### **REVIEWS OF TOPICAL PROBLEMS**

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# Ultrafast electron diffraction and electron microscopy: present status and future prospects

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<u>Abstract.</u> Acting as complementary research tools, high timeresolved spectroscopy and diffractometry techniques proceeding from various physical principles open up new possibilities for studying matter with necessary integration of the 'structuredynamics-function' triad in physics, chemistry, biology and materials science. Since the 1980s, a new field of research has started at the leading research laboratories, aimed at developing means of filming the coherent dynamics of nuclei in molecules

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and fast processes in biological objects ('atomic and molecular movies'). The utilization of ultrashort laser pulse sources has significantly modified traditional electron beam approaches to and provided high space-time resolution for the study of materials. Diffraction methods using frame-by-frame filming and the development of the main principles of the study of coherent dynamics of atoms have paved the way to observing wave packet dynamics, the intermediate states of reaction centers, and the dynamics of electrons in molecules, thus allowing a transition from the kinetics to the dynamics of the phase trajectories of molecules in the investigation of chemical reactions.

### 1. Introduction

The discovery of electron diffraction by G P Thomson and C J Davisson (1927) coupled with the development of the electron microscope by R Rüdenberg (1931), M Knoll, and E Ruska (1931) laid the basis for a highly powerful research tool for investigations into the structure of matter with the employment of electron beams (see monograph [1]). The advent of two remarkable instruments, the electron diffraction apparatus and electron microscope, permitted the observation of electron diffraction by a sample and determine internuclear distances, crystal lattice parameters, and mean amplitudes of thermal oscillations of atoms when

solving the inverse problem. The electron microscope, unlike the electron diffraction apparatus, makes possible measurements unrelated to electron diffraction with a spatial resolution in the subnanometer range. Such limiting resolution depends largely on magnetic lens aberration. Adding spherical aberration compensation to operation of a transmission electron microscope with an accelerating voltage of 200 keV increased the spatial resolution up to  $\sim 1$  Å and thereby allowed investigations at the resolution level of individual atoms and molecules. However, the study of atomic and molecular motions requires the use of probes ensuring not only high *spatial* but also *temporal* resolution for recording the structural dynamics of matter.

Studies of samples with high spatial and temporal resolutions are of great interest for solid state physics, molecular physics, chemistry, biology, and materials science. There are numerous examples of phase transitions in condensed media and as many processes in free molecules proceeding on nano-, pico-, and even femtosecond time scales. By way of illustration, scientific community [7] showed keen interest in the results of observing ultrafast, subpicosecond melting of crystalline bismuth under the effect of femtosecond laser radiation [6]. The question has raised here: how could lattice atoms so quickly 'understand' that the sample had melted if they had no time to undergo even a single oscillation?<sup>1</sup> The mechanisms of this phenomenon can be elucidated using an experimental probe for recording processes within time periods of such a duration.

Originally, continuous electron beams were used in electron diffraction and microscopy. In most cases, they are still used to the same effect. However, such experimental techniques do not allow studying dynamic processes within short time intervals. For this purpose, an electron beam needs to be split into separate short bunches. In other words, temporal modulation of the beam and synchronization of electron pulses with the processes proceeding in the sample are needed [2, 3]. Unfortunately, the seemingly explicit method of beam splitting into short electron bunches of a given length by the electronic pulse technique fails to yield the desired ultrashort electron bunches. A breakthrough in the development of time-resolved electron diffraction/microscopy came with the exploitation of ultrashort laser radiation for both pulsed excitation of the sample and the generation of ultrashort (photo)electron probing bunches.

The new paradigm of the electron diffraction method and the first successful experiments were described in Refs [4, 5]. In this scheme, one of the synchronized pulsed laser beams is directed toward the cathode to produce photoelectron bunches, while the other is focused onto the sample for its excitation. The time lag  $\Delta \tau$  between laser pulses can be controlled by means of an optical delay line [4].

The concept implying the usage of ultrashort laser pulses in combination with electron optics, supported by the development of the pulsed laser technology and the advent of readily available and reliable commercial femtosecond lasers, created important prerequisites for the achievement of a temporal resolution on the order of tens of femtoseconds, commensurate with the characteristic time of atomic oscillations in molecules. Attainment of this goal can be instrumental in the creation of 'molecular movies', i.e., the observation of atomic dynamics in the spacetime continuum, which in addition to purely fundamental great importance has great practical significance.

Experiments made some three decades ago [2, 3] marked an important milestone in the development of the timeresolved electron diffraction method (nanosecond resolution was reached in Ref. [3], and picosecond resolution in Refs [4, 5]). Temporal resolution determined in the first place by the duration of electron pulses is a key parameter in absolutely all experimental setups designed for monitoring the fast processes using superhigh-speed electronography and 4D electron microscopy<sup>2</sup> [6–8]. Meanwhile, the main experimental difficulties reside in both the creation and transportation of short electron bunches and in the reliable measurement of their duration. To recall, Coulomb repulsion and the difference among velocities of accelerated electrons in a bunch make the formation of femtosecond electron pulses difficult. Without application of additional compressing devices, all this restricts the potential of the method of interest as regards nonrelativistic electrons to hundreds of femtoseconds at best. The development of radio-frequency field-based compression systems is underway to overcome the 100-fs barrier [9]. Acceleration techniques allowing us to achieve relativistic electron energies can also be used for the same purpose [10].

As compared to classical devices with continuous electron beams, those designed to observe fast processes are characterized by high peak particle densities in the bunches, which can pose difficulties for transmitting and focusing such electron pulses. For example, a 100-fs long bunch containing only two electrons corresponds in terms of the current *I* to ~ 1  $\mu$ A. However, when a commonly applied 80-MHz femtosecond laser is used [8], the mean particle flux does not exceed a few dozen picoampers. For observation of dynamic processes expanded over a time scale, the signal needs to be recorded by a position-sensitive detector (in the electron microscope or electron diffraction regime) many times at different time lags  $\Delta \tau$ . All this imposes rather serious requirements on the recording system: it must ensure maximally effective detection of electrons.

Irreversible fast processes are of special interest. However, their investigation with the use of pulsed electron beams is only possible under very rigorous conditions. On the one hand, a single electron bunch must contain a rather large number of electrons,  $10^4 - 10^5$  and more, to ensure a distinct signal per pulse. On the other hand, such a beam must be short enough. These requirements are somewhat contradictory, because Coulomb repulsion smears out electron pulses in time and space. It should be mentioned that this problem has already been resolved for subpicosecond time intervals [11].

Methods based of ultrafast electron diffraction are being rapidly developed at present. Recent progress in the formation of ultrashort electron pulses [6-11] makes it possible to invoke attosecond resolution and observe the coherent dynamics of electrons inside molecules.

This review describes modern methods of ultrafast electron diffraction and electron microscopy using pico-, femto-, and subfemtosecond electron bunches for the study

<sup>&</sup>lt;sup>1</sup> According to Ref. [6], Bi melting time recorded in the electron diffraction regime is about 190 fs, whereas the characteristic oscillation period  $A_{1g}$  of lattice atoms is twice as long.

 $<sup>^{2}</sup>$  4D marks the four-dimensional space: *x*, *y*, *z*, and *t*. The term '4D electron microscopy' was proposed by Ahmed H Zewail, Nobel Prize winner in Chemistry 1999.

of the structural dynamics of matter in the gas phase and condensed state.

### 2. Time-resolved electron diffraction method

Formulation of the main principles of the time-resolved electron diffraction method and pioneering experiments showing the possibility of introducing a time coordinate in electron diffraction date back in the USSR to the late 1970s and early 1980s [2, 4, 12, 13]. Flash photolysis method proposed by Norrish and Porter [14] in 1949 was used as a prototype. By that time, it had been understood that spectral methods provide only indirect information on the structural dynamics of the molecule's nuclear subsystem (see Refs [15, 16] for a detailed discussion of this point).

The concept of the time-resolved electron diffraction method is illustrated in Fig. 1. A primary unscattered electron beam is blocked by a Faraday cylinder, as in the standard continuous electron diffraction method. Pulse lengths  $\tau_e$  and  $\tau_L$  depend on the character of the process being investigated. The duration of laser and electron pulses in the studies of coherent processes of nuclear dynamics must be part of the total time of the process, i.e., a snapshot in which events are averaged over time  $\tau_e$  for obtaining 'molecular movies', with the exciting and probing pulses being generated by the same source. The controlled delay time between  $\tau_e$  and  $\tau_L$ , denoted in the figure by  $\tau_d$ , also depends on the character of the process being investigated [2, 4, 12, 13].

### 2.1 First experiments

The first setup for studying structural dynamics and intermediate states of a chemical reaction by stroboscopic



**Figure 1.** Illustration of the concept of time-resolved electron diffraction method:  $I - \tau_e$ -long probe electron pulse transverses the molecular beam 2, pulsed or continuous, in the scattering region 3; 4 — exciting laser pulse with frequency  $\nu$  and length  $\tau_L$ . Electrons scattered into  $2\theta$  angle (5) are recorded by the detector in plane 6.

electronography was designed in 1980 by a group of researchers of the Chemical and Physical Faculties of Lomonosov Moscow State University and the Institute of Laser and Information Technologies, Russian Academy of Sciences (designated at that time as NITsTL AN SSSR). An electromagnetic lock was exploited in obtaining 20-ns long electron pulses.

The gaseous target ( $CF_3I$  molecules) was excited by a TEA  $CO_2$  laser. Diffraction patterns of  $CF_3$  free radicals (the products of multiphoton infrared (IR) dissociation of  $CF_3I$  molecules) were recorded for the first time:

$$CF_3I + nhv \rightarrow CF_3 + I$$
.

It was crucial for experimental integrity in studies [2, 12] that almost 100% of the CF<sub>3</sub>I molecules dissociated under the effect of a single  $10^{-7}$ -s IR laser pulse [17], yielding CF<sub>3</sub> radicals. This means that the diffraction pattern of scattering was recorded from the bulk (inside the IR laser beam caustic) containing no molecular components besides CF<sub>3</sub>; the resulting diffraction pattern was *unambiguously associated* with CF<sub>3</sub> radicals. To record the diffraction pattern with the use of a secondary electron multiplier, the pulse-resonance method was employed [18, 19].

In 1984, paper [3] reported the application of stroboscopic electronography for the study of  $ClO_2$  photolysis with a resolution of ~ 100 ns:

$$ClO_2 \rightarrow ClO + O$$
.

To investigate coherent structural dynamics processes, an experimental setup was designed in which a single pulse of an Nd:YAG laser with optical line-controlled delay was utilized to generate picosecond electron pulses and excite the target (Fig. 2).

The electron pulses were generated by the fourth harmonic of laser radiation 40 ps in duration at a wavelength of 266 nm. Electrons were ejected from the tip of a V-shaped tantalum cathode with a high quantum effectiveness ( $\sim 10^{-3}$ ) of the single-photon effect for the fourth harmonic and a slight excess of laser radiation energy over the cathode electron work function. At the same time, the initial alignment of the setup was possible in the continuous electron beam thermoemission regime [4, 13, 20]. This apparatus was operated in the regime of generation of



Figure 2. Schematic of the first TRED setup for the study of coherent nuclear dynamics of free molecules and condensed matter with picosecond resolution: 1—Nd:YAG laser, 2—single-pulse generator, 3—amplifiers, 4—SHG, 5—FHG, 6—quartz prism, 7—filter, 8—lens, 9—photosensitive commutator, and 10—registration plane [4, 13, 20].

individual electron pulses allowing one to measure the pulse lengths ( $\tau_e \sim 100 \text{ ps}$ ), and as a rectilinear scanning chamber to determine the mean number of electrons per single pulse ( $\sim 1000$ ) at a radiation power density  $\sim 10^{10} \text{ W cm}^{-2}$  of the Nd:YAG laser; in addition, diffractograms of thin films made from polycrystalline zinc oxide were obtained. A comparison of electronograms taken in pulsed and continuous regimes showed excellent agreement between them.

The present-day facilities used in the time-resolved electron diffraction (TRED) method combine a few constituents, first and foremost a device generating femtosecond laser pulses and then ultrashort electron pulses; an electron-optical system forming electron bunches, synchronizing exciting laser pulses with diagnostic electron pulses; a system recording electron diffraction patterns with subsequent computer-assisted data collection and primary processing. Moreover, they contain systems for measuring pulse lengths and electron flux density, maintaining high vacuum (usually ~ 10<sup>-6</sup> Torr), and mass-spectral control of the study sample. Construction of such facilities began in the 1990s and thereafter depended on the degree of development of the relevant base of elements [20, 21].

### 2.2 Development of the method

Further development of the TRED experiment is described in Ref. [21]. The following elements were utilized: (1) a pulsed nozzle for injection of study matter, which favored marked enhancement of gas density in the scattering volume; (2) a system for amplification of the optical signal detected by a charge coupling device (CCD) camera that markedly increased the signal-to-noise ratio for a measured electron scattering intensity; (3) an internal standard (high-purity nitrogen molecules) for calibration of the diffraction pattern [22]. In this setup (Fig. 3), two synchronized pulses from a femtosecond laser are used for photogeneration of electrons and excitation of the object with the optical delay line between exciting and probing pulses.



**Figure 3.** Schematic of an experimental TRED setup. A 500-fs optical pulse (496 nm) is generated by a Lambda-Physik FAMP DFDL laser system, then the frequency is doubled by the second harmonic generator (SHG), and the resulting pulse (248 nm) is amplified as it passes twice through the synchronized krypton fluoride excimer laser, thus producing a subpicosecond pulse with an energy up to 10 mJ. Then, the beam is split by passing through controllable time-delay circuits to obtain pulses for the photoelectron sensor and optical pumping [16, 21].



Figure 4. Experimental 40-keV electron scattering intensity curve obtained with a single 20-ns electron pulse ( $10^4$  electrons) in the setup shown in Fig. 3 [22].

Figure 4 presents an electron scattering intensity curve  $(\sim 40 \text{ keV})$  for sulfur hexafluoride gas, obtained using a single pulse containing 10<sup>4</sup> electrons. The structural parameters of an SF<sub>6</sub> molecule are consistent with the results for the continuous electron diffraction regime [22]. The maximum concentration of scattering particles was reached by utilizing a pulsed nozzle for inputting gas into the diffraction chamber. The use of pulsed sources allowed the signal-to-noise ratio to be significantly improved by virtue of increased maximum concentration of particles in the scattering volume; simultaneously, the vacuum conditions were also improved. The combination of a pulsed source of gas supply and an ordinary effusion nozzle proved especially efficacious. In this device, the outlet opening of the pulsed nozzle was extended as a thin (0.2 mm) cylindrical channel, which allowed maintaining a high vacuum (10<sup>-6</sup> Torr) and control concentration of molecules in the scattering volume at the nozzle edge, usually at a level of  $10^{13} - 10^{16}$  mm<sup>-3</sup>. The use of the carrier gas for the injection of the study substance through the pulsed nozzle permitted avoiding undesirable adiabatic cooling of the gas.

The authors of Refs [23, 24] designed a setup for generating ultrashort electron pulses with a high repetition rate (5 or 50 kHz). The pulses were emitted from a copper cathode. The second harmonic of a Ti:sapphire laser was utilized. The electrons were accelerated to 20 keV and intersected the effusion flux of the molecules of interest. The diffraction pattern was recorded by a CCD camera cooled by liquid nitrogen. The molecular targets were excited by the 200-fs third-harmonic laser pulse at 265 nm (Fig. 5). The diffraction pattern was imposed on the luminophor and optically projected onto the CCD sensor [24]. The electron current intersecting the molecular beam was 20 pA, and corresponded to  $\sim 2500$  electrons per pulse on the average, which reduced to a minimum pulse lengthening due to Coulomb repulsion (see Ref. [25]).

It should be noted that any instability of laser radiation evolving during electron pulse generation is transformed into pulse instability. To minimize this effect, the laser radiation is focused on a diaphragm 200  $\mu$ m in diameter. In this case, only the central part of the laser radiation is



transmitted, while most of the second-harmonic power is lost. The diaphragm is mapped on the photocathode surface; therefore, the above instabilities of laser radiation are reduced to a minimum in the photocathode region from which electrons were generated. The quantum efficiency of photoemission is rather high, which makes it possible to reach an electron current of about 200 pA near the photocathode. To decrease the influence of electron Coulomb repulsion, the current was lowered to 20 pA, when the beam traversed the diaphragm with a diameter of 30  $\mu$ m in front of the target. The central beam of unscattered electrons was removed by a Faraday cylinder  $375 \,\mu\text{m}$  in diameter. This apparatus was employed to study the structural dynamics of chemical reactions, in particular, the electrocyclic ring-opening reaction of 1,3-cyclohexadiene [23].

Figure 6 displays a schematic of experimental arrangement for the study of ultrafast electron diffraction (UED). The diffraction chamber in this third-generation unit (UED-3) is coupled with a time-of-flight mass spectrometer (MS-TOF) [26].

The arrangement consists of four separate vacuum chambers, viz. an electron gun, scattering chamber, detection chamber, and MS-TOF for *in situ* control of the gas composition and detection of potentially corrosive compounds [26]. A vacuum at the level of  $\sim 10^{-7}$  Torr is produced in the scattering chamber in the absence of a gas sample; the pressure builds up to  $10^{-4}$  Torr when the molecules studied are introduced into the chamber. The pressure in the sensor chamber was maintained at the level of  $10^{-2}$  Torr to avoid condensate formation on the thermoelectrically cooled surface. Special attention was given to avoiding parasitic electric or magnetic fields capable of distorting the trajectories of scattered electrons.

The detection system is of primary importance in the ultrafast electron diffraction method. The electron flux should be maintained at a very low level to ensure ultrafast temporal resolution of the system. The UED-3 apparatus contains a system for two-dimensional detection of the diffraction pattern based on a CCD matrix with a low noise level. Because scattering intensity in the course of electron diffraction rapidly decreases as the scattering angle increases (by 6–8 orders of magnitude), a changeable symmetric optical filter representing an analog of the rotating sector in conventional gas electronography is applied in the radial direction on the back wall of the scintillator [1]. Naturally, there are no moving mechanical parts here. The filter permits simultaneously measuring diffraction intensity over a



Figure 6. Experimental URE-3 setup coupled with a time-of-flight mass-spectrometer (MS-TOF), allowing for *in situ* control of the gas phase composition [26].

dynamic range spanning more than seven orders of magnitude, which significantly increases the determination accuracy of structural parameters of the study sample. A typical UED experiment implies recording of 1000 frames per second for an exposition time 240 s (at a pulse repetition rate of 1 kHz). Averaging is performed over 100 diffraction patterns. Modern mathematical methods are applied to process signals as described in Ref. [27]. A series of studies on the dynamics of free molecules and transition states of chemical reactions were carried out at UED-3 facility (see Ref. [26] for details).

### **2.3 Determination of initial time of recording diffraction pattern**

Further important achievement in the development of the experimental technique for time-resolved electron diffraction method was the use of the electron-electron correlation concept to determine the initial time of recording diffraction pattern  $(t_{Z0})$  in the spatial-temporal coincidence of probing and exciting pulses. A synchronization accuracy of  $\sim 100$  fs was reached [23, 28, 29]. Variations in the diffraction pattern over the pico/femtosecond range were recorded by the newly devised ion-induced focusing method [27, 28, 30] with multiphoton ionization of the CF<sub>3</sub>I gas in a TRED (UED) apparatus. Photoelectrons escaping from the ionized region leave behind positively charged ions. The electric field in the newly produced plasma acts as an effective lens and focuses the electron beam only when laser and electron pulses overlap in time. By this means a zero time  $t_0$  can be identified. Notice that the progress in laser techniques and electron optics achieved in the last decade has greatly facilitated improvement of the method (see reviews [31, 32] and monograph [33]).

