Ultrasoft x-ray study of the s-ionization mechanism for noble gases

I. P. Zapesochnyĭ, I. G. Zhukov, and P. V. Fel'tsan

Uzhgorod State University

(Submitted April 3, 1973)
Zh. Eksp. Teor. Fiz. **65**, 1357–1366 (October 1973)

Electron-impact excitation functions of ultrasoft x-ray doublets of Ne, Ar, Kr, and Xe are measured from the threshold up to 160 and 600 eV. The excitation functions of the investigated doublets reflect accurately the energy dependence of the s-ionization cross section. The experimental results, in conjunction with recent theoretical work on the direct s-ionization cross sections, show that the interaction of the $nsnp^6\ ^2S_{1/2}$ level with $^{2,4}L_{1/2}$ levels of $ns\ ^2np\ ^4n'l'$ configurations ($l'=0$ and 2), as well as Auger decays of the $nsnp\ ^5n'l'n''l''\ ^{\kappa}L \rightarrow nsnp\ ^6\ ^2S_{1/2}$ type, play important parts in the s-ionization mechanism. This conclusion is confirmed by an analysis of the excitation function for the Ar II λ920-Å ultrasoft x-ray doublet component as measured with an electron beam having a very low energy spread.

INTRODUCTION

The simple ionization of inert gas atoms (except helium) takes place by detachment of the outermost p electron. As the energy of the incident electrons is increased, the efficiency for single ionization rises, particularly as a result of detachment of a deeper s electron from the outer electron shell of the atom.

Ordinary electron impact ionization experiments do not enable one to determine the relative contribution of s-electron detachment to the total ionization. However, considerable information about this process can be derived from measurements of the ultrasoft x radiation emitted when the s vacancies are filled by p electrons of the same outer electron shell of the inert gas atom.

A number of papers reporting the observation of electron-impact excitation of ultrasoft x radiation of this type have appeared in the last three or four years. Thus, Hertz[1] investigated the intensity of the neon ultrasoft x-ray doublet of interest in this connection as a function of the incident electron energy (up to 500 eV), and Dutch, American, and Canadian physicists[2–5] have investigated the behavior of one component the corresponding argon doublet at electron energies up to several keV. In addition, the cross sections for excitation of these lines in various inert gases have been estimated from indirect data[6,7].

However, almost all the papers cited above lack any serious discussion of the processes leading to the ultrasoft x-ray emission. The role of configuration interactions in the production of s vacancies in the outer electron shell of an inert-gas atom was discussed for the first time in[7], and there have recently appeared two interesting theoretical papers[8,9] on the inner-electron ionization of atoms, including the s ionization of inert gases.

It has accordingly become necessary to perform new and better experiments in a systematic study of electron-impact excitation of ultrasoft x radiation in inert gases, particularly at low incident electron energies, and to analyze the results in the light of the new theories of s ionization. The present work was undertaken in an effort to help fill this need.

APPARATUS

In our study of the excitation of ultrasoft x-ray doublets of inert gases we used apparatus that works efficiently in the vacuum ultraviolet. It consists of a source of monoenergetic electrons, a miniature gas-filled cell, a vacuum monochromator, and a radiation recording system capable of counting single photoelectrons.

The apparatus is shown in Fig. 1. The gas cell and the radiation detector were mounted in a vacuum chamber that was differentially pumped and was connected with a vacuum seal to the monochromator chamber. With continuous admission of the working gas to the cell, the differential pumping system maintained a pressure drop of at least two orders of magnitude between the cell and the vacuum chamber around it (1—5 Torr within the cell and 8—10 μTorr outside it). The gas pressure within the cell was adjusted and held constant with the aid of an oxygen reducer and a needle valve, and was measured with a thermocouple vacuum gauge.

The gas-filled cell GC was made of stainless steel. Two of the walls of the cell were provided with holes for passage of the electron beam, and in one wall there was a slot (8 mm long) that served as the entrance slit for the vacuum monochromator. The slot was made as close to the electron beam as possible (4 mm); this, together with the large pressure drop between the cell and the surrounding vacuum chamber, minimized the effects of self-absorption and entrapment of atomic resonance radiation on the results of the measurements.

