay minerals, changes in the spectra occur at three ranges: 715-610 cm$^{-1}$ – the range of the bands due to pseudolattice vibrations; 1250-850 cm$^{-1}$ – the range of the bands assigned to asymmetric Si-O(Si,Al) and bending Al-OH vibrations and 3750-3200 cm$^{-1}$ – the range of the bands originating from OH- groups stretching vibrations. The most essential changes in the clay minerals are found in the second range.

Results of IR-spectroscopic studies have been compared with those obtained by atomic absorption spectroscopy, from which the proportion of ion exchange to chemisorption in the process and the effective cation exchange capacity of the individual samples have been estimated.

Next results indicate possibilities of applying the used natural sorbents for the obtainment of new building materials having favourable composition and valuable properties. The zeolite was used for obtaining autoclaved materials with an addition of CaO, and the clay minerals for ceramic sintered materials with an addition of quartz and clinoptilolite were produced.

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Coexistence of magnetism and electrical conductivity is one of the most important directions in the synthesis of multifunctional organic-based materials. The TTF (tetra-thiafulvalene) and its derivatives are the most frequently used donor molecules for building conducting supramolecular architectures. In particular, TCE-TTF (2,3,6,7-tetrakis(2-cyanoethylthio)tetrathiafulvalene) is functionalized with four electron-withdrawing groups which are able to coordinate transition metals to produce polymeric architectures. Here we present infrared and Raman spectra of the series of TCE-TTF-based isostructural salts with paramagnetic (CoII, MnII), and diamagnetic (ZnII, CdII) ions, where short S⋯S contacts between TTF cores of the 2D polymeric network create a 3D architecture [1]. These materials crystallize in the P21/c space group of the monoclinic system and display semiconducting behavior. In our analysis of the vibrational spectra, we focus on the normal modes related to the C≡C stretching vibrations of the TCE-TTF donor molecule, which are sensitive probes of the local charge on the molecule and can be used in order to estimate the ionization degree. These modes appear in the spectra in the frequency range 1400 – 1560 cm⁻¹. Another important vibrational features centered at about 2290 cm⁻¹ are related to the stretching modes of the C≡N groups, which are coordinated with metal atoms. Some differences between materials are discussed.

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STRUCTURE AND PROPERTIES OF (NH₄)₃BiCl₆

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The ionic compounds of the general formula RₐMₐXₐ+3b, where R – organic cations, M – Sb(III) or Bi(III) and X = Cl, Br, I, have been the subject of careful studies since their ferroic properties were discovered [1, 2]. The characteristic feature of these compounds is a rich diversity of anionic sublattices composed of deformed MX₆ octahedra either isolated or connected with neighbouring octahedra by corners, edges or faces. Different organic cations may be involved in the crystallization of halogenoantimonates(III) and halogenobismuthates(III), from alkylammonium to aromatic amines. However, there is little information in literature about the simplest – ammonium cation with chlorobismuthate(III) [3, 4]. Therefore, we decided to undertake systematic studies on (NH₄)₃BiCl₆. Calorimetry, linear thermal expansion and dielectric methods were applied to characterize the physical properties of this compound. The structure of the title compound is determined by means of X-ray diffraction at room temperature and has been redetermined at 100 K. It is reported to crystallize in the orthorhombic symmetry with space group Pnma. The optical observations under polarizing microscope revealed the ferroelastic domain structure at the room temperature phase. Differential scanning calorimetry (DSC) reveals one reversible phase transition at 414/403 K (cooling/heating) of the first-order type. The dielectric studies in the frequency range 3 kHz – 1MHz disclose a relaxation process below room temperature. The mechanism of the phase transition is discussed.

References
The preferred conformations of the 2-methyl-2-(1H-tetrazol-1-yl)propan-1-ol molecule (TOH) and their vibrational spectra were studied using DFT method and matrix-isolation Fourier transform infrared spectroscopy. A systematic search on the potential energy surface at the B3LYP/6-311++G(2d,2p) level for the TOH molecule revealed the presence of twelve different minima. One of these structures possesses the $C_s$ symmetry while eleven belong to the $C_1$ symmetry point group and have their mirror-image structures of the similar energy; the latter species will not be considered further. Two most stable species (TOH1, TOH2) of almost equal energy are characterized by a presence of the intramolecular hydrogen bond formed between O-H group and one of the nitrogen atoms (N1) of the tetrazole ring. The third most stable isomer (TOH3) characterized by the unbonded OH group is only ca. 1 kJ/mol less stable than the hydrogen bonded structures. All other stable conformers are by 6-14 kJ/mol higher in energy than the global minimum. The calculated relative Gibbs free energies of the TOH conformers do not follow the order of the zero-point corrected relative energies. The gas phase abundance at 298K equals 44.3, 17.7 and 29.3%, for TOH1, TOH2 and TOH3, respectively while other conformers have a negligible population.

The FTIR spectra of TOH reveal the presence of both hydrogen bonded and non-hydrogen bonded species isolated in argon matrices. The assignment of the experimental IR bands is based on the analysis of the theoretically predicted spectra and the potential energy distribution (PED) matrices obtained for the most stable conformers. Peculiar intensity changes of the bands assigned to the hydrogen bonded and non-hydrogen bonded conformers are observed on matrix annealing indicating that a temperature induced inter-conversion process occurs in the studied matrices.
FT-IR INVESTIGATIONS OF WOLLASTONITE/POLY-E-CAPROLACTONE NANOCOMPOSITES FOR MEDICAL APPLICATIONS

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The bone tissue is the second most frequently transplanted human tissue and in the medical market a demand is growing for new materials for reconstitution of bone defects. Polymer nanocomposites belong to a new class of hybrid materials consisting of polymer matrix and inorganic nanoparticles. Nanocomposites consisting of resorbable polymer and bioactive nanoparticles are very attractive materials for medical applications.

The aim of this work was to obtain new nanocomposite materials consisting of resorbable polymer (PCL) matrix and ceramic (wollastonite) nanoparticles for medical use in the field of bone tissue regeneration. Poly-e-caprolactone (PCL) is a biodegradable polymer belonging to the aliphatic polyesters group. It is a non-toxic material, which has a good ability to mix, and is mechanically compatible with many other polymers and organic and inorganic compounds. This biocompatible polymer has been widely used also in the tissue engineering. Wollastonite is a bioactive and biocompatible material, which may become an interesting alternative to hydroxyapatite, in particular due to higher than in the case of other bioactive materials rate of apatite formation on its surface after incubation in SBF, and due to its ability of chemical integration with the bone.

