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Investigation of structural dynamics of substances using ultrafast electron diffraction and microscopy

(50th anniversary of the Institute of Spectroscopy, Russian Academy of Sciences)

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Contents

Abstract. The structural dynamics of matter, induced by powerful and most often femtosecond laser pulses, is manifested in an atomic-molecular 'movie', a collection of processes, the exploration of which is of immense interest for today's natural sciences. Studying this global phenomenon requires an ultrahigh spatio-temporal resolution that involves the development of dedicated research methods. Laser spectroscopy may be applied to determine energy states of samples and track their evolution in time; however, the structural dynamics of matter can only be disclosed from that information by indirect methods. We present here direct techniques for studying laser-perturbed substances in the spatio-temporal continuum where matter is probed with ultrashort electron and X-ray pulses. We also describe the first series of experiments performed with the aid of a femtosecond electron diffractometer and picosecond transmission electron microscope at the Institute of Spectroscopy of the Russian Academy of Sciences based in Troitsk, Moscow.

Keywords: structural dynamics, time-resolved electron diffraction and electron microscopy, femtosecond laser radiation, coherent optical phonons

1. Introduction

The study of structural dynamics of matter opens up new prospects for the further development of both basic sciences (physics, chemistry, biology) and numerous applications. The scale of wavelengths in the optical spectral range is such that the use of optical methods based on the application of ultrashort laser radiation does not allow directly imaging subtle movements of atoms and molecules. Probing laser-induced processes for the detailed elucidation of their spatial and temporal patterns requires the use of ultrashort X-ray bundles or electron bunches time-synchronized with powerful light pulses irradiating the substance of interest [1–6].

A pioneering experiment [7] performed by Soviet researchers in Moscow in the 1980s with the aid of a gas-phase electronorgraph allowed the high temporal resolution of a pulsed laser to be combined with the subatomic spatial resolution provided by electron beam probing.[1] Advances in pico(femto)second laser technology and the formation of dense ultrashort electron pulses predetermined a breakthrough in ultrafast electron diffraction [1–6]. In the early 21st century, Caltech scientists and engineers reported the first series of experiments conducted with a transmission electron microscope[2] modified for investigations into the structural dynamics of matter in the nano- to picosecond range with a view of extending them to the femtosecond timescale. This work marked the advent of ultrafast electron microscopy (UEM).[3]

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[1] It is appropriate to cite here the following comment made by R J D Miller in his lecture entitled Making the Molecular Movie. Quest For the Structure-Function Correlation of Biology: "The first use of electrons for time-resolved structural studies of short-lived gas phase intermediates was the work of Ischenko et al. — *Appl. Phys B* **32** 161 [1983]." These studies were continued in the USA [8] due to a lack of research funding in Russia in the 1990s.

[2] A tendency to improve the resolving power is clearly discernible in the history of microscopy [9]. In the mid-20th century, the resolving power of an electron microscope was comparable to that of the then best optical microscopes, whereas on the verge of the 21st century, aberration-corrected electron optics ensured subangström spatial resolution of electron microscopy [9, 10]. The advent of UED/UEM gave a new impetus to the development of electron microscopy [1–6].

[3] It is pertinent to mention the important contribution to the development and application of the stroboscopic technique in electron microscopy made in the 20th century in the USSR (Spivak and co-workers) [11] and Germany [12].

Unlike purely optical techniques for the study of laser-disturbed matter, methods based on the use of electron bunches and X-ray bundles make it possible to obtain information on the structural dynamics of a sample directly from the time-dependent diffraction pattern and observe the coherent dynamics of atoms within an elementary cell exposed to powerful pulsed laser radiation. An important advantage of UED is the small size of a tabletop apparatus; it makes the method more accessible compared with that based on the use of synchrotrons and free-electron lasers. On the other hand, probing solid objects with electrons in a transmission mode is possible only in the case of thin (a few dozen or hundreds of nanometers) high-quality samples, which imposes special requirements on the preparation of study materials.[4] Let us consider some characteristic examples illustrating the potential of these methods as applied to the investigation of condense media.