# **2.4 Reference frame method** and structure synchronization

The TRED method makes use of synchronized sequences of ultrafast (laser) pulses to initiate reactions, and electron pulses to probe subsequent structural changes in molecular samples. Then, time-dependent diffraction patterns are recorded by a CCD camera. One of the main phenomena of electron diffraction is electron scattering from all atoms and atom-atom pairs in a molecular sample. In other words, a probe electron pulse is sensitive to all particles encountered along its path and can detect structures unrecognized by spectroscopy in which a probing laser pulse is tuned to certain transitions [26, 33]. The reverse side of this advantage of the TRED method is the problem of retrieval of information about changes in the molecular structure. Diffraction patterns contain distributions from both incoherent atomic scattering and coherent molecular interference of atom-atom pairs. Incoherent atomic scattering from gases is an order of magnitude higher due to the lack of long-range order that enhances coherent interference. The fraction of molecules subject to changes being small (usually 10% or less), an appreciable contribution to the electronogram also comes from molecules that have not reacted, thus giving a parasitic signal.

The key factor in obtaining information about the structural dynamics of a small set of varying structures, integrated into the strong background signal, was the application of the *reference frame method* [26]. It utilizes synchronization of electron pulses in such a way that a baseline reference signal is established *in situ*. Usually, these are either structures in the ground state emerging at a 'negative time', i.e., before a pump laser pulse excites the

sample, or one of the structures evolving at a positive time. For different reference times  $t_{ref}$ , selected changes can be distinguished. Currently available numerical treatment makes it possible to reveal the difference between each time-resolved electronogram and a separate reference signal, as demonstrated by a few examples, in particular, by a two-step deiodination reaction of 1,2-tetrafluoroethane [26].

The reference frame method has a number of advantages. First, the strong undesirable background signal from atomic scattering makes a general contribution to all diffraction patterns, regardless of time delay and the character of the reaction. This means that it can be practically eliminated by computing the difference. In other words, the reference frame curve is dominated by the intensity of molecular scattering, despite the predominance of background intensity in the overall diffraction signal. Second, any initial error in the detection system can be effectively eliminated or substantially reduced by computing the difference. Third, each sample with the selected reference frame reflects the comparative contribution of each reactant and transient structures. In contrast, in original unprocessed data only a relatively small fraction of signals comes from transient structures, most signals being produced by the components that failed to react. Consequently, the significance of a contribution from transient structures increases considerably in samples with the selected reference frames [26].

The progress of reference frame method, in conjunction with the high sensitivity attained with the use of a CCD camera for detection, creates conditions for the study of various molecular processes by the TRED method. However, other problems need to be overcome as well. To begin with, it is very difficult to determine zero time (of synchronization) in TRED experiments with an accuracy up to a few femtoseconds. Moreover, electron-electron repulsion is known to occur in ultrashort electron bunches. Spatial charge effects increase the pulse length, which necessitates the search for a compromise between temporal resolution and electron pulse density. Finally, the low sample density in the gaseous phase compared with solid state samples and the surface leads to reducing the intensity of diffraction patterns.

### **2.5** Space charge and energy distribution effects in an electron bunch

The space charge and energy distribution effects in an electron bunch constitute a central problem in the development of the time-resolved electron diffraction method and dynamic electron microscopy [33, 34]. Tao et al. [35] report a detailed experimental study and simulation of the influence of a space charge on the lengthening of high-intensity electron pulses, taking account of the initial energy distribution in electron bunches obtained by laser emission. It should be mentioned that seminal theoretical and experimental results of research on the influence of a space charge on the length of electron pulses in electro-optical converters (EOCs) were obtained in our country in the 1950s-1960s at the Kurchatov Institute of Atomic Energy (now the National Research Centre 'Kurchatov Institute') and further developed at the Department of Photoelectronics, Prokhorov Institute of General Physics (IGP), Russian Academy of Sciences (see Section 9).

The main question can be formulated as follows: Is it possible to generate a high-brightness electron beam without loss of high spatial-temporal resolution? Two factors smear out the phase space of an electron bunch: space-charge





**Figure 7.** (Color online.) Ultrafast electron shadow projection imaging and measurement results. (a) Experimental scheme. For illustration purposes, the angular dimensions of the shadow are significantly enlarged compared with the typical value of  $\sim 1$  mrad. For this reason, the projection is close to linear. (b) Snapshots of normalized images for 20, 50, and 80 ps;  $\sim 33$ -fold enlargement of image projection:  $x_0$  is the distance from the cathode (Au) surface, *L* is the distance from the cathode surface to the detector, *d* is the position on the detector screen, *t* is the time, and P is the point source of electrons [35].

limitation in high photoemission fluxes, and Coulomb repulsion during electron beam movement. The ultrafast electron shadow projection imaging technique [36] was applied in Ref. [35] to reveal space charge effects after photoemission and in the course of free electron bunch expansion in space. The dynamics of photoelectrons emitted by a cathode made from a gold-coated transparent thin (30 nm) quartz substrate was initiated by 50-fs laser pulses at a 266-nm wavelength (4.66 eV); this technique ensured the generation of high-intensity electron bunches  $(10^5 - 10^8)$ electrons per pulse). The photon energy was somewhat higher than the electron work function for gold (4.0–4.6 eV); this accounted for the narrow enough electron distribution over energies. A CCD camera was used as a detector. The repetition rate of the laser pulses was equal to 1 kHz; images with the desired signal-to-noise ratio were formed by accumulating  $10^5 - 10^6$  pulses in each experiment differing in delay time. The experimental layout and measurement results are presented in Fig. 7.

The quantitative results were obtained by comparing experimental data and analytical expressions for the ultrafast



**Figure 8.** (Color online.) (a) The principle of electron pulse injection and pulse compression in a microwave resonator. (b) Electron bunch dynamics before and after passage through the microwave resonator cavity. Modeling for  $10^4$  electrons with an energy of 30 keV [35].

electron shadow projection imaging technique [36]. Figure 7b presents the results of direct visualization of Coulomb repulsion in an electron bunch; Fig. 8 displays the results of modeling the dynamics of a bunch containing 10<sup>4</sup> electrons. A microwave resonator was used to compress the beam [35].

Unlike other techniques for studying the characteristics of ultrashort electron pulses [16, 21, 26, 37, 38], the method proposed makes it possible to simultaneously determine parameters of an electron bunch in both longitudinal and transverse directions. This substantially facilitates the comparison of experimental and simulated data, which is of interest for the development of electron optics for ultrafast electron diffraction and microscopy.

### 2.6 Coherent nuclear dynamics: molecular movies

The TRED method utilizes fast (30–100 keV) electron diffraction in a molecular flow of rarified gas or vapor of the study substance. At such electron beam energies, elastic electron scattering predominates. TRED constitutes an integral method. The recorded intensities of scattered electrons are the superposition of incoherent atomic scattering and diffraction patterns obtained from all nuclear pairs of the starting substance and intermediate products present in the scattering ensemble. This superposition is averaged over the diagnostic electron pulse length. Interpreting experimental data obtained by the TRED method requires the development of the theoretical basis for processing diffraction intensities in conjunction with the results of spectral research on coherent molecular dynamics in a strong laser radiation field [33].

The authors of Refs [4, 5] considerably modified the experimental method described in Ref. [2]. They proposed exploiting pulsed laser photoemission of electrons from a cold cathode. In doing so, a pulse from a single radiation source was split into two parts to generate picosecond electron bunches and excite the study sample (ZnO film [4] and Al film [5]) (see also review [20] and monograph [33]). One part of the laser pulse was directed toward the cathode, the other to the substance of interest with the aid of the optical delay line. Time-dependent diffraction patterns were obtained by varying the path length of the light pulse, exciting the study sample, in the optical delay line. This

experimental approach enabled the authors to observe diffraction patterns of the *coherent excitation process and the subsequent evolution of the system, as well as to study coherent nuclear dynamics* with temporal resolution in the pico- and femtosecond range. Deceleration of the electron bunch, e.g., on a copper plate, gave rise to X-ray pulses. This approach was realized in a later study addressing the time-resolved X-ray diffraction (TRXD) method [39].

# 2.7 Electron scattering by equilibrium and nonequilibrium molecular ensembles

Further development of the TRED method and subsequent modifications of the proposed technique for diffraction experiments with temporal resolution seem to be impossible without the elaboration of a theory for interpreting timedependent electron scattering patterns. With this inference in mind, the present section is designed to describe fundamentals of the theory, allowing us to find approaches to the interpretation of TRED data for time-dependent electron scattering intensities [16, 20, 33, 40, 41].

Electrons scattered from each atom in a molecule can be described by a spherical wave [42]:

$$\Psi_i(R,\theta) = \frac{\exp\left(ik|\mathbf{R}-\mathbf{r}_i|\right)}{|\mathbf{R}-\mathbf{r}_i|} \exp\left(ik_0 z_i\right) f_i(\theta) \,.$$

Here,  $\theta$  is the scattering angle,  $f_i(\theta)$  is the atomic scattering amplitude depending only on the nature of the atom and incident radiation wavelength  $\lambda$ , **k** is the wave vector,  $k = |\mathbf{k}| = 4\pi/\lambda$ ,  $\mathbf{k}_0$  and  $\mathbf{k}_s$  are the wave vectors of incident and scattered electrons, **s** is the momentum transfer vector,  $s = |\mathbf{k}_0 - \mathbf{k}_s| = (4\pi/\lambda) \sin(\theta/2)$ ,  $\mathbf{r}_i$  is the radius vector of an atom with respect to the molecule's center of mass, **R** is the distance between the scattering center and detector, and  $z_i$  is the projection of  $\mathbf{r}_i$  onto the primary radiation axis (Fig. 9).

In the framework of the independent atom model adopted in gas electronography, the wave function of a scattered electron is calculated on the assumption that the wave function of each atom is roughly described by the sum of



**Figure 9.** Definition of electron scattering coordinates:  $\theta$  is the scattering angle,  $\delta(\theta)$  is the correction to the scattering angle caused by Coulomb repulsion in the electron bunch,  $\mathbf{k}_0$  and  $\mathbf{k}_s$  are the wave vectors of incident and scattered electrons, respectively, s is the momentum transfer vector in the laboratory system of coordinates (x, y, z),  $\lambda$  is the electron wavelength, C—cathode, A—anode, ML—magnetic lenses, D—diaphragm,  $\tau_L$  is the laser pulse length,  $\tau_e$  is the electron pulse length, *l* is the electron bunch semiaxis in the direction of motion, *R* is the electron bunch semiaxis in the transverse direction, and  $\tau_d$  is the delay time between the exciting laser pulse and the diagnostic electron pulse.

localized atomic functions. Then, for a molecule consisting of N atoms one has in the far-field region  $(\mathbf{R} \gg |\mathbf{r}_i|)$  [42]:

$$\Psi = \sum_{i=1}^{N} \Psi_i = \frac{\exp\left(ikR\right)}{R} \sum_{i=1}^{N} f_i(s) \exp\left(i\mathbf{sr}_i\right)$$

The intensity of scattered electrons is given by [33, 41, 42]

$$I(\mathbf{s}) = I_0 \operatorname{Re}\left[\frac{1}{2\mathrm{i}k_0} \sum_{i=1,N} (\Psi_i^* \nabla \Psi_i - \Psi_i \nabla \Psi_i^*)\right]$$
  
=  $\frac{I_0}{R^2} \left[\sum_{i=1,N} |f_i(s)|^2 + \operatorname{Re}\left[\sum_{i \neq j=1,N} |f_i(s)| |f_j(s)| \exp\left(\mathrm{i}\Delta\eta_{ij}(s)\right) \exp\left(\mathrm{i}\mathbf{sr}_{ij}\right)\right],$  (1)

where  $I_0$  is the intensity of incident electrons.

The first part of the sum in the last line of formula (1) describes so-called atomic scattering unrelated to the spatial distribution of the atoms in the molecule. The second part describes electron scattering characterized by the instantaneous position of the atoms in the molecule. Quantities of higher orders, in the first place three-atom scattering, make an appreciable contribution to overall intensity and should be taken into account first and foremost for symmetric molecules containing heavy atoms. The methods proposed in papers [43–45] can be applied for this purpose. The effects of chemical bond formation manifested in the region of small scattering angles are usually disregarded in the structural analysis [42, 46].

Thus, the molecular constituent  $I_{mol}(s)$  of the total electron scattering intensity (1) can be represented as the sum taken over all atomic pairs of a molecule:

$$I_{\text{mol}}(\mathbf{s}) = \frac{I_0}{R^2} \operatorname{Re} \sum_{i \neq j} |f_i(s)| |f_j(s)| \exp\left(\mathrm{i}\Delta\eta_{ij}(s)\right) \exp\left(\mathrm{i}\mathbf{s}\mathbf{r}_{ij}\right),$$
(2)

where  $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$  is the instantaneous internuclear distance, and  $\Delta \eta_{ij}(s)$  is the phase shift for scattered electrons.

Due to the integral nature of gas electronography, the recorded diffraction intensities are the superposition of diffraction patterns obtained from all molecules making up the scattering ensemble. This suggests the necessity of averaging contributions in Eqn (2) in conformity with the probability density function (PDF) that characterizes the spatial position of the atoms in molecules [averaging over orientations,  $P(\alpha_{ij}, \beta_{ij}, t)$ , rotational and vibrational states, large amplitude movements,  $P(r_{ij}, t)$ ]. When a nonequilibrium ensemble is investigated, as in studies of molecules excited by laser radiation, the PDF must also include time dependence characterizing structural and dynamic changes of the system [33, 47].

Because an individual process of fast electron (> 10 keV) scattering proceeds in the attosecond range, electrons collide with molecules 'frozen' in certain rotational and vibrational states. This fact is possible to take into consideration by using a PDF characteristic of the ensemble being investigated. Given nonequilibrium ensembles, as in the case of molecules excited by an ultrashort laser pulse, the time-dependent PDF characterizing the structural evolution of the system must be invoked. Moreover, molecular rotational and vibrational movements can be separated adiabatically due to the fact that the latter motion involves much faster processes. Such

averaging yields the expression [47]

$$\begin{split} I_{\text{mol}}(s,t) &= \left\langle I_{\text{mol}}(s) \right\rangle = \frac{I_0}{R^2} \sum_{i \neq j=1,N} |f_i(s)| |f_j(s)| \\ &\times \text{Re}\left[ \exp\left(i\Delta\eta_{ij}(s)\right) \left\langle \exp\left(i\mathbf{sr}_{ij}\right) \right\rangle \right] \\ &= \frac{I_0}{R^2} \sum_{i \neq j=1,N} |f_i(s)| |f_j(s)| \cos\left(\Delta\eta_{ij}(s)\right) \\ &\times \int P(r_{ij},t) \left[ \iint P(\alpha_{ij},\beta_{ij},t) \exp\left(i\mathbf{sr}_{ij}\right) \sin\alpha_{ij} \, d\beta_{ij} \, d\alpha_{ij} \right] dr_{ij} \, . \end{split}$$
(3)

In Eqn (3),  $\alpha_{ij}$  and  $\beta_{ij}$  are the angles in the spherical polar coordinate system, determining the orientation of the internuclear distance vector  $\mathbf{r}_{ij}$  in the electron scattering reference frame (see Fig. 9). For isotropic molecular ensembles,  $P_{\rm sp}(\alpha_{ij}, \beta_{ij}) = 1/4\pi$ , and Eqn (3) is simplified:

$$\begin{split} I_{\text{mol}}(s,t) &= \frac{I_0}{R^2} \sum_{i \neq j=1,N} \left| f_i(s) \right| \left| f_j(s) \right| \cos \left( \Delta \eta_{ij}(s) \right) \\ &\times \int P(r_{ij},t) \, \frac{\sin \left( sr_{ij} \right)}{sr_{ij}} \, \mathrm{d}r_{ij} \, . \end{split}$$

The Russian school of gas eletronography usually relies on the reduced molecular constituent of electron scattering intensity [33]:

$$sM(s,t) = \frac{sI_{mol}(s,t)}{I_{at}(s)}$$

where  $I_{at}(s)$  is the atomic constituent of scattering intensity [the first term in the right-hand side of Eqn (1)]. Whence, one finds

$$sM(s,t) = \sum_{i \neq j=1, N} g_{ij}(s) \int P(r_{ij},t) \, \frac{\sin(sr_{ij})}{sr_{ij}} \, \mathrm{d}r_{ij} \,, \tag{4}$$

where

$$g_{ij}(s) = |f_i(s)| |f_j(s)| \frac{\cos(\Delta \eta_{ij}(s))}{\sum_{i=1,N} |f_i(s)|^2}$$

are the reduced atomic scattering factors.

Formula (4) indicates that the diffraction pattern taken from an ensemble of polyatomic molecules can be represented as a superposition of terms, i.e., diffraction patterns from each nuclear pair entering the molecule. In Eqns (3) and (4),  $P(r, t) = |\Psi(r, t)|^2$ , and it is suggested in general that  $\Psi(r, t)$ can describe a mixed quantum state. The wave function  $\Psi(r, t)$  can be represented in the form of an expansion in orthonormalized basic functions  $\psi_n(r)$ :

$$\Psi(r,t) = \sum_{n} C_{n} \psi_{n}(r) \exp\left(-\mathrm{i}\omega_{n} t\right)$$

where *n* is the quantum number of the state with energy  $E_n$ ,  $\omega_n$  is the oscillation frequency, and  $C_n$  is the probability amplitude. Then, Eqn (4) can be written down as

$$sM(s,t) = \frac{I_0}{R^2} g(s) \sum_{m,n} \rho_{mn} \exp\left(\mathrm{i}(\omega_m - \omega_n)t\right) \\ \times \left\langle \psi_m(r) | \exp\left(\mathrm{i}\mathbf{sr}\right) | \psi_n(r) \right\rangle, \tag{5}$$

where  $\rho_{mn}$  are elements of the density matrix.

It follows from Eqn (5) that molecular scattering intensity in the TRED method explicitly depends on the quantum state of the molecular system. Accordingly, the probability density function P(r, t) that can be derived from the TRED data as the Fourier transform of expression (5) has the form

$$P(r,t) = \left(\frac{2}{\pi}\right)^{1/2} \frac{R^2}{I_0} \int sM(s,t) [g(s)]^{-1} \exp\left(-\mathbf{i}\mathbf{s}\mathbf{r}\right) ds$$
$$= \left(\frac{2}{\pi}\right)^{1/2} \sum_{m,n} \rho_{mn} \exp\left(\mathbf{i}(\omega_m - \omega_n)t\right)$$
$$\times \int \langle \psi_m(r) | \exp\left(\mathbf{i}\mathbf{s}\mathbf{r}\right) | \psi_n(r) \rangle \exp\left(-\mathbf{i}\mathbf{s}\mathbf{r}\right) ds, \qquad (6)$$

it depends on the internuclear distance  $\mathbf{r}$  and time t, and contains in an explicit form all information about the quantum state of the system, being the projection of the Wigner function W(p, r, t):

$$P(r,t) = \int W(p,r,t) \,\mathrm{d}p$$

As a result, one finds [16, 32, 33]

$$sM(s,t) = g(s) \operatorname{Re}\left[\left\langle \int d\mathbf{p} \int d\mathbf{r} W(\mathbf{p},\mathbf{r},t) \exp(i\mathbf{s}\mathbf{r}) \right\rangle_{\operatorname{sp}}\right],$$
 (7)

where **p** is the momentum.

The interference term arising in the intensity of electron scattering from molecules upon coherent excitation of the molecular system [Eqn (5) and its Fourier transform (6)] gives the possibility, in principle, of determining the density matrix  $\mathbf{p}$  and tomographically restoring the molecular quantum state of the system under consideration [16, 32, 33]. To conclude, the temporal sequence of scattering intensity measurements sM(s, t) by the TRED method and the usage of Fourier transform (6) transferring description from the space of scattering variable  $\mathbf{s}$  to the space of internuclear distances r provide the necessary information for tomographic restoration of the Wigner function W(p, r, t) [16, 32, 33].