Nanocomposite polycaprolactone/wollastonite foils with a varying content of the ceramic nanoparticles were prepared. The nanocomposites and wollastonite nanoparticles were investigated using FT-IR and PIXE techniques. FT-IR method is a particularly efficient tool for the surface analysis of nanosized and nanocomposite materials. This technique was used to determine structural changes of the polymer caused by the presence of wollastonite nanoparticles. We observed a correlation between the concentration of nanoparticles and structural changes of the nanocomposite surface. PIXE was used to study the nanocomposites surface and their interaction with simulated body fluid (SBF).

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FTIR STUDY OF BIOACTIVITY CERAMIC LAYERS

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Vibrational spectroscopy has been extensively used for in vitro and in vivo investigations of degradation mechanism and kinetics of different biomedical devices as well as it has been used to characterize the crystalline and amorphous domains in bio-mineralization process.

Modern medicine requires high quality implant materials. Bio-ceramics have revolutionized orthopedic and dental repair of damaged parts of the bone system. Some of biomaterials due to their biocompatibility allow manipulation and adaptation to the shape and dimensions of bone defects.

Titanium and its alloys are the materials which widely applied for the fabrication of bio-implants. The nature of their surfaces can directly influence cellular response, ultimately affecting the rate and quality of new tissue formation. In order to improve titanium implants properties, they are usually covered with various kinds of ceramic layers. The bio-inert ceramic materials have attractive properties, such as strength and fracture for medical applications.

In vitro tests, where the materials immersed in simulated body fluids and/or artificial saliva, have been used to evaluate the biocompatibility of biomaterials. This kind of tests are a wide range of repeatable and reproducible methods, which are regulated by international standards for commercial use and scientific development of new materials and products.

The aim of this work has been to examine zirconia silicate films obtained by sol-gel method on titanium. The bioactivity of the composite films was studied by immersing the coatings in synthetic body fluids (SBF). Changes in phase composition of biomaterials were determined by FTIR reflection technique based on focal plane array (FPA) detection system. The study of the interaction of components of artificial body fluids with ceramic layers being subjected to different environmental conditions by FTIR imaging is shown.

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PREPARATION AND SPECTROSCOPIC CHARACTERISATION OF MONTMORYLONITE - CHITOSANE NANOCOMPOSITE MATERIALS

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Nanocomposites from renewable sources are materials which properties can be controlled in a wide range. Area of potential applications of the nanocomposites is still growing, since they can play role of structural materials, renewable materials and biomaterials. However, successful preparation of the nanocomposites still encounters many problems mainly related to proper dispersion of nano-fillers. High surface area, and high free surface energy are the cause of agglomeration of the nanoparticles which then lose ability to create first- and second-order interactions with a polymer matrix. In the result, the nano-filler becomes submicron or micron phase which because of its low fraction, not exceeding 5% (volume or weight), act as a defect weakening the polymer matrix.

The nanocomposites from renewable sources are considered to be a group of perspective materials. The main advantage of the nanocomposite materials based on natural biopolymers such as polysaccharides e.g. alginates or chitosane is their simple utilisation and safe products of degradation. The additional advantage of nanocomposites based on chitosane and montmorylonite (MMT) is availability and low cost of the component materials.

In the work efforts of production of a series of nanocomposites based on natural chitosane and nano-clay (MMT) were taken. The nanocomposites materials was obtaining by casting method. Ultrasound stirrer was used to better homogenization between nanoclay particles and biopolymer matrix. Four types of MMT with different particle size (DLS) and specific surface area (BET) were used. In two cases, MMT nanoparticles were organophilised with third-order amine. The nanoparticles morphology was examined with electron microscopy (SEM/TEM). In each nanocomposite, the nano-filler amount was 3.5 wt.%. Dispersion of the nano-filler within the polymer matrix was investigated with the use of FT-IR method (transmission mode, FT-IR microscopy).

It was shown that the best dispersion nano-clay in chitosane matrix characterized materials which as a modified was used commercial MMT named K5 and K10. High agglomerisation of nanoparticle MMT was observed when was used MMT modified by amine in spite of the same forming condition.

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SPECTROSCOPIC AND MOLECULAR DYNAMICS INVESTIGATION OF WATER STRUCTURE AROUND HEN EGG WHITE LYSOZYME

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Hen egg white lysozyme is a small globular protein with molar mass equal to 14.3 kDa. It is composed of 129 amino acid residues, including 8 cysteine residues forming 4 disulphide bridges. The dominant secondary structure is α-helix (40-46% residues), while β-sheet structure is adopted by 9-10% residues. The lysozyme molecule might be divided into two subdomains with predominant α or β secondary structure [1]. Lysozyme is often used as a model protein, e.g., in the studies of protein folding processes [2]. Since it is suggested that electrostatic interactions play a key role in lysozyme’s structure and activity [3], the interaction of this protein with water is a particularly intriguing subject.

Vibrational spectroscopy is an ideally suited method for investigation of solute hydration. Spectra of HDO isotopically diluted in H2O are free from numerous experimental and interpretative problems connected with H2O spectra. The vibrations of decoupled OD oscillators function as a very sensitive and ideally suited probe of hydration phenomena, giving valuable structural and energetic information pertaining hydration spheres.

To extract information about the interactions inside the hydration sphere, the contribution of bulk water should be eliminated from the solution spectrum to obtain the solute-affected water spectrum. The appropriate quantitative method of spectral data analysis was formulated inter alia in our laboratory [4]. The possibility to transform the vibrational spectrum profile to interatomic oxygen-oxygen distribution function enables comparison with experimental and computational methods that directly reveal the structural information.

Molecular dynamics (MD) serves as an important tool in the determination of protein structure and dynamics. We already successfully applied MD coupled with HDO vibrational spectroscopy to elucidate the hydration of amides in an aqueous solution [5]. In this work, we apply both techniques to investigate water structure around hen egg white lysozyme in its native form in an aqueous solution. The structural information from molecular simulations is confronted with affected water spectra to obtain complementary picture of the protein’s hydration spheres.