The monoenergetic electron beam was produced and shaped by a three-anode electron gun or a 127° electrostatic electron selector[10] ES, which provided a wide range of beam currents (from 1 to 500 μA) while keeping the energy spread within 1.5 eV for 90% of the electrons. A ribbon electron beam (width, 7 mm) was employed to ensure that the beam would fully cover the monochromator entrance slit. The electron gun or selector was mounted on the cell itself, and this entire assembly was rigidly connected to the supporting flange of the large chamber by a tube through which gas could be admitted to the cell, and was surrounded by an oven (not shown on the drawing), which was used to clean the cell and the electron gun or selector between runs and to prevent their becoming contaminated during the measurements.

We used the 70° Sai-Namioko design for the vacuum monochromator, which employed a one-meter concave diffraction grating DR measuring 50 × 60 mm. The grating was ruled (1200 lines/mm) on aluminum and coated with rhodium; at λ = 812 Å it concentrated 42% of the reflected light in the first-order spectrum. The reciprocal linear dispersion of the vacuum monochromator was ~7 Å/mm. The grating rocking mechanism included a synchronous motor so arranged as to ensure virtually linear scanning of the spectrum from the zeroth order to ~3500 Å in first order.

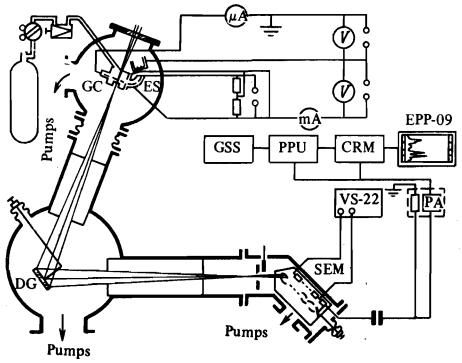

FIG. 1. Experimental setup.

The photon detector was an open type (model VÉU-OT-8M) secondary electron multiplier (SEM). In recording the weak ultrasoft x radiation we used the SEM in the most efficient manner possible, i.e., as a counter of single electron pulses[11].

After preamplification, the SEM pulses were fed simultaneously into two channels. The first channel consisted of a preamplifier PA and a unique scalar unit PPU that combined a wide-band amplifier, a pulse-height discriminator, the scaling circuit proper employing decatrons, and a time relay to control the exposure. When the gain and the discriminator threshold were properly set, the numbers of pulses recorded in equal time intervals were proportional (after subtraction of the dark count) to the numbers of photons reaching the SEM photocathode. The second channel included a counting-rate meter CRM whose output was matched to a type ÉPP-09 automatic recording potentiometer; this channel was used for visual monitoring and plotting of the spectra.

The region of the spectrum in which our spectrophotometric equipment operates efficiently lies between 400 and 1300 Å in the first order spectrum and is virtually free from overlap of the second and higher order spectra; it is limited on one side by the reflectivity of rhodium, and on the other by the red limit of the photoresponse of the oxidized beryllium bronze photocathode.

RESULTS AND DISCUSSION

1. Using the apparatus described above, we undertook a systematic study of the excitation functions of components of the ultrasoft x-ray doublets of all four inert gases (neon, argon, krypton, and xenon), first from threshold to 160 eV, and later out to 600 eV. The pertinent information on the ultrasoft x-ray doublet components is collected in Table I, which also gives their spectroscopic and x-ray classification. Figure 2 shows the measured excitation functions[1)] for all these lines in the electron energy range from threshold to 160 eV.

We repeatedly measured the excitation functions for all the investigated lines. Statistical analysis of the results showed that the 90% confidence interval for the relative measurements does not exceed 10—15%. Our results also agree within these limits with the most reliable data of other investigators.

The first obvious conclusion to be drawn from Fig. 2 is that the excitation functions for both components of the ultrasoft x-ray doublet

$$ns^2np^5\,{}^2P^0_{1/2,3/2} - nsnp^6\,{}^2S_{1/2}$$

TABLE I

Transition i		$ns^2np^5\,{}^2P^0_{1/2} - nsnp^6\,{}^2S_{1/2}$		$nsnp^6\,{}^2P^0_{3/2} - nsnp^6\,{}^2S_{1/2}$	
Ion	n	X-ray notation	λ, Å	X-ray notation	λ, Å
Ne	2	$L_I - L_{II}$*	462.39	$L_I - L_{III}$*	460.73
Ar	3	$M_I - M_{II}$*	932.05	$M_I - M_{III}$*	919.78
Kr	4	$N_I - N_{II}$*	964.96	$N_I - N_{III}$	917.43
Xe	5	$O_I - O_{II}$	1244.76	$O_I - O_{III}$*	1100.43

The asterisks mark lines whose excitation functions were measured in the present work.

