RECENT ADVANCES
IN LASER SPECTROSCOPY
AND LASER TECHNOLOGY

Lodz, Poland, May 29-31, 2007
Conference Topics

- Recent advances in generation and measurement
- Time-resolved optical and time-resolved x-ray diffraction studies
- Ultrafast processes in physics, chemistry and biology
- 2D spectroscopy
- Real world applications of ultrafast laser technology: laser medical diagnostics, fiber optical communication
- Photonic materials and devices
- Other important topics related to optical molecular spectroscopy
Conference Chair:

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Scientific Advisory Committee:

- **Prof. S. Bratos**, Universite Pierre et Marie Curie, CNRS, Paris, France
- **Prof. Th. Elsaesser**, Max-Born-Institute, Berlin, Germany
- **Prof. Ch. Hirlimann**, Institute de Physique et Chimie des Materiaux de Strasbourg, France
- **Prof. M. Handke**, AGH University of Science and Technology, Poland
- **Prof. Shaul Mukamel**, Department of Chemistry, University of California, USA
- **Prof. Nasser Peyghambarian**, University of Arizona, College of Optical Sciences, USA
- **Prof. Wolfram Schröer**, University of Bremen, Fachbereich 2 (Biologie/Chemie), Germany
- **Prof. Rick Trebino**, Georgia Research Alliance-Eminent Scholar Chair of Ultrafast Optical Physics, USA
Invited speakers

- **Prof. S. Bratos**, Universite Pierre et Marie Curie, CNRS, Paris, France
- **Prof. Th. Elsaesser**, Max-Born-Institute, Berlin, Germany
- **Prof. Ch. Hirlimann**, Institute de Physique et Chimie des Materiaux de Strasbourg, France
- **Prof. Shaul Mukamel**, Department of Chemistry, University of California, USA
- **Prof. Nasser Peyghambarian**, College of Optical Sciences, University of Arizona, USA
- **Prof. Cz. Radzewicz**, Warsaw University, Poland
- **Prof. R. Trebino**, Georgia Research Alliance-Eminent Scholar Chair of Ultrafast Optical Physics, USA
AGENDA OF SESSIONS

**Tuesday, May 29, 2007**

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**Wednesday, May 30, 2007**

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| 9.30 a.m. – 10.00 a.m. | **MCC–I**
|               | Marie Curie Chair inauguration lecture   | IFE      |
| 10.00 a.m.- 10.30 a.m. | Coffee Break                             | IFE      |
| **10.30 a.m.–12.30 p.m.** | **MCC–II**
|               | From femtoseconds to attoseconds, from mid IR , XUV
to X-ray spectral regions | IFE      |
<p>| 10.30 a.m.–11.10 a.m. | <strong>S. Bratos:</strong> Time- resolved optical and time-resolved x-ray diffraction studies of molecular dynamics of liquids | IFE      |</p>
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<td>11.40 a.m.-12.00 p.m.</td>
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<td>1.30 p.m. – 2.10 p.m.</td>
<td>• R. Trebino, P. Bowlan, P. Gabolde, and S. Akturk: Measuring everything you've always wanted to know about an ultrashort pulse but thought couldn't be done</td>
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<td>• Cz. Radzewicz: Noncollinear Optical Parametric Chirped Pulse Amplifier</td>
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<td>• Mukamel S., Zhuang W., Abramavicius D., Li Z. and Hayashi T.: Multidimensional Coherent Optical Spectroscopy of Proteins: Femtosecond Analogues of Multidimensional NMR</td>
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<tr>
<td>5.10 p.m.-5.50 p.m.</td>
<td>• Th. Elsaesser: Two dimensional vibrational spectroscopy of hydrogen bonds in liquids, Lecture</td>
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| 9.10 a.m. -9.30 a.m | • S. Draxler, S. Malkmus, Th. Brust, F. O. Koller, B. Heinz, M. Braun, W. Zinth:  
Ultrafast reaction dynamics of indolyfulgimide |            |
<p>| 9.30 a.m. -9.50 a.m | • G. Burdzinski: Femtosecond UV-VIS and mid-IR spectroscopy of aryl azides |            |
| 9.50 a.m. -10.10 a.m | • I. Lampere, J. Bonin, B. Soroushian, P. Pernot, M. Mostafavi: Formation and solvation dynamics of electrons in three diols |            |
| 10.10 a.m. -10.30 a.m | • Lecture                                                                 |            |
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| <strong>11.00 a.m.–12.30 p.m.</strong> | <strong>MCC-VI</strong>                                                                 | IFE |</p>
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<td>• H. Abramczyk: From femtosecond dynamics to breast tissue cancer diagnosis by molecular spectroscopy</td>
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<td>11.40 a.m.–12.20 p.m.</td>
<td>• W. Schröer: On the Dynamics of Multiple Scattering: Theory, Simulation and Experiments</td>
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<td>• A. Tortschanoff, A.A.Oskouei, A. Cannizzo, O. Bräm, F. van Mourik, M. Chergui: Solvation Dynamics in the UV with Photon-Echo and Fluorescence Up-coversion,</td>
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<td>2.00 p.m.–2.40 p.m.</td>
<td>• Ch. Hirlimann: Low intensity two-photon absorption by means of photonic jets</td>
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Social Programme

Welcome Reception:
Qubus Hotel
Tuesday May 29 (6 p.m.)
In the restaurant: Swedish buffet and a welcome drink.
A social greeting party – meeting in the hotel after supper
Live piano music – popular themes in jazz arrangements add to the atmosphere of a private, casual meeting.

Conference Dinner:
Poznanski's palace
Wednesday May 30 (7.30 p.m.)
Leave for the Poznanski's Palace (short sightseeing + dinner gala – guests sit at the round tables). Accompanying dixieland band plays popular Polish and other themes from the 20’s and 30’s / or an artistic programme based on French songs. During the dinner we propose a group picture made by a photographer dressed in vintage 19th century outfit and a proper old camera.
How to reach the Poznanski's Palace:
by buses provided by the organizers

Thursday May 31
Guests will have an opportunity to see the most interesting parts of Lodz. Because of relatively little time that the guests have, they will see mostly the vicinity of Piotrkowska Street, including the most beautiful factories, residences and palaces. During a 3-hour long tour an English-speaking professional guide will show the group Lodz to remember.
After sightseeing a farewell gala will take place at the European Insitute or at the Alcide de Gasperi Memorial Conference and Teaching Center located also on Piotrkowska Street
20.00- 22.00 hrs. – conference reception

Optional excursions /guests’ choice/
1. Museum of Textile Industry  www.muzeumwlokiennictwa.pl
2. City of Lodz Museum of History  www.poznanskipalace.muzeum-lodz.pl
Excursions lasting up to three hours.
1. **Echoes of the Textile Industry Empire.** Route: tour begins with visiting the Central Museum of Textile Industry, located at the former White Factory of Ludwik Geyer. Next we go to the John Paul II Place and see the Cathedral, Bishops’ Palace and The Schweikerts’ Villa. We ride down Tymienieckiego Street past Kopisch’s Bleachery towards "Ksiezy Mlyn" - a factory and residential complex of Karol Scheibler. At "Ksiezy Mlyn" we see workers’ dwellings, spinning factory, school, fire station, Herbst’s Palace. Transportation: car, touring bus or a minibus.

2. **The Rise of a One-Street City.** Route: the tour starts from Wolnoścī Place, the heart of the very first early 19th century factory settlement. During the ride or a walk on a 4-kilometer long part of Piotrkowska Street you will learn about the history of cotton lords dynasties, see their beautiful monumental residences and contemporary city. Transportation: rickshaw ride or walking.

**Long excursions**

1. **Villas and Palaces of Lodz.** Tour of the greatest and most beautiful cotton lords’ residences (choice of): I. K. Poznański’s – present City of Lodz Museum of History, K. W. Scheibler’s – present Museum of Cinematography, E. Herbst’s – present Museum of Art (19th century interiors), L. Kinderman’s – present Municipal Gallery, R. Schweikert’s – present European Institute, K. Poznanski’s – present Academy of Music, R. Richter’s – present rector’s office of the Technical University. The palaces’ interiors house many interesting decorations and works of art, showing the aesthetical taste of factory owners, the residences are often connected with factory buildings and surrounded by parks. Duration: 5 hours for 3 – 4 objects, including walking routes.

2. **Our Promised Land, or Lodz in a nutshell.** Route: the tour starts from Wolnosci Place, the heart of the very first early 19th century factory settlement. We walk down Piotrkowska Street, towards the former Meyer’s arcade and Rubinstein’s Piano. We ride to the John Paul II Place to the Cathedral, next to the former Ludwik Geyer’s White Factory. Next we ride down Tymienieckiego Street past Kopisch’s Bleachery towards the factory and residential complex of Karol Scheibler. Finally we visit the museum at Herbst’s Palace. Transportation: rickshaw ride down Piotrkowska Street, then by car, touring bus or a minibus.
3. The Melting Pot of Nations, or sightseeing the city of four religions. Route: the tour begins with visit to the Museum of History and seeing an exhibition „The Triad of Lodz. Next we ride to the cemetery on Ogrodowa Street to see the Karol Scheibler’s Chapel. Next we go to the Jewish Cemetery on Bracka Street. Next stops are: Alexander Nevsky’s Orthodox Church, St. Matthew’s Evangelical Church and the Cathedral of Lodz. The tour may end with an organ concert at St. Matthew’s church.

