The second part of this talk concerns a new type of X-ray source, *betatron*, based on the relativistic laser-plasma interaction in gas. This source produces a polychromatic and highly collimated X-ray beam with duration about 25 fs. Its applications in time-resolved EXAFS and Laue diffraction, together with its comparison with other existing pulsed X-ray sources, will be presented.

[1] Rischel C., Rousse A., et al., 1997, *Nature*, **390**, 490-492. [2] Rousse A., Rischel C., et al., *Nature*, 2001, **410**, 65-68. [3] Sokolowski-Tinten K., et al., *Nature*, 2003, **422**, 287.

Keywords: time-resolved X-ray diffraction, phase transitions and structure, laser plasmas

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How do Signaling Photoreceptors Respond to Light?

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Signaling photoreceptors harness the energy derived from the absorption of a photon to generate a structural signal which is then transmitted to downstream partners and ultimately modulates a biological process such as phototropism in plants or swimming behavior of bacteria. To accomplish this with high efficiency, competing de-excitation pathways such as fluorescence and vibration have to be shut down (or greatly minimized). How are structural signals generated at the atomic level, by processes such as light-driven isomerization, bond breaking and bond making? We address these questions by nanosecond time-resolved crystallography, in which molecules in a single crystal of a photoreceptor are stimulated by a brief laser pulse and the subsequent structural changes probed by a synchrotron-derived, polychromatic, intense X-ray pulse. These time-dependent changes are revealed over the time range from nsec to sec: molecular movies. We illustrate these experiments by considering the fully-reversible photocycles of the bacterial blue light photoreceptor, photoactive yellow protein, and the heme domain of the O_2/CO sensor, fixLH. We extract by singular value decomposition the number of structurally-distinct components, identify whether a chemical kinetic mechanism characterized by a small number of distinct states exists and if so, determine the structures of these time-independent, intermediate, short-lived states.

Keywords: time-resolved crystallography, Laue diffraction, signal transduction

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Femtosecond Electron Diffraction: Making the "Molecular Movie"

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Femtosecond electron diffraction (FED) harbours great potential for providing atomic resolution of structural changes as they occur. This ability to watch atoms move in real time—to directly observe transition states—has been referred to as making the molecular movie. Many-body simulations of ultrashort electron pulse propagation [1] enabled the recent development of sources for femtosecond electron pulses with sufficient number density to execute near single shot structure determinations. This is a necessary requirement to allow studies of irreversible processes. With the realisation of joint femtosecond temporal resolution and sub-Angstrom structural resolution, an atomic level view of melting of a thin film of Al under strongly driven conditions [2] has been obtained in which the process can be desribed as a thermally driven phase transition that takes place in ~3.5 picoseconds. Subsequent studies of the slower melting of Au have further elucidated the mechanism for melt zone propagation.

Ongoing development in electron gun design has further improved the temporal resolution of FED for the observation of transition states in molecular systems. The camera for "making the molecular movie" is in hand.

[1] Siwick B.J., Dwyer J.R., Jordan R.E., Miller R.J.D., *J. Appl. Phys.*, 2002, **92**, 1643. [2] Siwick B.J., Dwyer J.R., Jordan R.E., Miller R.J.D., *Science*, 2003, **302**, 1382.

Keywords: ultrafast electron diffraction, electron pulse propagation dynamics, ultrafast melting

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The Mechanism of Coherent Phonon Generation

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Coherent acoustic phonons in solids can be generated by impulsive optical excitation through ultrafast heating of lattice and electrons. The former is the thermal lattice expansion related to anharmonicity of ion-ion interaction. The latter is the thermal pressure of free electrons. Previous studies using fs optical probes indicate that both driving forces contribute the phonon generation. However, these optical measurements are indirect probes of lattice motions. Here, we report the study of coherent acoustic phonon generation mechanism by directly measuring the associated structural dynamics with femtosecond electron diffraction (FED). FED provides a quantitative measurement of the temporal evolution of both coherent and thermal lattice motions with sub milli-ångström spatial resolution and on the sub-ps timescale. The damped single-mode breathing motion of 20-nm-thick Al film along the surface normal was recorded as the coherent oscillation of Bragg peak position with a period 6.4 ps, as determined by the 1-D standing wave condition. The lattice temperature (thermal motion) evolution with a time constant of 600 fs was measured by following the associated Bragg peak intensity attenuation. By fitting these data with the differential equation of a harmonic oscillator using a driving term including both lattice and electron heating, we find that the electron pressure contributes more significantly than the lattice heating for the first half cycle of the lattice vibration. These results provid a direct and clear evidence of the non-thermal generation mechanism of coherent acoustic phonons.

Keywords: lattice dynamics, time-resolved diffraction, electron phonon coupling

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Time-resolved Diffraction Studies of the Combustion Synthesis of NiAl/TiC Composite

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Combustion synthesis is a cheap and easy technique to fabricate a large range of materials, including ceramics and composites. It is possible to synthesize a compound by exploiting the exothermic properties of the chemical reaction. Two combustion modes exist depending on whether the synthesis occurs in the form of a wave traveling through the sample (Self-propagating High-Temperature Synthesis SHS) or if it occurs simultaneously in the whole sample (Explosive mode). Despite a lot of advantages, combustion synthesis is barely used in industry due to a lack of understanding of the synthesis mechanisms.

