Use of electron spectroscopy to investigate resonance phenomena and post-collisional-interaction effects in collisions between electrons and magnesium atoms

S. M. Kazakov and O. V. Khristoforov

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Electron spectroscopy is used to measure the energy dependences of the differential cross sections for elastic and inelastic scattering of electrons by magnesium atoms at low energies. The singularities observed in the cross sections are due to formation and decay of short-lived negative Mg^- ions. The spectra of the electrons released as a result of the decay of the autoionizing states at bombarding-electron energies lower than 17 eV are also studied. A post-collisional effect that leads seemingly to a shift of the autoionizing-state thresholds is recorded.

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INTRODUCTION

Results by many workers¹⁻⁸ demonstrate the existence of subtle structural singularities in the energy dependences of the cross sections for the scattering of slow electrons by magnesium atoms. The most complete information on the nature of their formation was obtained by an optical method.⁷ From an analysis of the number of excitation functions (EF) of the energy levels, it is concluded in Ref. 7 that the structure in the cross sections is due to the production and decay, in the course of the collision, of short-lived states of negative Mg⁻ ions, and near the autoionizing states (AIS), in addition, also to the post-collisional interaction (PCI) of the slow scattered electron and the fast electron emitted by the atom as a result of the autoionization.

The results of the optical method, however, by virtue of certain factors, call for further confirmation and development. With an aim at a detailed explanation of the mechanism whereby the structure is produced in the cross section, we have used electron spectroscopy to measure the energy dependence of the differential cross sections (DCS) of the elastic and inelastic scattering of electrons by magnesium atoms and investigated the electronic spectra of the low-lying autoionizing states at low values of the exciting-beam energy.

The experimental setup, which makes it possible to investigate under conditions of one experiment the spectra of both scattered and emitted electrons, was described earlier.⁹ The energy resolution of the appara-



FIG. 1. Spectrum of electrons scattered by magnesium atoms at a primary beam energy 16 eV, $\theta = 90^{\circ}$.

tus was 0.3-0.5 eV in the measurement of the DCS and 0.05 eV when the AIS spectra were recorded. Just as in Ref. 9, the angle at which the scattered (emitted) electrons were observed was 90° .

SPECTRUM OF SCATTERED ELECTRONS

A typical spectrum of electrons scattered by magnesium atoms is shown in Fig. 1. The discrete lines of the spectrum correspond to elastic scattering (in this case the energy loss is zero) and to excitation of specific energy levels. In particular, the $3^{3}P$ and $3^{1}P_{1}$ resonant levels are well resolved. As expected, the most intense line of the loss spectrum is due to excitation of a singlet resonant level of magnesium. Of considerable intensity is also the line A, the energy loss for which is 5.86 ± 0.02 eV, corresponding to the excitation of several levels, the most probable of which are $4^{3}P$, $3^{3}D$, and $3^{1}D$. The less intense lines B and C characterize high-lying states with excitation energies in the range 6.7-7.1 eV. Above the single-ionization limit ($E_{I} = 7.644 \text{ eV}$) there are also discrete lines corresponding to excitation of AIS. Comparison with the electronic AIS spectra obtained in Ref. 10 leads to the conclusion that the line D corresponds to excitation of an unidentified state with threshold energy $E_a = 8.69 \text{ eV}$, which is observed also by us in the spectra of the emitted electrons (see below). The lines E and F, can be related to the states $3p3d {}^{1}F$ and $3p4d {}^{1}D$ ($E_{a} = 9.99$ and 11.07 eV). Notice must be taken of the high intensity of the lines lying beyond the ionization boundary, thus indicating an appreciable probability of electronic excitation of the autoionizing state of magnesium even at such low beam energies.

We present below the measured energy dependences of the intensities of some of the spectral lines, which reflect the energy dependences of the differential cross sections for the corresponding processes.

DIFFERENTIAL CROSS SECTIONS

The result of our measurements of the energy dependence of the DCS for elastic scattering of electrons in the 0.1-3 eV range is shown in Fig. 2. As seen from the figure, at an energy 0.2 ± 0.05 eV the DCS contains



FIG. 2.

an intense minimum, which we attribute to the existence of a *p*-wave shape resonance previously observed in experiments on the passage of an electron beam through magnesium vapor,^{2,3} as well as in the total cross section for electron scattering.⁸ Moreover, the appearance of a resonance in the form of a minimum in the cross section for scattering through 90° confirms its p-wave origin and allows us to conclude that it is due to the $(3s^23p)^2P$ state of Mg⁻. Even more interesting is the first observation of a singularity at ~1.5 eV. The appreciable width of the structure ($\sim 1 \text{ eV}$) and its distance from the ancestor $3^{1}S_{0}$ state of Mg are typical of shape resonances. The energy position of the resonance is close to that predicted by an analysis of the levels of the isoelectronic atoms and ions.³ All this allows us to regard this singularity as a resonance due to the $(3s^23p)^2D$ state of the Mg⁻ ion. Extrapolating the background of the potential scattering, as shown in Fig. 2, we can note that the resonance has a characteristic Fano profile. A graphic analysis based on the resonance formulas, just as in Ref. 11, has made it possible to determine more precisely the energy of the resonance. It was found to be 1.49 ± 0.05 eV. The profile index is q = 1.1, i.e., the resonance is almost symmetrical.

