

bution function and is not related to the profile of the first pulse. In the case of a strong pulse, the length of the echo signal can, of course, be used as a source of information on the half-width  $T_2^{*-1}$  of the inhomogeneously broadened line. Partial or complete reproduction by the PE profile of the shape of the first pulse will occur in the opposite situation in the case of an essentially nonequivalent excitation of the line when  $\theta_1 < 1$  and  $\delta_1 \gg T_2^*$ , i.e., in the case of a weak field ( $\mathcal{E}_1 < \hbar/dT_2^*$ ) first pulse.

It is interesting to note that, with this choice of parameters, we have the possibility of being able to investigate the shape of the inhomogeneously broadened line itself.

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## Effects of negative-ion formation and post-collision interaction in collisions between magnesium atoms and electrons

O. B. Shpenik, I. P. Zapesochnyi, E. É. Kontrosh, É. I. Nepiřpov, N. I. Romanyuk, and V. V. Sovter

*Uzhgorod State University*

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Results are presented of investigations of the excitation of magnesium atoms by monoenergetic electrons from the excitation threshold to 11 eV. The structure of the optical excitation functions is investigated in detail both up to and above the ionization threshold. It is established that the structure of the excitation functions up to the ionization threshold is governed by the decay of the short-lived states of the negative magnesium ion, while above the ionization threshold it is governed by the post-collision interaction of the emitted and scattered electrons. Possible negative-ion states and auto-ionization levels of the magnesium atoms, which lead to singularities of the excitation functions of the spectral lines, are discussed.

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### INTRODUCTION

Experiments aimed at studying the excitation of atoms of alkaline-earth elements by electron impact have recently been performed.<sup>1,2</sup> The effective cross sections

for the excitation of spectral transitions and energy levels were determined, and some singularities of the excitation of the lower levels of these atoms were revealed. To obtain a more detailed and complete information for atomic physics, precision investigations of

excitation by electron beams that are highly homogeneous in energy are required. This is precisely the purpose of a cycle of investigations that we have started with a group of alkaline-earth elements.

Alkaline-earth elements are rather convenient objects for precision investigations of the mechanism of excitation of energy levels by a spectroscopic method, since most spectral transitions lie in an accessible region of the spectrum. In addition, they have sufficiently high two-electron excitation probabilities, and have near the single-ionization threshold an appreciable number of autoionization states whose role in the population of the energy levels of the atoms by electron impact can be appreciable. At the same time, the chemical activity and the high working temperatures raise considerable difficulties in the realization of such experiments. From this point of view, magnesium is preferable to the other atoms of this group because of the relatively low working temperatures, the most convenient location of the intense spectral lines, and the limited number of well-resolved autoionization states.

The apparatus and the investigation procedure are in the main similar to those described in Ref. 3. The beam of exciting electrons was shaped by a trochoidal electron monochromator, passed through a collision chamber, and was incident on the electron collector. The radiation of the excited atoms was detected by a photomultiplier system that counted individual photoelectrons. However, the specific properties of the alkaline-earth elements required some improvements in both the experimental procedure and in the apparatus itself. Thus, for example, to decrease the changes that occur in the contact potential difference in time, all the electrodes of the electron-optical system were made of molybdenum instead of stainless steel. This decreased noticeably the drift of the contact potential difference (to 0.02 eV in 24 hours of continuous operation).

The electron-beam energy was calibrated against the emission threshold of the most intense spectral lines of magnesium, with correction for the instrumental function. The accuracy of this calibration method was  $\pm 0.03$  eV. The full width at half maximum of the electron energy distribution function was 0.1 eV.

We present here the first experimental results on the excitation of magnesium atoms by monoenergetic electrons in the energy region from the threshold of the process to several electron volts above the single-ionization threshold.

### ENERGY DEPENDENCES OF THE TOTAL SPECTRAL-LINE EXCITATION CROSS SECTIONS

In our experiments we investigated thoroughly the energy dependences of the total cross sections for the excitation of the deepest *S*, *P*, and *D* levels of the magnesium atoms by detecting the optical emission of the following spectral lines:  $\lambda = 2852, 2938, 3992, 3332, 3838/32/29, 4167/65, 4571, 4703/30, 5184/73/67$  and  $5528 \text{ \AA}$ . The results of the measurements are given in Figs. 1-4.