Observations of laser-induced molecular movements in modified protein myoglobin by the time-resolved X-ray diffraction technique set another milestone in the study of the structural dynamics of composite systems [21]. In this experiment, several thousand reflections recorded while probing a sample with pulsed short-wavelength radiation of the Grenoble synchrotron were processed at each time step of the evolution of a laser-disturbed protein. The data obtained allowed movements of the CO ligand to be reconstructed in the protein with high spatial (≈ 1.8 Å) and temporal (100 ps) resolutions

To study the structural dynamics by applying the ultrahigh electron diffraction technique, simpler instruments are needed. In Ref. [22], a laser-induced ultrafast insulator–conductor phase transition in the organic compound $(\text{EDO-TTF})_2\text{PF}_6$ was observed using a desktop femtosecond electronograph that allowed molecular movements to be traced in the spatio-temporal continuum. A new metastable state was found on the $\sim$ 10-ps time scale. The same method was employed to study nonthermal melting in bismuth under the effect of powerful femtosecond laser irradiation of the semimetal [23]. UED showed that when a 387-nm laser pulse with an energy density around 20 mJ cm^{-2} (the second harmonic of a femtosecond Ti:Sa laser) irradiated a Bi crystal, the solid-to-liquid transition occurred for a record-breaking 200 fs.

It can be concluded that the UED/UEM method opens up totally new prospects for the study of matter. For this purpose, novel experimental techniques have been developed at the Institute of Spectroscopy of the Russian Academy of Sciences, designed to elucidate the laser-induced structural dynamics in a substance with the use of pico(femto)second electron beams strictly synchronized with exciting femtosecond laser radiation to observe the state of the matter of interest in the spatio-temporal continuum. The newly constructed femtosecond electronograph and the reconstructed ultrafast transmission electron microscope were invoked to carry out a first series of experiments.

[4] A detailed comparison of the two approaches to the study of structural dynamics is presented in Ref. [13]. It should be noted that the cross section of elastic scattering of fast electrons (100 keV) is $\sim 10^5$ times that of short-wavelength electromagnetic radiation (photon energy 10 keV); moreover, probing with a nonrelativistic electron beam is less destructive for the sample [14]. However, UED makes it rather difficult to ensure ultrahigh temporal resolution largely dependent on the duration τ_e of electron pulses and to overcome the 100-fs barrier [15, 16]. In this context, it is worth mentioning that the UED/UEM experiments reported to a meeting of the German Physical Society (11–16 March 2018, Berlin) were confined to pico-subpicosecond or subfemtosecond temporal resolution. Thus far, experiments on the generation of attosecond electron pulses for UED/UEM have had only an illustrative character [17]. In fact, reports on temporal resolutions in the range from a few to 100 fs were virtually absent at the said meeting, which should be attributed to the unresolved problem of the compression of dense electron bunches. The development of a number of promising methods [18] for compressing photoelectron pulses are currently underway, including the use of a cavity with radio frequency compression [19] and a reflectron-based electrostatic mirror [20].

2. Femtosecond electronograph

A general view and schematic of a compact electronograph are presented in Figs 1a and 1b [24, 25]. The UED method is based on the 'pump–probe' principle, well known in ultrafast spectroscopy, with the first pulse exciting the sample and the second one, delivered after a controlled delay, probing it. A peculiar feature of the method presented is the use for pumping of the fundamental frequency of a femtosecond Ti:Sa laser with wavelength $\lambda_1 \approx 800$ nm, a pulse length of approximately 50 fs, and pulse repetition rate $f_{\text{laser}} = 1$ kHz. The probe beam is formed from photoelectron bunches by irradiation of a semitransparent photocathode (a 30-nm thick silver film on a quartz plate) by the third harmonic of the same master laser with wavelength $\lambda_2 \approx 266$ nm. This approach ensured precision synchronization of optical and photoelectron pulses for the study of coherent phonons in a $\sim$ 30-nm thick antimony film on a carbon substrate used in transmission electron microscopy. To excite phonons, the sample was irradiated at a 45° angle by weakly focused linear-polarized laser radiation with the energy density around 1.5 mJ cm^{-2} (≈ 1 eV Å^{-2}) per pulse. The pulsed photoelectron beam with an energy of 20 keV and diameter 100 μm was formed in the sample region by a permanent magnet-based lens. This allowed attaining an extremely short free path from the cathode to the sample (12 mm) and thereby reducing to a minimum the spread of the probe electron pulse. Electrons diffracted by the sample were recorded by a 2D detector consisting of paired microchannel plates, a luminophore, and a charge-coupled device (CCD camera).

Figure 1c presents a diffractogram of a thin antimony film obtained with the use of a pulsed photoelectron beam in the absence of optical excitation. The presence of bright reflections is unambiguous evidence of the crystalline nature of the study sample. Changes in the diffraction pattern in its separate parts due to optical excitation were recorded with different delays (60-fs steps, signal accumulation time 1s) between exciting optical and probing photoelectron pulses.