References

A possible existence of planar (NPX_2) cyclophosphazenes, where X = H, F, Cl and Br, or nonplanar (PXNX)_3 was studied with the Gaussian 03 software package using density functional theory (DFT) at the B3LYP/6-311++G** level of calculations. A linear correlation of total electronic energy difference ($\Delta E = E_{\text{nonplanar}} - E_{\text{planar}}$) on electronegativity of the X substituent was observed. The more stable nonplanar form was predicted ($\Delta E = -43.49$ kcal/mol) only in case of X = H. The remaining planar halogenocyclotriphosphazenes are more stable, in agreement with a few available experimental data. The HOMO – LUMO differences also nicely correlate with the stability of the planar and chair-like structures. Natural bond orbital (NBO) analysis was performed for the investigation and comparison of P-N bond strengths in planar and nonplanar cyclotriphosphazenes.
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SPECTROSCOPIC AND STRUCTURAL CHARACTERISTICS OF N-BENZYL-2-METHYL-4-NITROANILINE (BNA) CRYSTAL

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The N-benzyl-2-methyl-4-nitroaniline (BNA) crystal has been studied because of its interesting properties. First of all the BNA crystal shows 1.7 times more efficient second harmonic generation than the 2-methyl-4-nitroaniline (MNA) crystal [1]. It also reveals widely tunable THz generation [2].

The crystal structure of BNA has been determined and compared with the previous data [3]. The infrared, Raman and UV-Vis spectra of BNA have been studied: the IR spectra of BNA in CHCl₃ solutions and KBr pellet were measured in the 400-10000 cm⁻¹ region, Raman spectra were recorded in the CHCl₃ solution and crystal. The Raman spectra were excited by the red (647.1 nm), green (514.5 nm) and blue (488.0 nm) line of a Spectra-Physics Ar-Kr laser. DFT (B3LYP/6-31G++(d,p)) quantum chemical calculations of wavenumbers and potential energy distribution (PED) have been performed to facilitate complete assignments of bands to normal vibrations and an analysis of measured spectra. The near IR (NIR) spectra of crystal were also recorded in order to assign overtones and combination bands which are interesting from the point of view of anharmonicity.

BNA crystallizes at least in two different crystal structures, orthorhombic [3] and monoclinic, in which two types of hydrogen bond: N–H···O (the shortest bond is 2.487 Å) and C–H···O occurs, respectively.

The phenomenon of polymorphism in various BNA crystals form different solutions has been studied by differential scanning calorimetry (DSC). Furthermore, the possibility of the polymorphism has been checked with the Cerius² program [4].

Despite of the well-defined phase transition deficiency in the BNA crystal the cold crystallization [5] has been observed which can be connected with an amorphous phase.

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VISIBLE LUMINESCENCE OF DYSPROSIUM IONS IN OXYHALIDE LEAD BORATE GLASSES

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Dysprosium-doped oxyhalide borate glasses with PbO and PbX2 (X = F, Cl) were studied using X-ray diffraction and various spectroscopic techniques (Raman, infrared, absorption, excitation and luminescence). The results on glass preparation, short-range-order structure and optical studies are presented. X-ray diffraction analysis evidently indicates that the fully amorphous system was prepared. Coexistence of trigonal BO3 and tetrahedral BO4 units was evidenced by Raman and FT-IR spectroscopy. The electronic states of Dy3+ ions in oxyhalide glasses were determined from the absorption and the excitation spectra. Luminescence spectra registered in the visible spectral region correspond to 4F9/2 – 6HJ/2 (J = 11, 13, 15) transitions of Dy3+. Decay curves are nearly single exponential and the measured luminescence lifetime for 4F9/2 state of Dy3+ ions is slightly longer for sample with PbF2 than PbCl2. The systematic studies indicate that multicomponent oxyhalide glasses containing Dy3+ ions are promising solid-state materials for yellow/blue luminescence.

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RARE EARTH - DOPED LEAD BORATE GLASSES AND TRANSPARENT GLASS-CERAMICS: STRUCTURE-PROPERTY RELATIONSHIP

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Lead borate glasses and glass-ceramics containing rare earth ions have been examined. Rare earths as an optically active ions were limited to Eu³⁺ and Er³⁺ ions. Correlation between short-range-order structure and optical properties of Eu³⁺ ions in lead borate glass was clearly evidenced by Raman, FT-IR and photoluminescence spectroscopy. Structurally different borate groups can be found in lead borate glasses. The obtained results indicate that the BO₃↔BO₄ forward/back conversion strongly depends on the relative PbO/B₂O₃ ratios in glass composition, giving important contribution to the luminescence intensities associated to 5D₀-7F₂ and 5D₀-7F₁ transitions of Eu³⁺.

Lead borates doped with Er³⁺ ions were analyzed before and after thermal treatment, which introduces transformation from glass to transparent glass-ceramic material. X-ray diffraction analysis revealed that the orthorhombic PbF₂ crystallites are successfully formed in these systems, independently on thermal treatment conditions. The spectroscopic consequence of transformation from glass to glass-ceramic is the elongation in the ⁴I₁₃/₂ luminescence lifetime and the narrowing of near-infrared luminescence band at 1.5 μm due to main ⁴I₁₃/₂-⁴I₁₅/₂ laser transition of Er³⁺.

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STRUCTURAL CHARACTERIZATION, THERMAL, DIELECTRIC AND VIBRATIONAL PROPERTIES OF (C₃H₅NH₃)₃SbBr₆

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Halogenoantimonates(III) and halogenobismuthates(III) described by the general formula RₐMₐX₉ and R₅M₂X₁₁ [3,4] have been found to exhibit interesting ferroic properties [1, 2]. From among these compounds, in the salts crystallizing with the chemical composition R₃M₂X₆ and R₅M₂X₁₁, the ferroelectricity has been found to appear. The compounds of R₃MX₆ type were studied roughly so far. Recently have been synthesized and characterized several new halogenoantimonates(III) and halogenobismuthates(III) analogs containing in the crystal structure the allylammonium cations. The paper is devoted to the structure and physical properties of the tris(allylammonium) hexabromoantimonate(III), (C₃H₅NH₃)₃[SbBr₆]. It revealed three thermal anomalies at about 255, 211 and 190 K. The structure is composed of [BiCl₆]⁻ octahedra and allylammonium cations. The organic and inorganic moieties are attracted to each other by a network of the N–H…Br hydrogen bonds. The relationship between corresponding parameters of the unit cells has been found. The thermal (DSC) and dielectric studies showed that the phase transitions of the order-disorder type are attributed to the ordering of one non-equivalent allylammonium cation in the low-temperature phase. The vibrational (IR) measurements revealed a significant role of the organic cations in the phase transition mechanism at low temperatures.