Let us dwell on some general regularities of the measured excitation functions of the lines. Most excitation functions are characterized by a sharp increase of the intensity of the emission at the threshold. Thus, for individual lines the interval between the threshold and the first maximum on the excitation function does not exceed the energy homogeneity of the exciting electron beam, thus attesting to a resonant character of the near-threshold section of the excitation function. This is particularly clearly observed on the excitation functions of the lines that start from the levels  $5^3S_1$  and  $4^3D_{123}$  (Figs. 2 and 3), and also in the case of the excitation functions of the unresolved lines that start from the upper levels  $^1S_0$  and  $^1D_2$  (Fig. 4).

As seen from the results, the excitation functions of most levels reveal also a large number of narrow extrema (maxima, minima, and abrupt changes in the slopes of the curves), both below and above the threshold of single ionization. The energy positions of the extrema below the threshold of single ionization correlate well on the excitation functions of different transitions. Worthy of particular attention is the correlation of the extrema in the energy region 5.65-5.80 eV on the excitation functions of the lines that start from the resonant singlet  $3^1P_1$  and triplet  $4^3S_1$  levels (see Fig. 1). A similar phenomenon was registered earlier in Ref. 4 for the excitation function of an analogous pair of energy levels of the cadmium atom. In contrast to cadmium, however, at this energy the excitation function of the magnesium triplet reveals a deep minimum (in place of a narrow maximum for cadmium), while the excitation function of the singlet resonant levels shows an alternation of a minimum and a maximum instead of a dip

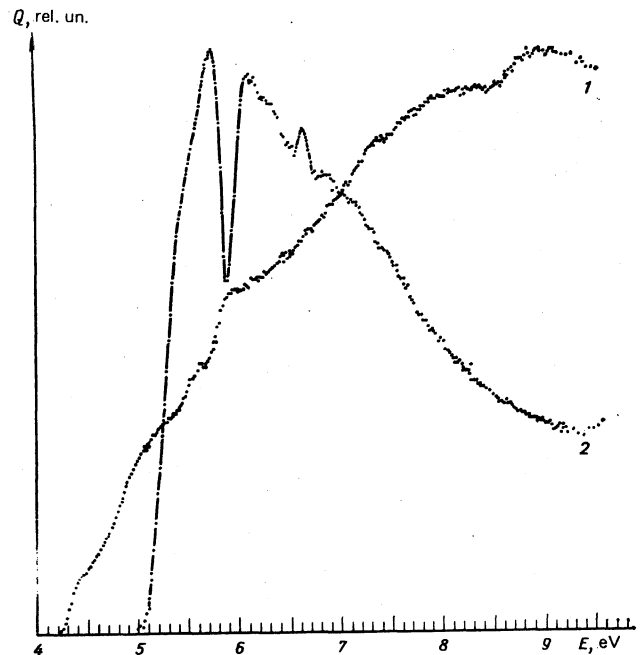


FIG. 1. Excitation function of spectral lines of the magnesium atom: 1— $\lambda 2852 \text{ \AA}$  ( $3^1S_0 - 3^1P_1^0$ ), 2— $\lambda 5184/73/67 \text{ \AA}$  ( $3^3P_{012}^0 - 4^3S_1$ ).