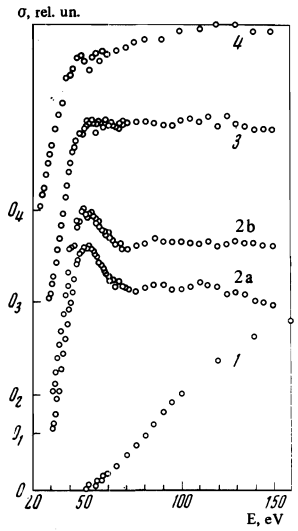

FIG. 2. Excitation functions for components ultrasoft x-ray doublets of inert gases: 1—NeII λ461 Å + NeII λ 462 Å, 2a—ArII λ 932 Å, 2b—ArII λ 920 Å, 3—KrII λ 965 Å, 4—XeII λ 1100 Å.

have the same trend (at least within the experimental errors). Thanks to this circumstance we can concentrate our efforts on a more detailed study of those ultrasoft x-ray doublet components that are not overlapped by other atomic or ionic lines and can therefore be examined with fairly wide (up to 2 mm) monochromator entrance and exit slits.

Moreover, while the excitation curve for neon rises very slowly to a single broad maximum at E ≈ 250 eV (i.e., at $E/E_{th} \approx 4-5$, where E_{th} is the threshold energy), quite a different behavior is seen for argon and the other gases: their excitation function rises rapidly from the threshold and very soon reaches a prominent maximum at $E/E_{th} \approx 1.5-2.0$ (i.e., at E ≈ 50 eV for argon). For these gases the excitation curve also exhibits a second maximum, which is broad and very weak, in the vicinity of 100 eV.

Since the $nsnp^6\,{}^2S_{1/2}$ level, which is the initial state for the ultrasoft x-ray doublets of all the inert gases under consideration, can decay in no other way[2)] than by the allowed radiative transitions to the $ns^2np^5\,{}^2P_{1/2,3/2}$ levels, it is evident that the observed excitation functions for these ultrasoft x-ray doublets must accurately reproduce the energy dependence of the efficiency for the production of s vacancies in the outer s subshell of the inert gas atom in electron-atom collisions, or, in other words, the efficiency of the s-ionization process.

2. It is well known that experiments on the single ionization of atoms only provide data on the over-all efficiency of the process, even when mass spectrometry is employed to separate the ions according to their charge. Of interest in this connection is a recent paper[14] whose authors were able to determine the relative contribution

made to the over-all ionization of argon from direct detachment by one of the outer $3p^6$ electrons, and to measure separately the principal cascade contributions to the direct p ionization, which are due to autoionization decay of the deepest $3s3p^64p$ and $3s3p^63d$ states of the atom.

However, it seems impossible at present to derive any information concerning single s ionization of inert gas atoms from electrical measurements. Hence the excitation functions for the ultrasoft x radiation arising from the formation of s vacancies in the outer ns^2 subshell in electron-atom collisions provide the only source of information about the s-ionization mechanism and its role in the total efficiency of single ionization of inert gases.

The features mentioned above of the excitation functions for the ultrasoft x-ray doublets of the several atoms (see Fig. 2) suggest that it is only in the case of neon that the production of s vacancies in the outer $2s^2$ subshell in collisions of an external electron with the normal atom is due almost entirely to direct ejection of a 2s electron, while other mechanisms apparently play no significant part in the excitation of the $2s2p^6\,{}^2S_{1/2}$ level. In the case of argon and the remaining inert gases, however, the first, prominent, maximum in the excitation function can be attributed to a significant contribution from some other processes than direct s ionization to the population of the $nsnp^6\,{}^2S_{1/2}$ level.

In principle, the following processes might contribute to the population of the $nsnp^6\,{}^2S_{1/2}$ level: 1) direct single s ionization; 2) allowed radiative cascades; 3) decay of autoionization states of the excited atom with the ejection of an Auger electron; and 4) configuration interactions.

In discussing processes 2)—4) we shall make use of the results of the theoretical treatment of the single ionization of various atoms in the first Born approximation by Omidvar et al.[8] In Fig. 3 we compare the theoretical energy dependences of the s-ionization cross sections of inert-gas atoms with our excitation functions for the ultrasoft x-ray doublets, which were measured at electron energies up to 600 eV and were normalized to the theoretical curves in the energy region in which the Born approximation is assumed to be valid.