Intensities measured in different parts of the diffraction pattern were normalized to signal amplitudes in the respective regions of the electronogram in the absence of optical excitation. The dynamics thus registered was characterized by a well-apparent oscillating component with a picosecond period. Fourier analysis of coherent oscillations (Fig. 1d) shows that the observed signal modulation was due to four modes with frequencies of 1.1, 3.4, 4.6, and 6.4 THz, respectively, three of which were observed in earlier optical experiments [26, 27]. Based on these findings, it proved possible to relate the 4.5- and 3.5-THz frequencies to totally symmetric A_{1g} and doubly degenerate E_g optical phonons of antimony, and the frequency of 1.1 THz to differential optical vibrations $A_{1g} - E_g$. The 6.4-THz frequency corresponding to the second-harmonic E_g was not observed earlier for anti-

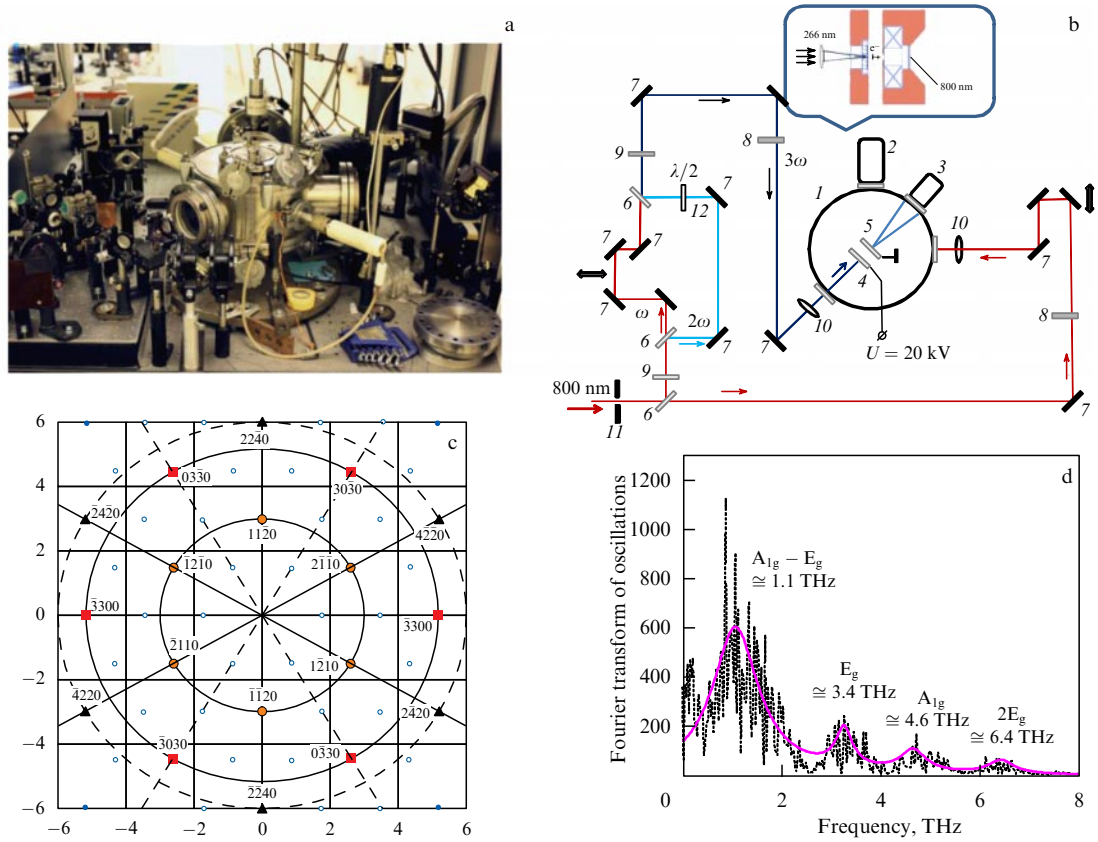

Figure 1. Photograph (a) and schematic diagram (b) of femtosecond electronograph: *1* — vacuum chamber, *2* — turbomolecular pump, *3* — electron current amplifier comprising microchannel plates and CCD camera, *4* — silver photocathode, *5* — anode + target, *6* — beam splitters, *7* — mirrors, *8* — radiation attenuator, *9* — converters of laser radiation to 2nd and 3rd harmonics, *10* — lenses, *11* — diaphragm, *12* — laser beam polarization rotator (inset shows the main elements of the setup: photocathode, anode, magnetic lens, and sample). (c) Electronogram of antimony sample. (d) Fourier-spectrum of laser-induced oscillations of the diffraction signal in an Sb film: dashed curve — experiment, and solid curve — approximation of experimental data by Lorentz functions.

mony. These studies and their theoretical analysis give evidence that the proposed compact electronograph ensured temporal resolution $\tau_e \approx 300$ fs [24, 25].