References
FT NIR RAMAN STUDIES OF ALGINIC ACID–BENZIMIDAZOLE POLYMER COMPOSITE

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Membranes with high anhydrous proton conducting have received growing interest for their application to the polymer electrolyte membrane fuel cell (PEFC). Recently using of proton conductivity of heterocyclic molecules like imidazole, pirazole in polymer membranes was proposed by Kreuer [1]. When heterocyclic structures are doped into acidic polyelectrolytes, these protogenic units form complexes through proton exchange reactions and proton transport occurs predominantly over azole units. Synthesis of heterocyclic molecules with biopolymers appeared to be extremely attractive proposal as PEFC [2,3].

In this study, new proton conducting polymer electrolyte networks consisting of alginate acid (AA) and benzimidazole (BnIm) were prepared and their properties were characterized by NIR Raman spectroscopy as well as XRD.

Alginic acid, one of the elements of marine algae, is a natural polysaccharide containing linear chains of 1,4’ linked β-D-mannuronic acid and α-L-guluronic acid. AA is a biodegradable, biocompatible, non-toxic and low cost polymer. Benzimidazole belongs to aromatic heterocyclic molecules, in which the atoms with protons or without may act as donors and acceptors respectively, in reaction of proton transport.

The AA-BnIm composites with three different content of BnIm: 1 mole of AA with 0.5; 1; 1.5 mole of BnIm were prepared. Thin transparent and homogeneous films with thickness 25-70 μm were obtained.

In structural studies of AA:BnIm composites it was found that benzimidazole is embedded in the alginate acid chain.

Raman spectra recorded at room temperature revealed, that the spectra of AA-BnIm composites differ from that which was observed for a mixture of AA and BnIm powders. A significant changes in the range of 1300-1800 cm⁻¹ were found for the AA:BnIm films. Intensity of the band at ~1730 cm⁻¹ related to stretching vibration νC=C in –COOH group decreases for 1:0.5 ratio of AA:BnIm, whereas it disappears for ratios of 1:1 and 1:1.5. Such behaviour is related to disappearance of –COOH group in the new compound and appearance of –COO⁻ group. As a consequence new intense bands at ~1454 cm⁻¹ and 1510 cm⁻¹ related to –COO⁻ group vibrations were observed in the Raman spectra of alginic acid-benzimidazole composites.

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References

Metal materials like titanium or its alloys are commonly used as dental or orthopaedic implants due to their good mechanical properties. Covering metal base by ceramics layers makes chance to improve their bioparameters. The surface, where the growth of apatite during simulated body fluid (SBF) soaking is observed can be treated as potential bioactive one.

The projected layers were composed of two parts: titanate-silicate underlayer for better adhesion and titanate-phosphate-silicate layers for potential bioparameters. The layers with different addition of hydroxylapatite were deposited on titanium and Ti6Al4V alloy bases using dipping sol-gel method. The selection of sol / suspension composition, depositing time and layer heating treatment conditions have the conclusive influence on the layers parameters. The obtained layers should be very thin and almost amorphous.

All obtained samples were compared on the base of XRD analysis data (GID technique), SEM with EDX measurements and FT IR spectroscopy (transmission and reflection techniques) before and after soaking in simulated body fluid. FT IR spectroscopy with mathematic treatment of the spectra (BIO-RAD Win IR program, Arithmetic-subtract function) was used to detect the increase or decrease of any phosphate phases during SBF soaking. On the base of FT IR results the processes of hydroxyapatite growing or layer solution were estimated.

The layers deposited on titanium base are more crystalline then the ones deposited on Ti6Al4V. During SBF soaking process the growth of small amount of microcrystalline carbonate hydroxylapatite was observed on titanium base. The layer on Ti6Al4V base contained amorphous apatites. The Ti6Al4V base seems to be more advantageous in context of potentially bioactive materials obtaining.
SBF Soaking Test of the Phosphate-Silicate Layers Modified by Calcium and Hydroxyapatite

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The layers modifying the properties of metal base can be deposited using different methods such as CVD, sol-gel, electrophoresis etc. The sol-gel method is classified as low temperature one. It enables to obtain the layers of different chemical composition and very good homogeneity on the different shapes bases. The adequately chemical composition of multilayer, combining with depositing time and layer heating treatment conditions, can activate bioparameters of material and pretend it to be used as bioactive implants.

Ti6Al4V alloy was used as a base material. The experiment was concentrated on the layer chemical and phase composition planning. The initial titanate-silicate sol was modified by different hydroxyapatite (HAp) and calcium additions. All the samples were soaked in simulated body fluid, in temperature of 310K, during the period of 3-6 weeks, to check the possibility of hydroxylapatite growth.

The specific character of ceramic layers on the metal base disqualify some measurements methods or make it difficult to interpret the measure results. The results of the XRD analysis data (GID technique), SEM with EDX measurements and FT IR spectroscopy (transmission and reflection techniques) enabled to characterise the changes of sample layers during SBF soaking.

The greater growth of apatites during SBF soaking was observed, mainly taking into account relative growth of intensities of bands characteristic for P-O bonds vibrations, in case of samples with calcium and hydroxyapatite additions when in case of samples subsidized only by HAp. The apatite growing during soaking in simulated body fluid is amorphous carbonate calcium apatite dispersed on silicate or titanium-silicate amorphous layer. During heating treatment above about 870-920 K the apatite transforms into carbonate hydroxylapatite.
THE EFFECT OF INVERSION OF MATRIX AND INCLUSIONS COMPOSITION IN LIQUATION PHOSPHO-SILICATE GLASSES

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Silico-phosphate glasses of XCaPO₄-SiO₂ and XCaPO₄-AlPO₄-SiO₂ (X = Na⁺ and/or K⁺) system have been the subject of the presented investigations. Glasses belonging to those systems are characterized by a liqation phenomenon – spherical amorphous inclusions dispersed in an amorphous matrix. Thorough EDX investigations have shown that introduction of aluminum ions into the structure of phospho-silicate glasses results in inversion of matrix and inclusions composition, when XCaPO₄ exceeds 25-35% mol. Such a substantial influence of aluminum ions on phospho-silicate glasses texture as well as matrix and inclusions composition (inversion) must be a result of structural changes.

²⁷Al MAS NMR research stated that aluminum ions in structures of XCaPO₄-AlPO₄-SiO₂ phospho-silicate glasses always acts as a glass-forming ion – i.e. aluminum always occupies fourfold coordinated sites.