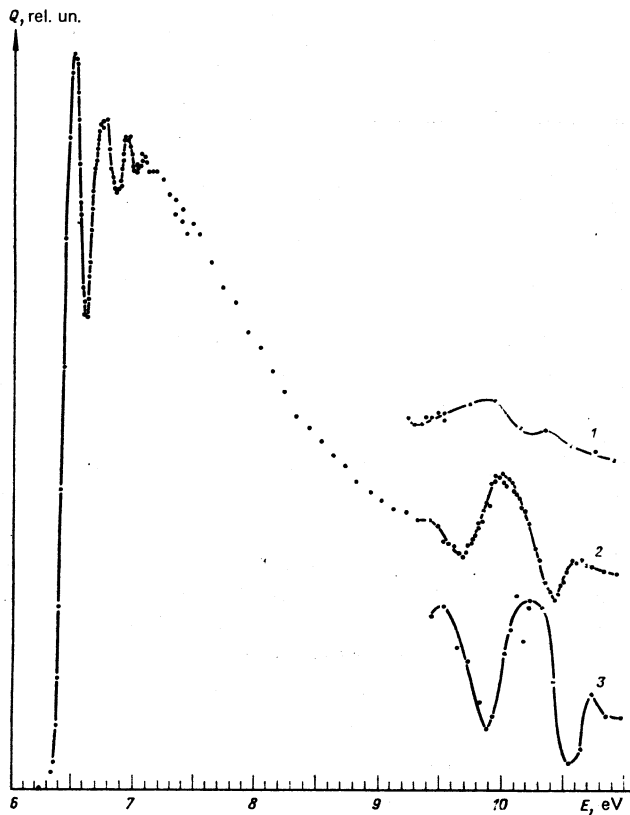


FIG. 2. Excitation functions at the spectral lines of the magnesium atoms  $\lambda 3337/32/30 \text{ \AA}$  ( $3^3P_{012}^0 - 5^2S_1$ ) (curve 2) and sections of the excitation functions of the spectral lines:  $\lambda 5184/73/87 \text{ \AA}$  ( $3^3P_{012}^0 - 4^3S_1$ ) (curve 1) and  $\lambda 2942/38/37 \text{ \AA}$  ( $3^3P_{012}^0 - 6^3S_1$ ) (curve 3).

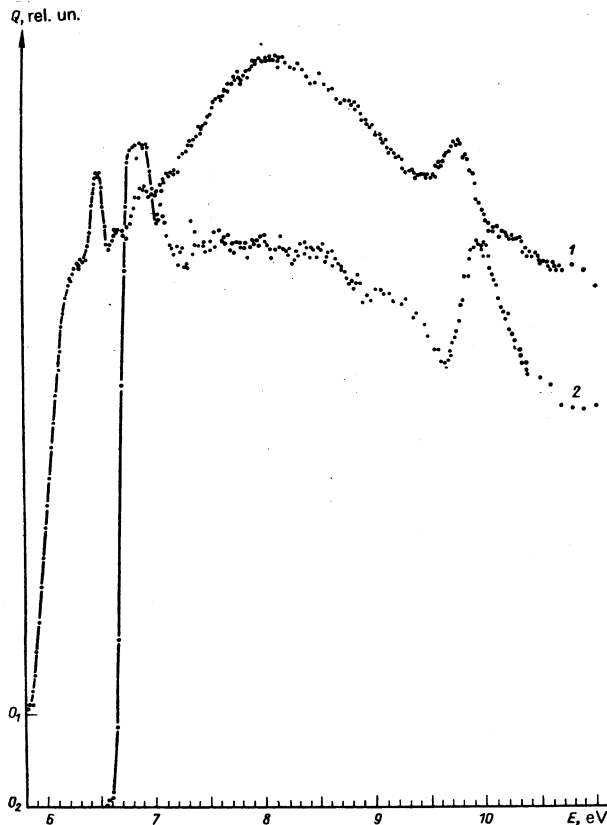


FIG. 3. Excitation functions of spectral lines of the magnesium atom: 1— $\lambda 3838/32/29 \text{ \AA}$  ( $3^3P_{012}^0 - 3^3D_{123}$ ), 2— $\lambda 3097/93/91 \text{ \AA}$  ( $3^3P_{012}^0 - 4^3D_{123}$ ).