In other words, our experiment provided direct insight into the generation of coherent optical phonons in antimony applying the UED technique [24, 25]. These studies were continued by our German colleagues [28, 29]. Specifically, Ref. [29] illustrates the mechanism of excitation of in-phase optical vibrations in an Sb lattice by powerful laser pulses (1–2 mJ cm^{-2}) of femtosecond duration.

3. Ultrafast transmission electron microscope

Unlike the electronograph, the electron microscope (a technically more sophisticated device) opens up opportunities for investigations of structural dynamics making use of the UED and UEM methods.[5] To reconstruct our Hitachi H-300 transmission electron microscope (Fig. 2a), originally designed to be operated with a 75-keV continuous electron beam and spatial resolution of 5.4 Å in the microscopic regime, a number of important problems had to be solved. To begin with, the injection of a laser beam into the microscope encountered difficulty owing to the design characteristics of the commercial device. Also, control over the spatio-temporal alignment of photoelectron and laser pulses on the sample surface in the confined vacuum space had to be ensured and the so-called zero reference point found, i.e., the '$t = 0$ problem'[6] needed to be solved. To recall, ultrashort optical/electron pulses provide high temporal resolution, on the one hand, but make difficult determining the zero reference point, on the other hand, especially in the absence of direct visual access to the sample.

Reconstruction of the device allowed successfully solving the above problems, including the use of a position-sensitive luminophore-based detector and CCD camera instead of photographic recording of electrons [31]. Figure 2b presents images and diffractograms obtained in photoemission and thermoemission regimes. UV second-harmonic radiation from a Mai Tai femtosecond laser with $f_{\text{laser}} = 80$ MHz was applied to activate the photocathode. The experimental data, other than the signal level, proved virtually identical, which confirms the operability of the reconstructed microscope. Numerical analyses of photoelectron beam propagation in

[5] In 2018, the German Professor S Schafer, a young co-worker of the Nobel Laureate in Chemistry 1999 A Zewail, was awarded the Walter Shottky Prize for a series of research projects with the use of an ultrafast TEM having a tip-shaped cathode. An important advantage of this approach is the possibility of reaching ultrahigh transverse spatial coherence, even if with a relatively small number of photoelectrons in each bunch; therefore, signal integration requires a laser source with a high pulse repetition rate, e.g., a femtosecond fiber-optic laser.

[6] The '$t = 0$ problem' is the calque from the text of Ref. [30].