²³Na and ³¹P MAS NMR research has shown that the inversion of matrix and inclusions composition, brought about by introduction of aluminum ions into the structure of phospho-silicate glasses, is an outcome of a change in phosphorous and alkaline ions coordination.

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STRUCTURAL ROLE OF FE IN THE SOIL ACTIVE GLASSES

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Usually Fe is considered as a component of glasses having an influence on their optical properties. In a different kind of glasses containing biogenic elements (macro and microelements) and releasing them in the soil biological environment in the form available for plants [1] iron can perform the role of a microelement. Its influence on development of plants is connected with the processes of energy transformation needed for photosynthesis, regulation of the ox-redox reactions, and participation in the metabolism of nucleic acids. Biological activity of glasses defined as control release fertilizers (CRF) is conditioned by the type and the amount of the components entering into the composition of the silicate-phosphate network and the position occupied by the particular components.

Glasses of the SiO₂·P₂O₅·K₂O·MgO·CaO system modified with the addition of a microelement in the form of Fe, are the subject of the presented work.

The object of the work is to explain the influence of Fe on the solubility of the glasses mentioned above, in the conditions simulating soil biological environment on the basis of the examination of the glasses structure.

In order to establish the position occupied by the Fe in the glass structure, the glasses were examined by X-ray method and FTIR, NMR and Mössbauer spectroscopies. The chemical activity of glasses was defined with the use of a test used in the agricultural chemistry based on their dissolving in the 2 wt.% citric acid solution [2]. Leaching of glass components was investigated by ICP-AES method.

It has been found that Fe appears in the examined glasses both in the form of Fe³⁺ ions (85%) as well as Fe²⁺ ions with the tetra- and octahedral positions. The increasing amount of Fe in the glasses structure causes the creation of phosphate-ferric domains, and this type of medium structure arrangement can be the reason for the decreasing chemical activity of the examined glasses.

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References

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SPECTROSCOPIC AND CHEMICAL CHARACTERIZATION OF SOME RARE EARTH FLUOROCARBONATE MINERALS (PARISITE-(CE) \(\text{Ca(CE,La)}_2\text{(CO}_3\text{)}_3\text{F}_2\) AND SYNCHYSITE-(CE) \(\text{Ca(CE,La)}\text{(CO}_3\text{)}_2\text{F}\)) FROM PEGMATITES OF THE STRZEGOM-SOBÓTKA MASSIF, LOWER SILESIA, SW POLAND

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Specimens of investigated fluorcarbonates were found within pegmatite in Zimnik quarry (Strzegom-Sobótka granitic massif, Lower Silesia, SW Poland). The phases crystallized as one from the last minerals of pegmatite within massive calcite on the hydrothermal stage. They form brown prismatic pseudohexagonal crystals up to 1 cm in length.

Parisite-(Ce) and synchysite-(Ce) belong to bastnäsite-(Ce) group minerals [1]. The grains of fluorcarbonate were hand-picked and mounted in a resin for electron-microprobe analyses and Raman spectra. Powdered sample was used to IR spectroscopic measurements.

Back-scattered electron investigations showed heterogeneity of fluorcarbonate minerals. The crystals are built of two phases with identical chemical composition but different atomic density. Those phases form intergrowths within single crystals. Electron-microprobe analyses reveal presence of two phases: parisite-(Ce) (light areas of the crystal) and synchysite-(Ce) (dark areas of the crystal).

Literature data [e.g. 2] concerning carbonates allowed the precise assignation of bands to the corresponding vibration type on the MIR and Raman spectra. The influence of non-tetrahedral cations on the shape of the spectra and the positions of bands has been analysed and the crystal-line field splitting effect has been discussed.

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References

THE ROLE OF ALUMINIUM IONS IN THE GEOPOLYMERS ACTIVATION PROCESS

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The geopolymer term was introduced for the first time by Davidovitz as a description of alkali activated aluminosilicate materials [1]. The main goal of such materials’ examination are economical and ecological reasons. To produce the geopolymers, the blast furnace slags (BFS) can be used. BFS is a material which is still stored in large amounts on slag heaps.

For this paper the examinations were conducted on the synthetic glasses, that have got modeled composition. The composition of glasses is placed on the gehlenite and anortite crystal fields. Such glasses are the most popular in industrial slags. Basing on the spectroscopy examinations (MIR, MAS NMR), there was observed that in the examined glasses, aluminum ions are occurred only in tetrahedral coordination – they are building the glass structure.

The model glasses were hydrated in different conditions and with different amounts of activator. As the activator the NaOH was used. On the hydrated samples the XRD, NMR, IR and strength tests were carried out.

The examinations of hardening time show that the gehlenite type glasses are the most active ones. The activity of anortite glasses is significantly lower. The 27Al MAS NMR examinations of NaOH activated glasses pastes show that in case of gehlenite type glasses, the activation process brings the change of coordination of aluminium ions from tetrahedral to octahedral. In case of anortite type glasses, this phenomenon wasn’t observed. This fact allows to state that relocation of aluminium ions plays a key role in alkali activation process of the aluminosilicate glasses.

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COMPARISON OF COUNTERION INTERACTIONS IN 2-AMINOPYRIDINE BETAINES SALTS AND THEIR QUATERNARY CYCLIC DERIVATIVES

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Betaines make a special class of zwitterions, in which net uncharged molecules containing separate cationic and anionic sites [1]. The positive charge is localized on N⁺, S⁺ or P⁺ atoms which have no hydrogen atom, while the negative charge is on COO⁻, O⁻ SO₂O⁻ or R-P=OO⁻ groups. Betaines have a variety of applications in medicine, pharmacy, biology and other scientific fields [2,3]. An interesting group of betaines are those whose molecules contain pyridine ring, which are easily obtained by quaternization of pyridines with haloacetic acids as well as their salts and esters. Quaternization of 2-aminopyridine with X-CH₂-COOH (X = Cl or Br) is more complex, because it depends on reaction temperature.

![](image)

This contribution reports the spectroscopic properties of 2-aminopyridine betaine (1-carboxymethyl-2-aminopyridinium inner salt) and its complexes with HCl, HBr, HNO₃ and HClO₄. (1-2) These complexes on boiling in ethanol cyclized to 1-H-2-oxo-imidazo[1,2-a]pyridinium salts (chloride, bromide and perchlorate) (3) and to 1-H-2-oxo-pyrido[2,1-b][3,4]dihydropyrimidinium salts (chloride, bromide, perchlorate and nitrate) (4). In this poster the effect of the NH₂ substituent in position 2 of pyridine ring and counterions on the structure, conformation and hydrogen bonds of the 2-aminopyridine betaines salts and their quaternary cyclic derivatives are analyzed. Structures of the compounds investigated were studied by X-ray diffraction, FTIR, ¹H and ¹³C NMR spectra and B3LYP calculations.