In the framework of the small harmonic oscillation model on which traditional electronographic investigations are based, the result of averaging electron scattering intensity (4) for a stationary case has the form [48–50]

$$sM(s) = \sum_{i>j} \frac{g_{ij}(s)}{r_{a,ij}} \exp\left(-\frac{s^2 l_{a,ij}^2}{2}\right) \sin\left(sr_{a,ij} - \kappa_{a,ij}s^3\right).$$
(8)

Here, subscript *a* signifies that averaging is performed with the help of function P(r)/r, with  $r_{a,ij}$  being the mean internuclear distance, and  $l_{a,ij}$  the root-mean-square amplitude of vibrational motion, while parameter  $\kappa_{a,ij}$  characterizes the asymmetry of the distribution function P(r).

In early electronographic experiments, the parameters of interest were statistically averaged characteristics of equation (6):  $r_{a,ij}$ , and sometimes  $\kappa_{a,ij}$ , given the simple molecules containing a small number of internuclear distances to which well resolved peaks in the radial distribution function curve corresponded. As experimentally examined molecular systems became increasingly complicated, such an approach proved impracticable. Besides an increased number of molecular parameters to be determined, the problem of their geometric matching arose, since mean internuclear distances are geometrically mismatched. Starting from paper [51], the problem of transition to a geometrically consistent structure, e.g.,  $r_{\alpha}$  [50], was addressed by calculating corrections based on

dynamic models of intramolecular motions. An important contribution to the calculation of dynamic corrections, including anharmonic ones, came from Refs [52–62] and pioneer attempts to determine equilibrium geometric parameters, even if for relatively simple molecules. Results of molecular structure research in terms of parameters of the potential energy function using electronographic data combined with the findings obtained by other methods are reviewed in Ref. [63].

The cumulant expansion theory elaborated in several studies with reference to electron scattering intensity [16, 60, 64–66] gives an opportunity to write down a more general analog of equation (4). The general form of the cumulant expansion of electron scattering intensities can be represented as

$$sM(s,t) = \sum_{i>j} \frac{g_{ij}(s)}{r_{ij,c}(t)} \exp\left(\sum_{k=1} \frac{(is)^{2k}}{(2k)!} r_{ij,c}^{2k}(t)\right) \\ \times \sin\left(\sum_{k=0} \frac{i^{2k}s^{2k+1}}{(2k+1)!} r_{ij,c}^{2k+1}(t)\right).$$
(9)

Expression (8) ensues from scattering intensity (9) if consideration for a stationary case is confined to the first three terms. The problem of cumulant computation and elucidation of relationships between them is discussed in detail in monograph [33]. As mentioned above, the traditional approach to the interpretation of electronographic data implies that the parameters entering Eqn (8) are directly determined quantities. Dynamic models of a molecule describing its oscillations (including anharmonic ones) and taking account of a large-amplitude movement allow these parameters to be determined from the parameters of the molecular potential energy function.

In the case of rigid molecules, one may confine oneself to considering the first three or four terms of expansion (9), in accordance with the worldwide accepted practice. The cumulants are expressed in terms of equilibrium geometry parameters and quadratic and cubic terms of expansion of the molecular potential energy function. The computation procedure with the solution of the inverse structural dynamics problem is detailed in monograph [33].

# **2.8** Difference method for the analysis of time-dependent diffraction data

The observed diffraction patterns depending on time delay between exciting and diagnostic pulses,  $\Delta I(s, t_{ref}, t)$ , are the difference curves related to structural changes in the transient state:

$$\Delta I(s, t_{\rm ref}, t) = I(s, t_{\rm ref}) - I(s, t) \,.$$

Accordingly, we arrive at

$$\Delta sM(s, t_{\rm ref}, t) = sM(s, t_{\rm ref}) - sM(s, t) \,,$$

and may obtain as well difference curves for radial distribution,  $\Delta f(r, t_{ref}, t)$ , in the space of internuclear distances r following Fourier transformation of the difference curves  $\Delta sM(s, t_{ref}, t)$ .

The theoretical analog of time-dependent scattering intensity should be calculated taking account of the nonequilibrium distribution in the system of interest with the employment of the cumulant representation for scattering intensity and, say, the stochastic approach to the analysis of diffraction data, shown to be effective in TRED analysis of  $SF_2$  photodissociation [67]. An alternative approach, taking into account in the explicit form the excitation process induced by ultrashort laser pulses and subsequent studies of coherent nuclear dynamics by the TRED method, is based on the theory described in papers [68, 69]. The difference method was shown to be highly effective for the analysis of TRED data [26].

# 3. Picosecond and subpicosecond electronography of gas phase molecules

The application of femtosecond laser pulses made it possible to observe for the first time the real-time dynamics of fast elementary molecular processes and to obtain snapshots of molecules at different stages of chemical reactions. The new discipline, femtochemistry [70–73] or coherent chemistry [74], emerged. The temporal resolution provided by femtosecond laser pulses proved sufficient for investigations into the nuclear dynamics in the molecule. However, studies of the electron subsystem dynamics require the application of even shorter, attosecond pulses. The generation of attosecond pulses became possible only in the early 21st century based on nonlinear-optical interactions between high-intensity ultrashort laser pulses with a stabilized phase. The shortest pulse (12 as) was generated by Koke et al. [75].

Interactions between intense laser radiation and inert gas atoms give rise to higher harmonics of the fundamental frequency, which are emitted into the vacuum UV and soft X-ray spectral regions. Atomic photoionization becomes essential at power densities above  $10^{14}$  W cm<sup>-2</sup>. The optical field decreases for a short time the effective Coulomb potential that couples valence and core electrons. An electron tunnels through the potential barrier or passes over it. This electron first moves away from the ion and thereafter returns to the parent ion or to the surrounding ions, recombines, excites bound electrons, and causes emission of UV or X-ray radiation. If the pulse length decreases to a few lightwave periods, ionization can develop at a certain intensity level for a fraction of the period. In this case, the electron does not have enough time to detach from the atomic core.

Ultrashort laser pulses very quickly (for fractions of the period) induce high fields that deform the Coulomb potential coupling a valence electron with the ion. Field decay results in the electron-ion recombination, while the interaction becomes dependent on the oscillation phase. Higher harmonics are generated with a maximum energy near the field peak. The higher harmonics can be emitted only once ( $\varphi = 0$ ) or twice ( $\varphi = \pi/2$ ) per pulse, depending on the carrier phase with respect to the envelope. Special attention in generating attosecond (and femtosecond) pulses is given to the synchronization principle. In femtosecond systems, synchronization of longitudinal modes of the laser resonator becomes crucial. The required synchronization of optical harmonic phases in the generation of attosecond pulses is achieved by stabilizing the phase of the fs pulse carrier. An attosecond pulse arises from spectral filtration of the proper part of the higher harmonics [76, 77].

Figure 10a presents the optical schematic of attosecond pulse generation. A phase-stabilized 5-fs pulse with an energy of 0.3 mJ is focused into a gas tube filled with neon under a pressure of 160 mbar (power density of the focused pulse



**Figure 10.** (a) Optical schematics of attosecond pulse generation [78]. (b) Measurement of attosecond pulse length with a time-of-flight electron spectrometer [79].

reaches  $7 \times 10^{14}$  W cm<sup>-2</sup>). Interactions between intense laser radiation and neon atoms initiate generation of higher harmonics of the fundamental frequency. A multilayer mirror spectrally filters vacuum UV photons, introduces a fixed delay time between fs and as pulses, and focuses the two beams onto the next target. The target comprises an atomic gas flow from which vacuum UV photons knock out electrons in the presence of a laser pulse. The pulse length is deduced from the electron distribution over energy analyzed in a timeof-flight electron spectrometer (Fig. 10b).

Changing the fs pulse phase to calibrate the TOF spectrometer gives rise to the generation of two attosecond pulses separated in time by an oscillation half-period of 1.2 fs at a wavelength of 750 nm (Fig. 10b); the attosecond pulse length was 250 as [79].

### **3.1** Creation and compression of ultrashort electron bunches and methods for measuring their length

Results of an investigation into ultrashort electron pulse interactions with the sample studied provide the main information on the structure and dynamics of the system of interest; this accounts for the importance of interaction time. The duration of electron photoemission from the surface of a solid cathode (hence, the initial length of the photoelectron bunch) depends, as a rule, on the length of the laser pulse incident on the cathode [80]. The tapping of currently available 40-fs laser pulses allows electron bunches of the respective fs length to be formed. However, the duration of the electron beam increases as it travels from the photocathode toward the target. Let us consider the three main factors governing this process.<sup>3</sup>

Experimentally examined photoelectrons need to be accelerated up to a kinetic energy of tens or hundreds of kiloelectron-volts, which leads, in particular, to a decrease in the de Broglie wavelength. It is easy to show that this process is responsible for the smearing of an electron pulse by an amount equal to the time-of-flight chromatic aberration

$$\Delta \tau_{\rm EF} = \frac{\sqrt{2m_{\rm e}\Delta E_{\rm e}}}{eF} , \qquad (10)$$

where  $m_e$  and e are the electron mass and charge, respectively,  $\Delta E_e$  is the electron kinetic energy spread, and F is the strength of the accelerating electric field. The subscript EF (electric field) denotes electron bunch smearing due to electron acceleration in the electrostatic field. The simplest way to arrive at Eqn (10) is to solve the quadratic equation for the motion of a uniformly accelerated electron over an *l*-long accelerating gap:

$$v_0 t + \frac{(eF/m_e) t^2}{2} = l.$$
(11)

Whence follows that

$$\Delta v_0 + \frac{eF}{m_{\rm e}} \,\Delta t \approx 0 \,, \tag{12}$$

from which the expression for time-of-flight chromatic aberration is arrived at once. Here is a numerical example as a useful illustration. At  $\Delta E_e = 0.3$  eV and  $F \approx 10^8$  V m<sup>-1</sup>, roughly corresponding to the maximum allowable static field strength<sup>4</sup> near thoroughly polished electrodes, this contribution is  $\Delta \tau_{\rm EF} \approx 60$  fs. Accordingly, at  $F \approx 10^7$  V m<sup>-1</sup>, ensuring reliable work,  $\Delta \tau_{\rm EF} \approx 0.7$  ps. Notice that a decrease in  $\Delta E_e$ may result in shorter electron bunches.<sup>5</sup> Relevant experimental approaches are discussed at the end of this section.

Furthermore, the motion of electrons with initially different kinetic energies is accompanied by time-of-flight lengthening expressed as

$$\Delta \tau_{\rm TOF} \approx t_{\rm TOF} \, \frac{\Delta E_{\rm e}}{2K} \,,$$
 (13)

where  $t_{\text{TOF}}$  is the time needed for photoelectrons accelerated to the kinetic energy K to reach the target. For example, it turns out that  $\Delta \tau_{\text{TOF}} \approx 5$  fs at K = 30 keV,  $\Delta E_e = 0.3$  eV, and  $t_{\text{TOF}} \approx 1$  ns.

Coulomb repulsion between charged particles in a beam is not infrequently the key factor limiting the potential of an experiment. Let us consider a simple model of an electron bunch propagating in a field-free region to estimate the influence of this mechanism on the beam temporal proper-

<sup>&</sup>lt;sup>3</sup> The evolvement of picosecond/femtosecond electro-optical chronography and its influence on the development of the ultrafast electron diffraction method are described in Section 9. Here, we disregard smearing of electron pulses due to the slight difference between trajectories (therefore, path lengths) along which electrons propagate from the cathode to the sample.

<sup>&</sup>lt;sup>4</sup> The opposite situation leads to a vacuum breakdown between the electrodes, even if they underwent preliminary mechanical and ion-beam treatment.

<sup>&</sup>lt;sup>5</sup> Naturally, the spread in energy  $\Delta E_e$  cannot be too small if the possibility of the existence of ultrashort electron bunches is to be maintained.

ties. The total energy (V + W) of a bunch consisting of N electrons must be naturally conserved:

$$V + W = \sum_{i,j} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} + \sum_i \frac{m_e v_i^2}{2} = \text{const}.$$
 (14)

Here, V is the Coulomb interaction energy, and W is the electron bunch kinetic energy. The characteristic spread in repulsing electron velocities,  $\delta v$ , can be conveniently deduced from the expression

$$m_{\rm e} \, \frac{\delta v^2}{2} \approx \frac{e^2 N}{16\pi\varepsilon_0 \delta r} \,, \tag{15}$$

where  $\varepsilon_0$  is the dielectric constant, and  $\delta r$  is the initial size of the photoelectron cloud. In this model, the spread in velocities accounts for electron pulse smearing by an amount of order  $\Delta \tau_{\rm C} \approx t_{\rm TOF} \, \delta v / v_{\rm e}$ , where  $v_{\rm e}$  is the beam propagation speed. This expression can be rewritten in the form

$$\Delta \tau_{\rm C} \approx \frac{t_{\rm TOF}}{v_{\rm e}} \sqrt{\frac{e^2 N}{8\pi \varepsilon_0 \delta r m_{\rm e}}} \,. \tag{16}$$

At  $v_e \approx 10^8 \text{ m s}^{-1}$ ,  $N \approx 10^4$ ,  $t_{\text{TOF}} \approx 1 \text{ ns}$ , and  $\delta r \approx 10 \ \mu\text{m}$  (the last value coincides by the order of magnitude with the size of the focal spot of a sharply focused laser beam); this contribution is  $\Delta \tau_C \approx 1.4$  ps in the framework of the approximation employed. Naturally, the use of a higher accelerating voltage, e.g., 200 kV instead of 30 kV, permits decreasing electron bunch smearing due to Coulomb repulsion; in this case, however, atoms of lighter elements can be knocked out of the sample.<sup>6</sup> Therefore, this method, to a certain degree, ceases to be nondestructive, which may complicate investigations, in particular, of organic materials containing light elements.

A rise in accelerating voltage to  $\sim 1$  MV or more increases the possibility of the formation of relativistic electron beams.<sup>7</sup> Interestingly, Coulomb repulsion in such conditions is not a strongly limiting factor, which makes it possible to obtain 100-fs electron bunches [81]. This advantage is easy to explain by the known fact that time slows down in a reference frame associated with a relativistic beam, where ultrafast electrons simply have no time to undergo repulsion. It is this time dilation effect that is known to underlie observation of shortlived cosmic particles under earthly conditions.

There is a direct method to avoid Coulomb repulsion by using one-electron pulses formed, for example, with the help of relatively low-intensity pulses from an fs laser generator with a frequency of 80 MHz [82]. Such an approach finds application in transmission electron microscopes adapted for observations of fast processes; it is considered in Section 7.

To sum up, it can be argued that a temporal resolution of 100 fs in electron-optical measurements is the threshold value which is difficult to overcome. In general, the improvement of temporal resolution in a given experiment can be achieved by additionally compensating one way or another for electron pulses. At present, this goal is attained using radiofrequency compression systems [83]. This work done at the Max Planck Institute (Germany) represents actually an extension of theoretical and experimental studies carried out at the Department of Photoelectronics of A M Prokhorov Institute of General Physics (IGP), Russian Academy of Sciences (see Section 9).

In Ref. [83], a special pulse synchronized with an fs laser triggered an oscillating field in a cell traversed by a photoelectron bunch preliminarily produced with fs laser radiation. The oscillating radiofrequency field, whose vector was parallel to the direction of electron beam propagation, slowed down actually faster electrons and accelerated slower ones. According to the estimates [83], such an approach would allow not only surmounting the 100-fs barrier, but also forming in the future electron pulses as long as several femtoseconds. The development of this method is currently underway [84].

At the same time, an alternative approach unrelated to radiofrequency compression technique (requiring synchronization between a high-frequency field and pulsed laser) is also known to exist. For this purpose one can employ a system based on a time-of-flight reflectron, having found wide application in heavy-ion mass spectrometry. An electrostatic mirror permits lengthening the trajectory of initially faster electrons and, accordingly, shortening the path of slower electrons. This may result in the 'collapse' of the beam in a certain space region, when its length becomes minimal. References [85-87] report on a theoretical analysis of this issue. It should be noted that the number of publications considering this approach is much smaller than those dealing with radiofrequency compression. Studies currently underway at the Institute of Spectroscopy, Russian Academy of Sciences (Troitsk) utilize a double mass-reflectron for the generation of ultrashort electron pulses in an adapted transmission electron microscope. Making use of two electrostatic mirrors is expected to simplify the design of the instrument and improve the characteristics of such a compressor.

Observation of the diffraction pattern created by a single ultrashort electron bunch remains a serious challenge. Note that Tokita et al. [88] were the first to record the diffraction pattern from a thin gold plate formed by a *single subpicosecond electron pulse*. The bunch generated by the irradiation of a special cathode with ultrahigh-intensity fs laser pulses and containing some  $4 \times 10^4$  photoelectrons was compressed using a magnetic sector; as a result, a 500-fs resolution was reached.

Femtosecond laser pulses not only ensure the formation of electron pulses due to photoemission from a solid cathode, but also allow measuring the temporal characteristics of photoelectron bunches and additionally compressing electron beams. This inference needs clarification, because it implies control of free electrons by a high-intensity laser beam.

At first sight, it is at variance with the well-known fact that free electrons cannot absorb electromagnetic radiation due to the impossibility of simultaneously satisfying the laws of conservation of energy and momentum. However, free electrons can scatter such radiation. From the quantummechanical standpoint, stimulated Compton scattering in a laser field occurs in such a case.

The possibility of acting on the translational degrees of freedom of charged particles, such as free electrons, by a spatially nonuniform electromagnetic (EM) field was theoretically predicted in the mid-1950s by Gaponov and Miller

<sup>&</sup>lt;sup>6</sup> The energy  $2p^2/M$  is a maximum one for light atoms with mass *M*. Here, *p* is the momentum transferred to a lattice atom as a result of electron impact.

<sup>&</sup>lt;sup>7</sup> The use of relativistic electron beams for the structural analysis of matter is considered in Section 5.

[89]. This mechanism pushes the charged particles from the strong high-frequency field region. In the event of using high-intensity laser radiation, the Gaponov–Miller force (GMF),<sup>8</sup> defined as the spatial gradient of ponderomotive potential  $U_{\text{pond}}$ , can be strong enough to provide a basis for the effective ultrafast control of electron beams in a vacuum.

For a nonrelativistic electron,<sup>9</sup> the notion of a ponderomotive potential in a spatially nonuniform EM field,  $E = E_0(r) \sin(\omega t)$ , is most easily introduced through averaging the respective Hamiltonian over fast oscillations with frequencies  $\omega$  and  $2\omega$ :

$$H = \frac{\left\langle \left( p + eE_0(r)\sin(\omega t)/\omega \right)^2 \right\rangle}{2m_{\rm e}} = \frac{p^2}{2m_{\rm e}} + \frac{eE_0^2(r)}{4m_{\rm e}\omega^2} = \frac{p^2}{2m_{\rm e}} + U_{\rm pond} , \qquad (17)$$

where  $\langle \ldots \rangle$  denotes averaging. As a result, the expression for GMF can be written as

$$F_{\text{pond}} = -\frac{e^2 \lambda^2}{8\pi m_{\text{e}} \varepsilon_0 c} \nabla I_{\text{las}}(r, t) , \qquad (18)$$

where *c* is the speed of light, and  $\lambda$  is the wavelength. By way of illustration, if the intensity of sharply focused laser radiation amounts to  $10^{15}$  W cm<sup>-2</sup> in the center of the focal spot with diameter  $d_{1/e} = 2 \mu m$  (determined at the 1/e level) and  $\lambda = 800$  nm, then one obtains  $U_{\text{pond}} \approx 60$  eV,  $F_{\text{pond}} \approx 10^{-11}$  N, i.e. the result coinciding with the absolute value of the repulsive force between two electrons spaced 5 nm apart.

