ferroelectric) data recording. A strong near field can also be used for control and local modification of biological objects. In addition, interesting possibilities are opened up for linear and nonlinear nanooptical studies of single nanostructures and molecules base on this method: surface enhanced Raman scattering controlled with a nanotip, nanolocal second-harmonic generation, etc.

The most attractive is the possibility to use the above-mentioned near-field spectroscopy in conjunction with methods of femtosecond spectroscopy to achieve even higher time resolution. For this purpose, for example, a normal pump-probe method can be used [3], by focusing pump and probe femtosecond pulses near an SPM tip over a sample.

In this case, the combination of high spectral and time resolutions contradicts the uncertainty relation between energy and time. Indeed, the duration of spectral measurements can be arbitrarily long, while the time resolution is determined by the delay of the probe pulse relative to the pump pulse and depends on the difference between the paths of these pulses (i.e., the time resolution is determined in this case by the accuracy of measurements of distances). Thus, this method allows one to obtain high spatial, time, and spectral resolutions in one experiment. This can also be achieved by combining femtosecond spectroscopy with near-field microscopy using a tip made of a glass fiber (possibly partially coated with a metal film).

In this connection, note the possibility of using the near field of a fiber laser (in particular, a femtosecond laser) as a microscope tip.

Another interesting possibility for nanolocal femtosecond spectroscopy is the determination of the cross-correlation function of laser pulses from a change in the tunneling current caused by the action of these pulses or the use of photoelectron emission from an SPM tip for this purpose.

Note that the sensitivity of a fiber-laser microscope can be sharply increased if the measurements are performed near the generation threshold and the lasing spectrum is studied. In this case, in contrast to the method of intracavity laser spectroscopy, dips in the lasing spectrum are related to characteristic losses of the laser near field outside the cavity.

Finally, consider one realized possibility — the nanolocal modification of a surface by the near field of femtosecond laser pulses near a scanning tunneling microscope (STM) tip ('a light pen') [4] (see also Ref. [5] and references therein), which can be used in principle for ultrahigh-density data recording. The use of ultrashort laser pulses in nanolithography is advantageous for the following reason. Femtosecond laser radiation produces nonstationary states in a sample, which can cause nonthermal instability and photoinduced phase transitions on the sample surface. One of the examples is the specific femtosecond melting of solids. Another example is the production of a quasi-dimensional grating on a surface with the help of femtosecond laser pulses.

Radiation from a Ti:sapphire laser with wavelengths of 813 and 406 nm, a pulse duration of 40 fs, and a repetition rate of 82 MHz was used. The radiation power was varied with light filters to 80–100 mW at a wavelength of 813 nm. The maximum power of the second harmonic (406 nm) was 5–7 mW. The diameter of a spot on the sample surface was 1 mm. The dependence of the effect on the radiation exposure was studied over a broad range from 2 s to 15 min. The angle of incidence ϑ of the laser beam was restricted by the design of the experimental setup and was $\vartheta \geqslant 76^\circ$. Pyrolytic graphite, gold films, etc. were used as samples.

The experimental procedure was as follows. First, the same area of a sample was examined several times with the help of an STM, the image reproducibility was checked, and the transverse drift was estimated. Then, one of the figures — a point, a line, or a cross, was drawn by positioning the STM tip at given points, with simultaneous illumination of the contact region by laser pulses. Upon positioning to a point, the tip was displaced by 4 nm from the surface and then returned. The lines and crosses consisted of such points. After irradiation, the processed region was repeatedly examined with an STM to find photoinduced modifications of the surface. The experiments revealed the following effects:

(1) The appearance of an X-like structure after being drawn by a local laser radiation field by positioning point by point. The lines of the persistent X-like structure were typically 100 nm thick and 1.5 nm in depth.

(2) The formation of a groove 20 nm in width and 5 nm in depth in the region of the action of a tip and radiation upon positioning of the tip point by point.

The formation of a persistent structure after the nanolocal action of femtosecond laser radiation shows that this method of nanolithography is promising. Optimum regimes and the specific mechanism of the nanolocal action of femtosecond laser radiation require further investigation. It is possible that this mechanism represents the condensation of photoinduced vacancies. It is likely that the formation of a one-dimensional grating with a period of 100 nm on a pyrolytic graphite surface, which we observed under the action of normally incident femtosecond laser pulses, is described by a similar mechanism.

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Spectroscopy of ions with the 5d electrons in the ground state

A N Ryabtsev

The spectra of ions with the 5d electrons in the ground state have recently been extensively studied in the Laboratory of Atomic Spectroscopy of the Institute of Spectroscopy, RAS. The renewed interest in these ions was stimulated, on the one hand, by the recent observation of spectral lines of 5d elements in chemically peculiar stars detected with the help of the high-resolution spectrometer of the Hubble Space

Telescope [1]. On the other hand, 5d ions characterized by large relativistic and correlation effects are of interest for the development of the theory of atomic spectra.