4. Artistic Lodz, or Following the Traces of Tuwim, Strzeminski, Kobro, Rubinstein.
Route: we visit an exhibition of modern art at the Museum of Fine Arts on Wieckowskiego Street. We ride to Ogrodowa Street to Poznanski’s Palace, and see the exhibition devoted to Artur Rubinstein. Next we walk on foot to Wolnosci Place, and take a ride in rickshaws to the Lodz Walk of Fame. Finally we ride to Targowa Street to visit the Higher School of Film.

5. Following the Traces of a Lost Nation. Route: the tour starts with a visit to the Museum of History at the former Izrael Poznanski’s palace. Next we walk to his former factory to visit the „Manufaktura” mall center. Next we go to the Old Town Park to see the Monument of Ten Commandments. The last stop is the Jewish Cemetery on Bracka Street. Transportation: car, touring bus or a minibus.
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2. **Cz. Radzewicz**: Noncollinear optical parametric chirped pulse amplifier
3. **R. Trebino, P. Bowlan, P. Gabolde, and S. Akturk**: Measuring everything you’ve always wanted to know about an ultrashort pulse, but thought couldn’t be done
6. **E. T. J. Nibbering, O. F. Mohammed, D. Pines and E. Pines**: Recent advances on bimolecular aqueous proton transfer probed with infrared spectroscopy
7. **H. Abramczyk**: From femtosecond dynamics to breast tissue cancer diagnosis by molecular spectroscopy
8. **N. Peyghambarian**: Photonic materials and devices
9. **Ch. Hirlimann**: Low intensity two-photon absorption by means of photonic jets

Oral presentations

1. **K. de Lange, O. Vieitez, T. Ivanov, A. Sprengers, W. Ubachs, B. Lewis, G. Stark**: Perturbation and predissociation in the electric dipole spectrum of \( \text{N}_2 \) studied with XUV spectroscopy
2. **H. Iglev, M. Schmeisser and A. Laubereau**: Ultrafast IR spectroscopy of ice-water phase transition
3. **S. Draxler, S. Malkmus, T. Brust, F. O. Koller, B. Heinz, M. Braun and W. Zinth**: Ultrafast Reaction Dynamics of an Indolylfulgimide
4. **G. Burdzinski**: Femtosecond Uv-vis and mid-IR spectroscopy of aryl azides.


7. **A. Tortschanoff**, A.A. Oskouei, A. Cannizzo, O. Bräm, F. van Mourik, and M. Chergui: Solvation Dynamics in the UV with Photon-Echo and Fluorescence Up-conversion

**Posters**

1. **Issaoui N., Rekik N., Ghalla H., Oujia B., Wójcik M. J.**: Theoretical study of both combined effects of multiple Fermi resonance and indirect relaxation of IR spectral density of medium strength H-bond

2. **Kolek P., Leśniewski S., Parowska K., Najbar J.**: LIF excitation spectra of jet-cooled deuterated anthranilic acid

3. **Kozanecki M., Pastorczał M., Ułański J.**: The resonance Raman effect in water revisited


5. **Esser M. J.Daniel, Bolling C., Preussler D.R., Jacobs. C., Koen W. S., Bernhardi E. H.**: High power diode and pumped Tm:GdVO₄ laser operating at 1818nm and 1915nm

6. **Konieczny P, Świderski J., Zając A.**: Spectroscopy and transitions dynamics of Er³⁺ ions in selected crystals

7. **Kurdi G., Varju K., Osvay K.**: Higher order dispersion control of femtosecond CPA lasers

8. **Kwiatkowski J., Gorajek Ł., Jabczyński J.K., Żendzian W.**: Spectral and energetic properties of wide-bandwight Tm fiber laser

9. **Kwiatkowski J., Zdanowski P., Jabczyński J.K., Żendzian W.**: Compact, multi-wavelength pulsed laser set up for spectroscopy
10. **Koziński M., Garrett-Roe S., Hamm P.**: Vibrational spectra diffusion of CN- in water


12. **Fischer M. K., Iglov H., Laubereau A.**: Optical manipulation of electron photodetachment dynamics of aqueous halide

13. **Gutman M., Hilczer M.**


15. **Brust T., Malkmus S., Draxler S., Lederer F., Braun M., Zinth W.**: Ultrafast photochromism of molecular switches: indolylfulgides and indolylfulgimides


17. **Kirillov S.**: Raman line profile analysis: recovery of depolarization ratio of composite lines and studies of conformation equilibria in liquids


19. **Piątkowski P., Gadomski W.**: Some preparation dependant properties of PbS nanocrystals

20. **Khelifi N., Oujia B. and Gadea F. X.**: Dynamic couplings, radiative and nonradiative lifetimes of the $A^1\Sigma^+$ and $C^1\Sigma^+$ states of KH
Plenary lectures
TIME-RESOLVED OPTICAL ABSORPTION AND TIME-RESOLVED X-RAY DIFFRACTION STUDIES: COMPARISON OF THE TWO TECHNIQUES

S. Bratos

Laboratoire de Physique Théorique de la Matière Condensée, Université Pierre et Marie Curie, Paris, France

Time-resolved optical absorption spectroscopy and time-resolved x-ray diffraction are the two principal techniques used to study molecular dynamics of liquids. In both of them, the system is first brought out of equilibrium by an intense optical pump pulse. Its evolution is probed next by a time-delayed optical pulse in absorption, and by a time-delayed x-ray pulse in x-ray diffraction. The corresponding experimental techniques are sketchily described. They are widely different in conception, dimension and price. Theoretical methods are described next. Contrary to above, they are basically similar in both these fields, and employ the same statistical mechanics of non-linear optical processes. A similar language can thus be used here and there.

These techniques are illustrated on the following two examples. (i) X-ray diffraction techniques are illustrated by monitoring hydrodynamics of laser heated methanol on atomic scale. The same motions are also studied using macroscopic hydrodynamics. Although belonging to the same physical reality, these motions appear very different at these two length scales. Atomic and macroscopic hydrodynamics are dissimilar. (ii) Laser spectroscopic techniques are illustrated by determining time-dependent OH…O atom pair distribution function $\Delta g_{\text{OH...O}}(r, t)$ of water. It is shown theoretically that, at times longer that pump-probe correlation time, the $\nu_{\text{OH}}$ pump-probe signal $\Delta S(\Omega, \tau)$ parallels completely $\Delta g_{\text{OH...O}}(r, t)$ of water. Laser spectroscopic techniques can thus be used to determine this function. This is important as these short time scales are still inaccessible to time-resolved X-ray diffraction.
NONCOLLINEAR OPTICAL PARAMETRIC CHIRPPED PULSE AMPLIFIER

Cz. Radzewicz
MEASURING EVERYTHING YOU’VE ALWAYS WANTED TO KNOW ABOUT AN ULTRASHORT PULSE, BUT THOUGHT COULDN’T BE DONE

Rick Trebino, Pamela Bowlan, Pablo Gabolde, and Selcuk Akturk

Georgia Institute of Technology, School of Physics
837 State St NW, Atlanta, GA 30332, USA

Abstract: We present two techniques for measuring the complete spatio-temporal intensity and phase, $E(x,y,z,t)$, of an ultrashort pulse, one in and near a focus and the other for a single pulse.

Most applications of ultrashort pulses, such as multi-photon microscopy or ultrafast micromachining, involve focusing the pulse. In order to optimize the pulse at the focus, it is important to be able to directly measure the electric field as a function of space and time. While techniques for characterizing the temporal or spatial field alone exist, measuring the complete spatio-temporal field is much more difficult, especially at or near a focus or on a single shot. So we introduce, to our knowledge, the first method that measures the complete $E(x,y,z,t)$ at and near a focus and the first technique to measure $E(x,y,z,t)$ on a single shot.

One technique is based on spectral interferometry (which measures a pulse vs. time or frequency), and we call it SEA TADPOLE (see Fig. 1).1 Because the entrance to SEA TADPOLE is an optical fiber with a core size of only a few μm (or less), it can measure a tiny region of a collimated, diverging, or converging beam, or it can measure a focused beam. Additionally, the entrance fiber can be scanned along the unknown beam in space so that the intensity and phase as a function of transverse and/or longitudinal position can also be measured.

Another technique is based on holography, and we call it STRIPED FISH (see Fig. 2).2 It yields the complete $E(x,y,z,t)$ for a single pulse. It involves measuring simultaneously holograms for each frequency in the pulse—using only two optical elements! Both SEA TADPOLE and STRIPED FISH can be self-referencing, as the reference pulse can be obtained from the unknown pulse and measured using FROG.

Fig. 1. Left: Experimental setup for SEA TADPOLE. Right: The reconstructed electric field (color indicates the instantaneous frequency) vs. space and time for a focused pulse.

Fig. 2. STRIPED FISH. The unknown and reference pulses cross at a small vertical angle, $\alpha$. The coarse 2D grating is rotated by a small angle, $\gamma$, about the z-axis, and the wavelength filter is rotated by an angle, $\beta$, about the y-axis. The inset shows one of the holograms.