The resonance next in intensity in the analyzed energy interval is the one at 2.75 eV, in the immediate vicinity of the excitation threshold of the $3^{3}P$ level. We, just as the authors of Ref. 8, believe that the singularity in the scattering cross section at 2.7 eV is due to the opening of a new scattering channel, namely excitation of the $3^{3}P$ level. Moreover, as shown by measurements of the energy dependence of the DCS for the excitation of the $3^{3}P$ level (see Fig. 3), the minimum of the elastic-scattering cross section correlates in energy within 0.02 eV with the maximum of the excitation cross section. This correlation offers additional evidence of the interrelation between the channels.

At 5.2 eV, the DCS for elastic scattering contains a rather pronounced singularity that points to the presence of a resonance in this region. As seen from Fig. 3, a structure is present at this energy also in the DCS for the excitation of the $3^{3}P$ level. Thus, the resonance noted in Ref. 12 in the polarization of the radiation of a single resonance line was observed by us additionally in two scattering channels. A resonance at E = 5.2 eV was observed in Ref. 7 also on the λ 285.2 nm optical EF line. The $4^{3}S$ level of the atom should be regarded as responsible for the formation of this resonance. The energy dependence of the DCS for the excitation of the



FIG. 3. Energy dependence of the DCS of elastic scattering of electrons: 1) elastic scattering, 2) initial section of $3^{3}P$ level excitation curve, 3) DCS for the excitation of the $3^{3}P$ level.

singlet $3 {}^{1}P_{1}$ level is shown in Fig. 4. This level, as is practically the case for all transitions with change of multiplicity, is characterized by a monotonic decrease of the cross section with increasing energy. Comparison with the optical EF of the resonance line of magnesium⁷ is evidence of the full agreement in the behavior of the curves. All the singularities typical of the excitation function (including the one at E = 5.2 eV) are present in the DCS.

Thus, the use of electron spectroscopy has made it possible to confirm once more the assumption that short-lived states of negative ions play a primary role in the mechanism of formation of the structure in the



FIG. 4. Energy dependence of the DCS for the excitation of the $3^{1}P_{1}$ level.



FIG. 5. Spectra of emitted electrons at primary beam energy 14.7-11.2 eV.

scattering cross sections, as well as the register heretofore unknown resonances and regularities in the cross sections.

ELECTRON SPECTRA OF AUTOIONIZING STATES

Some of the autoionizing-state spectra recorded by us are shown in Fig. 5. One notices a relatively low intensity of the lines in the spectra. This indicates that another, radiative decay takes place effectively when the probability of the electronic excitation of the AIS is large.

To interpret the spectra we used as the reference, just as in Ref. 10, the narrow and sufficiently intense line 9, which corresponds to decay of the 3p3d¹F state $(E_a = 9.99 \text{ eV})$. The line energies reckoned from this reference are listed in Table I. In each case we chose the average result of 15 and more independent measurements for beam energies exceeding the AIS thresholds

TABLE I.

Line No.	E _a , eV	E _{em} , eV	[10]	State	æ	k	r, eV
1	8.39	0.75	0,81	3p3p1S	-	-	_
2	8,69	1.05	-	- 1	-	- 1	-
3	8.92	1.28	-	-	- 1	-	- 1
4	9.16	1.52		- 1	-	-	-
5	9,29	1.65	-		- 1	- 1	-
6	9.52	1.88	1.90	3p4s ³ P	- 1	-	1 -
7	9.72	2.08		-	- 1	-	-
8	9.84	2.20	-	-	- 1	-	-
9*	9.99	2.35	2,35	$3p3d^{1}F$	-	-	-
10 **	10.14	2.50	2.50	3p3d ¹ D	0.89	0,08	0.05
11 **	10,22	2.58	-	-	1.74	0.07	0.04
12	10.37	2,73	2,74	-	- 1	-	-
13 **	10.65	3.01	3,00	$3p3d^{1}P$	1.88	0.05	0.03
14	10.87	3.23	3.21	$3p5s^{3}P$	-	-	-
15 **	11.07	3,43	3 .43	3p4d ⁴ D	{ 0.55	0.09	0.05
46	11 34	370	371	3n6s3P	(1,10	0.00	-
17 **	11 47	3.83	3.80	$3n5d^4F$	0.66	0.06	0.03
18 **	11.68	4 04	4 01	$3n6d^4F$	(0.33	0.06	0.03
10	11.00	-1.01	01	op Sur I	1.00	0.04	-
19	11.83	4.19	4.20	$3p9s^{1}P$	- 1	- 1	1

*Reference used to determine the absolute energy scale. **Lines for which a shift was observed. by at least 3 eV. The energy-determination accuracy is estimated at ± 0.01 eV. As seen from the table, the agreement with the data by others is good.