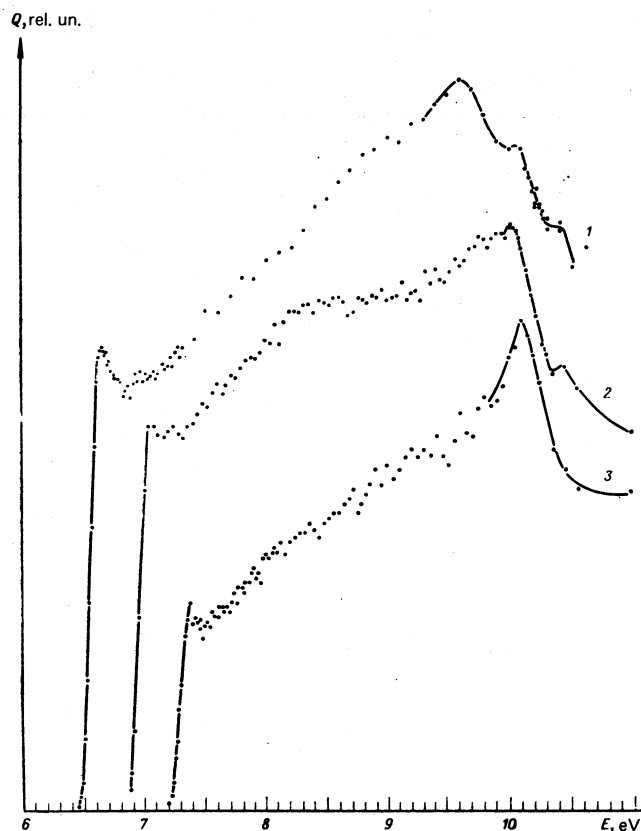


FIG. 4. Excitation functions of spectral lines of the magnesium atom: 1— $\lambda 5528 \text{ \AA}$  ( $3^1P_1^0 - 4^1D_2$ ), 2— $\lambda 4730/03 \text{ \AA}$  ( $3^1P_1^0 - 5^1D_1, 6^1S_0$ ), 3— $\lambda 4167/65 \text{ \AA}$  ( $3^1P_1^0 - 7^1D_1, 8^1S_0$ ).

on the excitation function of the analogous level of cadmium. Leep and Gallagher<sup>2</sup> also found in the indicated energy region a structure in the degree of polarization of the resonant emission of the magnesium atoms.

On the other hand, it was established that above the single-ionization threshold the extrama on the excitation functions of lines of a definite spectral series shift gradually toward higher energies with increasing principal quantum number of the initial level of the line. This shift is shown graphically in Fig. 5a. It is seen that all the extrama beyond the single-ionization threshold can be fitted to three curves that have horizontal asymptotes.

Thus, it can be concluded from the foregoing that in our experiments we have observed two types of fine-structure extrama on the excitation functions of the levels of the magnesium atom.

#### EXCITED STATES OF NEGATIVE ION

A part of the structure observed by us on the excitation functions of magnesium and located below the single-ionization potential ( $E_i = 7.65 \text{ eV}$ ) can be attributed to the production and decay of short-lived states of the negative  $\text{Mg}^-$  ion.<sup>5</sup> To determine the energy position of the resonant structures, we use a previously proposed<sup>3</sup> method of graphic analysis of excitation functions. We

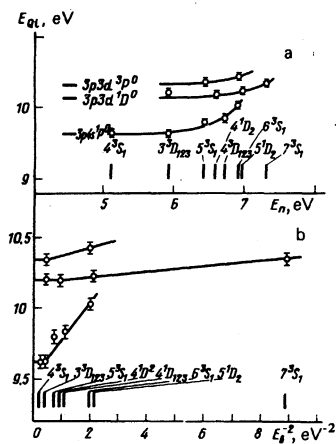


FIG. 5. Dependence of the apparent positions of the autoionization states  $E_{ai}$  and the energies of the levels to whose excitation functions they contribute: a—dependence of  $E_{ai}$  on the excitation thresholds of the initial levels  $E_n$  reckoned from the ground state; b—dependence of  $E_{ai}$  on the reciprocal squares of the binding energies  $E_b$  of the initial levels relative to the ionization potential.

assume here that in the region of each resonance the background is a slowly varying function. Then the resultant structure is the difference between the measured curve and the extrapolated background. The position of the resonance is determined from the Fano formula. The results of the reduction of the curves are given in the table.

We proceed now to discuss the possible negative magnesium ion states, that can lead to singularities in the level-excitation cross sections. We use for this purpose the sequence of levels of doubly excited states of the aluminum atom, which is isoelectronic to  $Mg^-$ . The basis for the comparison of the levels of  $Mg^-$  and  $Al^{**}$  is that, according to the data of Sternheimer,<sup>6</sup> levels of light and medium atoms with identical values of  $k=n+l$  (where  $n$  and  $l$  are the principal and orbital quantum numbers) are energywise ordered in a definite sequence with respect to the values of  $l$ , forming a certain  $l$ -structure. This structure is in general independent of  $k$  and is determined by the closed outer shells of the core. Thus, for example, singly excited states of Na, Mg,  $Mg^-$ , Al, and  $Si^+$  form a cluster having a structure