References
MULTIDIMENSIONAL COHERENT OPTICAL SPECTROSCOPY OF PROTEINS:
FEMTOSECOND ANALOGUES OF MULTIDIMENSIONAL NMR

Shaul Mukamel, Wei Zhuang, Darius Abramavicius, Zhenyu Li and Tomoyuki Hayashi

Department of Chemistry, University of California, Irvine
Irvine, California 92697-2025, USA

The response of complex biomolecules to sequences of ultrafast optical pulses provides multidimensional snapshots of their structure and electronic and vibrational dynamics. Two-dimensional correlation plots of the signals show characteristic cross-peak patterns which carry information about structures, equilibrium binding fluctuations and relaxation processes. The lineshapes provide information on conformational and solvent induced fluctuations. The fundamental concepts underlying the design and interpretation of these coherent nonlinear experiments will be surveyed. New pulse sequences may be constructed for probing specific coherences, building upon the analogy with multidimensional NMR. Computational techniques for simulating the necessary multipoint response functions will be presented. Applications will be made for probing ideal secondary structural motifs of peptides, protein folding dynamics, Amyloid fibrils and hydrogen bonding. Resolution may be enhanced by applying novel polarization configurations of the optical fields which also provide chirality-specific information. The use of pulse shaping coherent control strategies and sensitivity analysis to simplify complex spectra and retrieve and enhance desired features will be demonstrated. A Quasiparticle representation of the coherent nonlinear optical response of coupled excitons based on the nonlinear exciton equations (NEE) will be discussed. Signatures of multiquantum coherences and exciton transport in two-dimensional signals are identified. Future extensions to core hole excitons probed by attosecond x ray pulses will be discussed.


TWO DIMENSIONAL VIBRATIONAL SPECTROSCOPY OF HYDROGEN BONDS IN LIQUIDS

T. Elsaesser\textsuperscript{1}, N. Huse\textsuperscript{1}, S. Ashihara\textsuperscript{1}, A. Espagne, J. Dreyer\textsuperscript{1}, E.T.J. Nibbering\textsuperscript{1}, M.L. Cowan\textsuperscript{2}, B.D. Bruner\textsuperscript{2}, J.R. Dwyer\textsuperscript{1,2}, R.J.D. Miller\textsuperscript{2}

\textsuperscript{1}Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Str. 2 A, D-12489 Berlin, Germany
\textsuperscript{2}Departments of Chemistry and Physics, University of Toronto, 80 St. George St., Toronto, Ontario, Canada M5S3H6

Vibrational excitations underlie structural dynamics and chemical processes in hydrogen-bonded systems, frequently occurring in the ultrafast time domain. Femtosecond nonlinear vibrational spectroscopy has developed into a major tool for studying such phenomena. In this paper, we discuss recent results of two-dimensional (2D) vibrational spectroscopy for two prototype systems, (i) cyclic dimers of acetic acid forming two coupled O-H...O hydrogen bonds [1,2], and (ii) neat liquid water, a fluctuating network of intermolecular hydrogen bonds [3,4].

Different vibrational couplings in acetic acid dimers are separated and determined quantitatively by combining 2D photon-echo spectroscopy with ab-initio theoretical calculations. Fermi resonances of the O-H stretching vibration with over- and combination tones of fingerprint vibrations results in strong off-diagonal peaks in the 2D spectra and also dominate the envelope of the linear O-H stretching absorption band which is essentially homogeneously broadened. In addition, the O-H stretching mode couples to underdamped low-frequency modes of the intermolecular hydrogen bonds, giving rise to multilevel quantum beats. Both types of anharmonic couplings have absolute values of the order of 100 cm\(^{-1}\).

Neat liquid water represents a highly disordered system with a pronounced inhomogeneous broadening of the O-H stretching absorption. The 2D infrared spectra give evidence of an extremely fast sweep of O-H stretching frequencies on a 50 fs timescale and a concomitant decay of the initial inhomogeneous distribution of sites. We attribute this behavior mainly to librational excitations resulting in a high-frequency component of the fluctuating force exerted on the O-H stretching oscillator. On a somewhat slower time scale, energy transfer contributes to spectral diffusion. Sub-200 fs lifetimes and couplings of the O-H stretching and bending vibrations and of librational modes are derived from pump-probe studies in a broad range of frequencies [4].

RECENT ADVANCES ON BIMOLECULAR AQUEOUS PROTON TRANSFER PROBED WITH INFRARED SPECTROSCOPY

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Modern discussions of acid-base reactions have evolved from the seminal studies of Eigen and Weller[1,2]. The general kinetic approach for acid-base reactions in aqueous solutions consists of three reaction branches [2]: (a) direct proton exchange between acid and base, (b) acid dissociation to solvent followed by proton scavenging by the base, and (c) water hydrolysis by the base followed by the neutralization reaction of the acid by the hydroxyl anion. Judging by the magnitude of the reaction radius in typical (diffusion-controlled) acid-base reactions it has been estimated that up to 2-3 water molecules separate when acid and base exchange a proton through pathway (a) [1]. In reality, however, this value is likely to be an averaged value of several encounter complexes (with n rearrangements steps) leading to proton transfer.

Photoacids can be used as a means to follow proton transfer dynamics to a neutralising base in real time by photoinitiation. The outcome of the observed dynamics, i.e. the reaction rates and yields depend on the relative strengths and concentrations of acid and base. We have investigated the aqueous neutralization reaction of the photoacid pyranine and carboxylate bases (‘OOCCH₃₋ₓClₓ) (x = 0-3) with femtosecond infrared spectroscopy [3]. Here we are able to dictate the outcome of the reaction dynamics by tuning the number of chlorine atoms x. We have identified two innermost types of encounter complexes (tight and loose), resulting in a sub-150 fs proton dissociation lifetime of the photoacid [4-6]. The proton transfer in both encounter complexes is found to be reversible. The step-wise, von-Grotthuss type [5-6], proton transfer in loose complexes involves a first step leading to a H₃O⁺ like cation resembling the proton solvation core in the Eigen cation, H₉O₄⁺ and a second and final transfer to the base on much slower picosecond time scales. The stability of the hydrated proton in the loose complex increases with decreasing reactivity (basicity) of the carboxylate base as measured in bulk water. We have applied a unified reaction dynamics model in which we have approximated all possible configurations between acid and base by tight (n = 0), loose (n = 1) and solvent switch (n > 1) complexes, as well as acid and base fully separated by the solvent. Whereas the fully separated acid and base first have to diffuse, all other complexes are connected to each other through reversible proton transfer steps. Step-wise proton shuttling through water provides a route for proton transfer which circumvents further desolvating the acidic and basic groups necessary for direct transfer.

FROM FEMTOSECOND DYNAMICS TO BREAST TISSUE CANCER DIAGNOSIS
BY MOLECULAR SPECTROSCOPY

H. Abramczyk
PHOTONIC MATERIALS AND DEVICES

N. Peyghambarian
LOW INTENSITY TWO-PHOTON ABSORPTION BY MEANS OF PHOTONIC JEST

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Recent advances in the physical understanding of light interaction with few wavelengths diameter dielectric particles have shown the possibility with micrometric particles to concentrate light in the near field. This new possibility can have a great interest for non-linear optics. We theoretically and experimentally demonstrate this interest.

Dielectric spherical particles with a diameter size that can be compared with the wavelength are able to focus light. Because of the scale of the problem, this focus point does not obey to the geometrical laws. According to their refractive index, the focus point can be outside or inside the dielectric spheres. When the focus point is right on the surface or in front of the sphere, its FWHM can be smaller than the wavelength and a high intensity concentration is reached. We are beyond the diffraction limit. If a non-linear effect can occur in the medium around the dielectric sphere, this intensity concentration enhances this phenomenon.

To carry out a rigorous evaluation of this intensity concentration, we have used the Mie theory. This method makes it possible to analytically find the solutions of the vectorial propagation equation of Helmholtz for a dielectric sphere. The focused beam, called photonic jet, has been computed. The intensity concentration is demonstrated.

In order to verify our assumption that nonlinear effect will be enhanced, an experiment has been carried out. As dielectric spheres, we have used silicate balls of 400 nm diameter, produced by Stöber reaction. The nonlinear medium is the umbelliferon 47 dye dissolved in ethanol. This medium is known for its ability of two-photon absorption. The emitted photon is blue. The incident source is a pulsed Ti:sapphire LASER of wavelength 750 nm. A small volume of dielectric spheres has been added in the dye solution. Because of the low concentration of spheres, electromagnetic interactions between spheres are negligible. The comparison between light emitted with and without dielectric spheres allows us to illustrate the significant enhancement of the non-linear light absorption.

This experiment opens a new way for using optical non-linear effects at much lower intensities. Low intensity non-linear imaging for example can now be envisioned.
Oral presentations
Molecular nitrogen is the most abundant molecule in the Earth’s atmosphere. The molecule hardly absorbs visible and UV radiation, but in the extreme ultraviolet (XUV) below $\sim 100$ nm $N_2$ is predominantly responsible for the absorption of solar radiation at altitudes of $\sim 150$ km. The excited states responsible for these strong absorption features are usually coupled to underlying dissociative states. The resulting predissociation produces atomic nitrogen in ground and excited states that plays a significant role in the atmospheric reaction dynamics in the stratosphere. Clearly, a good understanding of the molecular spectroscopy of nitrogen is relevant for any reliable description of the atmosphere.

The molecular spectroscopy of nitrogen is notoriously complicated. Since the molecule possesses a triple chemical bond, even the lowest excited states are relatively high in energy and cannot be accessed in one-photon transitions from the $^1\Sigma_g^+$ ground state in the visible or UV spectral regions. Hence, the experimentally much more demanding method of extreme ultraviolet (XUV) excitation in the range of 92.6 - 93.5 nm, followed by one-photon ionization with a visible or UV photon is the method of choice. The very high spectral resolution associated with this technique allows the observation of separate rotational states and of lifetime broadening of such spectral features. The lowest accessible excited states possess $^1\Pi_u$ and $^1\Sigma_u^+$ symmetry. These states undergo complex interactions among themselves, and with nearby dissociative triplet states. Since both homogeneous and heterogeneous interactions occur, their spectral analysis is far from trivial and has led to a rich literature on the topic.