Ultrashort laser pulses exert direct force action on electrons propagating in a vacuum on the fs time scale; hence, the possibility of both creating ultrashort fs electron bunches and measuring their duration [37]. Determination of temporal characteristics of a pulsed electron beam is based here on scanning the time delay between laser radiation forming a photoelectron bunch and a sharply focused laser beam modulating photoelectron distribution by velocities under the influence of GMF (Fig. 11a).<sup>10</sup> Such a method surpasses, in principle, the potentialities of a standard streak camera-based technique [37].

It will be recalled that electrons in a streak camera deflect in the rapidly changing high-voltage electric field before they reach the position-sensitive detector. The variation rate of a high-voltage electric field determines the temporal resolution of the device, which does not exceed  $\sim 200-300$  fs, even in the most expensive models. At the same time, the required temporal synchronization of a high-voltage electric pulse in the streak camera with an fs laser pulse forming the ultrashort photoelectron bunch to be analyzed is frequently a difficult engineering task. Here there is certainly a relationship with the radiofrequency compression scheme in which the vector of the electric field component is parallel to electron beam propagation.



**Figure 11.** Diagrams illustrating the practical applications of the Gaponov–Miller force produced by ultrashort laser radiation to measuring the duration of photoelectron bunches and creating fs electron beams (a), as well as to compressing the initial electron pulse and forming already attosecond bunches (b) [95].

Studies of the influence of a spatially nonuniform EM field on free electrons that began soon after the publication of Gaponov's and Miller's work were first devoted to the creation of traps based on the microwave technique [91]. Much attention in experiment was paid at that time to the passage of electrons with a given kinetic energy through the ponderomotive potential since it allowed determining  $U_{\text{pond}}$  [91, 92].

Of special interest is the measurement of GMF, with which sharply focused laser radiation acts on electrons propagating in a vacuum [93], first of all for *in situ* spatial– temporal diagnostics of high-intensity laser fields and verification of the accuracy of measuring the ultrashort electron pulse length based on irradiation of an electron bunch with high-intensity laser pulses.

Let us consider two examples of GMF application [94]. Figure 11a depicts two sharply focused laser beams propagating from opposite directions and forming a standing wave in which part of the electron pulse deflects.

The proposed scheme has a dual purpose. First, it allows the length of the initial electron bunch to be determined by scanning delay times between laser pulses creating the standing wave, and properly recording the deflected wave (in the general case, also the scattered electron component) with the aid of a position-sensitive detector. Second, the length of a deflected electron pulse can be shorter than the initial electron beam.

A couple of remarks are in order. The above scheme [37, 95] utilizes a standing wave, which requires spatial-temporal matching of two fs laser pulses to the initial ps electron bunch. The application of a single laser beam for implementing electron scattering is a simpler option. However, spatial nonuniformity of the EM field in a standing wave amounts

<sup>&</sup>lt;sup>8</sup> An alternative term is the ponderomotive force.

<sup>9</sup> Materials of Ref. [90] can be used in a relativistic case.

<sup>&</sup>lt;sup>10</sup> This scheme is presented here by way of an illustration for an electron pulse of a small enough ( $\sim \lambda/4$  or less) transverse size. Also, it is assumed that standing wave antinodes do not coincide with the electron beam line (shifted somewhat down in the figure). Notice that in general the electron beam scattering diagram is more complicated than shown in this figure.

to  $\sim \lambda/2$ , which is technically difficult to realize, having an isolated strengthened fs laser beam. For example, a short-focal length parabolic mirror usually permits focusing strengthened fs laser radiation with a wavelength of 0.8 µm onto a spot with diameter  $d_{1/e} \sim 6$  µm. Therefore, when the laser pulse energy, laser wavelength, and focusing conditions remain unaltered, all other things being equal, electron scattering in a pulsed standing wave is more pronounced.

The other remark concerns the limiting capabilities of this approach. To begin with, we are interested in what the measuring accuracy of the temporal characteristics of the initial electron pulse and what length of the deflected electron bunch can be reached in experiments. These quantities are directly related to the time of flight of electrons through the laser focal spot:

$$\tau_{\rm fl} \approx \frac{d_{1/e}}{v_{\rm e}} \,. \tag{19}$$

For example, at  $d_{1/e} = 6 \,\mu\text{m}$  and  $v_e \approx 10^8 \,\text{m s}^{-1}$  (corresponding to  $K = 30 \,\text{keV}$ ),  $\tau_{\rm fl}$  is only  $\approx 60 \,\text{fs}$ . This means that a sharper focusing of intense laser radiation is needed to obtain a 30-fs electron bunch (see footnote 3) by the deflection method and to diagnose such pulses from electron scattering patterns in a spatially nonuniform EM field. It may be a nontrivial technical problem. According to formula (19), measurement errors can be reduced exploiting electrons with higher kinetic energies; however, this implies the usage of stronger laser fields.

It seems appropriate to dwell on an interesting method for obtaining attosecond electron pulses described by Baum and Zewail [95]. In the experimental scheme proposed (Fig. 11b), a subpicosecond photoelectron bunch is irradiated by two laser beams with different wavelengths propagating from opposite directions and in pursuit of the bunch. The wavelengths of both beams coincide in the fast electron frame of reference due to the Doppler effect, which results in origination of a stationary wave. The ponderomotive forces push electrons from the antinodes of the standing wave of a strong laser field. As evidenced by calculations [95], this may cause the formation of attosecond electron bunches. Strictly speaking, the duration of the initial electron bunch is conserved but, importantly, an attosecond temporal structure arises inside the initial pulse.

Bearing in mind the uncertainty relations for the existence of ultrashort (in the present case, attosecond) pulses, a wide enough energy spectrum,  $\Delta E_e$ , is needed. For example, a 100as electron bunch must have  $\Delta E_e$  of at least 6 eV. An initial photoelectron pulse resulting from cathode irradiation from an fs laser does not possess such spectral properties. The desired broadening may be due to the action of GMF. Let us write down the equation for work of the force in the classical form, where the energy gain is defined as

$$\Delta E_{\rm e} = e F_{\rm pond} v_{\rm e} \tau_{\rm L} \,; \tag{20}$$

here,  $\tau_L$  is the length of the laser pulse, and the force is roughly defined as

$$F_{\rm pond} \approx \frac{2U_{\rm pond}}{\lambda^*} \,,$$
 (21)

where  $\lambda^*$  is the laser radiation wavelength in the fast electron reference frame. In a numerical experiment [95], the following values were putted:  $U_{\text{pond}} \approx 0.2$  eV,  $\lambda^* = 370$  nm,

 $v_e \approx 10^8$  m s<sup>-1</sup>, and  $\tau_L = 300$  fs. Hence,  $\Delta E_e \approx 32$  eV, in excess of the above-mentioned value.

The authors of Ref. [95] proposed a rather elegant scheme, but it should be remembered that measuring the duration of attosecond pulses is a highly not prime experimental problem. It is probably easier to generate an ultrashort bunch than to measure it.

As mentioned above, the duration of photoelectron beams can be controlled by varying the initial spread of electron kinetic energies,  $\Delta E_e$ . In Ref. [96], photoemission of electrons was examined using a tunable source of fs UV pulses. As revealed through the study,  $\Delta E_e$  turned out to be minimal when the photon energy practically coincided with the work function of the cathode material. Accordingly, the experiment demonstrated shortening of the bunches prepared. It is important that a decrease in  $\Delta E_e$  results in an increased coherence length. As a consequence, the scope of applications of electron diffraction can be broadened.

It proved possible to employ to the same effect laser cooling of atoms [97]. In Ref. [97], rubidium atoms preliminarily cooled in a magneto-optical trap turned into electron sources under laser irradiation. Tuning of the laser wavelength to the photoionization threshold of Rb atoms made it possible to form a bunch of cold electrons with characteristic temperature  $T_b \approx 10$  K, while the coherence length  $(L_c \sim T_b^{-1/2})$  reached  $L_c \approx 8$  nm, a record-breaking value for ultrafast electron diffraction [84]. Such a cold gas source was subsequently employed in a demonstration experiment designed to observe electron diffraction from graphene [84] (see Section 5.3).

### **3.2** Molecular dynamics and electron density tomography

Itatani et al. [98] had recourse to computed tomography (CT) for image reconstruction and obtained a 3D image of a single molecular orbital. The notion of one-electron wave functions (orbitals) was introduced to describe the electron structure of molecules. It characterizes the state of an individual electron resided in an averaged field of all other electrons and nuclei. This notion has remained a 'mathematical abstraction' for many decades because of the impossibility of directly observing them till the advent of methods allowing detailed investigations of intramolecular electron density distribution. Such investigations are carried out using, for instance, scanning tunneling microscopy of molecules on a solid surface (with the inevitable distortion of electron density distribution). Moreover, there are methods for work with molecules in the gaseous phase, such as a variant of photoelectron spectroscopy, permitting the 'illumination' of molecules by electrons from the inside and thereby recording the diffraction pattern reflecting the electron wave propagation in the three-dimensional potential of the molecule. However, none of the available methods permitted us to obtain an undistorted 3D image of the electron wave function and information about its phase.

Computed tomography was applied in Ref. [98] for the study of complex objects, including reconstruction of the image of an object with a complicated internal structure based on the analysis of spatial distribution of radiation intensity that passed through the object (3D image reconstruction from a large number of one- or two-dimensional projections). The highest filled orbitals responsible for the formation of chemical bonds are the most interesting objects studied. The authors of Ref. [98] reconstructed nitrogen molecule orbitals, generating higher harmonics by intense fs laser pulses. As already noted, this method is currently employed to obtain EM radiation pulses of extremely short duration, i.e., attosecond pulses.

The desired set of projections can be obtained by rotating a molecule. Because the researchers had to work with a macroscopic number of molecules rather than with an isolated nitrogen molecule, an indispensable preliminary stage of the experiment was the same alignment of molecular axes. For this purpose, a stream of nitrogen molecules with a diameter of 1 mm was tentatively subjected to a 60-fs laser pulse, which caused them to rotate. The rate of rotation depended on their initial orientation with respect to the axis of laser radiation polarization. At some instant of time after the passage of the preliminary pulse, all the molecules became uniformly oriented. Thereafter, the oriented molecules were subjected to a second (more intense) fs laser pulse (wavelength 800 nm, duration 30 fs). Radiation power density  $(2\times 10^{14}~W~cm^{-2})$  was high enough to ensure tunnel ionization of the highest filled molecular orbital by virtue of suppressing the Coulomb potential barrier with an electric field of the laser pulse. Part of the electron wave function was liberated in the course of tunnel ionization: this electron wave packet began to move under the action of a varying electric field of the laser pulse.

The packet first moved away from the molecule, but then returned and interacted with it. While the electron wave packet travelled back to the donor molecule, it expanded in the direction perpendicular to the direction of motion up to roughly 9 Å, i.e., much in excess of the molecule size  $(\sim 1-2 \text{ Å})$ . The returning wave packet can be regarded as a set of plane waves 'probing' a properly oriented molecule. As the returning wave packet and the molecule collide, the packet overlaps the remaining part of the molecular orbital. Because both packets originate from a single source, the coherent combining of two wave functions takes place (it is this fact that permits 'working' with a separate molecular orbital). The arising asymmetric electron density distribution varying in time (as the wave packet travels back) can be regarded as an oscillating dipole which emits EM waves. The spectrum of EM radiation thus generated depends on both the molecular orbital shape and the molecule orientation; it is limited from above by the kinetic energy of the oncoming wave packet.

Having registrated the set of spectra ('projections') for different orientations of the molecular axis with respect to the axis of laser radiation polarization (with a  $5^{\circ}$  step) makes it possible to reconstruct the 3D structure of an individual molecular orbital (Fig. 12).

The natural extension of work [98] involves the observation of modification of molecular orbitals in chemical reactions. Moreover, this technique can be applied to reconstruct both the highest occupied molecular orbitals and the deeper ones.

Theoretical studies of electron diffraction and X-ray radiation, as well as simulation of the coherent dynamics processes in a molecular electron subsystem, were undertaken for the first time in Refs [99, 100].

As shown in the preceding sections, ultrafast electron diffraction makes possible the observation of transient structures in chemical reactions and nonstationary events in condensed media. *However, the temporal resolution, from femto- to picoseconds, proves insufficient to study electron motion in atoms and molecules.* Recently proposed methods for generating attosecond pulses [96, 101–105] open up new



**Figure 12.** (Color online.) (a) CT image of  $2p_{\sigma g}$  molecular orbital; (b) *ab initio* structure calculation of the same orbital; (c) shape of the wave function along the internuclear axis (dashed line—reconstruction from experimental data, and solid line—*ab initio* calculation) [98].

principal possibilities for investigations into the 4D coherent dynamics of electrons in a molecule.

A laser pulse a few femtoseconds in duration creates the superposition of electronic states that are further diagnosed using an attosecond one-electron pulse with an energy of 10 keV at different delay times. The dynamics of coherent electronic state superposition in atomic hydrogen (H) and the tritium molecular ion  $T_2^+$  were theoretically studied in Ref. [106]. The diffraction patterns reflect the time dependence of the effective radius of charge electron density. Changes in the diffraction patterns, in turn, reflect the localization or delocalization of charge electron density oscillating in time, in fact its 'breath'.

Figure 13 illustrates the electron dynamics of a  $T_2^+$  molecular ion.

It may be hoped that the exploration of the 4D dynamics of electron density in a benzene molecule (see monograph [107]) will help to discover Dewar structures and experimentally confirm the main concept of the resonance theory put forward in the early 1930s [108, 109].

### 3.3 Laser-induced electron diffraction

Let us imagine a 3D 'molecular movie' of a photochemical reaction showing shot-by-shot changes in atomic positions inside a molecule. In a traditional scheme of molecular structure research, particles or waves propagating from a sufficiently remote source are scattered in collisions with atomic nuclei or their electron shells, thus producing a diffraction pattern [1, 110, 111]. The new paradigm [112]



**Figure 13.** (Color online.) Left column: tritium  $T_2^+$  ion charge density oscillation. Right column: differential cross sections of an electron bunch with an energy of 10 keV and length of 0.1 fs. Figures from top to bottom correspond to delay times 0, T/4, and T/2, respectively [106].

proposes utilizing repeated collisions of electrons with ionized source molecules on which the electrons are scattered. Such an approach to molecular visualization was termed laserinduced electron diffraction (LIED) [112, 113]. This principle, related to ordinary electron diffraction, implies the employment of spatial coherence of repeatedly colliding electrons. Measurements of 3D pulses of scattered electrons provide information needed when reconstructing atomic positions in a molecule [114, 115]. Moreover, the coherence of a repeatedly colliding electron differs from that of an electron generated from the molecular external region, because this electron is derived from a single electron orbital and governed by coherent light. This opens up the possibilities for electron holography [114]. For example, one part of a laser pulse can produce a reference wave packet (when circularly polarized light is used), while the other, coherently coupled part, can produce a wave packet that repeatedly collides with the ion. The resulting interference pattern represents a hologram of the 3D scattering potential. In this way, D Gabor's original dream of electron holography [116] (to shot holographic movies) can be realized.

The three major methods for determining the molecular structure, viz. X-ray, neutron, and electron scattering, are based on the measurement of molecular diffraction patterns. The idea of LIED was further developed in paper [117], where a fundamentally new method was proposed for the simultaneous investigation of ultrafast nuclear and electronic dynamics in molecules. The authors of above-cited work used a laser field to eject electrons from the molecule of interest. These electrons were then accelerated, and some of them collided with the parent ion and diffracted from it; the entire process proceeded within a fraction of the laser radiation period. It was shown that the distribution of the momentum of the ejected electron is a 'fingerprint' of the highest occupied molecular orbital, whereas the diffraction pattern of electrons elastically scattered from the molecular nuclear subsystem can be used to determine their coordinates. Thus, photoelectrons carry detailed information on both the electron orbitals and positions of nuclei in the framework of a single method.



**Figure 14.** (a) Tunneling creates a filtered projection of molecular orbitals. Approximately half of the electron wave packet reaches the detector. (b) The remaining part goes back to the parent ion. Figure shows the central part of a repeatedly colliding wave packet diffracting by the molecule. The outer part of the wave packet (not shown) weakly interacts with the ion potential. The relative amplitude of each component depends on the filtered projection of molecular orbitals, and consequently on the spatial alignment of the molecules [117]

Molecular multiphoton ionization in the tunneling limit (Fig. 14a) is akin to electron tunneling in a scanning tunneling microscope (STM). In both cases, electrons are ejected from orbital external regions into a continuum, i.e., a vacuum for the multiphoton ionization of molecules in the gas phase, or the conduction band in the tip of the metal needle in STM. The sample is fixed in STM, while the probe needle moves. Rotation of a molecule about the field direction is an analog of needle tip movement. The resulting angular dependence of ionization probability provides information about molecules that is analogous to the tunneling current dependence on the detector coordinates in STM. The electron wave packet entering a vacuum in the course of tunneling conserves information about the orbitals of the study molecule.

Unlike the STM static field, the electric field in a laser pulse fluctuates and makes part of the tunneled electron wave packet return to the parent ion, where it may diffract (Fig. 14b). In the case of LIED, the study molecule serves simultaneously as a photocathode, whereas the laser field maintains an accelerating voltage for electrons. This method permits obtaining extremely high current densities and attosecond electron pulses.

Paper [117] reports the results obtained by molecular tunneling spectroscopy (MTS) and LIED. MTS was applied to measure the 3D momentum distribution of electrons generated by spatially oriented  $O_2$  and  $N_2$  molecules. A comparison of theory and experiment demonstrated that the electron momentum distribution in two directions perpendicular to the field is determined by the highest occupied molecular orbital and can be observed through the filter of the laser field-suppressed coupling potential [118, 119], through which the electron tunnels. Thus, a series of measurements simultaneously determine the orbital wave functions of a molecule and the positions of atomic nuclei.

Laser induced tunneling and diffraction involve different parts of the electron wave packet produced by the ionization of the molecule under study. The wave packet originated upon field decay returns to the parent ion, from which it may scatter both elastically (diffract) and inelastically or recombine (interact) with the orbital from which it was ejected. These three scattering processes open up different prospects for the investigation of molecules.

Electron tunneling through the potential barrier, underlying the LIED technique, provides a possibility for probing the electron structure of a neutral molecule. Recombination radiation known as high harmonic emission yields information on the orbital structure of neutral molecules. Nevertheless, these processes should be separated before the method will be generalized to the investigation of complex orbitals, because the generation of high harmonics starts with tunneling and ends in interference.

Elastic and inelastic electron scattering occur on a molecular ion, the source of the electron. The action of an ultrashort laser pulse on a molecule may cause multiple ionization, followed by Coulomb repulsion between small molecules, as predicted by the Keldysh theory (see review [119]). Data on the molecular structure can be derived from the vectors of momenta of correlated ionic fragments. Elastic scattering of electrons is also sensitive to the structure of the molecular ion potential. Here, the molecular structure is encoded in the diffracting electron wave packet, which allows this visualization technique to be applied to the study of more complex molecules.

Electron diffraction occurs at the de Broglie wavelength on the order of the molecule size. Small diatomic molecules have an internuclear distance of about 1-2 Å ( $\sim 2-4$  a.u.). An electron must acquire a kinetic energy of  $\sim 150 \text{ eV}$  to have a like wavelength. Such a level of kinetic energy is readily reached by electrons that are accelerated in the laser radiation field and repeatedly collide with the starting molecule. Cold target recoil ion momentum spectroscopy (COLTRIMS) was utilized to record electron momenta resulting from tunnel ionization of spatially oriented O<sub>2</sub> and N<sub>2</sub> molecules. COLTRIMS allows measuring 3D vectors of single electron and ion momenta with the coincidence method. The possibility of coincidence is utilized to measure O2 and N2 structures simultaneously and under identical conditions in a gas mixture, also permitting us to eliminate any contribution to electron inelastic scattering spectra resulting from fragmentation or multiple ionization of molecules. Measurement of coincidences permits studying weak fragmentation channels providing information on the quality of the spatial orientation of the molecules being studied.