Hydroxyapatite (HA) – Ca_{10}(PO_4)_6(OH)_2 is a basic inorganic model component of hard biological tissues such as bones and tooth. The significant property of HA is its ability to exchange Ca^{2+} ions which influences crystallinity, physico-chemical and biological properties of modified hydroxyapatite materials. The exchange mechanism is determined by the type of applied substitution method and by the type of metal cation [1]. One of the possible modifier of calcium phosphate materials is manganese. It has been demonstrated that divalent manganese (Mn^{2+}) ions in Ca_3(PO_4)_2 (TCP) structure positively influence bioactive surfaces thus promoting higher potential for proliferation and better viability of cells on the Mn doped β-TCP coatings obtained by pulsed laser deposition technique [2].

In this work, FTIR and XRD techniques were used to determine thermal stability and chemical and phase composition of modified hydroxyapatite. Mn substituted HA (MnHA) was prepared by coprecipitation method. Manganese acetate was added to H_3PO_4 solution in such concentrations that final MnHA contained 0.1, 0.5 and 1.0 wt % of Mn. Unmodified hydroxyapatite powder was used as the reference material. All samples obtained on the basis of initial powders were sintered at 800 and 1250ºC.

FTIR measurements allowed to determine chemical composition of Mn-doped hydroxyapatite. Intensity of bands attributed to OH^- group vibrations, was decreasing when manganese content was increased at higher sintering temperatures. It has been demonstrated, that manganese influenced a thermal stability of hydroxyapatite and changed its composition. MnHA MIR spectra were characterized by several bands, which were not visible in unmodified hydroxyapatite spectrum.

XRD studies confirm FTIR analysis. Samples calcined at 800ºC showed the presence of hydroxyapatite as the only crystalline phase. At higher temperature MnHA decomposed partially to α-TCP. The secondary phase content (TCP) was increasing with the amount of manganese added.

It has been concluded that after heat treatment, the studied materials changed color depending on sintering temperature – from light blue (intensity of the color increased with manganese content) to gray and even black (at highest sintering temperature).

The biological in vitro studies revealed that the number of MG-63 cells cultured on the surface of HA samples modified with 1.0 wt % of Mn was reduced compared to the unmodified HA and to the positive control. In contrary to the above results, correct morphology of cells determined by their adherence and spread was confirmed.

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There has been an ongoing research in our laboratory on molecular crystals showing nonlinear properties, one of which is 1,3-dinitrobenzene crystal. It generates second harmonic (SHG) up to 5 times more efficiently than KDP [1]. Previous studies could not indicate the origins of its nonlinearity since it possesses two electron accepting groups. However, in the paper by G. Wójcik et al. [2] it was proposed that the charge transfer may occur between oxygen atoms of two neighbouring molecules. This fact is very well pronounced in polarized IR spectra where one can observe unusually enhanced bands arising from out-of-plane deformation vibrations of nitro groups. From the reflectance IR spectra we were able to obtain some information regarding LO-TO splitting on the basis of four-parameters semi-quantum model. The splitting in the case of 1,3-dinitrobenzene crystal is at most equal to 10 cm$^{-1}$ and is mostly pronounced within nitro groups vibrations. Similar values of LO-TO splitting were observed in the case of 3-chlorobenzene [3] or trioxane [4].

We also performed the low temperature studies in order to learn more about the dynamics of nitro groups. Considering FWHM (of two bands originating from NO$_2$ deformation vibrations) vs. temperature and applying Arrhenius-like relation [5,6] we estimated the values of activation energy of nitro groups reorientation. They are much lower than expected and equal to 2.86 and 8.31 kJ·mol$^{-1}$. Such a low value may be explained if we take into account O...O interactions which would facilitate the movement of the whole nitro group.

The anharmonicity is a direct consequence of electron-phonon coupling. However, as it was proved by L. Del Freo and A. Painelli, it affects most appreciably the hyperpolarizability [7] which, along with polarizability, governs nonlinear optical properties. It was also shown that the presence of conjugated double bonds in a material can be almost as important as the lack of center of symmetry as far as nonlinear optical properties are concerned [8]. However, no such bonds are present in the title crystal (which is certified by the values of HOMA aromaticity indicator) thus leaving room for mutual nitro group interactions.

References

PHOTOCHEMISTRY OF BIS-METHACRYLIC POLYMERS: IR STUDIES

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Bis-methacrylic polymers form a new class of photoaligning materials for liquid crystals (LC) [1,2]. They provide high thermal and photo-stability of LC alignment, rather strong anchoring and a full range of pretilt angles.

The present study is focused on photochemical transformations of bis-methacrylic polymers, which determine orientational ordering and thus alignment properties of the films of these compounds with regard to LC.

The poly(p-methacryloylaminophenyl methacrylate) was chosen as a representative of the class of bis-methacrylic photoaligning polymers. Theoretically, three photochemical transformations in this polymer are possible: two Fries rearrangements and photocrosslinking/photopolymerization of side methacrylic groups (cases (a) and (b) in Fig. 1). These reactions were studied by IR spectroscopy capable to monitor separately reactions in NH-C=O (amide group), O-C=O (ester group) and C(CH₃)=CH₂ (methylene group) groups during irradiation. To find positions of these groups, modeled compounds were synthesized in which one or more reactions mentioned above were excluded. The changes in FTIR spectra under ultraviolet illumination reveal an occurrence of both Fries rearrangements and a conversion of C=CH₂ methacrylic bonds in poly(p-methacryloylaminophenyl methacrylate).
The absorption dichroism detected in all polymers in UV/Vis range suggests photoselection mechanism of photoorientational ordering. Besides, all these materials provide LC photoalignment. This allows us to conclude that all three photochemical reactions discussed contribute to LC photoalignment. However, they differently influence photoalignment properties; while Fries rearrangement causes strong azimuthal anchoring, crosslinking reactions provide high alignment stability.