In this work, in-situ time-resolved diffraction using synchrotron radiation has been applied to determine the crystallographic changes occurring during the SHS in air of a mixture of Al, Ni, Ti and C. Time-resolved diffraction is the only in-situ technique able to provide information about the synthesis mechanisms without influencing the propagation of the combustion front. The experiments were performed in transmission using a small X-ray beam of 200x200 µm (E=45keV). During the reaction, 2D diffraction patterns were acquired with a frequency of one pattern every 135 ms (25 ms of acquisition time and 110 ms of readout time). The results show a complex sequence of reactions including the formation of several intermediate phases, which then lead to the formation of a simple biphasic product of small round particles of TiC embedded in a large grained NiAl matrix. A possible synthesis mechanism has been proposed to explain the formation of this composite. In order to determine if both combustion modes lead to the same synthesis mechanisms, recent results on the same reaction studied in explosion mode using time-resolved neutron diffraction will be presented and compared with the time-resolved X-ray diffraction results.

Keywords: time-resolved diffraction, combustion synthesis, NiAl/TiC composite

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MS56 ANALYSIS COMBINING SANS AND SAXS EXPERIMENTS

Chairpersons: José Teixeira, Roberto Triolo

MS56.27.1

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Hydrophobic Polyelectrolytes: Combined Small-angle Neutron and X-ray Scattering Studies

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The structure of salt-free aqueous solutions of highly charged hydrophobic polyelectrolytes was investigated using high-resolution small-angle neutron and X-ray scattering. The choice of one technique rather than another was driven by the contrast between the solvent (H_2O and/or D_2O) and the species (macroions and/or counterions) we want to look at. Various architectures of sulfonated polystyrene macroions with distinct sulfonation rates as well as distinct counterions were considered.

We will present scattering results that show strong evidence for the existence of necklace conformations with dense charged aggregates connected by stretched chain parts. Such conformations have been predicted on the basis of scaling arguments for weakly charged polyelectrolytes under poor solvent conditions [1] and have been confirmed by low-resolution small-angle X-ray scattering studies [2] and molecular dynamics simulations [3]. They result from the balance between the tendency to precipitate, the electrostatic repulsion and the entropic degrees of freedom. It was however suggested that fluctuations should impose a severe obstacle in observing these necklace structures [4]. Here, we are more concerned with quenched polyelectrolytes and the non-sulfonated sequences may form microdomains. The resulting shape could therefore be similar, though the physical case is not the one theory was made for.

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Keywords: SANS, SAXS, hydrophobic polyelectrolytes

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Utility of Absolute Calibration in SANS and SAXS Studies of Polymers and Colloids

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Absolute calibration forms a valuable diagnostic tool for the detection of artifacts in SANS and SAXS experiments. This lecture emphasizes the importance of placing data on an absolute scale, in units of cm^{-1} and reviews the methods available to accomplish this. In order to minimize the time associated with calibration, emphasis is placed on the development of strongly scattering standards which may be run in brief time periods, and special attention is paid to those that can be used for both neutron or X-ray experiments. Independent calibrations of such standards may be tested by comparison with the theoretical relationship between the x-ray and neutron cross sections.

The use of absolute units is not essential for measuring the spatial dimensions, though the cross section is a sensitive indicator of whether an appropriate structural model has been chosen. Thus, scattering from colloidal micellar solutions may be modeled by core-shell structures as a function of a set of parameters such as the inner/outer radius etc. On an arbitrary scale, it is possible to produce excellent fits of the *shape* of the scattering, which may be in error by *orders of magnitude* in intensity. Absolute calibration allows such artifacts to be recognized, and to restrict the model parameters to those which reproduce the observed cross section. Conversely, even an approximate (± 25%) calibration is sufficient to confirm the assumptions of the structural model chosen. The utility of absolute calibration in small angle scattering will be illustrated by examples comparing model calculations and experimental data from a range of polymeric and colloidal systems.

Keywords: X-ray scattering, polymers and colloids, neutron scattering

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The Structure of DNA+Cationic Liposome Aggregates Studied using SAXS and SANS

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DNA forms aggregates with electrostatically neutral phospholipids in the presence of metal cations or cationic surfactants. These aggregates can be used as nonviral vectors for DNA transfer and expression in cells [1, 2]. Synchrotron small-angle X-ray diffraction (SAXD) shows the formation of condensed lamellar phase L_α^c of periodicity d~7-8 nm with DNA monolayers intercalated between lipids bilayers due to interaction of DNA with unilamellar or multilamellar liposomes from saturated and monounsaturated phosphatidylcholines in the presence of divalent cations (Ca^{2+}, Mg^{2+}). Lipid bilayer thickness was determined by analyzing small-angle neutron scattering (SANS) curves of unilamellar liposomes according to three shells model, which devides the bilayer into two polar head group regions separated with nonpolar hydrocarbon region [3]. The inter-helical DNA-DNA distance d(DNA)~4-6 nm was observed in aggregates formed with multilamellar liposomes. Applying repeated heating-cooling process, reflection from DNA helices organization disapeared.

[1] Lasic D.D., *Liposomes in Gene Delivery*, 1997. [2] Zhdanov R.I., Kutsenko N.G., Fedchenko V.I., *Vop. Med. Khim*., 1997, **43**, 3. [3] Kučerka N., Kiselev M.A., Balgavý P., *Eur. Biophys. J*., 2004, **33**, 328.

Keywords: DNA-cationic liposome, SAXD, SANS

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The Subunit Arrangement of the Type I Restriction Modification Enzyme M.AhdI

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Type I restriction-modification (R-M) systems encode multisubunit/multidomain enzymes. Two genes (M & S) are required to form the trimeric 160kDa methyltransferase that methylates a specific base within the recognition sequence and protects DNA from cleavage by the endonuclease. SAXS revealed an unusually large structural change in the methyltransferase following DNA binding; this involves a major repositioning of the subunits of the enzyme, resulting in a 60Å reduction in the dimensions of the enzyme on forming a complex with DNA.

The type I R-M enzyme M.AhdI has been prepared in two