with decreasing values of the orbital quantum number  $l$ , i.e., a  $fdps$ -structure. For the doubly excited states of the aluminum atom one can see an analogous ordering of the levels, and it must be assumed that the doubly excited states of aluminum considered by us converge in the limit to  $3s3p$  of  $Al^+$ . In this case the states  $3s3pnl$  of  $Al^{**}$  form a sequence of levels where only the outer electron is "excited." These levels indeed are grouped together energywise and form the  $l$  structure. It can therefore be assumed that this structure is observed on going from the aluminum atom to negative  $Mg^-$  ions. Thus, the arrangement of the  $Mg^-$  levels should correspond to the structure of the  $Al^{**}$  levels.

The indicated correlation of the singularities on the excitation functions of the  $3s3p^1P_1$  and  $3s4s^3S_1$  levels of magnesium at 5.7 eV, which is the consequence of interference in the population of the initial levels by direct transitions of the electron from the ground state of the atom to an excited state and via short-lived states of the negative  $Mg^-$  ion, facilitates to a considerable degree the identification of the resonances observed by us with actual states of the negative  $Mg^-$  ion. This fact is evidence that the most probable  $Mg^-$  state configuration that causes the singularity on the excitation of functions of the indicated levels is  $3s3p4s$  of  $Mg^-$ . In the aluminum spectrum, this configuration corresponds to the autoionization states  $3s3p4s^4P_{1/2, 3/2, 5/2}$  at an average energy 7.65 eV. The ratio of the energies of these levels is  $\sim 0.75$ . Next, if the energy spacings between the  $Al^{**}$  levels are changed by a factor 0.75, then we obtain a sequence of shifted  $Al^{**}$  levels that duplicate well the resonances observed by us for the excited magnesium atom (see the table). In addition, the ratio of the ionization energy of the Mg atom ( $E_i(Mg)=7.65$  eV), as a limit of the series of the resonances, to the limit of the series of the doubly excited  $3s3p$  states of  $Al^+$  ( $E_i(Al)=10.63$  eV) also gives a close value for the "shrinkage" coefficient. Thus, analysis shows that when slow electrons collide with magnesium atoms the realized states of  $Mg^-$  correspond to autoionization states of the aluminum atom.

### EXTREMA ABOVE THE IONIZATION THRESHOLD AND POST-COLLISION INTERACTION

As indicated above, the structure observed by us above the threshold of single ionization of the magnesium atom

TABLE I.

Electron configuration of $Al^{**}$ or $Mg^-$	Positions of $Al^{**}$ levels, eV	Expected position of Mg levels, eV	Obtained position of Mg levels, eV	Mg levels with excitation functions that reveal resonances										
				$3p^1P_1$	$3p^1D_{1,2}$	$4s^1S_0$	$4D^1, 3S^1, 3S^1$	$4^1D_{1,2}$	$5s^1S_0$	$5^1D_2, 6^1S_0$	$6s^1S_0$	$7^1D_2, 8^1S_0$		
$3s3p^2^2S_{1/2}$	6.42	4.7	4.7	+										
$3s3p^2^2P_{1/2, 3/2}$	7.03	5.2	5.2	+										
$3s3p4s^4P_{1/2, 3/2, 5/2}^0$	7.65	5.7	5.7											
$3s3p3d^2D_{3/2, 5/2}^0$	8.30	6.3	6.3				+							
$3s3p3d^2P_{3/2, 5/2, 7/2}^0$	8.83	6.6	6.5		+									
$3s3p3d^4D_{3/2, 5/2, 7/2}^0$	8.83	6.6	6.5				+			+				
$3s3p3d^4P_{3/2, 5/2, 7/2}^0$	8.95	6.7	6.7		+									
$3s3p5s^2P_{1/2, 3/2}^0$	9.05	6.8	6.7						+	+				
$3s3p4d^2P_{3/2, 5/2}^0$	9.45	7.1	7.0						+	+	+	+		
$3s3p6s^2P_{1/2, 3/2}^0$	9.75	7.3	7.4						+	+	+	+	+	

