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The Possibility of ESCA Microscopy with Laser Femtosecond EUV–X-Ray Pulses

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The Letter proposes the photoelectron spectroscopy (ESCA) for observation of 2D- molecular structure with nm-spatial resolution and chemical selectivity using EUV–X-Ray femtosecond laser pulses.

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Femtosecond pulses amplified to ultrahigh intensities [1] enable one, to obtain high-order femtosecond harmonics in the EUV and soft X-ray regions [2, 3]. This is of principal importance, for this method makes it possible to transfer coherence from the optical to the X-ray region of the spectrum. In that case, there is no need to make radiation coherent by means of positive feedback, this being very difficult to implement in the X-ray region on a femtosecond time scale. This Letter proposes the method of study of structure of individual biomolecules based on the joint use of optical and EUV–X-ray femtosecond laser pulses. Gaining direct information on the molecular structure of individual biomolecules, especially such as DNA and proteins, is a very important problem facing the physicists developing new techniques and instruments for other domains of science (one can cite as an example X-ray crystallography, electron microscopy, etc.).The requirements for the potential method are exceptionally stringent: (1) atomic specificity, (2) ultrahigh sensitivity, and (3) nm-Å spatial (lateral, longitudinal) resolution. Combining all the above characteristics in one method would make it possible to determine the 3D molecular structure of *individual* biomolecules.

The following methods can be regarded as potential. First, these include the femtosecond versions of the well-known classical X-ray diffraction and electron diffraction techniques, each being capable of being extended to atomic-resolution holography. These techniques, however, require that the specimens be either crystals or ensembles of oriented molecules. Moreover, for these techniques to be implemented, it is necessary that a many X-ray photons or electrons in individual shots be coherent. The latter requirement requires the intensity of the X-ray radiation that can cause damage to the structure of the specimens on a femtosecond time scale [4].

An alternative is to extend the well-known ESCA technique [5]. This technique is incoherent and can be used with individual biomolecules, and information can be accumulated in the course of many irradiation pulses of not very high intensity. Besides, the photoionization cross section of atoms exposed to X-rays is much greater than the scattering cross-section.

To obtain a 2D image of the surface under study, one have to refuse the traditional electron spectroscopy techniques, i.e., one whould use the time-of-flight method for selecting photoelectrons. It is exactly for this purpose that the possibilities of using femtosecond optical and X-ray pulses jointly prove very suitable.

Fig.1 is a simplified illustration of the idea of ESCA microscopy with the atoms of the desired element in

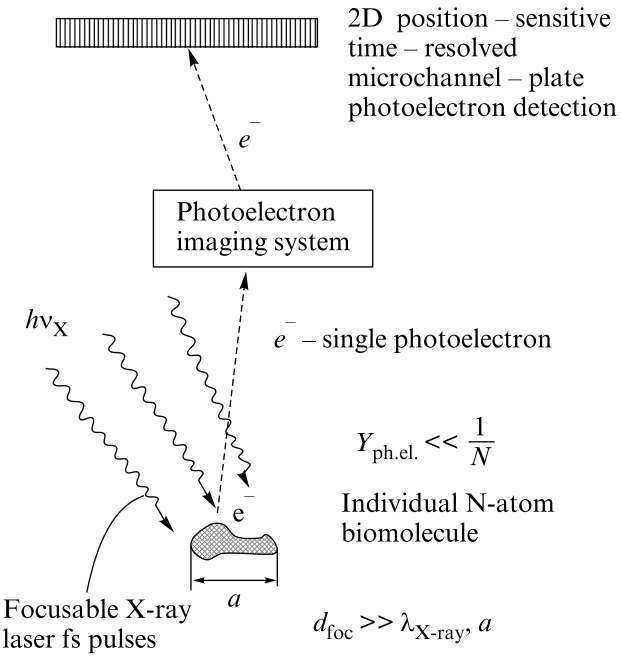

Fig.1. The simplified general idea of femtosecond ESCA 2D-microscopy

an individual molecule being ionized by focussed X-ray pulses having a energy of $h\nu_X$. The focal spot diam-