Out of many available examples, we shall focus on a recent 1 XUV and 1’ UV study of the Rydberg-valence complex between $^1\Pi_u$ ($v=1$) and $b^1\Pi_u$ ($v=9$) states. For $^{14}N_2$, these states cross, and close to the crossing point a homogeneous interaction is apparent. Our XUV study provides new and detailed information on the perturbed rotational structures, oscillator strengths, and predissociation linewidths. For $^{14}N_2$ the heterogeneous L-uncoupling interaction with the near-degenerate $b^1\Sigma_u^+$ ($v=6$) state is also apparent. In addition, an interesting two-level quantum-mechanical interference effect has been found between the o-X(1,0) and b-X(9,0) transition amplitudes. This interference is totally destructive for the lower-energy levels just above the crossing point, making it impossible to observe transitions to b($v=9$, J=6). A similar interference effect is found to affect the o($v=1$) and b($v=9$) predissociation linewidths observed with photoabsorption spectroscopy employing synchrotron radiation. Our study of the Rydberg-valence complex between $^1\Pi_u$ ($v=1$) and $b^1\Pi_u$ ($v=9$) provides a textbook example of the role of perturbations in the spectroscopy of molecular nitrogen [1].

ULTRAFAST IR SPECTROSCOPY OF ICE-WATER PHASE TRANSITION

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The structural changes in ice that undergoes melting are governed by the properties of the hydrogenbonded network of the water molecules. The relaxation dynamics of the H-bonded groups include many elementary steps in the femtosecond and picosecond time domain. Obviously, the microscopic understanding of ice-water phase transition requires investigations of the process on ultrashort timescales.

We have performed ultrafast temperature jump measurements in neat and isotopically mixed ice using IR double-resonant spectroscopy with sub-picosecond time resolution. The hydroxilic stretching vibrations (OH and OD) possess sub-picosecond population lifetime that allow a rapid energy redistribution and heating of the ice lattice. The same modes can be used as fast and sensitive probes of local temperature and structure.

The method is verified for an isotopic mixture of ice at 200 K and ambient pressure. It is important to recall the isochoric character of the ultrafast temperature jump because of the slow volume expansion of the shock-heated sample (see Figs. a and b). In other words, a pressure increase is involved that is also measured with our technique. The temporal evolution of temperature and pressure in the sample are determined by comparison of the measure time–resolved absorption changes to steady-state differential spectra.

The experiments close to the melting point show that shock laser heating of bulk ice can avoid the common surface melting, leading to substantial superheating of the ice lattice. The thermal stability of the straight H-bonds in the crystal lattice near the melting point appears to be much higher as assumed until now. For larger energy deposition ultrafast melting of bulk ice was observed. For this process a time constant of 33 ps was determined, while the consumed energy amounts agree with the latent heat of melting (see Figs. c and d).

Further details of the kinetics of bulk melting of ice will be presented and the mechanism of the melting process discussed.

Figure (a) Transient differential spectra measured with tunable sub-picosecond pulses 40 ps after OH- (hollow squares) or OD-pumping (filled diamond) of HDO:D2O ice at 200 K. The curves represent steady-state differential spectra for $\Delta T = 15, 20$ and $25$ K and constant ambient pressure. (b) Same experimental data as in (a) but compared to steady-state differential spectra for isochoric temperature jumps. (c) Temporal evolution of the amount of molten liquid observed in the ultrafast melting experiment. (d) Transient latent heat $LH$ consumed by the melting process compared to the steady-state value of 321 J/cm$^3$ (dashed line).

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ULTRAFAST REACTION DYNAMICS OF AN INDOLYLFULGIMIDE

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Fulgimides are photochromic molecular switches [1] including the cyclohexadiene motif as reactive core, which undergoes an ultrafast photoreaction to all-trans hexatriene. Especially indolyl-substituted fulgimides are known for the thermal stability of their isomers and low chemical fatigue. The three isomers E, Z and C can be converted reversibly into each other upon light illumination. The C-form (closed ring) shows a pronounced absorption band in the visible range whereas the E- and Z-form (both in the ring-opened state) display absorption only in the UV. The C-E ring-opening reaction can be induced by illumination in the VIS, whereas the E-C ring-closure occurs under UV radiation.

Fulgimides have been used as molecular switches to trigger energy transfer [2] or fluorescence yield [3]. For the use in data storage molecular switches are desired that are not only well addressable, but also exhibit ultrafast switching processes for write, erase and read out operations. Fulgimides turn out to be promising candidates for such applications.

In this work the complete reaction cycle, C→E and E→C, of an indolylfulgimide [4, 5] is analysed via ultrafast spectroscopy using transient absorption in the UV, VIS, and mid-IR and ultrafast fluorescence broadband spectroscopy by a Kerr gate [6]. For the transient absorption measurements Ti:Sa amplifier systems working at 1 kHz repetition rate were used. The excitation pulses for the C-form were created by a white-light seeded NOPA set-up, for the E-form the second harmonic of the Ti:Sa laser fundamental was used. Probe pulses in the VIS were generated by a NOPA. For the UV probe pulses second harmonic generation of the NOPA output at 700 nm was used. Broadband Mid-IR probe pulses for vibrational spectroscopy were generated by a multistage parametric process [5].

For the VIS induced C→E reaction we find consistently with all techniques an exponential time constant of ~2 ps for the S1 decay and the S0 repopulation. Furthermore, we observe non-exponential signatures which occur in the 20 ps time domain and are assigned to the cooling of hot molecules in the electronic ground state. In addition we find that the UV induced E→C reaction occurs within less than 1 ps and we also observe vibrational cooling. Due to different absorption spectra of the C- and E-form, the disappearance of the educt signal and the rise of the product signal can be observed. Thus, both ring-opening and ring-closure reaction are completed within a few picoseconds. This can be regarded as the ultimate time regime of write and erase operations in a data storage application. An ultrafast, non-destructive read out method [8] can be accomplished via IR probing.

FEMTOSECOND UV-VIS AND MID-IR SPECTROSCOPY OF ARYL AZIDES

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Femtosecond Uv-vis and mid-IR transient absorption techniques, with the support of modern quantum chemical computational methods is a powerful tool to describe light induced photochemical and photophysical processes. We have studied photolysis at 270 nm of aryl azides (para and orthobiphenyl azide) in acetonitrile. The photoexcited azide in the S2 state absorbs broadly in the visible and rapidly (within a few hundred femtoseconds) deactivates to the S1 state through Internal Conversion (IC). This is followed by fast fragmentation leading to a hot nitrene and molecular nitrogen. Quantum chemical calculations predict that the S1 state of the azide is involved in fragmentation due to a small barrier for nitrene formation (2 kcal/mol). Vibrational cooling (11 ps) was recorded for long-lived para-biphenyl nitrene (~9 ns). The lifetime of ortho-biphenyl nitrene is shorter (16 ps). In both cases a ketenimine is a major product due to nitrene isomerization. Ketenimine formation was clearly observed by mid-IR transient absorption spectroscopy in the region of 1880 cm\(^{-1}\). An IR band rises with a time constant of 10 ps, while sharpening and blue shift indicate that ketenimine is born with excess of vibrational energy. However, in the case of para-biphenyl azide, we could not record any positive signal, since the larger rearrangement barrier (6.8 kcal/mol) prohibits nitrene isomerization on the picosecond time scale.

FORMATION AND SOLVATION DYNAMICS OF ELECTRONS IN THREE DIOLS

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The solvated electron is characterized by an intense absorption band in the visible or near infrared spectral domain depending on the solvent [1]. Thanks to the development of ultrashort laser pulses, great strides have been made towards the understanding of the solvation and early reactivity of the solvated electron, mainly in water and also in a few polar solvents. In alcohols, the formation of the solvated electron is slower than in water allowing a better insight into the solvation processes and precursor states [2,3].

Within this context, using pump-probe transient absorption spectroscopy we studied the salvation dynamics of the electron in liquid polyalcohols: ethane-1,2-diol, propane-1,2-diol, and propane-1,3-diol. The choice of the diols comes from their relatively high viscosity and the presence of two hydroxyl groups, allowing the investigation of the influence of the distance between the hydroxyl groups on the electron solvation process. In addition, for these alcohols, the maximum of the absorption band of the equilibrated solvated electron is located in the visible spectral domain, around 570 nm.

First, transmission measurements allowed us to assess that electrons were produced via two-photon ionization of the solvent with 263 nm femtosecond laser pulses, and to determine the two-photon absorption coefficient of the diols. Second, time resolved absorption spectra ranging from 430 to 710 nm were measured. Our study shows that the excess electron in polyalcohols presents an intense and wide absorption band in the visible and near IR spectral domain at early time after photoionization. Then, for the first tens of picoseconds the electron spectrum shifts toward the blue domain and its bandwidth decreases as the red part of the initial spectrum drops rapidly while the blue part hardly evolves [4-6]. Using Bayesian data analysis method, the observed picosecond salvation dynamics were reconstructed with different models: stepwise mechanisms, continuous relaxation models or combinations of stepwise and continuous relaxation. Comparison between the ability of models to reproduce the experimental kinetics is in favor of a heterogeneous continuous relaxation, mainly governed by solvent molecular vibrations and motions [5,6].