occurs at different energies on the excitation functions of the individual lines. Consequently, it cannot be due to production and decay of short-lived states of negative ions, nor to population of the initial levels of the lines by radiative transitions from autoionization levels. Another mechanism that leads to additional population of the atomic levels near the autoionization states in electron-atom collisions may be the mechanism of post-collision interaction (PCI) between the emitted and scattered electrons. Namely, it appears that this mechanism is responsible for the structure observed above the ionization threshold of the magnesium atom. It is known<sup>7</sup> that the PCI is the result of Coulomb interaction between a scattered slow electron and a fast autoionization electron in the field of the target ion. Even though this interaction has a long-range character, the effects due to the PCI occurs only under favorable conditions. An analysis by Nienhuis and Heideman<sup>7</sup> leads to the conclusion that the exchange of angular momenta between the emitted and scattered electrons has low probability, and that the largest energy exchange between the emitted and scattered electrons occurs when the scattered electron has practically zero energy immediately after the collision. The value of the exchange energy reaches in this case  $\sim 1$  eV. Consequently, the PCI mechanism should be suppressed on the excitation functions in those cases when the binding energy of the Rydberg electron in the final high-excitation state as a result of the PCI exceeds 1 eV. This statement can be experimentally verified by carefully measuring the resultant autoionization structure on the excitation functions above the threshold of single ionization of the atom. In the presence of PCI, as shown in Ref. 7, a gradual shift of the positions of the extrema (and naturally of the entire structure) should be observed near the position of the autoionization states of magnesium towards higher energies on the excitation functions of different lines of definite spectral series with increasing principal quantum number of the initial level. It is seen from Figs. 2-4 that this shift does indeed take place (see also Fig. 5a), and vanishes practically when the binding energy  $E_b$  of the Rydberg electron in the highly excited state is  $\sim 1.5$  eV.

Assuming that the profile of the observed extrema is close enough to the Beutler-Fano profile for autoionization states, we calculated the apparent positions of the autoionization states on Figs. 2-4 above. Analysis has shown that the observed structures correspond to three autoionization states.

To determine the apparent shift of the autoionization states on the excitation functions, we used the classical PCI model.<sup>7</sup> According to this model, the expected  $P_{exc}$  structure is described by the expression

$$P_{exc} = \exp \left\{ - \frac{\Gamma (R/E_1)^{1/2}}{E_1 + E_b} \right\} \frac{\Gamma}{(E_1 + E_b)^2} \left( \frac{R}{E_1} \right)^{1/2}, \quad (1)$$

where  $E_1$  is the excess energy of the incident electron

above the autoionization-state threshold,  $\Gamma$  is the half-width of the autoionization state, and  $E_b$  is the binding energy of the Rydberg electron in the final highly excited state (the energy of the initial level, reckoned from the ionization potential).

Inasmuch as  $E_1 \ll E_b$ , in our experiments and the half-width  $\Gamma$  of the autoionization state is constant,<sup>1)</sup> the observed dependence of the observed position of the autoionization state on  $E_b$  is given by the factor  $\Gamma E_b^{-2} (R/E_1)^{1/2}$ . The positions of the autoionization states as functions of  $E_b^{-2}$  are shown in Fig. 5b. From the slopes of the lines we can estimate the half-width  $\Gamma$  of the autoionization states.

An autoionization state at  $E = 9.62$  eV with relatively large half-width were observed by Trajmar and Williams<sup>8</sup> and identified with the configuration  $3p4s^1P^0$ . Our estimates show that the half-width of this autoionization state is  $\Gamma = 0.46$  eV. The other two autoionization states at  $E = 10.18$  and  $10.32$  eV agree well with the data of Moore<sup>9</sup> and according to our estimates their half-widths are 0.04 and 0.17 eV (the states  $3p3d^1D^0$  and  $3p3d^3D^0$ , respectively).

## CONCLUSION

Precision investigations of the excitation of atoms by electron beams that are highly homogeneous in energy make it possible to tackle the problem of classifying short-lived states of the negative ion of an atom. The Mg atom is the first simplest investigated object, while other alkaline-earth elements have a larger number of autoionization states. Their investigation can yield information on a new regularities in the formation of states of the negative ion of an atom, and also information on the role of the PCI in the population of the levels of an atom.

<sup>1)</sup>The classical PCI model presupposes that the average lifetime  $\tau$  of the autoionization state is not altered in the presence of the scattered electron.

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