eter d_{foc} is much greater than the wavelength λ_X of the X-ray radiation and the size a of the individual molecule of interest containing N ionizable atoms. The ionization probability of one such atom, $Y_{ph.ion}$, which depends on the fluence of the X-ray radiation pulse, $\Phi_X/h\nu_X$, and the photoionization cross section $\sigma_{ph.ion}$ ($Y_{ph.ion} \simeq \sigma_{ph.ion}\Phi_X$), is taken to be low ($< 1/N$). In that case, one X-ray pulse gives birth to no more than one photoelectron ($NY_{ph.ion} \lesssim 1$). This excludes the Coulomb repulsion of the photoelectrons produced with a low kinetic energy of $E_{ph.el.}$. An electron-optical system images these photoelectrons on the surface of a position-sensitive time-resolved (time-of-flight) electron detection system.

By appropriately selecting the X-ray quantum energy $h\nu_X$ one can ensure the necessary atomic specificity of photoionization [5].

Ultrahigh sensitivity can be attained without damaging the biomolecule under study by the focused X-ray pulses by taking their energy fluence adequately low. Consider as an example the case where the photoionization cross section is $\sigma_{ph.ion} \simeq 10^{-20}\,cm^2$ ($h\nu_X \simeq 1\,keV$). When an X-ray pulse with an energy of $E \simeq 1\,nJ$ in the spectral range $\Delta E \simeq 1\,eV$ is focused onto an area the size of $a \simeq 10\,\mu m$ (this provides for $h\nu_X\Phi_X \simeq 1\,mJ/cm^2 \cdot pulse \cdot eV$), the ionization probability of a single desired atom may come to some 10^{-7} photoelectron/atom·pulse, and for a molecule with $N \approx 10^5$ atoms, it will be $Y_{ph.ion} \approx 10^{-2}$ photoelectron/molecule·pulse. The energy of the X-ray pulse can probably be raised by a factor of 10^2 (up to a level of $0.1\,J/cm^2 \cdot pulse \cdot eV$) in order to provide for the production of about one photoelectron per pulse in the biomolecule.

Photoelectrons are produced at the X-ray penetration depth that is much greater than the monolayer thickness. To achieve surface (monolayer) selectivity, it is necessary to eliminate the background noise due to the photoelectrons formed throughout the bulk of the specimen. To this end, use can be made of the effect of the photoelectron escape depth minimum $E^{min}_{ph.el.} \simeq 30\,eV$ [6]. Selective detection of surface photoelectrons can be effected by at least two methods. First, use can be made of X-ray radiation with an energy of $h\nu_X = I + E^{min}_{ph.el.}$. This may be a monochromatized radiation of higher harmonics of laser pulses within a wide X-ray spectral range. Secondly, one can perform selective detection of photoelectrons with a kinetic energy of $E_{ph.el.} \approx 30\,eV$. In our case of constructing a photoelectron image, this can be attained by means of time-of-flight (TOF) photoelectron detection. The selection of photoelectrons having the necessary energy $E_{ph.el.} \approx 30\,eV$ (velocity $v_e \approx 3 \cdot 10^8\,cm/s$) in the energy range $\Delta E_{resol.}$ over the photoelectron flight path length $L_{el.fl.} \approx 1\,mm$ requires that the TOF system used should have a very high time resolution, at a level of $\tau_{resol.} \approx 10^{-12}\,s$. In principle, this is quite possible, provided that use is made of some of the energy of the initial high-intensity optical femtosecond pulses generating the X-ray pulses. This possibility is based in particular on the reflection of electrons from the strong light field of the femtosecond optical pulses [7].