### 4. Ultrafast electron crystallography

The ultrafast electron crystallography (UEC) technique allows the research to be made into transient nonequilibrium structures, yielding important information for understanding phase transitions and the coherent dynamics of nuclei in the solid state, on surfaces, and in macromolecular systems. This method has been extensively employed in recent years to study the dynamics of nanoobjects placed in a laser radiation field [8, 29, 120, 121].

The application of time-resolved electron diffraction in condensed state research provides information on the behavior of matter in the 4D spatial-temporal continuum. The possibility of combining the high spatial resolution (up to hundredths and even thousandths of an angström) and high temporal resolution (femtosecond range) makes it possible to study structural changes and energy redistribution in real time.

The apparatus for the realization of the UEC method comprises three ultrahigh vacuum chambers with a source permitting one to study low-energy electron diffraction (LEED), an Auger spectrometer, and a gas dosing device. The unit also includes a goniometer with a 0.005° angular resolution, and a system for cooling down to 110 K. The accuracy of measuring the internuclear distances reaches  $\sim 0.01$  Å, and the maximum resolvable distance amounts to  $\sim 50$  Å. The laser pulse length is 120 fs; laser radiation penetrates as deep as 4 nm at a wavelength of 266 nm, and 7 µm at a wavelength of 800 nm.

The UEC method permits the study of coherent structural dynamics in photoinduced phase transitions in nanoparticles and macromolecules, on solid surfaces, in thin films, and in interphase regions. Moreover, dynamic processes at the level of the system's constituent elements can be investigated [120, 122, 123].

A general schematics of the UEC method is presented in Fig. 15a. A bunch of electrons with an energy of ~ 30 keV (wavelength ~ 0.07 Å), denoted as the wave vector  $\mathbf{k}_i$ , is incident at angle  $\theta_i < 5^\circ$  on a crystal containing absorbed atoms or molecules. The resultant diffraction pattern contains information about the surface structure determined by the substrate and adsorbed particles. The substrate temperature was controlled in Ref. [123] by IR laser pulses (usually, 120 fs in duration with a wavelength of 800 nm); UV radiation at 266 nm was also tapped. The time reading point at which both exciting and diagnostic pulses simultaneously arrive at the crystal surface was defined as zero time  $t_0 = 0$  (see inset to Fig. 15a).

A vacuum of  $10^{-10}$  Torr was maintained in the apparatus. The observed diffraction patterns depending on the delay time between exciting and diagnostic pulses,  $\Delta I(\theta_i, s, t_{ref}, t)$ , represent the difference curves reflecting structural changes in the transient state:

$$\Delta I(\theta_{\rm i}, s, t_{\rm ref}, t) = I(\theta_{\rm i}, s, t_{\rm ref}) - I(\theta_{\rm i}, s, t) ,$$

because reference time  $t_{ref}$  can be chosen either before or after the arrival of the exciting pulse. The diffraction pattern in such an experimental geometry reflects the structure in a reciprocal space (Fourier transform). In a 2D atomic monolayer in the reciprocal space, diffraction 'rods' can be seen spaced by 1/a and 1/b (see Fig. 15) in the reciprocal lattice space. The rods correspond to constructive coherent wave interference. Since the monolayer is inserted into the crystalline substrate, the rods in the diffraction pattern undergo changes caused by modulation of interplane distances (see Fig. 15). For electrons, Ewald spheres defined by vector  $\mathbf{k}_i$  have a large radius, and the diffraction pattern depending on  $\theta_i$  contains both stripes at small scattering angles and Bragg spots at large angles in the Laue zones. In the case of high-energy electron scattering, these reflexes provide information about the static structures of both the surface and the lattice. Given a high enough temporal resolution, an additional dimension can be introduced for the following reasons. First, it is possible to diagnose structural changes in the surface layer (and its reconstruction) directly in the real-time regime. Second, the time scale is essentially separated for processes proceeding in the surface layer and in the perpendicular direction, which allows distinguishing and diagnosing the initial nonequilibrium



Figure 15. (a) Schematic of UEC method. The electron bunch is directed toward the Si(111) crystal surface at angle  $\theta_i < 5^\circ$ . Ewald spheres and Laue zones (L0, L1, ..., see text) are shown. (b) The structure of and distance between bilayers (3.136 Å). Atoms and molecules are adsorbed on the surface layer [123].

structures rather than structures emerging in association with the spread of action of the exciting pulse.

### 4.1 Surfaces and crystals

An example of research demonstrating the potential of the UEC method is reported in Ref. [124]. The authors studied the structural dynamics of the crystalline GsAs surface following a rise in crystal temperature. Variations in Bragg diffraction (shift, line width, and intensity) indicated that both 'contraction' and 'expansion' were of the same order (from -0.01 to +0.02 Å) and that 'transient temperature' (Ref. [124] offers no exact definition) rose to a maximum value of 1565 K for 7 ps (Fig. 16). The evolution of nonequilibrium structures suggested that the onset of structural changes lags behind a temperature rise.

These findings were compared in Ref. [20] with the results of nonthermal fs optical probing [125]. The GaAs surface was functionalized with a monolayer of chemically bound chlorine atoms. Observations over ultrashort time intervals revealed contraction followed by expansion due to a rise in phonon temperature. On longer intervals, structural rearrangement and evolution to the equilibrium state were revealed. Such structural dynamics can be divided into three regimes, viz. changes involving electron redistribution without nuclear motion (from femto- to several picoseconds), coherent nonequilibrium lattice expansion (starting from 7th ps), and structural rearrangement and heat diffusion (from 50 ps to nanoseconds).

Similar studies were carried out with silicon crystals in the presence of adsorbates and without them [120, 123]. The choice of a ground-state structure as the reference frame is indicative of structural changes caused by the starting pulse with respect to the sample ground state for a 'negative' delay time till the changes observed at a positive time. A structural change was apparent as a time shift in the curve of in-phase Bragg peak rocking, while an increase in the oscillation amplitude influenced broadening of the peaks. The motion of surface and bulk atoms was observed as in the case of GaAs [123]. The femtosecond rise in electron temperature was followed by enhanced population of optical phonons that induced acoustic waves (lattice expansion and contraction) after a picoseconds delay and finally by lattice heating. The employment of UEC made it possible to observe ultrafast surface and bulk dynamics and follow up structural rearrangements of the object and heat diffusion over longer time intervals.



**Figure 16.** (Color online.) Study of GaAs crystal surface coated with chlorine atoms. Only changes in relative equilibrium positions of lattice constants are shown (see the text). (Taken from Ref. [120].)

By now, the possibility of employing the UEC method to study surface structural changes, as well as the influence of adsorbed molecules, and the transition from the crystalline phase to the liquid one, was demonstrated [8, 29, 120, 121]. Silicon surfaces containing adsorbed molecules of hydrogen, chlorine, and trifluoroiodomethane (CF<sub>3</sub>I) were examined. Laser radiation caused coherent restructurization of surface layers associated with subangström displacements of atoms, which follow an ultrafast laser pulse heating of the surface. The nonequilibrium dynamics of surface structural changes (with a 2 ps time-step and total duration up to 10 ps) was apparent from variations of interference lines, Bragg spots, and diffraction rings.

The oscillation amplitude falls to 0.1 Å upon transition from hydrogen to chlorine. The temporal response for a system containing chlorine atoms is similar to that for a system of hydrogen atoms; however, it is characterized by slower dynamics. In this regard, it is necessary to take into account an essential increase of both mass and electronegativity of chlorine compared with the respective parameters of hydrogen. Electron capture by the surface changes the potential and, accordingly, increases the amplitude of nuclear motion in an adsorbed molecule. Adsorption of trifluoroiodomethane molecules having lower effective electronegativity decreases the adsorption energy and the time of the system's dynamic response to external excitation [8, 29, 120, 121].

The first results of research demonstrate the possibility of direct observation of the structural dynamics of adsorbed layers and open up new prospects for the analysis of matter states on the surface in the 4D spacetime continuum.

#### 4.2 Molecular ensembles

Investigations into membrane structures were anticipated by the study of a fatty acid bilayer deposited on a hydrophobic substrate by the known Langmuir–Blodgett technology that permits the control of layer-by-layer deposition of ordered molecular films. This technology is employed to create model biological membranes.

The UEC method was applied in Ref. [126] to determine the structure and to recognize the orientation of aliphatic chains in a single bilayer of arachidonic (eicosanoic) acid (two  $C_{19}H_{39}COOH$  chains). These studies made it possible to determine the size of the molecular subcell ( $-CH_2-CH_2-$ ), to examine the structural dynamics of the bilayer on the substrate and the movements of its atoms; moreover, selforganization of the layers was also described [127].

All diffraction patterns consist of spots (and/or stripes) demonstrating a high quality of the two-dimensional crystalline structure of the arachidonic acid bilayer and the basal surface of hydrogen-functionalized Si (111). The diffraction patterns obtained at a negative delay time and the small angle of incidence of electrons in parallel and perpendicular directions give a near-zero chain tilt angle with the following bilayer subcell parameters:  $a_0 = 4.7$  Å,  $b_0 = 8.0$  Å, and  $c_0 = 2.54$  Å. Bilayer symmetry corresponds to rhombic packing R(001) with the (001) plane parallel to the Si(111) surface. These experimental values of lattice parameters differ from theoretical ones:  $a_0 = 4.96$  Å, and  $b_0 = 7.4$  Å [128]. The discrepancy is attributable to the fact that the predicted values were calculated for infinitely long aliphatic chains, disregarding the carboxylic end group of fatty acids. Moreover, the bilayer consists of only two monolayers, which accounts for the important role played by the substrate and deposition conditions (e.g., pressure or pH) in the location at the interface. Distance  $c_0$  between (CH<sub>2</sub>)-planes is consistent with the predicted value of 2.54 Å. The selective structural dynamics of the bilayer were investigated. Bragg spots became less pronounced as soon as  $\sim 1$  ps after arrival of a heating pulse. These changes were more noticeable over time (10-100 ps). Surprisingly, neither electron nor thermal pulses destroyed the bilayer due to their ultrashort length, as has been confirmed in many experiments.

The observed behavior of the diffraction pattern reflects the initial subcell expansion ( $\Delta c_0 = 0.1$  Å) in the bilayer after flash heating of the substrate followed by its restriction due to heat dissipation. The expansion occurs with a time constant of ~ 25 ps, whereas the same constant for subsequent contraction equals ~ 55 ps; a longer (restructuring) contraction occurs over the nanosecond range. No substantial changes manifested themselves in the plane perpendicular to molecular chains. It should be noted that the morphology and lattice parameters of the surface layer depend on the matrix and modification of the surface (see, for instance, Ref. [129]).

### 4.3 Time-resolved electron nanocrystallography

UED, UEC, UEM, and DTEM (dynamical transmission electron microscopy) techniques [34] permit directly observing structural changes in study objects in a real-time regime. They are currently applied in quantitative dynamic research of various phenomena in nanoobjects over pico- to femtosecond time intervals (see reviews [29, 130]). Recent studies have allowed significantly decreasing the paths of electron bunches and increasing the accelerating voltage [29, 130, 131]; as a result, femtosecond electron pulses have been generated. Electron pulse brightness was enhanced by the radiofre-



**Figure 17.** (a) Au nanoparticles (Au-NPs) are dispersed over self-organizing molecular interfaces. (b) Detection of the diffraction signal resulting from the photomechanical response of graphite multilayers. (c) Schematic of the UENC method. (d) Image obtained with a scanning electron microscope (SEM): 20-nm Au-NPs scattered on the substrate surface in the absence of buffering. (e) Diffraction pattern of 20-nm Au-NPs showing sites of Bragg signals from silicon substrate. (f) Rocking curves corresponding to the 20-nm Au-NPs diffraction pattern (figure e) with different values of the angle of incidence  $\theta_i$ . (g) SEM image of 20-nm Au-NPs with proper buffering. (h) Diffraction pattern corresponding to figure g and showing Debye–Scherrer diffraction rings and spots from the Bragg buffer layer (Si, N, C, and stack of layers in self-organizing aminosilane) (interval 2.2 Å, tilt angle 31°). (i) Rocking curve (figure h). (Taken from Ref. [136].)

quency electron grouping technique [132]. The electron field emission method was employed to increase spatial coherence [133, 134], and ponderomotive acceleration of the wave front to reduce the discrepancy between the velocities of light and electron pulses and electron bunch contraction [102]. These achievements considerably extended the scope of research on the coherent structural dynamics of nanomaterials with a femtosecond temporal resolution.

An important stage of nanoparticle research with the ultrafast electron nanocrystallography (UENC) technique is the preparation of the matrix surface for subsequent deposition of nanoparticles of interest. This stage is described in detail in review [135]. The effectiveness of the UENC technique was demonstrated in a number of graphite-to-diamond transition studies [136] and research on the photo-induced homogeneous structural transition of gold nanocrystals [137], interphase charge dynamics [138], and molecular electronics phenomena [139]. The high sensitivity and resolving power of UENC make the technique suitable for the

investigation of such processes as surface melting of nanoparticles, nonequilibrium structural dynamics of phase transformations, and the response of adsorbed molecules to nonequilibrium surface structural changes.

Reference [137] reports the use of the UENC method to study reversible surface melting and recrystallization of Au nanoparticles (2–20 nm in size) in the subpicosecond range with a spatial resolution up to several picometers (Fig. 17). Investigations into ultrafast photoinduced melting of nanoparticles under nonequilibrium conditions allowed distinguishing phases of initial lattice deformation, nonequilibrium electron–phonon interaction, the formation of collective bonds, and the breakdown of coordination among the atoms that transform nanocrystals into nanoliquids in the course of melting. Structural excitations in the pre-melting period and during coherent crystal-to-liquid transformation under conditions of phase coexistence during photomelting are different from the recrystallization process in which 'hot forms' of the lattice and liquid phase coexist as a consequence of thermal contacts. Importantly, the magnitude of structural changes and melting thermodynamics prove to depend on the size of nanoparticles [136].

The UENC technique is suitable for studying not only structural changes but also charge and energy redistribution at interphase boundaries (see review [135]). At present, it permits working at extremely low surface densities (~ 6 particles/ $\mu$ m<sup>2</sup>) and thereby creates conditions for examining individual nanoparticles. The advent of submicrometer diagnostic electron bunches may be expected to bring crucially new results in studies of the 4D dynamics of nanostructures by virtue of the combination of diffraction and spectral techniques with ultrahigh temporal resolution [103].

# 5. Diffraction of subpicosecond and femtosecond relativistic electron beams

Methods of ultrafast electron diffraction, crystallography, and microscopy were exploited in structural dynamics research on free molecules and condensed matter states, including coherent nuclear dynamics—from simple molecules to complex biological objects (see reviews [16, 26, 29, 31, 32, 34, 120, 135] and monographs [8, 33]):

• transfer of the energy of electronically excited atoms to the vibrational energy of photodissociation products;

• intermediate stages of molecular photoconversion reactions; conformer dynamics on complex potential energy surfaces;

- dynamics of water molecules on protein surfaces;
- interphase behavior of water molecules;
- dynamics of lipid bilayers and molecular ensembles;

• conformational transitions in protein, DNA, and RNA molecules;

• phase transitions including pre-melting and melting of nanocrystals;

- dynamics of crystal formation;
- crystal lattice dynamics;
- laser-induced oscillations in nanomechanical systems.

The principal goal of all these studies consists in elucidating the relationships between the main elements of the 'structure–dynamics–function' triad and thereby in reaching a new level of understanding and control of various physicochemical, chemical, and biochemical processes. Realization of this goal implies investigation not only of structural dynamics of starting compounds and intermediate (transient) states but also of the entire chain of transitions (molecular movies) [29, 31, 33]. However, most studies carried out thus far have not yet resolved these problems for the following reasons.

(1) Poor temporal resolution. The study of the coherent dynamics of nuclei in molecular systems requires a resolution of at least 10–100 fs, as has been shown in a number of publications since 1994 [15, 16, 140]. At the same time, the temporal resolution in all reported research designed to study the structural dynamics of various systems was no better than a few picoseconds. It may have been even worse bearing in mind the difficulty of measuring initial time  $t_0$  (see Section 2.3), controling the length of ultrashort electron pulses, synchronizing exciting laser and electron pulses, and maintaining the stability of experiments at large times of diffraction signal accumulation. Ultrashort laser pulses (10–50 fs) may be initially used to excite an object and generate ultrashort (femtosecond) electron pulses. However, such

factors as the substantial difference between group velocities of light quanta and electrons at the accelerating voltage of 30– 100 keV usually used in experiments, the smearing of electron bunches during their motion toward the object, target molecule delocalization in the case of TRED in the gas phase, and long electron paths in the sample (sliding reflection geometry) in UEC and UENC significantly increase the resolution time. As a result, the recorded diffraction patterns reveal structural and dynamic parameters of the study systems averaged over such long time intervals that details of the process simply escape observation. A similar situation takes place in the time-resolved X-ray diffraction method (see reviews [141–144]).

(2) The application of an inadequate electron scattering theory for the interpretation of diffraction data. The excitation of a study object by ultrashort laser pulses with high power density generates nonequilibrium distributions by electronicvibrational and rotational degrees of freedom. The departure from equilibrium may persist for a long time (up to nanoseconds); it is readily apparent in diffraction data as documented in a number of publications (see, e.g., Refs [15, 16, 140]). This fact requires radical modification of the theory and methodology for the interpretation of experimental findings. The traditional theory stemming from the classical work of Debye [145] and subsequently simplified to standard electron diffraction equations is widely applied today for equilibrium ensembles (see, e.g., monograph [111]). However, the use of standard equations for experimental data processing in structural dynamics research of nonequilibrium systems yields knowingly erroneous results [15, 16, 20, 33, 67–69]. Nonetheless, practically all known research carried out by relying on the UED, UEC, and DTEM methods has made use of various structural analysis options based on the Debye equation and its simplified versions proposed in later work [111]. Moreover, highly excited molecular vibrational states up to the dissociation limit are characterized by the largeamplitude motion of nuclei, which is not consistently regarded in the framework of the theory under consideration. For this reason, the results of research on the structural dynamics of free molecules require revision.

Considerable progress in the formation of short electron pulses and measuring their parameters has been achieved in the past 30 years since the publication of pioneering works [2– 5]. Simultaneously, methods for recording electron diffraction patterns have also been developed [26, 33, 84, 135, 146]. These achievements open up new possibilities for advancing structural dynamics research — further improvement of experimental techniques and methods for making 'molecular movies' with femtosecond resolution that allows one to represent real-time coherent nuclear dynamics by means of adequate analysis of a sequence of time-dependent diffraction patterns.

### 5.1 Experimental techniques

Three main lines of inquiry in developing the experimental technique for the ultrafast diffraction method may be distinguished now; they are intended for the achievement of femtosecond and attosecond resolutions:

(1) diffraction of relativistic bunches containing  $10^6 - 10^8$  electrons at an accelerating voltage of ~ 5 MeV and pulse length < 100 fs, which is attained under radiofrequency compression of the electron beam; the large number of electrons in a bunch permits us to obtain the diffraction pattern from a single pulse [34, 38, 81];

(2) diffraction of individual electrons with an energy of 30–200 keV at a high repetition rate of order 1 kHz and the large time of electron signal accumulation [8];

(3) temporal lens and nonorthogonal intersection of the wave front of exciting optical and probing electron pulses; diffraction of nonrelativistic low-intensity ultrashort electron pulses with a high repetition rate and oblique geometry of intersection of the wave fronts of electron and laser pulses, ensuring the pulse synchronization accuracy of < 1 fs despite the marked discrepancy between light and electron group velocities: 0.3–0.7 s at an accelerating voltage of 30–200 keV [101–104].