ON THE DYNAMICS OF MULTIPLE SCATTERING: THEORY, SIMULATION AND EXPERIMENTS

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In highly turbid samples the scattering intensity contains contributions of single and multiple scattering. New experimental techniques enable separating the single scattering from the multiple scattering. Vice versa multiple scattering contributions can be analysed, which is of interest in its own right and requires assessment of such contributions by theory and simulation.

In this contribution we report on the simulation of the scattering processes in Latex solutions of particles of different size (diameters 50, 100, 250 and 450 nm) and of mixtures in the vicinity of the critical solution point. The polarized and depolarized contributions to the intensity and the corresponding time-correlation functions are calculated for singly scattered light and the various multiple scattering contributions. Simulation results are compared with analytical calculations and experimental results. It turns out that, even in highly turbid samples, the majority of multiple scattering contributions reaching the detector involves essentially particles within the scattering volume, which is defined by the scattering geometry. Coherent backscattering is found in highly turbid samples as the maximum of the scattered intensity is shifted to such positions within the scattering volume, where the light–path is short. The time dependence of the correlation functions shows a universal structure: at short times the decay of the correlation functions is independent of the scattering angle given by the product of the multiplicity of the scattering with the angular average of the time constant for the decay of the correlation function of singly scattered light. At longer times the decay is determined by the intermediate scattering angles leading to the shortest light path. The crossover between the two regions is determined by the size of the particles, where the short time region becomes smaller with increasing size of the particles. In the Gaussian approximation the exponents of the form factor and of the time-correlation function of the single scattering form a universal parameter determining the intensities and the correlation functions of the various multi-scattering contributions.
SOLVATION DYNAMICS IN THE UV WITH PHOTON-ECHO AND FLUORESCENCE UP-CONVERSION

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Solvation dynamics play a crucial role for various chemical and physical processes in liquid media. At room temperature, the relevant processes span many timescales and different ultrafast experiments have been designed for their investigation. The most common techniques are femtosecond fluorescence up-conversion, which allows to follow the Stokes shift in real time, as well as photonecho techniques. The capability of photon-echo peak shift measurements to trace the band-gap correlation function has been discussed in much detail [1,2] and is widely used.

With the final goal of studying dynamics in wild-type proteins by exciting the aromatic amino acid tryptophan we have implemented these techniques with excitation at 290 nm. Here, we will report about first photon-echo peak shift experiments on an organic dye and on tryptophan in water, measured using the frequency doubled output of an optical parametric amplifier. Besides being a test system for the feasibility of the experiment, the dyes are interesting for the study of non-polar salvation and internal vibrational relaxation on the femtosecond timescale.

The photon-echo results are complemented by dispersed fs-fluorescence up-conversion experiments [2] with UV excitation. Analysis of the transient spectra, allows a detailed study of the very initial, internal dynamics in the UV dye and, in accordance with the photon-echo results, reveals sub-ps relaxation mechanisms.

Posters
THEORETICAL STUDY OF BOTH COMBINED EFFECTS OF MULTIPLE FERMI RESONANCE AND INDIRECT RELAXATION ON IR SPECTRAL DENSITY OF MEDIUM STRENGTH H-BOND

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Abstract: We extend a quantum non-adiabatic treatment of H-bonds [1] involving indirect relaxation and intrinsic anharmonicity of the fast mode, which is described by an asymmetric double well potential, by accounting for multiple Fermi resonance. The IR spectral density (SD) of the high frequency stretching mode is studied within the linear response [2, 3] theory from a full quantum mechanical point of view. The anharmonic coupling between the high frequency $X \rightarrow H \cdots Y$ and the low frequency $\bar{X} \rightarrow H \cdots \bar{Y}$ modes is treated inside the strong anharmonic coupling theory [4], whereas Fermi resonances are introduced in the spirit of the work of Witkowski and Wójcik [5]. The relaxation of the fast and bending modes (direct damping) is introduced in a phenomenological way, by assuming that the autocorrelation function disappears exponentially in time, as in the very fundamental model of Rösch and Ratner [6]. The IR SD is obtained by Fourier transform of the autocorrelation function of the dipole moment operator of the fast mode.

References:

LIF EXCITATION SPECTRA OF JET-COOLED DEUTERATED ANTHRANILIC ACID

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The LIF excitation spectra of anthranilic acid (AA) were measured for nondeuterated and deuterated samples in the spectral range 28800 – 30100 cm\(^{-1}\). In the present contribution a discrimination between the monomer and dimer species \cite{1, 2} was performed using different vapor pressures of AA in mixtures with Helium at 4 bars before supersonic expansion. Low energy part of the spectra measured when the oven containing the AA sample was heated to 353 K are shown in Fig. 1 (top). In these conditions the monomer species of AA are predominant. Partial deuteration of the AA sample with the exchange of O – H\textsuperscript{(1)} and O…H\textsuperscript{(2)} – N – H\textsuperscript{(3)} hydrogen atoms gives the LIF excitation spectrum of eight easily recognizable isotopomers. The corresponding spectrum is shown in Fig. 1 (bottom).

![Fig.1. LIF spectra of nondeuterated anthranilic acid monomer (top) and partially deuterated sample of AA (bottom)](image)

Partial assignment of vibrational transitions of deuterated species of AA has been performed using HF, CIS, DFT and TD DFT calculations of molecular geometry and vibrational transitions in \(S_0\) and \(S_1\) electronic states, respectively. The TD DFT calculations for AA indicate that the rotamer with the hydrogen bond – C = O…H\textsuperscript{(2)} – N – H is observed in the LIF excitation spectra \cite{3, 4}. The vibrational modes 253(5), 355(6), 419(8), 543(13), 594(14), 713(17) cm\(^{-1}\) give major contribution to the LIF spectrum of nondeuterated AA.

The largest deuteration shifts of the 00 transition are due to the exchange of the H\textsuperscript{(1)} hydrogen atom. The shifts are as follows: hhd = – 7, hdh = 43, hdd = 37, dhh = 10, dhd = 3, ddh = 53 and ddd = 47 cm\(^{-1}\). The deuteration shifts have been compared with the calculated zero point energies of isotopomers in the excited and ground electronic states using harmonic and anharmonic approximations \cite{5}. The intensity distributions in the LIF spectra have been analyzed using multidimensional FC factors. The displacement parameters were also fitted to reproduce observed intensities more closely. The evaluated geometry changes and some intramolecular hydrogen bond properties of AA are compared and discussed.

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THE RESONANCE RAMAN EFFECT IN WATER REVISITED

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Although water is one of the most intensively studied substances, many of its anomalously unique properties are still explained unsatisfactorily. It is obvious, that the water behaviours strongly depend on supramolecular structure formed via H-bonds. Raman spectroscopy seems to be very powerful technique to analyse the reorganisation of water molecules under various stimuli (pH, contaminations, temperature, pressure), because of its high sensitivity to intra- and intermolecular interactions [1-4]. The special attention should be focused on the range 2900-3800 cm\(^{-1}\) containing the Raman bands assigned to -OH stretching vibrations. However proper interpretation of Raman spectrum of water and its changes under various conditions requires detailed description of the dependency of the Raman intensity vs. excitation wavelengths, as it will be shown in this work.

The Raman resonance effect in water was already a subject of several publications. In most works the broad and structured Raman band with a maximum at c.a. 3400 cm\(^{-1}\) was considered as single peak and for the analysis integral intensity of the whole broad band was used [5-7]. Our results show that the shape of the water Raman spectrum in the range of 3000 - 3900 cm\(^{-1}\) significantly depends on the excitation wavelengths. It is of a high importance, as the particular peaks composing the broad 3400 cm\(^{-1}\) band reflect the supramolecular structure of water. Moreover, the ratio of the integrated intensities of two the strongest peaks (3400 and 3200 cm\(^{-1}\)) is widely used as a measure of the water structure in many systems, such as hydrogels, living cells, tissues and others.

In many cases, the resonance Raman effect results in changes of the depolarisation ratio of in-resonant bands. Our investigations of the polarised Raman spectra show that only the low frequency component depends on the excitation wavelengths. It is consistent with the results obtained by the time-resolved method by Woutersen and Bakker [7]. They have demonstrated that intermolecular transfer of vibrational energy is a crucial phenomena allowing for resonance effect in water. The intermolecular energy transfer is possible only if the water molecules are strongly jointed via H-bonds manifested in 3200 cm\(^{-1}\) Raman peak. The presence of the resonance Raman effect in water is also correlated with the obtained absorption water bands in visible region.

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Ultraviolet laser-induced fluorescence (LIF) of fluorescent biological substances provides a real-time technique for detecting airborne pathogens. Measurements of EM-EX matrices and calculations of the fluorescence cross-sections of 25 biological simulants and interferants (vegetative bacteria, spores, fungi and pollens) will be presented. The investigations are aimed at systematic creations of database used for comparison of various biological materials and possibility of their discriminations. Now there are not known emission characteristics of a large group of potential interferants.

Till-now, the designed systems of biological agents detections use one wavelength for fluorescence excitation. It is not satisfactory because many false alarms appear. The results found in the literature and obtained from our investigations on ten different bacteria confirm that only one wavelength is insufficient for discriminating of various group of biological agents. Multispectral excitation of different fluorophores increases the possibility of distinguishing biological agents from a background.