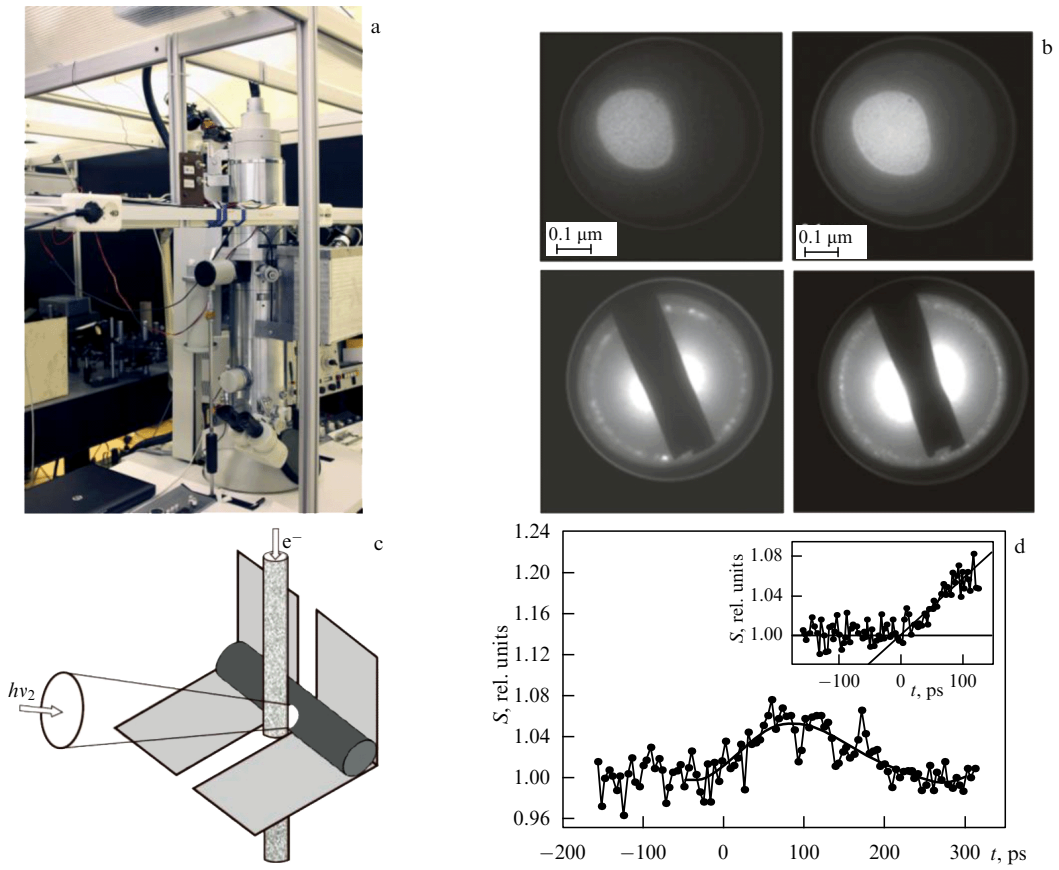

Figure 2. (a) Photograph of a picosecond transmission electron microscope. (b) Images of perforations in a carbon film and diffraction patterns of Al microparticles obtained in photoemission (left panel) and thermoemission (right panel) regimes. (c) Sample layout to converge electron and optical pulses and find zero reference point $t = 0$. (d) Electron signal S plotted versus time delay t between optical and electron pulses (inset shows $S(t)$ dependence at the initial stage of evolution): solid curve — approximation of experimental data.

the column showed that the duration of an electron pulse near the sample was $\tau_e \approx 7$ ps provided that a bunch contained ≈ 300 electrons; it made possible measurements with a picosecond temporal resolution [31].

The 'pump–probe' method was applied to visualize the ultrafast interaction of a 75-keV electron beam with a dense ensemble of slow electrons. A 3-mm long copper cylinder 0.5 mm in diameter and fixed at the intersection of two orthogonal copper plates with 0.1-mm wide slots served as the source of slow electrons (Fig. 2c). Radiation from a fiber-optic laser (ANTAUS, Avesta-Proekt, Troitsk, Moscow) with $f_{\text{laser}} = 250$ Hz–500 kHz at a wavelength of 1050 nm, pulse energy up to ~ 1.6 μJ, and pulse length of ~ 300 fs was converted into the 2nd and 4th harmonics. After their separation, UV radiation activated the Ag cathode and the 2nd harmonic irradiated the sample. A change in the time delay between the two harmonics allowed observing the dynamics of the passage of the 75-keV electron beam through the electron cloud resulting from the photoeffect under the action of powerful (~ 5 mJ cm^{-2}) laser pulses (Fig. 2d).

In the analysis of experimental data, it is worthwhile to relate the signal contour width to the characteristic time of slow electron propagation through the region of interaction with a 75-keV electron beam. The value of ≈ 39 μm found from this reasoning is close to the measured diameter of the 75-keV electron beam [31]. On the other hand, the zero reference point ($t = 0$) is determined, in accordance with a popular approach accepted in UED, by the intersection of two straight lines, one of which corresponds to a plateau and the other to the signal variation front resulting from a pulsed action on electrons [32]. The time-zero position determined in this way is smeared according to the expression $\Delta t_0 \approx 10.5$ ps, in good agreement with the numerical estimate of τ_e [31].

The above data indicate that the reconstruction of the Hitachi H-300 microscope ensured a temporal resolution of ≈ 7 ps. Together with the spatial resolution of electron microscopy, it opens up ample opportunities for further research on laser-stimulated structural dynamics in composite organic systems by UED/UEM techniques.

4. Conclusion

Rapidly developing methods of ultrafast electron diffraction and microscopy make it possible to trace the movements of atoms and molecules on natural spatio-temporal scales. To implement them into research practice, the Institute of Spectroscopy of the Russian Academy of Sciences created experimental setups in which laser-induced ultrafast processes in matter were probed by ultrashort electron beams. This equipment was used to conduct a first series of experiments and the world's first UED studies on coherent optical phonons in antimony. The Hitachi H-300 electron microscope was successfully reconstructed to ensure a ≈ 7-ps temporal resolution. The use of this instrument is of great interest for the elucidation of structural dynamics in proteins

and other composite organic substances. A molecular-cluster device, combined with the source of pulsed electrons and a highly sensitive 2D system, was designed to record a diffracted beam for investigations in molecular-cluster jets, including laser-induced intracluster reactions, the migration of energy, and structural phase transitions.

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