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BLACK PAINTED POTTERY, KILDEHUSE II, ODENSE COUNTY, DENMARK

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This work aimed at characterization of a black layer covering a bronze age (period VI) pot surface. Samples of an urn were submitted in two (ca. 0.8 x 0.4 mm) pieces. Following methods were applied to solve research problems: plane polarized light microscopy (PLM) with Olympus B5 apparatus, scanning microscopy with X-ray microanalyser (SEM/EDS) with Nano Nova FEI Company apparatus, Raman microspectroscopy with Renishaw InVia Raman spectrometer (excited with ion Ar+ laser, laser focus diameter ca 1-2 μm), FTIR microspectroscopy (FTS 40 Pro f-y Digilab, with UMA 500 Digilab microscope). All observations and conclusions refer strictly only to the investigated samples. Observation of the black layer under the PLM suggests that we deal with an opaque, isotropic layer, purposely put on leather hard, burnished surface of a pot. The pot itself must have been fired and burnished before action of painting: a very sharp contact between the layer and the pot surface points at it. No traces of organic substances that might have modified a pot surface before painting were detected. Lighter band just under the surface of the pot (ca. 0.6 mm of thickness), is expected to have appeared due to changes in firing regime. The black layer reveals all features of a painting layer executed with a dense substance: it coats the pot with a continuous layer of the thickness of 0.2 – 0.4 μm that is quite typical thickness of painting layer. The black layer must have been executed in hot or warm state: thin, cloudy band of irregularly penetrating, dispersed opaque spots just beneath the pot surface convinces of this. It is recognized that the black layer is a true painting layer. Spectroscopic analyses point at tar/pitch applied. Carbon black should be definitely excluded. The analyses organic substance is structurally ordered in various degrees, due to varying temperature influence. Some spectra reveal, in second-ordered region of the spectrum (> 2000 cm⁻¹), the graphite presence. Scarce points reveal the presence of inorganic admixtures: clay minerals, feldspars and quartz. Presence of magnetite and goethite is possible. Remarks on iron compounds purposely mixed with tar/pitch can be found here and there, but here they cannot be distinguished from casual admixtures. Most probably the black substance is a birch tar. The next question is then: is it an organic paint or a carbon-based, “mixed” paint. The problem was solved with the SEM/EDS observations: plane, compact areas with high carbon content dominate and the areas enriched in inorganic substance are scarce and irregular. Thus, it can be stated that the inorganic admixtures are only casual. Relatively high concentration of alumina is expected to have appeared due to Al mobility in acidic environment and this was provided by organic tar/pitch substances. Phosphorus (usually with calcium) concentrates mostly within clay minerals: hypothesis on bone powder or ash addition to tar/pitch should be excluded then. Some elements may originate not only from inorganic substances but also from wood ashes (in 210 g of fresh pine wood, 1.8 wt% S, 50 wt% Ca, 4.5 wt% Na, 21 wt% K and 3.9 wt% of P). No traces of a tool that was used to execute a painting layer were observed. This information should be collected in macroscopic observation of a whole pot.
FTIR STUDY OF COMPOSITES MODIFIED WITH NANOADDITIVES

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Polyoxymethylene (POM) is well known as one of the strongest and stiffest thermoplastic material. It shows very good chemical stability, high resistance to humidity and many solvents [1]. From the medical point of view such an attractive properties of POM cause that it is widely use in stomatology (dental implants and prosthetics), cardiology (cardiac valve prostheses) in orthopedics (artificial fingers and shoulder joints) and also in joint replacement components [2-3].

According to the relevant literature data in many cases for increasing antimicrobial efficacy against different types of bacteria and viruses silver nanoparticles have been used as composite modification [4]. Its high effectiveness against different microorganism lead to reduce post-operation infection. In order to improve implant osteointegration, bone repair and reconstruction biocompatible hydroxyapatite is widely used [5].

In this work polyoxymethylene modified with silver and hydroxyapatite nanoparticle is presented. Commercially available form of polyoxymethylene copolymer – POM (Ultraform®, BASF, Germany), silver nanopowder (Sigma Aldrich) and hydroxyapatite nanopowder (nGimat, USA) both of particle size below 100nm were used. Nanocomposites in the form of dumbbells were produced in thermoplastic processing (extrusion and injection moulding). The composites with different content of modifiers (silver and nano-hydroxyapatite) were obtained. As a reference sample the pure POM was advantaged.

Dispersion of the nanohydroxyapatite within the polymer matrix was investigated using FT-IR microscopy with ATR objective. Microstructure of the produced materials was examined by means of SEM with an attachment for chemical analysis of specimen microareas (EDS). The mechanical properties such as tensile strength and Young’s modulus were determined using universal testing machine (Zwick-1435) by stretching tests.

Studies of modified composite confirmed that nanopowders could be uniformly homogenized throughout the entire volume of nanomaterials.

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INTERACTION OF A PROTON WITH THE O, F AND Cl ATOMS OF ENFLURANE

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Enflurane (halogenated ether, CHFCl-CF2-O-CHF2) is one of a highly volatile narcotic gases. The mechanism of action of anesthetics depends on specific binding with proteins, therefore, the knowledge of their structural properties and their ability to form hydrogen bonds is very important. The properties of hydrogen bonds are closely related to the basicity of the centers involved in the interaction with a proton donor. In this work, the ab initio MP2 and density functional B3LYP methods were used to investigate the interaction of a proton with the O, F and Cl atoms of enflurane in the gas phase. The calculated proton affinities (PAs) of the O and Cl atoms are 154.5 and 139.8 kcal/mol respectively, whereas PAs of five of the fluorine atoms are between 143.6 and 165.5 kcal/mol (MP2 results). In contrast to protonation at the O and Cl atoms, protonation at each of the F atoms of enflurane reveals a striking result, it leads to a cleavage of the C−F bond and formation of an ion-dipole complex between the enfluranyl cation and neutral hydrogen fluoride. According to the SAPT results, the long range attraction in these complexes is dominated by the electrostatic term (70 %), whereas the induction and dispersion components contribute by about 15 % each. Protonation at the chlorine atom of enflurane does not lead to a cleavage of the C−Cl bond.
EXAMINATIONS OF ADHESIVE TAPES BY THE USE OF INFRARED SPECTROSCOPY
AND PYROLYTIC-GAS CHROMATOGRAPHY FOR CRIMINALISTIC PURPOSES

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It happens that adhesive tapes are used by offenders to bind hand and foot or to gag a victim as well as to prepare explosive charge or to seal threatening letters. The aim of criminalistic examinations of adhesive tapes is to identify the kind of the tape and to compare tape fragments originating from the crime scene with those originating from the suspect in order to state whether they originate from the same roll. The aim of this paper was to evaluate the usefulness of infrared spectrometry (IR) and pyrolytic gas chromatography coupled with mass spectrometry (Py-GC/MS) in examination of chemical composition of adhesive tapes and so their differentiation.