At high energies the experimental curves agree well

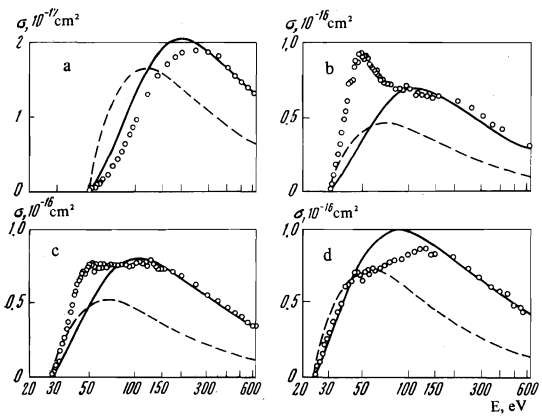

FIG. 3. The s-ionization cross sections of inert gas atoms (a—Ne, b—Ar, c—kr, d—Xe) vs. the incident electron energy E. The full curves were calculated for direct s ionization in the first Born approximation by Omidvar et al. [8]; the eircles represent the present experimental data normalized at E = 600 eV to the Born-approximation calculations [8]; and the dashed curves were calculated for direct s ionization, using Ochkur's classical formula [9].

with the theoretical curves over a range of several hundred electron volts, whereas at lower energies the experimental curve would always lie below the theoretical curve in its approach to the threshold if there were no contributions from other s-ionization mechanisms. Thus, in neon we see direct s ionization in virtually pure form, since the Born approximation always gives too large a cross section near the threshold. For the other inert gases, the prominent peak near the threshold projects above the theoretical curve as a result of the action of other mechanisms that lead to the production of s vacancies via intermediate states of the excited atom or singly charged ion.

Radiative cascade transitions of the type

$$A^{+*}ns^2np^4n'l'\,{}^{2,4}L^0 \to A^{+*}nsnp^6\,{}^2S_{1/2}+h\nu$$

can take place in inert gas atoms. Few of the corresponding lines have been observed[15] (only two for Ne II, seven for Ar II, nine for Kr II, and twelve for Xe II), and they are very weak[3)]. Further, as Lawrence showed for argon[3], such radiative cascades have practically no effect on the lifetime of the $nsnp^6\,{}^2S_{1/2}$ level. Hence these transitions cannot play any important part in the phenomena under discussion (i.e., they cannot be responsible for the comparatively high first maxima).

Published data also lead to the conclusion that autoionization states with $ns^2np^4n'l'n''l''$ configurations in inert-gas atoms decay to the $ns^2np^5\,{}^2P^0_{1/2,3/2}$ levels of the ion (this is essential for an explanation of certain features of the energy dependence of the p ionization) and that autoionization states with $nsnp^5n'l'$ configurations in the singly charged ions decay to $ns^2np^4(^1S, {}^1D, {}^3P)$ levels of the doubly charged ions. Thus, neither of these groups of Auger transitions contributes to the population of the $nsnp^6\,{}^2S_{1/2}$ level. However, states belonging to $nsnp^5n'l'n''l''$ configurations[16] can apparently make autoionization contributions to the cross section for excitation of the $nsnp^6\,{}^2S_{1/2}$ level.

Thus, of the three possible mechanisms leading to additional production of s vacancies in the outer shell of heavy inert gas atoms, there remains for our serious attention only configuration interaction of discrete $ns^2np^4n'l'\,{}^{2,4}L_{1/2}$ (l' = 0 and 2) levels of the excited ion with the $nsnp^6\,{}^2S_{1/2}$ level, which, with increasing incident electron energy, leads to Auger transitions of the type

$$nsnp^5n'l'n''l''\ {}^{*}L \to nsnp^6\,{}^2S_{1/2}.$$

3. It is advantageous to choose argon for a detailed study of this mechanism: first, because the first maximum in the excitation function for the ultrasoft x-ray doublet is most pronounced in argon; second, because of the relative abundance of theoretical and experimental data on the pertinent states of the argon ion.

We therefore undertook special experiments to examine in detail the excitation function for the stronger $(M_I—M_{III})$ component of the argon ultrasoft x-ray doublet at energies from the threshold to 60 eV, using the electron selector at reduced beam current, and thus somewhat reducing the energy spread of the electron beam. One of the resulting curves is shown in Fig. 4, together with the series of all the known $^{2,4}L_{1/2}$ states belonging to $Ar^{+*}3s^23p^4n'l'$ (l' = 0 and 2) electron configurations[15], the $Ar^*3s3p^5n'l'n''l''$ autoionization states[16], and the radiative cascade thresholds[15].