Bacteria fluorescence lifetime is an important parameter that confirms substance identifications. Time-resolved fluorescence was measured for biological species using stroboscopic technique and UV LEDs (280 and 340 nm) as a source of excitation. For all the examined species, the fluorescence lifetime was described by double exponential kinetics. In general, lifetimes and relative fractional contributions of components are various for particular biological species, however, they are not specific for one group, what causes difficulties in BWA classification with time-resolved fluorescence method only. Evaluation of the decay curves and emission spectra using PCA method allows discrimination of living bacteria and spores from interferants.
HIGH-POWER DIEDE-END-PUMPED Tm:GdVO\textsubscript{4} LASER OPERATING AT 1818 nm AND 1915 nm

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ABSTRACT

High-power solid state lasers operating in the 2 \(\mu\)m wavelength region are of interest for a wide variety of applications, including remote gas detection and laser spectroscopy, as drive lasers for high harmonic generation and attosecond applications for free-space optical communication. One approach to achieve high output power is to optically pump Tm doped lasers that can lase at 1.92 \(\mu\)m, with high-power laser diodes at 0.82 \(\mu\)m. The Tm laser output can then be used to pump Ho doped lasers that can produce output at 2.12 \(\mu\)m.

Tm:GdVO\textsubscript{4} is a relatively new laser material that has attracted attention due to its broad absorption spectrum centered around 799 nm which makes it particularly suitable to be pumped with commercially available high-power laser diodes. In addition, it has a broad emission spectra which makes it feasible to operate such a Tm:GdVO\textsubscript{4} laser over a wide wavelength range. Despite these advantages, there are a limited number of publications relating to the power scaling of this laser material. The highest output powers previously demonstrated from a continuous wave Tm:GdVO\textsubscript{4} laser was 2.6 W with its wavelength at 1910 nm [1].

In this paper we report on our initial experiments with diode-end-pumped Tm:GdVO\textsubscript{4} laser. The atomic doping concentration was 3 \% and the dimensions of the crystal 2.5 x 2.5 x 3 mm\textsuperscript{3}. The crystal was placed in a plano-concave resonator of approximate length 26 mm. Two output coupler mirrors were used during the experiments. The first coupler had 95 \% reflectivity at 1.9 \(\mu\)m with 300 mm radius of curvature. The second coupler had 28 \% reflectivity at 1.8 \(\mu\)m with 250 mm radius of curvature. The laser was pumped with a fibre-coupled laser diode from one end only, the fibre of which had a core diameter of 400 \(\mu\)m and N.A. of 0.22. The laser diode was operated in a quasi-continuous wave (QCW) mode with 60 W maximum peak power incident on the crystal at 800 nm. The duty cycle of the pump pulses was kept low in an attempt to prevent crystal fracture. The output at 1.9 \(\mu\)m was measured with PbS photo diode and a power meter.

The output wavelength of the laser with the 95 \% reflectivity output coupler was measured to be 1915 nm (\(\pm\)2.5 nm measuring uncertainty). The pump pulse had an on-time of 20 ms at 5 Hz repetition rate. The measured maximum peak power was 8.7 W for 37.3 W of incident power on the laser crystal. This corresponded to \(~\)175 mJ per pulse of output energy. Increasing the pump power beyond this point resulted in thermal fracture of the laser crystal.

Next the 28 \% reflectivity output coupler was used and the pump pulse on-time was reduced to 10 ms. The damaged crystal was replaced with a crystal of similar doping concentration and dimensions. The output wavelength of the Tm:GdVO\textsubscript{4} laser was measured to be 1818 nm (\(\pm\)2.5 nm). This reduction in wavelength was expected from the quasi-three level laser with an output coupler with high transmission loss. The maximum peak output power of this laser was measured to be 8.4 W at full pump power from the laser diode, corresponding to \(~\)84 mJ per pulse.

It was shown here for the first time to our knowledge that Tm:GdVO\textsubscript{4} laser can be used in QCW mode with a pulse width of 10 – 20 ms with multi watt output power. It was concluded that this laser is suitable to be used as a pump source for Ho doped lasers which have upper states lifetimes in the 7 – 15 ms range. In addition we have shown that the Tm:GdVO\textsubscript{4} laser wavelength can be operated over \(~\)100 nm by adjusting the laser resonator losses. This makes the Tm:GdVO\textsubscript{4} a suitable laser source for pumping different types of crystals doped with Ho. Our future work will include further power scaling and continuous wave operation of the Tm:GdVO\textsubscript{4} laser.

REFERENCES

ABSTRACT
Rare earth ions, which are used to doping glass matrix or crystals, are generally in trivalent state. These trivalent ions have outer electronic configuration of $4fn5s^25p^6$, where $n$ is integer value ranging from 1 for cerium to 13 for ytterbium [1]. The 4f electrons are shielded by 5s2 and 5p6 electrons, what is mean that these electrons are weakly perturbed by the crystal field of the host. This gives rise to the comparatively sharp energy level structure for transitions between the manifold of the 4f electrons [1].

When crystals such as YAG, YSGG or YLF are doped by rare earth ions their energy level structure is enriched and each of energy level is splitting on $(J+1)$ dublets (Stark effect) [2].

In Er:YAG, Er:YSGG and Er:YLF lasers the most important are three lowest energy levels of Er3+ ion. Transitions between these levels decide about wavelength of generated laser radiation. In Er:YAG laser these levels are: $4I_{15/2}$ (energy: 280 cm$^{-1}$), $4I_{13/2}$ (6710 cm$^{-1}$), $4I_{11/2}$ (10330 cm$^{-1}$) [2]. Er:YAG has many absorption lines mainly in visual and near infrared wavelength spectrum. This laser may generate optical radiation on two wavelength: 1.6 mm and 2.94mm. For the first wavelength Er:YAG work as a three level laser and the for second wavelength it work as a four level laser. In this case top laser level is $4I_{11/2}$ and down laser level is $4I_{13/2}$. Generated wavelength and work type may be selected by dopant concentration.

In lasers such as Er:YAG analysis of transitions between levels during optical radiation absorption and generation must take in consideration Boltzman distribution of occupation of energy levels and thermalization effects [3].

Authors have developed simulation software which allows analysing of transitions dynamics, laser output power/energy and rod’s temperature increase (during pulse generation) which depends on:
- pump properties,
- initial temperature,
- dopant concentration

Analysis may be carried on for monoimpulse generation as well for impulses series generation. This software allow to simplify Er:YAG laser application designing.

REFERENCES
HIGHER-ORDER DISPERSION CONTROL FOR FEMTOSECOND CPA LASERS

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ABSTRACT

To achieve the shortest pulse duration with the highest possible temporal contrast at the target, the residual dispersion of few cycle laser pulses has to be compensated to the fifth order at least. The otherwise popular acousto-optical modulators suffer from limited bandwidth and spectral range. Other approaches include complicated but efficient combination of grating and prism compressors, chirped mirrors and optical slabs. We show, that by creating an appropriate temperature profile in an optical slab inserted into the stretcher (or a compressor) of a chirped pulse amplification (CPA) laser, the dispersion can be adjusted theoretically to an arbitrary high order.

In a proof-of-principle experiment a 40 mm wide, 10 mm thick BK7 slab was placed into the compressor of a Ti:S CPA laser system (Fig.1). The spectral group delay (SGD) has been measured with spectrally and spatially resolved interferometry [1], for which the 18 fs, 800 nm pulses from the oscillator of a Ti:S CPA laser system has been split into reference and probe beams. The probe beam propagated through the whole laser system (stretcher, amplifiers, compressor) while the reference beam was compressed by a prism compressor. The two beams were combined on the entrance slit of a spectrograph. First the spectral group delay of the glass slab at room temperature was recorded as a reference (Fig. 2, dashed curve). Next the middle of the slab was heated with thermo-resistors while the edges were contacted with water tanks filled with water/ice mixture (Fig. 1), so that a parabola-like temperature profile has been created. Accordingly, the SGD curve become parabolic (Fig. 2, solid curve). Having reversed the temperature profile by stopping the heating at the middle along with inserting hot water into the tanks, the measured SGD curve was also reversed (Fig. 2, dotted curve).

We believe that this approach with a more elaborated heating-cooling system, like application of ITO layers and Peltier elements, could offer a more simple solution with extra degrees of freedom for high order dispersion compensation of few cycle laser pulses even in UV and IR.

REFERENCE

Thulium doped fiber lasers of output powers in the range of several dozens of Watts are required in different applications as follows: laser spectroscopy, coherent pumps of holmium and chromium doped crystalline lasers, surgery, atmosphere monitoring etc. Thulium doped fiber laser are based on silicate [1, 2] or fluoride fibres [3], pumped at 0.79, 0.8 or 0.97-μm wavelengths depending on optional co-doping. The high slope efficiency (~0.4) of Tm laser is caused due to effective cross-relaxation processes resulting in quantum efficiency near 2.

Fig. 1. Optical scheme of Tm fiber laser pumped by 2 x 25-W fiber coupled laser diodes.

Fig. 2. Output power vs. pump power of Tm fiber laser pumped by 2 x 25-W fiber coupled laser diodes.