Fig.2 schematically illustrates the idea of reflection of electrons by the strong field of an evanescent light

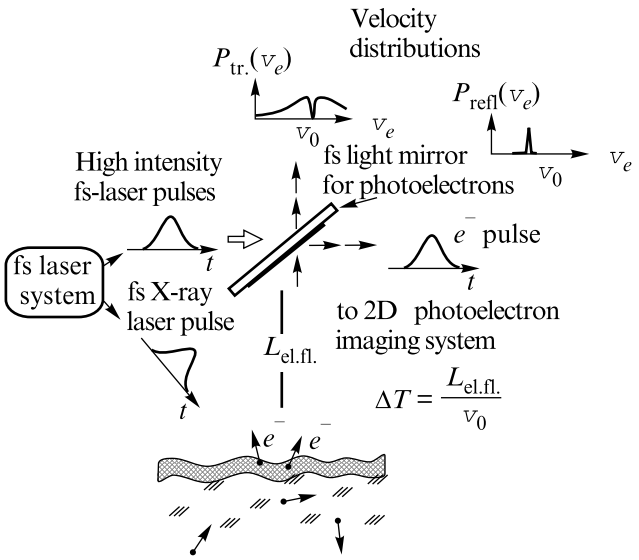

Fig.2. Idea of time-of-flight photoreflectron of photoelectrons by highly-intense femtosecond evanescent light wave

wave, as suggested in [7]. The intense evanescent wave formed on the total internal reflection of a femtosecond light pulse penetrates into the vacuum to a depth of the order of the wavelength λ. The change in the electron velocity can be described in terms of the effective index of refraction, $n_{el} < 1$ [7]:

$$n_{el} = \left[1 - \left(\frac{\mu^2}{\beta^2}\right)\sqrt{1-\beta^2}\right]^{1/2}, \qquad (1)$$

where $\beta = v_e/c$, $\mu^2 = \frac{r_e}{mc}\lambda^2 I$, v_e is the electron velocity, r_e is classical electron radius, I is intensity, and λ is wavelength. At the intensity in the range $10^{13}-10^{14}\,W/cm^2$ n_{el} drops perceptibly for $E_{el} \simeq$ $\simeq 10-100\,eV$.

Part of the powerful femtosecond pulse generating higher harmonics in the X-ray region is also capable of effectively reflecting electrons with the specified velocity v_0, whose time of flight from the surface, ΔT, is con-

trolled by the time interval between the X-ray and the optical pulse. The reflected photoelectrons with a narrow velocity distribution $P_{\text{refl.}}(v_e)$ should be directed into the imaging system used for 2D visualization purposes.

Naturally the photoreflection concept presented here is of rather qualitative character because this effect has not as yet been observed experimentally. However, it is of certain interest within the framework of "laser-induced electron optics" [7, 8]. Besides the possibility of velocity selection discussed above, it possesses the property of compensation of the velocity dispersion of the reflected electrons. Indeed the slower electrons (at the red edge of the peak of the distribution $P_{\text{refl.}}(v_{\text{el.}})$) must suffer reflection in a less intense light field of the molecules and cover a shorter distance. The opposite is true for the faster electrons. By using a curved evanescent wave, one can, in principle, attain electron beam focusing simultaneously with reflection. Of course, all these potentialities of "laser-induced" reflective electron optics should be the subject matter of future theoretical and experimental studies.

The concept of the TOF-selection of ejected photoelectrons through femtosecond photoreflection allows one, in principle, to solve the problem of detection of photoelectrons coming from a thin surface layer. The problem of attaining the high longitudinal resolution necessary to realize 3D microscopy with an atomic scale resolution still remains to be solved. It is possible that one will have to use the approach based on consecutive observation of thin surface layers, as demonstrated in [9].

As for the lateral spatial resolution in our experiments with one-photon ionization, with laser photoelectron microscopy [10, 11], we have achieved a resolution of around 30 nm [12], and the use of a sharp needle tip and two-photon femtosecond-pulse excitation has made it possible to improve resolution to some 5 nm [13]. Progress in the development of photoelectron microscopy allows one to hope that a resolution of the order of 2 nm will be attained [14].

Therefore, the method proposed here is potentially suitable for the table-top sequencing of DNA-like chain molecules with irregularly recurring molecular blocks spaced at some 1 nm on the average. To solve the entire problem, it would probably be necessary to combine several methods in a single setup.

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