### 5.2 Diffraction of relativistic electron bunches

The formation of ultrashort electron pulses in electron beams is hampered by Coulomb repulsion leading to electron bunch decay. However, the Coulomb repulsion effects are weakened as electron energy approaches relativistic values. Moreover, a relativistic particle beam contains a magnetic force of interaction among particles moving in parallel with a charge of the same sign; this force essentially compensates for Coulomb repulsion. The repulsion weakens  $\gamma^2$  times ( $\gamma$  is a relativistic factor equal to the ratio of the particle energy to the rest energy). Magnetic attraction of the like charges propagating in the same direction keeps them from flying apart in the direction perpendicular to their motion; it is  $1/\gamma^2$ as intense as with motionless charges. Therefore, an electron traveling at the periphery of a relativistic electron beam is subject to force  $eE/\gamma^2$ , where E is the field strength of the infinite cylindrical electron beam. Moreover, Coulomb repulsion at high enough  $\gamma$  can be compensated for by external fields.

A new approach to the implementation of the ultrafast TRED method was proposed in Ref. [81]. The initial energy of the electron beam generated at the LINAC facility (Stanford University, USA) reached 50 MeV. The electron beam generated by laser photoemission from the copper cathode of LINAC was subjected to radiofrequency compression which makes it possible, in principle, to obtain ~ 100-fs electron pulses. An accelerating voltage of 5 MeV allowed reaching the relativistic velocities of electrons and shortening the time of bunch delivery onto the target, thereby reducing smearing of the electron beam during its transport to the scattering point.

The key element of the concept is radiofrequency compression of electron pulses, used in free electron lasers. The physics of these electron sources is well known and combines the following advantages:

(1) electron energies of 5–6 MeV are easy to reach. Intense well-collimated beams can be generated [34];

(2) the electric field strength in an electron gun may be higher than 100 MV m<sup>-1</sup>. This means that electrons reach relativistic energies as they travel a few millimeters. Since the electrons have relativistic velocities, Coulomb repulsion in the longitudinal direction ceases to play an important role in pulse broadening, because the pulse needed to alter the velocity of relativistic electrons is much higher than for nonrelativistic electrons. Moreover, relativistic beams are characterized by a relatively narrow velocity distribution, which accounts for the minimal broadening of the pulse during its motion from the cathode to the target. The length of an electron pulse subjected to radiofrequency compression may be smaller than that of a laser pulse [147]. Hastings et al. [10] obtained the diffraction pattern from a thin aluminum



**Figure 18.** Diffraction pattern from a 160-nm thick aluminum foil, obtained in the scattering of a single 500-fs electron pulse with an energy of 5.4 MeV (solid line). Dashed line is the calculated curve. The inset shows a two-dimensional image of the respective experimental and theoretical diffraction intensities [10].

foil (160 nm) under the action of a single  $\sim$  500-fs electron pulse (Fig. 18).

In other words, the authors of Ref. [10] were the first to show the possibility of obtaining the electron diffraction pattern from a single ultrashort pulse with an energy of 5.4 MeV. The employment of relativistic electrons significantly reduces space-charge constraints in comparison with lower-energy beams. A single 500-fs pulse contains a sufficiently large number of electrons to produce a diffraction pattern, despite a marked decrease in the scattering cross section of relativistic electrons.

A similar design of relativistic electron diffraction experiments is exploited in the UCLA Laboratory (University of California, Los Angeles, USA) [148, 149]. The characteristics of the machine making possible the generation of < 100 fs electron pulses are listed in Table 1 [150].

 Table 1. Comparative characteristics of traditional and relativistic TRED methods.

Parameter	Traditional TRED	Relativistic TRED
Energy, keV	20-300	$(3-5) \times 10^{3}$
Accelerating gradient near cathode, MV m <sup>-1</sup>	2-5	80-100
Number of particles in an electron bunch	$10^4 - 10^5$	$10^7 - 10^8$
Pulse length, fs	$\sim 10^3$	$< 10^{2}$
Typical Bragg angle ( $d = 2$ Å), mrad	10	0,5
Mean free path in Al, nm	20	200

The authors of Ref. [150] also developed a method for measuring the length of ultrashort pulses of relativistic electrons and demonstrated the dependence of the duration of laser emission on the electron bunch charge for different areas of the cathode photoexcitable region. The velocity of relativistic electrons is close to the velocity of light, which allows the difference between group velocities to be significantly reduced and thus improving the temporal resolution of the experimental setup.

### 5.3 Investigation of thin film and individual crystals

The exploitation of an apparatus for the relativistic TRED method [149] made it possible to obtain diffraction patterns from 200-nm thick titanium and aluminum foils during a single 100-fs pulse containing  $10^8$  electrons (Fig. 19).

Electron diffraction intensities at an accelerating voltage of 5 MeV were simulated in Ref. [81] to study the possibility of obtaining a diffraction pattern from a 150-nm thick aluminum foil under the effect of a single fs pulse containing  $10^7$  electrons. Such pulses can be generated by radiofrequency compression in a linear electron accelerator. First, the possibility of relativistic electron scattering on the 150-nm aluminum foil was evaluated. The main contribution was found to come from singly scattered electrons, although the contribution from double scattering was also significant and amounted to ~ 30% of the single scattering. The marked discrepancy between experiment and theory (see Figs 18 and 19) may be due to the effect of multiple electron scattering [81].

The first result of experiments on the structural dynamics of laser melting of individual Au crystals with the use of a  $\sim$  100-fs relativistic electron beam was obtained in Ref. [149] reporting on the laser melting dynamics of isolated gold crystals. The sample was excited by Ti-sapphire laser radiation: the pulse energy reached 2 mJ, the wavelength measured 800 nm, and the pulse length was 40 fs. Diffraction patterns were obtained using isolated 100-fs relativistic pulses containing 10<sup>7</sup> electrons each and generated at an accelerating voltage of 3.5 MeV (extraction field gradient > 75 MV  $m^{-1}$ ) with a subsequent radiofrequency compression. Twenty-nm thick gold foil was explored. Changes in Bragg peak amplitudes under the effect of heating and melting were studied by scanning the sample-exciting pulse. The experimental data were in excellent agreement with the twotemperature model of thin foil heating [151].

The observed behavior of Bragg peak amplitudes provides a direct test for understanding the processes of laserinduced heating and melting of an individual metallic crystal. The laser energy is absorbed by the 7–8-nm thick surface layer and thus creates a population of fast electrons that ballistically move in the sample with Fermi velocities [152]. The electron distribution is rapidly thermalized due to strong electron–electron scattering, which accounts for the homogeneous electron temperature throughout the sample by the end of a 40-fs light pulse, when electron and crystal lattice temperatures also become equalized by virtue of electron– phonon interaction. A good approximation holding after the initial few hundred femtoseconds is that of ballistic electron transport under changes of penetration depth of the laser excitation energy and the employment of the two-temperature model [151]. An increase in lattice temperature causes a loss of Bragg peak coherence. The thermal motion induced by electron–phonon interaction smears the atomic positions in a crystal and lowers Bragg peak amplitudes (Debye–Waller effect). Calculated changes in Bragg peak amplitudes in the framework of the two-temperature model for Au crystals are demonstrated in Fig. 20.

The best agreement with experiment is achieved when electron-phonon coupling parameter  $\lambda$  (an important quantity in the theory of superconductivity) takes the value 0.15. This observation is consistent with the literature data [153]. It was also shown that higher diffraction orders disappear sooner than lower ones, in accordance with the scattering vector dependence in the Debye-Waller factor. The lattice temperature increases to above the melting point when energy density rises to 35 mJ cm<sup>-2</sup>. In that case, the solid phase first undergoes overheating, and then phase transition occurs, as is apparent from the deviation of the Debye-Waller factor calculated in the two-temperature approximation within 12-18 ps after starting laser excitation of the sample (see Fig. 20). Because relativistic electrons penetrate deep enough into the sample, further studies might include observation of the dependence of laser radiation action on the film thickness.

# 6. Coherent nuclear dynamics of spatially oriented molecules in a laser field

Because of the chaotic orientation of molecules in the gas phase, unlike X-ray diffraction by a crystal, the electronographic technique *in the absence of additional information* (e.g., about equilibrium configuration symmetry of the study system, equivalence of certain chemical bonds, character of vibrational energy distribution) permits determining only a one-dimensional molecular structure or a set of internuclear distances. It restricts applications of the electron diffraction method for studying the structure and dynamics of complex



Figure 19. (Color online.) Diffraction pattern from a 200-nm thick titanium foil, obtained in the scattering of a single 100-fs electron pulse with an energy of  $\sim 5$  MeV (solid red line). The black dashed line is the calculated curve. Bars on the radial distance *r*-axis show the position of diffraction rings [149].



**Figure 20.** (Color online.) (a, b) Changes of normalized Bragg peak amplitudes in individual Au crystals: (200)—black squares, (220)—red circles, under the effect of laser pulses with an energy density of 10 and 35 mJ cm<sup>-2</sup>, respectively. Solid line—results of calculations based on a two-temperature model (TTM, Ref. [151])). (c) Normalized scattering intensity in the region with s = 0.42 Å<sup>-1</sup>. Formation of the peak of the liquid corresponds to the exponential function with a time constant of 10 ps [149].

polyatomic molecules. The solution of a structure-related problem even in the case of relatively small molecules implies the involvement of results obtained by other experimental methods, such as vibrational spectroscopy and/or quantumchemical computation.

X-ray crystallography is believed to be the most adequate tool for the elucidation of the structure of complex polyatomic molecules. However, this method can be applied only for the study of crystalline objects. Moreover, the local environment of a molecule distorts its structure and makes it difficult to study the nuclear dynamics.

A new approach to structural research based on isolated molecule irradiation by a large number of photons contained in a single X-ray laser pulse was proposed in Ref. [154]. The use of rather short laser pulses enabled the researchers to obtain diffraction patterns before the study system was destroyed. Diffraction patterns for micro- and nanometer objects were taken with femtosecond pulses of soft X-ray radiation [155–158]. However, this method is currently employed only in studies of fairly large objects, such as nano-sized particles.

An alternative approach takes advantage of the TRED method as applied to anisotropic ensembles ('oriented' molecules whose dipole transitions are oriented in the direction of polarization of the laser radiation) in the gas phase. The anisotropic environment of laser-excited molecules can be formed, for example, under the effect of fs pulses of polarized laser radiation. It was theoretically predicted in Refs [16, 28, 47, 159–162] that the electron diffraction pattern from 'oriented' molecules in the gas phase furnishes an



Figure 21. Schematic layout of the UED experiment designed to study anisotropic ensembles of laser-excited molecules. The inset schematically presents the temporal sequence of dipole transitions in sample molecules in the UED scattering volume. At t = 0, a vertically polarized laser pulse traverses the volume and creates a population of excited states composed of molecules with dipole transitions oriented largely in the vertical direction (dark lines). Rotation of excited and unexcited molecules with different angular velocities causes dephasing of oriented molecules and the loss of the initial order. The order can be restored on significantly longer time intervals for the wave packet rotational revival [28].

opportunity of determining not only internuclear distances but also valence angles.

The experimental layout is presented in Fig. 21. A linearly polarized laser pulse ( $\varepsilon$ ) excites molecules in the gas phase and the sample is diagnosed by an electron pulse generated with a given delay time. The laser and electron beams intersect at 90°. The electron pulse scattered from the sample is a bunch of electrons; its longitudinal extent is  $v\Delta t$ , where v is the electron velocity, and  $\Delta t$  is the pulse length. The pulse (electron bunch) leaving the scattering volume makes up the central core of unscattered electrons surrounded by the expanding cloud of scattered electrons of varying intensity, shown in the figure in the form of rings. The electron diffraction pattern is taken far from the scattering center in a relatively small region of scattering angles on a flat detector, the center of which coincides with the incident beam axis. Each point on the detector is characterized by scattering angle  $\theta$  and azimuthal angle  $\phi$ , corresponding to the wave vector **k** and the momentum variation vector s. The radial distance between the registration point and the center of the unscattered beam denoted by s' is presented in the figure as the expression through quantities s and k; the camera distance between the scattering point and the center of the diffraction pattern on the detector is denoted by L.

The theory was first confirmed experimentally in Refs [163–165] for adiabatically oriented  $CS_2$  molecules using the TRED method with a resolution of 10 ns.

To elucidate the structure of organic molecules, such as low-molecular weight proteins scarcely amenable to crystallization, the authors of Ref. [166] used a jet of liquid gel droplets and a continuous electron beam producing a diffraction pattern. Organic molecules, e.g., small proteins, in a droplet or inside a glassy ice shell can be spatially oriented under the effect of polarized radiation of a powerful continuous wave laser. Iterative methods for solving the phase problem have been proposed.

### 6.1 Illustration of peculiarities

### of a diffraction signal for excited molecules

The division of a diffraction signal obtained in scattering of fast electrons from a molecular ensemble into incoherent 'atomic' and coherent 'molecular' constituents,  $I_{\text{total}}(s) = I_{\text{atomic}}(s) + I_{\text{mol}}(s)$ , is a mathematical construction allowing the oscillating component to be separated from the overall scattering intensity  $I_{\text{total}}(s)$  which rapidly decreases with increasing *s* (roughly as  $s^{-6} - s^{-7}$ ). However, it is a simplified representation; it would be wrong to state that the scattering by a molecular ensemble consists of different additive constituents, i.e., atomic and molecular contributions. Rather, the diffraction signal is the Fourier transform of a molecular structure, defined by the total molecular function of probability density, including electronic, vibrational, and rotational constituents, as well as their interaction.

The small modulation depth of the observed diffraction signal for molecules in the gaseous phase is related to orientational averaging over the isotropic molecular ensemble and to the fact that the probability density of internuclear distance distribution for equilibrium ensembles (averaged over ensemble temperature) is the Gaussian function. It is therefore interesting and instructive to consider diffraction patterns resulting from the excitation of concrete, wellspecified quantum states in a molecule. Such results were obtained for CS<sub>2</sub> molecules in certain vibrational states [161]. It was shown that motions of carbon and sulfur atoms are manifested in wave function oscillations. The mass of sulfur being much larger than that of carbon, the latter's shift is significantly greater: in fact, the hydrogen atom oscillates between sulfur atoms that reside virtually in a stationary state. Vibrational excitation of molecules in such a state introduces additional modulations into diffraction patterns [161].

Figure 22 illustrates resulting diffractograms from molecules fixed in concrete orientational states with respect to the incident electron beam and the outcoming scattered beam. When  $CS_2$  molecules are oriented perpendicular to the directions of observation (X) and the electron beam (Z), the molecular constituent of the diffraction intensity barely contains any structural information, i.e., waves scattered by each atom are (almost) always in phase (middle frame). The excitation of symmetric or antisymmetric stretching vibrations in a molecule causes no changes. Conversely, the excitation of the bend vibration (blue dashed line) leads to small modulations in the diffraction pattern.

In electron scattering in the X-direction from  $CS_2$ molecules oriented in the same direction (top frame in Fig. 22), the diffraction signal is more sensitive to the molecular structure, as is apparent from the rapidly oscillating intensity for the molecular ground state (black solid line). Excitation of either symmetric or asymmetric valence vibration causes additional intensity oscillations readily distinguishable in the diffraction pattern. In this geometry, the excitation of bend vibrations does not lead to changes in the diffraction pattern compared with the ground state. However, it does induce modulation in the diffraction pattern from molecules oriented toward the electron beam (bottom frame).

These concepts are easy to extend to diffraction intensities of large vibrationally excited molecules. References [159–161] present the results of calculations for molecules containing the six-membered aromatic ring of S-tetrasine  $(C_3H_3N_3)$  in the excited electronic state  $S_1$ . The diffraction signal that could be obtained were the molecules fixed in concrete orientations with respect to the incoming and scattered electron beams would have a well-structured character.



Figure 22. (Color online.) Diffraction patterns produced with different vibrational excitations of a  $CS_2$  molecule fixed in a given orientation (a). Figure (b) shows molecular components of diffraction patterns for the  $CS_2$  molecule in the ground vibrational state when four quanta of symmetric valence (s.s.), antisymmetric valence (a.s) and deformation (bend) vibration are excited [161].



**Figure 23.** (Color online.) Difference diffraction patterns between the ground and excited states of an S-tetrasine molecule. Polarized laser radiation excites distinguished vibronic states in the ensemble of isotropically oriented molecules. *X*-axis — angle of rotation about the electron beam at the angle  $\alpha = 0^{\circ}$  of laser radiation polarization; *Y*-axis — projection of vector **s** onto detector plane [160].

Vibrational excitation of a polyatomic S-tetrasine molecule introduces additional features in the diffraction signal structure due to variations of the probability density function of internuclear distance distribution for vibrationally excited molecules. Changes in the diffraction pattern, in contrast to the ground vibrational state, is inherent in isotropic ensembles excited by linearly polarized laser radiation introducing essential anisotropy and allowing the observation of the excitation of individual vibrational modes. This phenomenon for different vibrational movements in the excited  $S_1$ -electronic state of S-tetrasine is illustrated in Fig. 23. It is noteworthy that, similar to a linear CS<sub>2</sub> molecule, the bending strain of the cycle oscillation plane (vibrational mode 16a) produces a signal qualitatively different from the diffraction signal of valence vibrations excited in the cycle plane (vibrational modes 1 and 6a).

### 6.2 Orientation of molecules in a strong laser field

Let us consider a molecular ensemble in the ground electronic and vibrational states. It can be obtained by cooling the molecules in a pulsed gas jet when the gas enters the vacuum chamber through a small opening. In the pulsed regime, the vacuum pump load (i.e., the pumping rate) can be decreased.

Molecules in a jet are akin to a crowd of people on a subway station escalator during rush hour, i.e., the trajectory of each passenger is totally determined by the motion of the crowd, while the movements of individual persons are reduced to a minimum. Molecules in a prepared-for-use ensemble reside in different rotational states. It is well known that differences in energy between the neighboring levels linearly increase with an increase in the angular momentum of a molecule. But the picture changes when molecules are subjected to powerful linearly polarized laser radiation. (To recall, laser radiation must not cause strong ionization of molecular systems.) The molecular spectrum in a strong laser field transforms into a spectrum with equidistant distribution [167]. It turns out that a three-dimensional spatial distribution of molecules in a linearly polarized strong EM field tends to the one-dimensional case, i.e., the molecules are oriented in the laser field [168] but oscillate.

This is easy to understand from the following simple considerations. The electron polarizability of a molecule,  $\alpha_{\rm pol}$ , relating the induced dipole moment of the system to the external field amplitude is an anisotropic function. For example, the polarizability of the simplest (diatomic) structures along the molecule axis is  $\sim 1.5-2$  times that in the perpendicular direction. Therefore, when such molecules are aligned in the external field, their potential energy is minimum. In most cases, when laser radiation is out of resonance with electronic-vibrational transitions, it is convenient to make calculations taking into account only the static susceptibility of electrons instead of  $\alpha_{pol}$ . It should be emphasized that such aligned molecular states exist only for a very short time. The alignment rapidly disappears after the end of the laser pulse, and the ensemble ceases to be quasione-dimensional. Nevertheless, the alignment can be restored The region of interaction with the target is 100  $\mu m$  in diameter. The temporal resolution is 850 fs.



**Figure 24.** Alignment of molecules in a strong laser field. The first experiment in the gas phase with subpicosecond resolution [173].

under certain conditions, even in the absence of a laser pulse. Alignment is easier to perform for molecular beams where rotational temperature  $T_{\rm rot} \sim 10$  K and only several rotational states are excited. Theoretical and experimental studies in this field are reviewed in paper [169].

The process being considered is of interest for many applications, such as control of chemical reactions, simplification of analytical procedures (one-dimensional distribution instead of three-dimensional), and observation of molecule behavior in a strong laser field (generation of higher harmonics, investigation of photoionization of molecules upon a change in their orientation with respect to the axis of polarization of ionizing laser radiation, etc.).