Although the fine structure of the excitation function is still not so well resolved as might be desired, Fig. 4

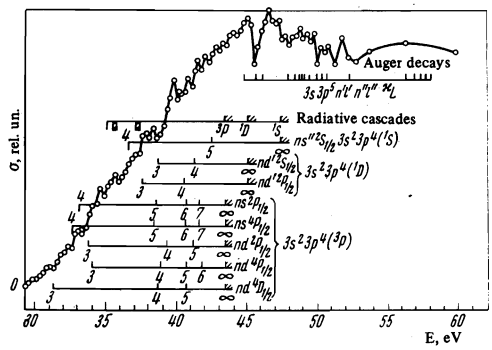

FIG. 4. Excitation function for the 920 Å component of the ArII ultrasoft x-ray doublet, measured using an electron beam having a very low energy spread.

shows that most of the fine-structure features can be attributed to configuration-interaction contributions to the s ionization. Indeed, the smooth trend of the excitation function near the threshold ceases as soon as the incident electron energy becomes high enough to excite the lowest 3d $^4D_{1/2}$ and 4s $^{2,4}P_{1/2}$ states of the $3s^23p^4n'l'$ configurations. All the subsequent fine-structure peaks of any significance correspond to definite groups of closely spaced levels that tend to the limits $3s^23p^4\ ^3P$, $3s^23p^4\ ^1D$, and $3s^23p^4\ ^1S$.

The relatively sharp dip in the excitation function near E = 45 eV corresponds precisely with the limits of the first two level sequences mentioned above, and the one at E = 47.5 eV, with the limit of the third sequence[4)]. It is just here, too, that we find the peak of the first maximum in the excitation function as recorded without resolution of the fine structure (see Fig. 2). As the electron energy increases further, the excitation function continues to fall off nonmonotonically because of the Auger decays of the autoionization levels of the $3s3p^5n'l'n''l''$ configurations. Only after reaching the limit (E = 61.3 eV) of the levels of these configurations does the experimental curve (see Fig. 3) come into coincidence with Omidvar's theoretical curve for direct s ionization of the argon atom.

The first maxima in the excitation functions for krypton and xenon also exhibit features analogous to those of the argon excitation function. The incident electron energies corresponding to the limits of the pertinent series are listed in Table II. In these atoms the allowed radiative transitions apparently play a relatively more important role. Table II also shows that the first configuration maximum for neon should be at the threshold itself.

Generalizing what was said above, we may suppose that the first maximum in the excitation function for the ultrasoft x-ray doublet of an inert gas actually represents the total effect of many narrow resonances[17] due to configuration interaction, superposed on the background of direct s ionization. Of course, in order to resolve these resonances clearly one would have to measure the excitation functions for the ultrasoft x-ray doublets, using an electron beam with an extremely low energy spread (of the order of 0.1 eV).

The fact that there is no significant interruption of the smooth trend of the s-ionization curve for neon can be explained on the assumption that LS coupling holds rigorously for this atom; in that case the selection rules ($\Delta S = \Delta L = \Delta J = \Delta\pi = 0$) forbid configuration interaction

TABLE 2

Ion	n	s-ionization threshold, eV	E_{min} threshold for excitation of $ns^2np^4n'l'$ $^{2,4}L_{1/2}$ levels, eV	E_{min} threshold for excitation of radiative cascades, eV	$ns^2np^4\ ^1S_0$ limit, eV	$nsnp^5\ ^1P_1^0$ limit, eV
Ne	2	48.5	48.8	55.8	69.6	98.5
Ar	3	29.2	31.2	35.0	47.5	61.3
Kr	4	27.5	29.1	31.2	42.7	56.2
Xe	5	23.4	24.1	26.0	38.0	48.1

between the $2s2p^6\ ^2S_{1/2}$ level and any levels except other $^2S_{1/2}$ ones.