The specific feature of the electronic structure of these ions is a strong interaction between their configurations in both the even $5d^N + 5d^{N-1}6s + 5d^{N-2}6s^2$ and odd $5d^{N-1}6p + 5d^{N-2}6s6p + 5d^{N-3}6s^26p$ level systems. The ground state in neutral atoms belongs to the $5d^{N-2}6s^2$ configurations, while the $5d^N$ configurations have high energies and are unknown in atoms. Upon moving along the isoelectronic sequence, the above configurations intersect, so that in doubly ionized atoms the ground state belongs to the $5d^N$ configuration. In this case, adjacent configurations of the same parity overlap and their energy structure and transition probabilities are strongly distorted. The spectra are complex not only quantitatively (hundreds of energy levels and up to a thousand intense spectral lines involved in the resonance transition), but also qualitatively, due to the overlap of configurations. Their analysis requires high-resolution spectral instruments in the UV region, systems and methods for fast measurements of spectrograms and obtaining wavelengths of the spectral lines, as well as reliable methods for the prediction and interpretation of the spectra.

The spectra were detected in the region from 50 to 2500 A with unique high-resolution vacuum spectrographs developed in the Institute of Spectroscopy, RAS: normal-incidence spectrograph with a 1200 lines mm^{-1} grating of radius 6.65 m, and grazing-incidence spectrograph with a 3600 lines mm^{-1} grating of radius 3 m with a resolving power of 5×10^3 and 2×10^5, respectively. In addition, we used spectrograms obtained in the U.S. National Institute of Standards and Technology, Paris Observatory, and St. F. Xavier University (Canada).

The spectrograms were measured by means of a precision system for scanning and processing photospectrograms developed in the Institute of Spectroscopy, RAS, which consisted of a scanning microdensitometer and a package of original graphic programs for spectra processing to obtain the wavelengths and parameters of the spectral line profiles.

The spectra were identified using the method of analysis of complex spectra developed earlier for interpretation of less complex 3d spectra of comparatively light elements. The method is based on the extrapolation of the energy parameters of the theoretical description of the ion structure rather than on the conventional extrapolation of wavelengths and energy levels along the electronic sequence. Because the parameters obtained from *ab initio* calculations (for example, by the Hartree – Fock method) do not provide the required accuracy, we used a semiempirical method: the parameters were treated as free parameters and were determined by fitting of their calculated values to known experimental energy levels. The effect of the remote configurations, which can be described using perturbation theory, was taken into account by introducing the effective parameters. The interaction with neighboring configurations was calculated explicitly. The successive use of this method for calculations of the 3d spectra showed that the electrostatic Slater parameters, spin-orbit, and effective two-particle electrostatic parameters changed smoothly along isoelectronic, isoionic, and isonuclear sequences, including the region of strong interactions between configurations. The extrapolation of the energy parameters to an unknown spectrum yields a reliable first approximation, which gives first experimental information that can be used for the refinement of the parameters for the identification of the spectrum by means of this iterative scheme.

The identification was performed using a program for the automated computer analysis of complex spectra [2], which has no analogs worldwide.

The table, which presents in the first column the spectroscopic symbols of ions (the spectrum of a neutral atom corresponds to I, that of a singly ionized atom, to II, etc.) and in boxes — configurations of the ground state corresponding to the spectrum of an atom or an ion, shows the degree of the study of spectra of 5d ions and our contribution

Table. Study of the spectra of ions of elements from W to Hg.

	W	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**
I	$5d^46s^2$	$5d^56s^2$	$5d^66s^2$	$5d^76s^2$	$5d^96s$	$5d^{10}6s$	$5d^{10}6s^2$
II	$5d^46s$	$5d^56s$	$5d^66s$	$5d^76s$	$5d^9$	$5d^{10}$	$5d^{10}6s$
III	$5d^4$	**$5d^5$**	**$5d^6$**	$5d^7$	**$5d^8$**	$5d^9$	$5d^{10}$
IV	$5d^3$	**$5d^4$**	**$5d^5$**	$5d^6$	$5d^7$	$5d^8$	$5d^9$
V	**$5d^2$**	**$5d^3$**	**$5d^4$**	$5d^5$	$5d^6$	$5d^7$	$5d^8$
VI	5d	$5d^2$	**$5d^3$**	$5d^4$	$5d^5$	$5d^6$	$5d^7$
VII		5d	**$5d^2$**	**$5d^3$**	$5d^4$	$5d^5$	$5d^6$
VIII			5d	**$5d^2$**	$5d^3$	$5d^4$	$5d^5$
IX				5d	**$5d^2$**	$5d^3$	$5d^4$
X					5d	**$5d^2$**	$5d^3$
XI						5d	**$5d^2$**
$5d^N$ — Spectrum is unknown;		$5d^N$ — Studied by others;			**$5d^N$** — Studied in our papers		

to this problem.

In the last six years, the spectra of some twenty ions have been investigated (see Refs [3 – 5] and references therein). The wavelengths and energy levels were measured with high accuracy and transition probabilities were reliably calculated. The reliability of these results was confirmed by the detection of the PtIII line in the spectrum of a chemically peculiar star [1]. Another result of the studies is the acquisition of semiempirical data on intraatomic interactions. In particular, the values of two-particle magnetic and three-particle electrostatic parameters were obtained for some ions. Data on the interactions of higher orders can be also obtained using semiempirical calculations with orthogonal parameters [6]. For this purpose, it is necessary to study the most complex spectra of the Ir, Pt, Au, and Hg ions, which we plan to do over the next three years.

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