Thus, molecules can be aligned in a linearly polarized laser radiation field. But what will happen if the axis of laser radiation polarization starts to rotate? Such a situation can be realized in experiment by adding two specially chirped laser beams [170, 171]. It turns out that under certain conditions (cold enough starting molecules and a rather intense laser field) many molecules of the ensemble begin to rotate with an acceleration following the laser field. Such molecular 'propellers' or superrotors can dissociate and even break down into atomic fragments after a sufficiently high rotational energy is acquired [171]. The current state of research in this very promising area of molecular physics is described in Ref. [172].

The alignment of molecules in a laser field is of great interest, since it can be used to restore their three-dimensional structure by the ultrafast electron diffraction method [173]. It was the first UED experiment with subpicosecond resolution using spatially oriented free polyatomic molecules and it produced an impressive result by showing that no additional parameters for restoration are needed if the molecules are aligned in a strong laser field (Fig. 24).

### 6.3 Spatially oriented intermediate structures in the absence of external orienting fields

It was mentioned in Section 6.2 that molecules can be spatially oriented by applying active laser excitation [169]. At the same time, oriented transient compounds can also be obtained by selective laser dissociation [162]. To form diffraction patterns in the early period, i.e., before the onset of dephasing of the particles under study due to their rotation, it is necessary to take advantage of ultrashort electron pulses.

Diffraction patterns from oriented intermediate products of 1,2-diiodotetrafluoroethane  $(C_2F_4I_2)$  photodissociation were first observed in Ref. [174]. The bond breaking resulted in a clear-cut signal in the time-dependent diffraction pattern, which simplified the study of the spatial orientation effect of a transient compound monoiodotetrafluoroethane (C<sub>2</sub>F<sub>4</sub>I). The photoexcited molecules dissociated under the action of a linearly polarized fs laser pulse. The respective absorption cross section is proportional to  $\cos^2 \alpha$ , where  $\alpha$  is the angle between the directions of laser radiation polarization and the transition dipole moment.

A supersonic gas jet was input into the vacuum chamber through a de Laval nozzle. The gas flow containing  $C_2F_4I_2$ molecules in buffer helium ensured rotational cooling. The calculated rotational temperature was equal to 168 K. The third harmonic of laser radiation with a wavelength of 800-267 nm (100  $\mu$ J), pulse length of 50 fs, and pulse repetition rate of 1 kHz was utilized. Laser UV radiation was focused to a beam 200 µm in diameter and directed inside the gas jet to excite the photodissociation reaction. A small part of the total laser pulse energy was split off and used to trigger the electron emission from the photocathode. An electron bunch containing some 10,000 electrons was accelerated to 29 keV prior to gas jet passage. Gas jet and electron and laser beams were mutually orthogonal. The primary electron beam was blocked, and the diffraction pattern was recorded by a CCD camera, into which it entered after passage through the fiberoptic system equipped with a luminescent screen. The electron pulse length at the target was 2.3 ps. The overall temporal resolution of the system amounted to 4 ps due to the discrepancy between electron and laser pulse velocities.

Figure 25a presents the resultant difference values, i.e., variations of the molecular constituent of scattering intensity,  $\Delta sM(s, \phi, t)$ , depending on the delay times between the exciting laser pulses and probing electron pulses. The intensity curves for unexcited molecules were consistent with the available data for  $C_2F_4I_2$  [175]. Figure 25a corresponds to  $\Delta sM(s, \phi, t = 0)$  for near-zero time delays. At this early stage, the dissociation signal is rather weak, as determined by the characteristic response time of the UED unit [174], but the diffraction pattern is strongly anisotropic. The scattering intensity is significantly higher in the direction of laser radiation polarization. This means that dissociated molecules are oriented along the direction of laser radiation polarization. The difference intensity curves computed on the assumption that only 1/3 of the starting molecules dissociated are in excellent agreement with experiment. The results presented in Fig. 25a can be utilized to calculate the degree of spatial orientation of C<sub>2</sub>F<sub>4</sub>I radicals,  $\langle \cos^2 \alpha \rangle = 0.5$ , which appears to be close to the theoretical value of 0.6 for the model under consideration. This value characterizes the mean magnitude of the orientation effect with respect to laser beam polarization. The value of  $\langle \cos^2 \alpha \rangle = 1/3$  corresponds to an isotropic ensemble, while the value of  $\langle \cos^2 \alpha \rangle = 1$  to a fully oriented ensemble. Figure 25b gives the results for a longer period, when anisotropy becomes weaker but is still apparent. The respective theoretical dependence was calculated as the weight-average between anisotropic and isotropic ensembles on the assumption that 2/3 of its molecules are randomly oriented with respect to the direction of laser beam polarization. Figure 25c presents the values of  $\Delta sM(s, \phi, t)$  at t = 8.3 ps. The diffraction pattern becomes isotropic. Rotation of the molecules leads to disappearance of their alignment in the polarized radiation field. Theoretical diffraction intensities depicted in Fig. 25c are calculated for an isotropic ensemble on the assumption that all C<sub>2</sub>F<sub>4</sub>I radicals were converted into the end product  $-C_2F_4$ .



**Figure 25.** Time-resolved 2D diffraction patterns. (a)  $\Delta sM(s, \phi, t)$  for a near-zero delay time between the exciting and diagnostic pulses: difference diffraction pattern is a result of averaging of electron scattering intensities over a 0–1.7 ps delay time range. Arrow indicates direction of laser radiation polarization. Top left panels of the figures present experimental results, bottom right panels show calculated values. The dark stripe in the center is due to projection of the initial beam stop. (b, c) The quantity  $\Delta sM(s, \phi, t)$  is a result of averaging of electron scattering intensities for 3.3–5.0 ps and 8.3–28.3 ps delay time ranges, respectively [174].

Analysis of TRED data in paper [174] showed that the spatial orientation of radical  $C_2F_4I$ , the initial product of  $C_2F_4I_2$  photodissociation, occurs almost instantaneously after the iodine molecule splits off. The spatial orientation of  $C_2F_4I$  molecules is characterized by a time constant of 2.6 ± 1.2 ps.

# 7. Ultrafast electron microscopy — a tool of the 21st century

The development of the ultrafast electron diffraction method for research on the coherent nuclear dynamics of molecules and condensed matter [33] made it possible to replace the electron diffraction apparatus by a more sophisticated instrument, the electron microscope [29, 34]. The first transmission electron microscope was adapted to observe fast processes at the beginning of the 21st century at the laboratory headed by Ahmed H Zewail in the California Institute of Technology. This approach is known now as 4D UEM. Initially, it was a 120-keV electron microscope, and 200-keV apparatus was developed later. An advantage of the approach is the fact that it extends the scope of research beyond the observation of electron diffraction alone [8, 33].

### 7.1 Phase transition in thin films

It is well known that vanadium dioxide  $(VO_2)$  undergoes a first-order phase transition from the low-temperature monocline phase (M) to the high-temperature tetragonal rutile phase (R) at  $\sim 67 \,^{\circ}$ C. This transition has been a subject of intensive research by various methods since its discovery almost half a century ago. It was examined for the first time by the 4D UEM method in work [176]. The sample was irradiated by femtosecond NIR laser pulses and simultaneously by single electron probe pulses. The microscope can be operated either in the nominal regime using a continuous beam or in the pulsed beam regime. In both diffraction patterns (atomic scale) and UEM images (nanometer scale), the structural phase transition in VO<sub>2</sub> nanoparticles appears (Fig. 26). Vanadium atoms in the experiment first move apart from one another for a very short time but then begin moving to their final location. Investigations of phase transition by the example of a vanadium dioxide sample proved successful





**Figure 26.** (a) Images obtained by the UEM method before (left) and after (right) phase transition in VO<sub>2</sub> films with a magnification of 42,000 (the scale corresponds to 100 nm). (b) Diffraction patterns obtained by the UEM method before (top) and after (bottom) phase transition in VO<sub>2</sub> films. Left panel—comparison of experiment (left) and theory (right) [176]. The 'pen' on the right side is a blind covering the zero (brightest) electron diffraction order.

and have good prospects. They showed, in particular, that the 4D UEM method can be employed to study ultrafast metal-dielectric phase transitions.

### 7.2 Visualization of nanostructure motion: from cantilever to 'musical nanoinstruments'

The advent of the UEM apparatus made possible direct observations of vibrational movements of nanostructures in the ultrasonic range that spans the frequencies from kilohertz to gigahertz [177]. To recall, optical interferometry methods do not ensure complete three-dimensional spatial resolution, whereas the potential of standard electron microscopy is restricted by temporal resolution at the level of  $\sim 30$  ms.

The authors of Ref. [177] made use of a quasi-onedimensional molecular material, a Cu(TCNQ) crystal with strongly anisotropic electrical and optical properties (TCNQ — 7,7,8,8-tetracyano-p-quinodimethane). It was revealed that filamentary microcrystals of the quasi-onedimensional semiconductor Cu(TCNQ) produce an optomechanical effect that can be applied in nanotechnologies. Irradiation of microcrystals by laser pulses lengthens their filaments, completely restoring their initial size after the pulse cessation. When a crystal is destroyed by a laser pulse, a  $10 \times 100$ -nm crevice forms at the fracture site. The crevice closes under the effect of laser irradiation and the crystal expansion, but develops again and comes back to its initial size after irradiation is completed. In other words, the effect is reversible.

Changes in crystallite parameters are attributable to the fact that the laser energy knocks electrons out of the Cu(TCNQ) molecules making up the crystal lattice. These electrons are partially captured by TCNQ fragments, and their charge distribution alters. As a result, the molecules lose their dipole moment, with a consequent their reorganization and a build up of sizes of the whole body, while the entire ensemble enlarges. In this case, the degree of crystal expansion must depend on radiation intensity. Cu(TCNQ) molecules were used for creating nano- and microcantilevers as thick as 300 nm and 2 µm, respectively. In such crystals, the optomechanical motion is initiated by a charge transfer from (TCNQ) to copper Cu(I). In experiments, the charge transfer occurred when the crystal was irradiated by 670-nm laser pulses. The resulting movements of the cantilever were visualized by a pulsed photoelectron beam with an energy of 120 keV. These data allowed determining the Young's modulus, measuring the resonance oscillation frequencies of the sample, and calculating the energy stored in the course of optomechanical expansion of the crystal under study.

Similar experiments were continued somewhat later with other materials. Specifically, photoelectron bunches with an energy of 200 keV were utilized to visualize the mechanical oscillations of a very thin (75 nm) graphite sheet in the submillisecond range, subjected to pulsed laser irradiation at a wavelength of 532 nm [8]. Initially, i.e., immediately after pulsed laser heating, individual groups of carbon atoms in the membrane (respective modes) were found to vibrate in a random order. But after a few dozen microseconds, the corresponding modes of the membrane began to be synchronized, resembling a drumbeat with a frequency of around 1 MHz.

The success with graphite nanosheets inspired the search for other musical nanoinstruments. A 'harp' and a 'piano', constructed at the nanoscale, were made using arrays of cantilevers. They were prepared by microstructuring multilayer workpieces of Ni/Ti/Si<sub>3</sub>/N<sub>4</sub> using sharply focused ion beams [178]. The workpieces consisted of 30-nm thick layers of nickel and titanium sequentially deposited onto a 15-nm Si<sub>3</sub>N<sub>4</sub> film. For the piano, the cantilevers had almost the same lengths, approximately 4.6  $\mu$ m, but their width varied from about 400 nm to 2.3  $\mu$ m. In the harp, the lengths and widths of individual elements varied in the range of 1.2–9.1  $\mu$ m and ~ 300–600 nm, respectively.



**Figure 27.** Ultrafast spectral visualization. The change in electron kinetic energy (electron spectrum) was measured as a function of the delay time between an exciting fs laser and probing electron pulses for each position of the probe (electron 10-nm pulse). Energy gain was measured in units of laser radiation quantum, hv = 2.4 eV [181].

A 'musical nanoinstrument' was first irradiated by nanosecond pulses of the second harmonic with a fixed repetition rate from an Nd:YAG laser. Heating of a sample consisting of layers with different thermal expansion coefficients caused mechanical deformation of its material which triggered vibrations of the instrument that were probed by photoelectron bunches generated by the treatment of the photocathode with the fourth harmonic of the Nd:YAG laser.

In the next series of experiments, the use of femtosecond laser radiation with a megahertz repetition rate ( $f_{\text{las}} \sim 25 \text{ MHz}$ ) of laser pulses made it possible to 'play' the instruments. A fiber laser generator with a tunable pulse repetition rate was tapped for this purpose. The pulse energy density ranged 20–30 µJ cm<sup>-2</sup>. Changes in  $f_{\text{las}}$  'triggered' different resonance frequencies of the nanodevices; their effect was apparent afterwards in micrograms obtained with the help of the electronic pulse technique.

Apart from a purely academic interest, the abovementioned musical nanosystems can have very specific applications. As an example, the authors of paper [178] report that such layered nanostructures can be utilized to precisely measure the temperature with a spatial resolution at the level of  $10 \,\mu\text{m}$  in combination with a microsecond temporal resolution.

#### 7.3 4D electron tomography

Electron tomography has been rapidly developing since the 1960s [179]. The progress in this field was mainly determined by the development of the electronic computing devices [179] needed to process a huge number of two-dimensional images and combine them into a single movie. Modern laser technologies allowed adding the fourth dimension, time, to electron tomography, thereby creating a unique technique.

4D tomography was applied by Kwon and Zewail [180] to study the nonstationary behavior of a carbon nanotube (CNT) some 4.4  $\mu$ m in length twisted in the form of a bracelet. Probing electron pulses with an energy of 200 keV were utilized. Femtosecond laser excitation caused CNT heating and, therefore, structural changes that started to appear at a picosecond time scale. A series of electron micrograms was obtained at different angles  $\alpha_{CNT}$  and delay times. In Ref. [180],  $\alpha_{CNT}$  varied in a range from  $-58^{\circ}$  to  $58^{\circ}$ (0° corresponded to the normal electron pulse incidence on the bracelet-shaped CNT) with an increment of 1°; the number of two-dimensional electron images amounted to 4000. The spatial resolution reached in the experiment proved sufficient to obtain correct images of the channels with a diameter of  $\sim 10$  nm, and thereby to visualize pico- and nanosecond mechanical oscillations of the carbon nanobracelet. To recall, the demonstration experiment [180] introduced no irreversible changes to the nanotube structure. The total dose delivered to the carbon sample during the experiment was approximately two orders of magnitude lower than the one needed to cause its irreversible deformation. This became possible mostly due to the extremely high detection effectiveness reached in the 4D electron microscope. The results [180] seem to have been interesting to a narrow circle of electron optics specialists, whereas a broad audience was more excited at the prospects of creating a video and, thereafter, a real atomic movie based on the achievements of 4D electron tomography.

### 7.4 Electron microscopy

### with high spatial-temporal and spectral resolution

It was mentioned in the preceding paragraphs that the combination of spatial nanoresolution and subpicosecond (femtosecond in the future) temporal resolution constitutes the basis of the atomic movie. However, the potential of an electron microscope of the new generation operating with ultrashort photoelectron pulses is higher than that. Measurements of the kinetic energy of electrons that pass through a sample by a commercial energy analyzer make it possible to determine the spatial, temporal, and spectral characteristics of the sample within a single experimental cycle. Notice that such an experiment is a serious challenge for the majority of modern research laboratories; hence, the importance of a precedent in this field.

This idea was realized by Yurtsever et al. [181] using a single metallic nanostructure (a triangular silver particle of characteristic length 130 nm and thickness 20 nm) previously placed on a graphene substrate (Fig. 27). The sample was irradiated by 520-nm fs laser pulses to excite plasma oscillations in the silver, which were probed with a beam of ultrashort electron bunches 10 nm in diameter that could be moved over the sample surface. The energy gain of the electrons that pass through the sample was measured, as were the *usual* spatial and temporal characteristics.

It should be emphasized that a field localized on the surface of a metal particle may cause electrons not only to lose kinetic energy as in an ordinary transmission microscope but also to acquire it. In principle, this process can be controlled by tuning the laser wavelength, the accuracy of  $\sim 1$  meV being determined by the laser pulse spectral width.

In this way, the plasmonic relief created by a femtosecond laser on a silver surface was measured. The data obtained clearly demonstrate that the plasmonic oscillation field excited by laser radiation is concentrated near the vertices of the triangular particle, in excellent agreement with the theory [181]. In other words, the first measurements of the sample in the 5D continuum encompassing space, time, and energy (spectrum) proved successful. But, what is their immediate utility in terms of applications?

It turns out that the method developed in work [181] permits us to determine the length of probing electron bunches. According to report [84], 0.4–0.6-ps long photoelec-

tron pulses can be generated in a 200-keV transmission electron microscope. This result demonstrates the possibility of diagnosing probe pulses without considerable modification of the microscope column.

A question is in order: Is it really necessary to employ ultrashort electron pulses in a modern microscope? Let us resort to an analogy. As is well known, photography mostly utilizes pulsed light beams transmitting information to a film or a matrix. Otherwise, optical visualization of many processes produces blurred images. For example, a long exposure photograph of a night city street is a blurred, even if artistically impressive, picture.

The history of microscopy reveals a tendency toward the enhancement of its resolving power. The electron microscope in the midtwentieth century was only slightly better than its optical analog. The introduction of electronic optics correcting aberrations at the dawn of the 21st century [182, 183] ensured atomic-scale spatial resolution of the electron microscopy. This, in turn, required the employment of ultrashort electron beams to avoid the distortion of images with an unprecedentally high degree of refinement.

To conclude this section, it should be noted that a commercial electron microscope adapted to study ultrafast processes usually operates in a single electron probe pulse mode, which allows Coulomb repulsion between particles in the beam to be neglected. This ensures nominal functioning of the magnetic lenses controling electron beams of standard low intensity and prevents smearing of electron bunches. In the limiting case, such a 4D microscopy actually operates with single-electron wave packets. As far as we know, however, their correct description, unlike that of multielectron wave packets, encounters serious difficulties. Is it possible to 'discover the electron again' by systematically observing its interactions with matter undergoing ultrafast changes? In other words, can some new, unusual properties of singleelectron wave packets be expected to emerge if an adapted transmission electron microscope is exploited as a testing device? Naturally, an affirmative answer to these questions would be a pretty bold claim. The identities of a new type recently reported in Ref. [184] allow densities of local pseudopulses to be transformed into the local pulse density in the analysis of electron wave packet dynamics, substantially simplifying their description.

### 8. Complementarity of spectral and diffraction techniques for studying the structural dynamics of matter

The preceding sections were designed to review current research on dynamic processes (including, in the first place, the structural dynamics of matter) by the ultrafast electron diffraction method and microscopy. It should be recognized, however, that a wealth of data in this field has thus far been obtained by light microscopy rather than its electron analog. A variety of optico-spectral techniques have been applied for the purpose. The history of structural dynamics research goes back to pulsed photolysis (flash photolysis) proposed in the late 1940s-early 1950s (see lecture [185]), which found wide prevalence and recognition (Nobel Prize in Chemistry 1967). Even with the adoption of classical light sources (flash lamps), this method allowed identifying intermediate products of photoinduced reactions with a temporal resolution up to the submicrosecond level. The advent of lasers with wide frequency tuning ranges, generating short light pulses, made it possible to develop a large number of methods for laser spectroscopy and to turn to the investigation of dynamic processes with femtosecond temporal resolution. The description of these techniques and their applications is beyond the scope of this review, because they are covered in the voluminous literature. By way of example, it can be found in a valuable monograph [186]. We confine ourselves to a brief discussion of problems closely related to the topic of the present work, such as first of all relaxation processes and intramolecular dynamics associated with the ground electronic state of the molecule.