4. It follows from the preceding discussion that the method developed by Omidvar and his collaborators for calculating the direct s ionization cross section is reliable. We therefore feel that the best estimate of the s-ionization cross section (and of the importance of the configuration contribution) at low electron energies can be obtained by fitting the observed excitation functions for ultrasoft x-ray doublets to the theoretical s-ionization cross sections in an energy region in which the Born approximation is valid. We made some calculations in the classical two-particle approximation, using Ochkur's formula[9]

$$\sigma_{is}(E)=\frac{2\pi e^4}{E+I_s+E_s}\left[\frac{1}{I_s}-\frac{1}{E}+\frac{2E_s}{3}\left(\frac{1}{I_s^2}-\frac{1}{E^2}\right)\right]F$$

in which E is the kinetic energy of the incident electron, I_S is the binding energy of an s electron in the outer shell, E_S is the kinetic energy of the s electron[5)], and F is the so-called focusing factor, and it is interesting that they, too, give fairly good results (see Fig. 3), especially in the region in which direct s ionization is most effective. In this connection the estimates of s-ionization cross sections reported in[7] on the basis of indirect measurements[6] seem to us to be much (almost an order of magnitude) too low. Of course direct absolute measurements of the s-ionization cross sections of inert gases with apparatus calibrated against synchrotron radiation remain of pressing importance.

In concluding, we should emphasize that measurements of the ultrasoft and soft x-ray spectra excited in collisions between electrons and atoms can yield exceptionally abundant and unique information concerning the characteristics and mechanism of the excitation of atomic electrons belonging to outer closed electron shells and to deeper shells.

The authors are grateful to E. P. Stakhno for fabricating the unique pulse processing unit, and to I. S. Aleksakhin and E. É. Kontrosh for valuable discussions.

1)Some of our data on the excitation functions for Ar, Kr, and Xe were published in brief communications [12,13].

2)Although $nsnp^6\ ^2S_{1/2}$ is the limit of the series of singlets and triplets of the $nsnp^6n'l'$ ($^{1,3}L$) configurations, and the levels of this series undergo Auger decay, $nsnp^6\ ^2S_{1/2}$ itself does not.

3)We note, however, that both transitions in NeII satisfy all the selection rules for electric dipole transitions, whereas the selection rules for L and S are clearly progressively violated in the sequence ArII, KrII, XeII, owing to the gradual strengthening of JI coupling.

4)It is also evident from Fig. 4 that individual peaks also coincide with the radiative cascade levels, which also have their upper limit at E = 47.5 eV.

5)In all our calculations with this formula we took $E_S = I_S$.

[1] H. Hertz, Zs. Naturforsch. **24a**, 1937 (1969).
[2] B. F. Luyken, F. J. de Heer, and L. Vriens, VI ICPEAC, Boston, MIT Press, 1969, p. 25.

[3] G. M. Lawrence, VI ICPEAC, Boston, MIT Press, 1969, p. 134; Phys. Rev. 179, 134 (1969).
[4] G. A. Govertson and D. K. Anderson, J. Opt. Soc. Am. 60, 600 (1970).
[5] J. W. McConkey and F. C. Donaldson, Bull. Am. Phys. Soc., Ser. II 16, 1345 (1971).
[6] A. F. J. van Raam, J. P. de Jongh, and J. van Eck, VII ICPEAC, Amsterdam, North Holland Pubs., Amsterdam 1971, p. 704.
[7] B. F. J. Luyken, F. J. de Heer, and R. Ch. Baas, Physica 61, 200 (1972).
[8] K. Omidvar, H. L. Kyle, and E. C. Sullivan, NASA preprint X-641-71-145; Phys. Rev. A5, 1174 (1972).
[9] V. I. Ochkur, VII ICPEAC, Amsterdam, North Holland Pubs., Amsterdam 1971, p. 883.
[10] I. P. Zapesochnyĭ and O. B. Shpenik, Zh. Eksp. Teor. Fiz. 50, 890 (1966) [Sov. Phys.-JETP 23, 592 (1966)].
[11] A. M. Tyutikov and Yu. A. Shuba, Opt. spektr. 9, 631 (1960).
[12] I. G. Zhukov, I. P. Zapesochnyĭ, and P. V. Fel'tsan, Opt. spektr. 32, 1049 (1972) [Optics and Spectroscopy 32, 569 (1972)].
[13] I. G. Zhukov, I. P. Zapesochnyĭ, and P. V. Fel'tsan, Opt. spektr. 34, 820 (1973).
[14] A. Crowe, J. A. Preston, and J. W. McConkey, J. Chem. Phys. 57, 1620 (1972).
[15] A. R. Striganov and N. S. Sventitskiĭ, Tablitsy spektral'nykh liniĭ neĭtral'nykh i ionizovannykh atomov (Tables of Spectrum Lines of Neutral and Ionized Atoms), Atomizdat, 1966.
[16] R. P. Madden, D. L. Ederer, and K. Codling, Phys. Rev. 177, 136 (1969).
[17] U. Fano, Phys. Rev. 124, 1866 (1961).

Translated by E. Brunner
139