Both, glue and carrier of 51 adhesive tapes of different kinds and producers were examined by the use of infrared spectrometry and pyrolytic gas chromatography. For spectrometric measurements the spectrometer FTS 40Pro + UMA 500 (Digilab, USA) was used. IR spectra in the mid-infrared range were recorded at the resolution of 8 cm⁻¹. Each spectrum represented a collection of 512 scans. For the Py-GC/MS analysis TurboMass Gold system (Perkin Elmer Instruments) was applied. Samples were pyrolysed by the use of CDS 2000 pyroliser (Analytix, USA).

On the base of the obtained IR spectra adhesive tapes were divided into eight groups of different composition of glue or carrier. Within each group the spectra were similar and it was not possible to differentiate between them effectively. The application of Py-GC/MS enabled further differentiation between the samples. It was found that only 4 pairs of examined samples were not distinguishable by the use of both methods. The composition of glue and carrier of each tape was obtained on the base of IR spectra and pyrograms.

The results demonstrated that Py-GC/MS appears as valuable analytical technique being complementary to the FT-IR technique in the field of investigation of chemical composition of samples of adhesive tapes. In the case when samples are undistinguishable on the base of their IR spectra the application of Py-GC/MS enables their successful differentiation.
APPLICATION OF INFRARED AND RAMAN SPECTROSCOPY IN EXAMINATION OF CAR PAINT CHIPS FOR FORENSIC PURPOSES

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The criminalistic examination of car paint samples includes the comparison of their chemical content in order to state if they could have originated from the same object. Typical car paint coat fragment consists of several layers of different colour and composition. The complexity of chemical composition of paints renders their analysis difficult. Application of infrared spectrometry enables one to identify polymer binder, some of the main fillers and pigments. Raman spectroscopy [1,2] is often used to supplement these investigations providing detailed information about pigment content of the examined samples. Both methods should help forensic chemist in the individualisation of paint samples. The aim of this work is to demonstrate the usefulness of infrared and micro Raman spectrometry in characterisation of paint coating for criminalistic purposes and so their differentiation.

40 samples of multilayered paint chips were examined directly on their cross-section (layer by layer) by the use of both methods. For spectrometric measurements the spectrometer FTS 40Pro + UMA 500 (Digilab, USA) was used. IR spectra in the mid-infrared range were recorded at the resolution of 8 cm\(^{-1}\). Each spectrum represented a collection of 512 scans. Raman spectra were measured by the use of InVia spectrometer (Renishaw, USA) using three excitation lasers: 514, 633 and 785 nm. The obtained spectra will be discussed in details.

It was found that application of FTIR and Raman spectroscopy proved to be a good tool for forensic identification of multilayer paints providing information on the chemical composition of the samples and complemented each other. Because no sample preparation is required both methods provide an excellent means to rapidly screen reference panels for the presence of certain pigments.

References
Printing inks are one of the most popular materials utilised in printing of documents. Their chemical composition is usually highly protected. Thus, forensic experts performing examinations of questioned documents have to rely on information obtained by their own studies. For this type of examinations a number of micro-spectrometric methods can be utilised: X-ray fluorescence for establishing the elemental composition, infrared spectrometry – polymer composition, Raman spectrometry – the presence of dyes, pigments or fillers and spectrometry in the visible wavelength range – the parameters of colour. The advantages of application of optical microscopy in combination with a spectrometric method is the possibility of performing of a non-destructive analysis of very small samples.

The analysis of printing inks used by Polish Security Printing Works for printing court tax marks of 50 and 200 PLN denomination will be presented as an example of forensic examinations. Printing inscription on each kind of mark consists in three graphic elements (the background, an inscription and the pattern) printed with the use of various kinds of inks. Printing inks used for the same type of graphic element in different kind of marks are not necessary identical.

Six kinds of printing inks were examined: one yellow-brown, one light blue and four dark blue. The measurements were performed using the following methods: XRF spectrometry (ED2000, Oxford Instruments Ltd.), IR spectrometry (FTS 40Pro, microscope UMA 500, Digilab), microspectrometry in Vis region (microscope Axioplan 2, Zeiss, DAD detector, Tidascope, J&M Spectralys 1.81 programs) Raman spectrometry (In Via, Renishaw, equipped with 514 nm helium-neon laser, 633 nm – argon laser and 785 nm – diode laser).

For each printing inks the elemental composition and the main polymer and also the kind of pigments and fillers for blue printing inks were established. CIEX*a*b* parameters of colour for dark blue printing inks were calculated and colours were compared. The obtained data were sufficient for classification of the examined inks into four groups. It reflected not only the differences in colour but also the end-use of given ink. The possibility of obtaining Raman spectra for three wavelengths allowed us additionally to differentiate samples within one group and the obtained results were sufficient not only for differentiation of inks, but also the printings on marks.
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Photocurable compositions are widely used in industrial applications. The monomers can be polymerized either as individual compounds or the mixture of two or more components. The polymerization course of the mixture of the two monomers highly depends on the feed composition. It may result from changes in the system viscosity as well as from intermolecular reactions between monomers which, in turn, depend on their molar ratio. One of the methods used in the investigations of the elastic properties of polymers is Brillouin scattering. Polymers of dimethacrylate-based networks formed during photopolymerization process are frequently used in high performance applications such as dental restorative materials and information storage systems.

In this work we report the results of investigations of Brillouin scattering of two-components system: 2,2-bis[4-(2-hydroxyl-3-methacryloxy)phenyl]propane / polyethylene glycol methacrylate (PM/bis-GMA) containing 0, 30, 50, 85 and 100 mol-% of PM.

The Brillouin light scattering investigations have been performed during polymerization process of the system, initiated by ultraviolet radiation ($\lambda = 360\text{nm}$) at temperature 20°C and 40°C. Some of the physical parameters characteristic for this system such as velocity $V$, attenuation coefficient $\alpha$ of acoustic waves, adiabatic compressibility $\beta$, real $M'$ and imaginary $M''$ parts of elastic modulus have been estimated from Brillouin spectra.

The obtained results have been discussed in terms of the influence of PM/bis-GMA system composition on its elastic properties during photopolymerization process.

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