We have developed the Tm fiber laser (see Fig. 1) pumped by both ends with two 25-W fiber coupled diode lasers operating at 0.79-μm wavelength. The pump beam (NA = 0.22 and 0.4-mm core width) after passing through relay optics of magnification m = 0.6 is launched into active thulium doped double clad fiber of NA = 0.46, and inner cladding width of 0.26 mm. The total launching efficiency is estimated to be less than 70%. We have used 5-m long Tm fiber with core width of 25 μm, and resulting beam quality M² parameter near 1. In the preliminary experiments the output 1.8-μm laser beams were reflected by the two flat mirrors inclined at 30° with respect to pump beam axis. The laser action started at 14 A threshold due to 5% Fresnel coupling at fiber facets. We have obtained above 12 W of output power (see Fig. 2) for maximum available pump power of 42 W. The laser spectrum centred at 1800 nm has width over 200 nm depending on pump power. Such a laser will be applied as a coherent pump of hybrid pulsed Ho:YAG laser destined for atmosphere sensing. This work was financed by the Polish Ministry of Science and Higher Education under project 0T00A00330.

REFERENCES

ABSTRACT

The pulsed, high peak power laser beams at different wavelengths in the visible und UV range of spectrum are required in several applications as follows: laser technology, LIDAR’s, spectroscopy etc. The aim of this work is to develop the simple laser set up enabling generation of high peak power (> 5 kW) pulses at several wavelengths in the visible and UV. The heart of laser system is a simple acousto-optic Q-switched laser delivering the pulses with peak power above 20 kW and repetition rates of several dozens of kHz (see Fig. 1).

The scheme of generation of II, III and IV harmonic out of cavity applying nonlinear crystals is routinely used (see Ref. [1,2,3]) to obtain efficient conversion to the 532, 355 and 266 nm wavelengths respectively. In preliminary experiments we have demonstrated efficient conversion to II harmonic applying KTP crystals (see Fig. 2) with averaged output power about 1.3 W and peak power > 5 kW. The prepared laser set up consists of a special “laser kit” which enables to obtain the required peak powers at desired wavelengths. We expect that such a simple laser set up will find applications in numerous university laboratories working in the area of laser spectroscopy and could be interesting for other applications as laser marking, microsurgery etc.

This work was financed by the Polish Ministry of Science and Higher Education under project PBZ-009/T11/2003 and Rector of Military University of Technology under the project PBW - 902.

REFERENCES

In this work we present 2D-IR spectra of a very weak IR absorber, $^{13}$C$^{15}$N$^-$ in D$_2$O by means of heterodyne detected three-pulse photon echo experiments [1]. The CN$^-$ vibrational frequency is sensitive to local solute–solvent interactions and additionally to hydrogen bonds between solute and solvent.

We used an actively phase–stabilized 3–pulse heterodyned photon echo setup to record spectra of CN$^-$ dissolved in D$_2$O.

At short population times, e.g. $T = 200$ fs, the 2D-IR bands are tilted and elongated along the diagonal. This tilt becomes less pronounced with increasing population time $T$ and disappears almost completely by 10 ps. The tilt reports a correlation between initial pump and final probe frequencies if the band is inhomogeneously broadened. Pump and probe frequencies are correlated as long as a memory of the initial frequency exists. Inhomogeneity in the solution phase is not static, but decreases with the time-scale of rearrangements of local structures around the solute molecule. Hence, the time-scale of the disappearance of the tilt directly reports on the lifetime of the local water structures around the $^{13}$C$^{15}$N$^-$ ion.

We find that the spectral dephasing of $^{13}$C$^{15}$N$^-$ dissolved in D$_2$O is governed by two processes: A fast, inertial process (time constant 200 fs) which is essentially in the homogeneous limit, and which gives rise to the larger fraction of the total line-width ($\approx 10$ cm$^{-1}$), and an additional slow spectral diffusion process with 5 cm$^{-1}$ line-width and 2.9 ps spectral diffusion time. The total frequency fluctuation correlation function is similar to that previously obtained for (N$^-$3$^-$) in D$_2$O. It is not surprising to get similar results in our case, since both N$^-$3$^-$ and CN$^-$ are small negatively charged ions and their interaction with solvent should be similar as well. The longer spectral diffusion time constant (2.9 ps, compared to 1.3 ps in N$^-$3$^-$) seems to suggest that the hydrogen bonds (which were attributed to be responsible for the spectral diffusion in the N$^-$3$^-$ case) are even more stable in the CN$^-$ case. This might be due to the more uniform charge distribution of the CN$^-$ ion, as opposed to alternating full charges in N$^-$N$^+$N$^-$.

Comparison of the presented data with recent MD simulations show the need of more sophisticated approaches than classical force fields to quantitatively describe spectral diffusion processes.

In conclusion, we present reliable experimental data for the vibrational dephasing of CN$^-$ in water, one of the weakest IR absorbers measured to date. As a diatomic molecule, this molecular system avoids the complications due to other intramolecular degrees of freedom. We consider it a benchmark system to develop theoretical models of vibrational dephasing of strongly interacting solutes in polar solvents.

REFERENCES

PUMP-PROBE SPECTROSCOPY FOR PRIMARY EVENTS IN BACTERIORHODOPSIN

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Abstract

Light absorption by the retinal prosthetic group of the light-adapted bacteriorhodopsin BR568 initiates a cyclic photochemical reaction which drives the transport of protons across the bacterial cell membrane.

Ultrafast time resolved electronic spectra have been measured by the femtosecond pump-probe spectroscopy in order to gain insight into dynamics of primary intermediates leading to photoisomerisation following the torsion about C_{13}=C_{14} bond. The results obtained clearly demonstrate the dominant role played by the intermolecular energy relaxation and the intramolecular resonance energy exchange processes between the vibrational modes. The high frequency C=C stretching mode is the primary reaction coordinate upon excitation, not the torsional coordinate. The coupling between S_1(B_u) and the torsional coordinate leading to the photoisomerization is achieved at the end of the sequence of the intramolecular energy exchange events within the first 3.5 ps upon excitation.
OPTICAL MANIPULATION OF ELECTRON PHOTODETACHMENT DYNAMICS OF AQUEOUS HALIDE

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We studied the electron photodetachment dynamics after excitation of aqueous bromide at 200 nm into the lowest charge-transfer-to-solvent (CTTS) state. The simplified energy level scheme used to account for the measured dynamics is presented in Figure A. The initially excited CTTS state leads to fast separation of the released electron and subsequent formation of atom:electron pair. To account for the two time scales two intermediates are introduced that are assigned to an atom:electron pair in a non-equilibrated solvation structure, \((\text{Br}:\text{e}^-)_{\text{hot}}\), and a quasi-equilibrated pair \((\text{Br}:\text{e}^-)_{\text{aq}}\). The subsequent slower dynamics indicated by an absorption decrease (see Figure B) is found to be temperature dependent and is explained by a competition of pair dissociation and geminate recombination.

The direct experimental verification of the proposed atom:electron pair is still a challenge since its absorption spectrum is very similar to those of the fully solvated electron. To overcome this limitation we applied a third femtosecond pulse at 800 nm, called repump pulse. Varying the temporal delay between the UV and NIR pulse we are able to excite different intermediates of the electron detachment process (see Fig. A). In this way the electron relaxation pathway can be manipulated providing novel information of the involved intermediates.

Examples for the time-resolved data obtained by Pump-Repump-Probe (PRep) experiment are shown in Figure B. In order to be sensitive to population changes, the relaxation dynamics is monitored at the absorption maximum of the solvated electron of 700 nm. It can be already seen that the excitation of \((\text{Br}:\text{e}^-)\)-pairs avoids the recombination and leads to additional solvated electrons.

Using the PRep spectroscopy we were able to separate the atom:electron pair and the \((\text{e}^-)_{\text{aq}}\) which have the same spectral signature and could not be distinguished with former simple pump-probe-techniques.

![Figure (A)](image)

**Figure (A)** Simplified energy level scheme used to account for the measured dynamics. CTTS state (black line), \((\text{Br}:\text{e}^-)_{\text{hot}}\) state (grey/black dotted line). The equilibrated pair \((\text{Br}:\text{e}^-)_{\text{aq}}\) and the fully solvated electron \((\text{e}^-)_{\text{aq}}\) show the same absorption spectrum (grey line).

**Figure (B)** Signal transients measured at 700nm after excitation of aqueous bromide at 200nm without (black circles) and with reexcitation (bright circles) 1 ps after the UV pulse. The dark circles shows the difference.

Gutman M., Hilczer M.
PHOTOINDUCED BIMOLECULAR ELECTRON TRANSFER INVESTIGATED BY FEMTOSECOND TIME-RESOLVED INFRARED SPECTROSCOPY

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Since the pioneering work of Weller and coworkers [1,2] bimolecular photoinduced electron transfer (ET) reactions have been intensively investigated. These processes are the simplest bimolecular reactions and have thus been object of many theoretical treatments. Furthermore, they play an important role in many areas of chemistry and biology and are involved in several practical applications such as solar energy conversion, and photopolymerization. Despite the numerous studies carried out on bimolecular ET, important questions still remain unanswered [3], such as the nature of the primary ET quenching product and the various steps leading to the formation of free solvated ions in polar solvents.

A major experimental problem is that ion pairs and free ions cannot be easily differentiated from their electronic absorption spectra. Here, we report on an investigation of the bimolecular ET quenching reaction of the electron donor perylene (Pe) and the acceptors 1,4-dicyanobenzene (DCB), and tetracyanoethylene (TCNE) in acetonitrile and dichloromethane using time-resolved IR spectroscopy [4]. Following vibrational marker modes on both donor and acceptors sides in real time provides direct insight into the structural dynamics during the reaction. By recording transient IR absorption spectra of the radical ions generated upon photoinduced ET and analyzing height and width of the corresponding bands, we can directly follow the generation of both products under identical conditions, which is often difficult to impossible in all-visible experiments. With this approach we are able to distinguish strongly and weakly coupled ion pairs in the bimolecular electron transfer reaction.