At low primary-beam energy we have observed a number of lines not observed by others. It can be assumed that the appearance of "new" lines at low energies is due to the effective population of the AIS through intermediate short-lived states of negative ions:

$$e + A \rightarrow A^{-} \rightarrow A_{\text{AIS}} + e_{\text{scat}}$$

$$\downarrow$$

$$A^{+} + e_{\text{em}},$$

where A and A_{AIS} are the atom in the normal and autoionizing states, respectively, and A^- and A^+ are respectively negative and positive ions. This process is probable only near resonance, therefore at other energies the lines may not be observed because of the low probability of their direct electronic excitation.

With the primary-beam energy approaching the AIS thresholds, we registered fifths of the maxima of a large number of lines towards higher energies, thus pointing to post-collisional interaction. As the energy is decreased (see Fig. 5), the lines higher in energy than the others begin to shift, since the initial beam energy above the AIS threshold, $E_1 = E - E_a$, becomes a small quantity for them. With further decrease of energy, more and more lower-lying lines join in the shift. Besides the shift, we could observe deformation of the line contours, the appearance of asymmetry, as well as line crossing. Such a crossing is seen in Fig. 5 for the lines 13 and 14, which are separated by 0.22 eV. The effect was most pronounced for line 15 (4p4d ¹D state). The maximum shift of this line exceeds 0.3 eV, and the width changes from several hundredths to 0.5 eV and more. In addition, it is characterized not only by asymmetry but also by appearance, on the left and on the right of the maximum, of weakly pronounced components, which are apparently due to the interference of the contour of the line predicted by the quantum theory of this effect.¹³

We have observed reliably in the investigated energy interval of the emitted electrons a shift of six spectral lines. A fact worthy of attention is all these lines (with the exception of the unidentified state 11) and 3pnd levels of the atom (see Table I).

The classical theory of the PCI effect, proposed by Barker and Berry,¹⁴ presupposes that the shift of the spectral lines of the emitted electrons obeys the law $\Delta E = eE_1^{-\alpha}$. The exponent $\alpha = 0.5$ agrees well with the experimentally obtained value.¹⁴ Later, however, a stronger dependence of the apparent shift on the energy E_1 was observed. Nienhuis and Heideman¹⁵ proposed and demonstrated theoretically that the law indicated above with $\alpha = 0.5$ should hold only at very small and very large E_1 . In the intermediate region the shift should be described by $\Delta E = kE_1^{-1.5}$. To determine the parameters α and k we investigated the dependence of the shift ΔE on the value of E_1 . This dependence is shown in a logarithmic scale for five lines of the spectrum in Fig. 6. For lines 15 and 18, the presence of two regions with different α is seen quite convincingly. The values of α and k determined from the plots are



FIG. 6. Dependence of the apparent shift ΔE of the AIS thresholds on the above-threshold energy of the primary beam $E_1 = E - E_a$. The number on a curve corresponds to the number of a line in Table I.

given in Table I. We were unable to register the kink of the curve on the side of large E_1 because of the small displacement, which was commensurate in this region with the line-energy measurement error. Starting from classical concepts, we can determine the widths Γ of the autoionizing states by assuming that their lifetime does not depend on the energy of the incident electrons. These calculated data are also given in Table I. Although the values obtained for Γ are estimates, since the theoretical premises developed for helium atoms cannot be transferred directly to so complicated an atom as magnesium, the numbers presented do not contradict the experimentally observed values.

Shpenik, Zapesochnyi, et al.,⁷ analyzing the structures of the excitation functions of the spectral lines that start out from low-lying energy levels of the magnesium atom, have reached the conclusion that the extrema that lie beyond the limit of single ionization are due to the PCI effect near three AIS. One of them is the 3p3d¹D state. A shift of line 10 and the spectra of the measured electrons, corresponding to the decay of this state, was observed by us (see Table I). Thus, we have confirmed the occurrence of PCI in this region by two independent methods. In addition, the state width determined in Ref. 7 is 0.04 eV, which is also in good agreement with our 0.05 eV.

Two other states with excitation energies 9.62 (Γ = 0.46 eV) and 10.32 eV (Γ = 0.17 eV) were identified

earlier as 3p4s ¹P and 3p3d ³D states. The line energy is given in Ref. 10 for these states are 2.17 and 2.69 eV, respectively. Our nearest narrow lines 8 and 12 do not shift when the energy is changed. It can be noted, however, that at energies near 2 and 2.5 eV our spectra contain very broad formations which are possibly manifestations of the indicated states. It is impossible to track rigorously their displacement with changing energy, in view of their large width and the superposition of narrow lines, but a noticeable tendency to shift to the right is nevertheless present.

The question why no shift of the structure is observed on the excitation functions of the high-lying state near other AIS subjected to the PCI effect can be answered as follows. It appears that, just as in the case of inertgas atoms,¹⁶ there is no one-to-one correspondence between the observation of the PCI effect in different channels, in the sense that a strong manifestation of the effect in the spectra of the emitted electrons does not necessarily manifest itself equally strongly in the excitation functions, and vice versa.

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