The advent of pulsed tunable IR lasers made it possible to initiate research on the processes associated with excited vibrational states in molecules due to direct excitation of their nuclear subsystems. This first of all promoted investigations into the collisional relaxation of vibrational excitation, including V–V exchange and V–T/R relaxation (see reviews [187, 188]). The employment of the IR multiple photon excitation (IR MPE) effect (see monograph [189] for details) made possible the investigation of relaxation processes in highly excited molecules. Specifically, it was shown in paper [190] that the rate of vibrational-translational (V-T/R)relaxation is the nonlinear function of the level of vibrational excitation in the molecules. The harnessing of the IR MPE effect made it possible to undertake (apparently, for the first time) an experimental study of intramolecular vibrational relaxation (IVR) that reflects stochastization of the vibrational motion of the nuclei in many-atomic molecules. (See Refs [191, 192] for more details on IVR processes and stochastization.) Reference [193] reported the first observation of the stochastization limit of vibrational energy. Subsequently, with the appearance of lasers generating ultrashort pulses, it became possible to use the methods of IR and RS (Raman scattering of light) spectroscopies to study IVR dynamics with ps and fs temporal resolutions. A detailed analysis of the results obtained in this field can be found in review [194].

In the excitation of vibronic states, in particular, in a simple diatomic molecule, the spectroscopic signal reflecting the wave packet dynamics can be related to the molecular structure dynamics [72]. The situation is complicated when the number of atoms increases and the retrieval of structural dynamics information becomes a difficult task, even for simple polyatomic molecules, let alone macromolecules [32, 33, 68, 69]. This can be accounted for by the fact that optical spectroscopy probes valence electron states affecting many parts of the molecular system. Therefore, they are only indirectly and ambiguously related to nuclear subsystem dynamics, with the exception of some favorable occasions that can be studied by vibrational spectroscopy [195–200] or coherent multidimensional spectroscopy [201-203]. Hence, the necessity of alternative or auxiliary methods directly providing information on the structural dynamics, such as those known under the general name of X-ray absorption fine structure (XAFS) methods for fine-structure research of the X-ray absorption spectrum in the vicinity of absorption jumps of the elements contained in the sample [204, 205].

X-ray absorption spectra at certain photon energies are known to have sharp edges (indicative of a sudden increase in absorption) called absorption jumps. When the energy of photons is slightly higher than the absorption edge energy, they can trigger ionization of inner electron shells of the atoms or ions and thereby generate photoelectrons with a certain energy. These photoelectrons travel in the vicinity of a resonantly absorbing (i.e., with a jump due to the production of a photoelectron) atom, undergo scattering by the surrounding electron density bunches (electron shells of nearby atoms/ions), and return to the site of origin by the end of the relaxation process, bringing with themselves information about neighbors (their type, number, and distance from the reference atom). This information is apparent as spectrum undulation in the  $\pm 40$  eV region with respect to the absorption jump that extends roughly1000 eV further. All this is generally called the XAFS spectrum [204, 205]. Given a theory describing this X-ray photoeffect from photon absorption to relaxation of the excited atom, a model of the process can be improved, taking account of the mutual arrangement of scattering atoms and the absorbing one, i.e., a short-range order structure can be determined. Such XAFS theory is presently well elaborated and widely applied for structural analysis of various substances based on the fine structure of their absorption spectra [204, 205]. Even this concise elucidation of the XAFS method sense implies that its experimental realization, i.e., detailed measurement of the absorption spectrum over a 1000-eV interval, requires the application of a specific probe, such as an X-ray beam either with a wide continuous spectrum or with a spectrum finely tuned in a broad energy range. Synchrotrons that became available for research in the early 1970s proved the most suitable radiation sources for such measurements. Since that time, the theory and instruments for the XAFS method have been rapidly developing [204, 205].

Although XAFS methods permit us to study only shortrange order structures at distances smaller than the mean free path of a photoelectron in a sample, they attract much attention from materials science specialists. To begin with, they can be applied to study matter in any aggregate state. Second, the measuring systems are very simple, requiring no sophisticated goniometers and vacuum equipment; suffice it to have a sample holder or a point detector measuring X-ray beam intensity before and after its passage through the sample.

The distribution of an EXAFS (extended X-ray absorption fine structure) signal can be tapped to mathematically calculate such characteristics as the distribution function  $g_{\alpha\beta}(r)$  of a pair of atoms  $\alpha$  and  $\beta$  of the system in the direct space. When function  $g_{\alpha\beta}(r)$  or a combination of partial functions  $G_{\alpha}(r)$  for concrete atoms or ions  $\alpha$ , and even full functions G(r) for all elements in a liquid are known, they can be utilized to determine interatomic distances, coordination numbers, and the degree of local order around the atom of interest. Analysis of the near-threshold region by the XANES (X-ray absorption near edge structure) method is essentially different from the analysis of the extended region by EXAFS.<sup>11</sup> XANES spectra can be sensitive to oxidation states [204, 205].

<sup>&</sup>lt;sup>11</sup> The difference between the EXAFS and XANES methods is especially well apparent when de Broglie wavelength  $\lambda_D$  for photoelectrons resulting from X-ray irradiation of a material is considered. If the quantum energy is close to (slightly higher than) the absorption edge for a given chemical element, the energy of produced photoelectrons is low and, accordingly,  $\lambda_D$  is high and may exceed the characteristic interatomic distance in the sample (XANES). In this case, multiple photoelectron scattering from the surroundings needs to be taken into consideration. In another limiting case (EXAFS), when the de Broglie wavelength is shorter than the characteristic interatomic distance, only single scattering can be regarded in the first approximation.

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The analysis of EXAFS data yields characteristics of the local environment of a selected absorbing atom, i.e., the type, number, and separation of back-scattering atoms from the resonantly absorbing reference atom. Notice that the scattering atoms should not be necessarily chemically bound to the absorbing atom. The distance measurement error in this method is usually about  $\pm 1\%$  within a 6-Å radius. However, the error in the measurement of the coordination number may be large and strongly depends on the system under study. Therefore, a comparison with other methods is highly desirable for the correct interpretation of EXAFS data and obtaining realistic results. Because the fine structure being observed is related to the absorption edge of a concrete type of atoms and the absorption edge energy depends on the chemical element and the degree of its oxidation, the EXAFS method investigates the local structure around the element of interest in a given oxidation state. A study involving several absorbing elements of the sample provides more comprehensive and reliable structural information [205].

Because the EXAFS and XANES techniques yield local structural information [204, 205], they can be used to record a signal from local laser excitation. EXAFS provides quantitative structural information with subangström resolution with the aid of the so-called EXAFS equation [206], whereas XANES brings quantitative information ('fingerprints') on the local geometry of a chemical bond, i.e. orbital hybridization in the immediate proximity to the atom(s) of interest [205], possibly facilitating the understanding of molecular dynamics in solutions where the solvent medium markedly affects the dynamics of the chemical reaction. Similar to timeresolved X-ray liquidography (TRXL) [207, 208], X-ray absorption spectroscopy has been employed in time-resolved research. A scheme with the use of a pump laser and an X-ray probe was applied in studies of charge transfer processes [206, 209-213] and spin crossover [214, 215] in coordination compound chemistry, radical solvation dynamics [216], and the structural dynamics of intermediate photodissociation products in the liquid phase [213, 217]. The structural information obtained from X-ray absorption is limited to the local surroundings of a concrete atom, unlike that obtained by diffraction methods recording signals with information about all the particles present in the scattering region. It is, however, an advantage of the EXAFS and XANES methods, since the locality of X-ray absorption ensures enhanced sensitivity. In other words, TRXL methods and time-resolved X-ray absorption spectroscopy are well complementary; their combination in the future may prove useful for obtaining more comprehensive and reliable information on the structural dynamics in solutions.

The temporal resolution in TRXL is currently limited by the length of X-ray pulses of synchrotron radiation (~ 100 ps). It can be considerably improved in the next generation of radiation sources, such as X-ray free electron lasers (XFELs) and linear accelerators (LINACs), where subpicosecond X-ray pulses with an enhanced photon flux and quasi-complete coherence can be generated. It is believed that a temporal resolution of < 100 fs will be reached with XFELs [218], which would make possible the study of atomic movements along the potential energy surface in real time, the formation and breaking of chemical bonds, and isomerization processes in the liquid phase. However, the employment of such short X-ray pulses is at variance with both the assumption of thermal equilibrium of a solute and the usage



Figure 28. Current applications of TRED and TRXD methods for research into structural dynamics in different phases and time domains. Up to now, the small penetration depth of electrons has limited the use of TRED by dynamic studies of free molecules, surfaces, nanoparticles, and thin films. The TRXD method is efficient for studying condensed media, e.g., reactions in protein crystal solutions. The main limiting factor is the relatively low temporal resolution of TRXD [235].

of hydrodynamic equations for a solvent [208]. This dictates the necessity of developing new theoretical methods for the analysis of TRXL data to be used in research on ultrafast structural dynamics. Once these problems are overcome, TRXL will be a valuable tool for dynamic research of chemical reactions in the condensed phase.

Replacement of the optical probe by the X-ray one [219-234] or the diagnostic electron pulse [33] opened up the possibility of studying molecular structure dynamics due to the fact that the diffraction (scattering) effect arises from the totality of atoms in real space rather than from optical resonances in the energy space. Unlike visible or IR light exciting electronic or vibrational transitions in chromophore groups, X-ray radiation and electrons undergo diffraction (or scattering) by all atoms and atom-atom pairs. Atomic pairs present in a molecule contain direct information on the molecular structure that can be deduced from time-dependent X-ray and electron diffraction data in the solution of the inverse structural problem. For example, most 3D protein structures were detected by means of X-ray crystallography. The application of pulsed X-ray beam diffraction method with excitation by synchronized laser pulses is a tool for protein structural dynamics studies. The data obtained by TRXD and TRED are compared in Fig. 28.

The electron scattering cross section is roughly a million times bigger than that of X-ray radiation; therefore, the TRED method is most suitable for probing the structural dynamics of free molecules or thin samples, such as molecules in the gas phase, surfaces, nanostructures, and thin films. On the other hand, the much smaller scattering cross section of X-ray radiation enables it to penetrate matter by several orders of magnitude more deeply than electrons. Therefore, it is more convenient to use X-rays instead of electrons for the investigation of crystalline and liquid samples as thick as a few dozen micrometers. Indeed, with the further development of synchrotron X-ray radiation sources and XFELs generating high-density radiation fluxes and the application of ultrashort hard X-ray pulses, TRXD methods may become a universal powerful tool for the investigation of the structural dynamics of matter, first of all in the condensed state. Currently, these methods have been successfully employed in dynamic studies of chemical and biological systems [219-235].

### 9. Conclusions

The late 1940s and early 1950s were marked by the development of a new branch of technical physics—pico-femtosecond electron optical chronography. In this country, its fundamentals were established by the work of the E K Zavoisky scientific school [236–240]. This highly informative method for the spatial–temporal analysis of fast processes is based on the use of electro-optical convertors (EOCs) for the transformation of optical images into their photoelectronic analogs with subsequent focusing, amplification, and deflection of the resulting photoelectron images over EOC outlet screen.

In 1949, J S Courtney-Pratt [241-243] reported the first experiments on scanning slot photoelectron images by a fastchanging magnetic field in which he obtained images of separate phases of exploding substance with a maximum temporal resolution of 300 ps. Practically at the same time, E K Zavoisky, S D Fanchenko, and co-workers at the Kurchatov Institute of Atomic Energy used the domestic UMI-95 multichamber EOCs (specially created for highspeed photography) to design the first chronographic camera [239, 240] in which they recorded individual luminosity phases of a high-frequency spark discharge with a temporal resolution of 10 ps at a scanning rate of  $10^9$  cm s<sup>-1</sup>. The multicascade brightness amplification  $(10^5 - 10^6)$  enabled the researchers to register practically each individual photoelectron leaving the input photocathode. In the year 1961, the same authors constructed the UMI-95V EOC [245], in which the electric field strength at the input photocathode was an order of magnitude higher than that in UMI-95 (up to 0.6 kV mm<sup>-1</sup>) and the scanning rate of point photoelectron images amounted to  $2 \times 10^{10}$  cm s<sup>-1</sup>, which ensured a 500-fs technical temporal resolution. The results of these unique experiments gave a powerful impetus to further development of the basics of high-speed electron-optical photography and determination of its threshold temporal resolution.

These achievements of Russian researchers in the experimental realization and substantiation of the physical principles of pico/femtosecond electron-optical registration of fast processes were duly appreciated by A M Prokhorov [246]. They soon set about designing EOC of the new generation with an accelerating grid near the photocathode and a microwave deflection system [247].

An analysis of the history of development of laser-assisted electron-optical instrument making demonstrates the important contribution of EOC application to the advancement of laser physics, ensuring the studies of fast processes since the 1960s. The progress in these fields would have been impossible with other methods and facilities, whereas the continuous evolution of lasers created a solid basis for the construction of EOC [248-251]. The keynote of this work was the continued improvement of EOC temporal resolution taking advantage of the progressive shortening of applied laser pulses to 10 ps (in 1968), 700 fs (1976), 200 fs (2001), and 100 fs (the best result so far). The most notable achievements include registration of Ti:sapphire laser radiation with an experimentally realized temporal resolution equaling 160-200 fs in the streak regime at a scanning rate of  $5 \times 10^{10}$  cm s<sup>-1</sup> [252].

Thus, the temporal resolution of EOCs has been improved by more than three orders of magnitude since the creation of the first streak camera. However, this tendency has been greatly slowed down in the last two decades in view of technical difficulties. This has hampered the achievement of the theoretically predicted 10-fs limit.

A major breakthrough in the experimental realization of femtosecond temporal resolution in photoelectronics was the compression of photoelectron beams in nonstationary focusing fields [253]. This method allowed an initial 7-ps photoelectron beam to be contracted to 280 fs. Theoretical considerations suggest the possibility, in principle, of generating attosecond electron beams in nonstationary focusing fields [254]. Such beams can be employed not only in timeresolved electron diffraction experiments but also to test EOC photoelectron image scanning systems for the estimation of the limiting accuracy of spatial-temporal measurements with fs resolution. Studies are currently underway based at the Prokhorov General Physics Institute in search of the most rational ways of expending future efforts in this direction [251, 255].

Thus, integration of electron optics and pulsed laser techniques into a single experimental layout provided an efficacious tool for the research into structural dynamics of matter with high temporal and spatial resolutions. The new trend gave rise to a very promising branch of modern physics and chemistry, advancing investigations in the 4D tied spacetime continuum for a better understanding both the dynamic properties of various molecular systems with an intricate landscape of the potential energy surface and the mechanisms of different phase transitions in condensed media, including nanovolumes of solid bodies.

A wide variety of instruments drawn into the study of natural and technological processes are needed, as is well known, in view of their characteristic duration. By way of example, Fig. 29 shows some typical time scales [256, 257] spanning an unprecedented 60 orders of magnitude, from Big Bang duration (time scale corresponding to the strong nuclear interaction) and the period of electron revolution about the nucleus (electron dynamics) to the age of the Universe.



**Figure 29.** Characteristic time scales in nature and technology. The current age of the Universe is 14 billion years  $= 5 \times 10^{17}$  s, the average human lifespan — 70 years  $= 2 \times 10^9$  s, cardiac rhythm — 1 s, computer speed —  $3 \times 10^{-10}$  s, terahertz pulse length —  $10^{-12}$  s = 1 ps, light field oscillation period —  $3 \times 10^{-15}$  s = 3 fs, period of electron revolution about a proton in a hydrogen atom —  $1.5 \times 10^{-16}$  s = 150 as, strong nuclear interactions —  $10^{-21}$  s = 1 zs, primeval fireball of the Big Bang (Planck time) —  $10^{-43}$  s [256].

The progress in the development of pulsed laser sources allowed electron dynamics to be observed in real time. Today, a wide scope of research is being carried out in picosecond, femtosecond, and even subfemtosecond ranges: from registration of ultrafast processes by spectroscopic techniques to characteristics of semiconductors with subpicosecond relaxation times. One more application is the so-called terahertz technology that gained new momentum with the advent of powerful commercial femtosecond lasers. Another important breakthrough with a high potential for practical application is the discovery of the possibility of controling chemical reactions with femtochemical resolution, femtochemistry with the involvement of ultrashort laser pulses tunable over a wide frequency range [70–73, 258].

The development of appropriate experimental facilities for ultrafast electron diffraction method and microscopy made it possible to combine a spatial resolution on the order of  $\sim 10^{-2}-10^{-3}$  Å with pico- and even subpicosecond temporal resolution into a single complex. Some authors have reported the generation of  $\sim 200$ -fs electron pulses [251, 259–263]. The preparation of 10-fs long pulses containing  $10^4-10^6$  electrons in future research would be of paramount importance for the observation of fast processes in matter and concomitant changes in its structure. Also needed is an effective method for the reliable measurement of such short temporal characteristics of electron bunches [251].

The present review is concerned with processes studied with the aid of modern sources of femtosecond laser radiation on a time scale from nano- to femtoseconds or shorter extending even to the subfemtosecond (attosecond) region. The reader may ask: Is it possible to make use of ultrafast electron diffraction in studying very short (say, shorter than 1 as) processes? In principle, such studies can be conducted in the case of diffraction of isolated relativistic electrons scattered with the characteristic time  $\tau = D_{\text{nucl}}/c \sim$  $10^{-22} - 10^{-23}$  s. Under favorable conditions, the results may open up new possibilities for the investigation of the dynamics of extreme states of matter [264]. Naturally, the development of such a new promising line of research will require great efforts by both experimentalists and theorists, as well as considerable financial investments, let alone the proper experimental base. It can be expected that the success of these activities will depend on how effectively the methods and approaches from different fields of physics and technology are combined into a single experimental layout [265, 266].

It cannot be ruled out that a combination of two different type microscopes, namely, an electron microscope and, for example, a scanning probe microscope, in a single experimental layout may turn out well justified to improve the characteristics of a unique measuring device as a whole, as described in Ref. [267]. It is worth mentioning an original method of scanning vacuum probe microscopy with a hollow tip, the development of which is underway at the Institute of Spectroscopy, Russian Academy of Sciences [268]. Such a tip, a dielectric or microcapillary coated with a thin metallic layer, may have a 100-nm aperture (commercial variant) or a 10-nm open hole (laboratory design) [269]. This instrument is expected to enable modification of surfaces with ion and electron microbeams or soft X-ray radiation directed to the sample through the capillary, and investigation of surface molecular complexes by passing photoions or photoelectrons through the scanning hollow tip. In the photoionic mode, time-of-flight mass spectrometry will make it possible to realize nanolocal photodesorption of molecular ions when

high spatial resolution is combined with high chemical, elemental selectivity. This method may add information about a sample to that obtained with an electron microscope.

We appear to be witnessing not only the new birth of electron microscopy but also its principally new achievements to come as it approaches the centenary of successful developments and wide practical applications. Today, it provides the principal possibility of studying the properties of matter in the spacetime continuum exploiting short photoelectron beams. Characteristically, there are 30–40 research laboratories all over the world experimenting or planning to experiment with ultrafast electron diffraction [84] and one tenth that number of centers possessing electron microscopes adapted to operate with ultrashort electron beams.

In this context, it is worthy of special mention that the Institute of Spectroscopy, the Institute of Laser and Information Technologies, and the Lomonosov Moscow State University of Fine Chemical Technologies have jointly developed a dynamic transmission electron microscope<sup>12</sup> built around the commercial Hitachi H-300 system and modern sources of femtosecond laser radiation. This new unique experimental complex will permit observing, for example, fast phase transitions with atomic-scale spatial resolution at picosecond time scanning. In doing so, special attention will be given to the investigation of new materials.<sup>13</sup> It should be emphasized that creating a new-generation electron microscope is of crucial importance, because successful realization of this project demonstrates the potential of leading national research centers and their ability to work at the forefront of modern science.

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<sup>12</sup> The microscope utilizes a 75-keV electron beam.

<sup>13</sup> One example is nanosilicon [270] having a wide range of applications.

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