With DCB as acceptor a band narrowing on a time scale of a few tens of picoseconds observed on the antisymmetric CN stretching vibration of the DCB radical anion indicates that a substantial part of the excess energy is dumped into vibrational modes of the product, despite the fact that the reaction is weakly exergonic. An additional narrowing of the same band on a time scale of several hundreds of picoseconds observed in acetonitrile only is interpreted as a signature of the dissociation of the geminate ion pairs into free ions [5].

Using TCNE as acceptor the obtained transient spectra clearly show two distinct components, permitting for the first time to clearly distinguish two independent sub-populations of the reaction product, strongly and weakly coupled ion pairs. The tightly coupled pairs originate from ultrafast “static” ET quenching and recombine to the neutral pair shortly after ET. The weakly coupled pairs are formed by diffusional quenching, undergo slower recombination and, thus, lead to free solvated ions. The relative yield of these sub-populations strongly depends on the TCNE concentration.

ULTRAFAST PHOTOCROMISM OF MOLECULAR SWITCHES: INDOYLFULGIDES AND INDOYLFULGIMIDES

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The molecule class of the fulgides is well known for its photochromism. These molecules undergo a pericyclic light-induced ring-opening reaction [1]. The three photoisomers C, E and Z of the indolylfulgides and associated indolylfulgimides have different optical absorption spectra. Only the Cisomer has a characteristic absorption band in the visible spectral range, so the ring-opening reaction is well accessible. Indolylfulgides and indolylfulgimides are thermally stable and have low chemical fatigue upon illumination. Because of these reversible structural changes indolylfulgides are interesting candidates for applications for energy transfer, optical switches or data storage [2,3]. In this contribution we report steady state and time resolved measurements of the ultrafast ring-opening reaction of the indolylfulgides and indolylfulgimides [4,5] under several chemical and physical conditions (chemical substitution, surrounding, temperature, excitation).

The ultrafast switching process is examined by femtosecond time-resolved spectroscopy in a pump-probe experiment. The ultrashort laser pulses are generated with a home-built Ti:sapphire based laser system with a repetition rate of 1 kHz [6]. Tunable broad-band pump and probe pulses in the visible spectral range are produced by two non-collinear optical parametric amplifiers (NOPA) [7]. After compression the pulse duration is about 15 fs.

For the ring-opening reaction a bi-exponential decay is observed. The time constants are strongly dependent on the chemical substitution (fulgide – fulgimide), solvent and temperature. The fast component (about 1 ps) is assigned to a solvent-solute interaction. The slow component describes the decay of the educt excited state and the rise of the product ground state. In a nonpolar and polar surrounding this decay time is in the range of 2 to 3 ps for indolylfulgimides and 8 to 12 ps for indolylfulgides. For higher temperatures the lifetime of the excited state decreases. No intermediate state was found. Additional cooling of the hot molecules is observed (time constants between 10 and 40 ps).

Quantum yields of the ring-opening reaction also depend on the chemical substitution, dielectric constant of the surrounding, temperature and excitation wavelength. The efficiency varies between 1 and 12 %. The results lead to an Arrhenius like behaviour, so a model with an energy barrier on the potential energy surface of the excited state and conical intersections with the ground state [8] can be discussed.

REFERENCES
PHOTOCHEMISTRY OF MAGNESIUM PHTHALOCYANINE BY RAMAN AND FEMTOSECOND LASER SPECTROSCOPIES

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Understanding photochemical mechanisms of phthalocyanines plays a crucial role in evaluation of their photodynamic activity because photochemistry and mechanisms of vibrational relaxation of these drugs affect their photobiology.

In our studies we concentrate on photophysical and photochemical behaviour of magnesium phthalocyanine and their tetrasulfonated derivative induced by laser irradiation with VIS light. Photochemistry of tetrasulfonated magnesium phthalocyanine in liquid solutions of water has been studied by femtosecond transient absorption spectroscopy. Spectra of magnesium phthalocyanine and their sulfonated derivative have been recorded also by Raman spectroscopy in the temperature range 293-77K in DMSO and in water to identify the nature of emissive bands.

Acknowledgement

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Theoretical description of vibrational line profiles plays very important role in analyses of vibrational and reorientational dynamics. In Ref. [1] a model time-correlation function has been introduced that can be Fourier transformed analytically and hence enables one to analytically describe the profile of vibrational line. Careful examination of this correlation function and examples of its use are reviewed in Refs [2,3].

There are numerous important applications, where considerations regarding the line profile are crucial for correct understanding the nature of the system under study. One of them is the analysis of depolarization ratios $\rho(\nu)$ in Raman spectra. $\rho(\nu)$ is a valuable tool in studies of the symmetry of probe molecules, assignment of molecular vibrations, distinguishing between fundamentals, overtones, and binary combinations, etc.

An analysis of $\rho(\nu)$ could be easily made in the case of single lines. However, if a line in question consists of several overlap components, any attempt to perform a quantitative analysis of the wavenumber-dependent depolarization ratio fails, since $\rho(\nu)$ of a composite line is not the additive function of the depolarization ratio of its constituents, and for a composite line representing an envelop of is single lines.

In this presentation, the method described in Refs [1-3] is employed simultaneously to composite isotropic and anisotropic Raman profiles and the spectrum of the wavenumber-dependent depolarization ratio $\rho(\nu)$. An idea of this approach is to restore isotropic and anisotropic contours of all components of a composite spectrum and to recover their partial $\rho(\nu)$ spectra. The solution of this problem is demonstrated for benzene, toluene and toluene-$d_8$, and other methyl substituted benzenes. For these molecules, the $\rho(\nu)$ spectra of all components are recovered, and assignment of overtones and hot bands is made.

Another application of the method described in Refs [1-3] is conformation analysis of aromatic compounds. The most obvious consequence of the concept of aromaticity is the common confidence that in aromatic compounds, bond lengths do not alternate and are between typical to the single and double ones. However, in 1994, it was discovered that a very surprising angular group induced bond alteration (AGIBA) effect can exist in some crystals [4,5]. In this presentation, the first possible evidence of spectroscopic manifestations of the AGIBA effect in liquids is analyzed. It is found that in the liquid toluene, instead of being single, the line corresponding to the ring breathing vibrations is clearly split by 1.0-1.4 cm$^{-1}$, thus indicating the presence of two AGIBA isomers. The energy difference between these isomers is determined as 6.68 kJ/mol.

APPLICATION OF RAMAN SPECTROSCOPY FOR BREAST CANCER DIAGNOSIS

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Investigation by Raman Spectroscopy ex vivo normal and lesions human breast tissues. We have examined healthy and lesioned breast tissues from 49 patients of M.Kopernik Hospital in Lodz. Samples have been examined without immersing in formaline. Raman spectra have been recorded using laser 514 nm excitation in CW regime with powers 25 mW and 100 mW.

Contrary to previous research efforts, he have collected spectra of a large number of samples, which can give information of statistical value.

In healthy tissues we have observed carotenoids and lipids bands which don’t show up in lesioned samples. Our current attempts are to find the differences between malignant and benign lesions using principal components analysis (PCA).

Raman spectra of healthy (A) and lesioned (B) tissue. Excitation with 514 nm laser line.
SOME PREPARATION DEPENDANT PROPERTIES OF PBS NANOCRYSTALS

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Semiconducting nanocrystals (NC) PbS are very interesting due to their peculiar optical properties, e.g. ultrafast dynamics of the excited states or strong nonlinear features in near infrared. Thanks to these properties quantum dots can be used for construction of photonic devices. The PbS nanocrystals have already been applied for construction of the laser mirrors used for light modulation [1,2]. Herewith we present optical properties of quantum dots PbS synthesized by use of different compounds passivating the surface, what should influence the relaxation time of excited molecules. In order to get nanoparticles of different sizes (what determines the appropriate widths of the restricted bands) the investigations have been performed at different temperatures. The size and the shape of the obtained nanocrystals are found by methods of small angle X ray Scattering and Atomic Force Microscopy. Absorption and stationary fluorescence measurements are applied for investigation of optical properties of the synthesized materials. The dynamics of the relaxation process is monitored by transient absorption measurements.

DYNAMIC COUPLINGS, RADIATIVE AND NONRADIATIVE LIFETIMES OF THE A $^1\Sigma^+$ AND C $^1\Sigma^+$ STATES OF KH

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ABSTRACT

In this paper, dynamic couplings for X-A, X-C and A-C, by using first and second derivatives terms neglected in the Born-Oppenheimer approximation, are calculated. Newly calculated radiative transition probabilities for the $A^1\Sigma^+\rightarrow X^1\Sigma^+$ and $C^1\Sigma^+\rightarrow X^1\Sigma^+$ emission bands of KH are used to calculate the radiative and non-radiative lifetimes of the various vibrational levels (0 $\leq v \leq 35$) and (0 $\leq v \leq 55$) of $A^1\Sigma^+$ and $C^1\Sigma^+$ states of diatomic potassium hydride, KH molecule. For higher vibrational levels, an estimate of the bound-to-free emission probability is also needed and included. Accurate positions, radiative and nonradiative lifetimes of states belonging to the adiabatic A and C states of KH molecule are estimated. The results come from a Fermi’s Golden Rule treatment in coupling calculation. That confirms the accuracy reached in both approaches and also in the treatment of the diabatic-adiabatic transformation. It involves, in particular, an effective phase choice that is needed to properly estimate nonadiabatic couplings.


REFERENCES

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