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INELASTIC ENERGY LOSS AND IONIZATION IN EXCITATION OF OUTER AND INNER ELECTRON SHELLS DURING ATOMIC COLLISIONS

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The inelastic energy loss spectra and ionization in deep collisions of He^+, N^+, Ne^+, and Cl^+ ions and Ne atoms with Ar atoms have been studied for initial energies in the keV region. The kinetic energies, charge states, and scattering angles of the two atomic particles involved in a single collision event were measured simultaneously. For all colliding particle pairs except He^+-Ar, on intersection of the inner shells discrete lines are observed in the inelastic energy loss spectra which are due to formation of vacancies in the inner shell of one of the particles. It follows from the experiment that vacancies are produced in the shell with lower electron binding energy. From analysis of the charge distributions of the scattered particles we can conclude that autoionized states involving excitation of outer shells decay during the collision while the particles are still interacting. An estimate shows that filling of internal vacancies occurs with approximately equal probabilities before and after the collision. In comparison of the experimental results on inelastic energy loss spectra and Auger electron and x-ray spectra, agreement is observed of the threshold internuclear distances at which the inner shells are excited and of the cross sections for vacancy production and the Auger electron yield. The experimental results are interpreted with a model which considers electronic transitions in the quasimolecule arising at the moment of collision. It is shown that the observed inelastic energy loss and vacancy formation probabilities can be explained in terms of the model. In vacancy formation in the systems N-Ar and Ne-Ar, it is shown that it is necessary to take into account the simultaneous interaction of a large number of electronic levels of the quasimolecule.

I. INTRODUCTION

WITH application of the coincidence technique[1,2] in the physics of atomic collisions, it became possible to measure simultaneously the charge states of the two particles which undergo a collision, the distance to which the particles approach at the moment of collision, and the inelastic energy loss. Knowledge of the charges of the two colliding particles permitted direct study of the elementary processes of the change of charge state and determination of that part of the inelastic energy which is expended in ionization.

In addition to ionization, the inelastic energy is expended in two other channels: it is carried away in the form of kinetic energy of electrons and by radiation. We note that under the conditions of deep collisions the so-called excess inelastic energy expended in these two channels is comparable with or greater than the ionization loss. The principal cause of this at comparatively low collision rates is the excitation of autoionized states.

In study of deep collisions of many-electron atomic particles of keV energies[1-3] a discrete structure has been observed in the inelastic energy loss spectra. Further studies[4-7] showed that the cause of the discrete spectra is the formation of vacancies in the inner electron shells of the colliding particles. In the energy loss spectra, inelastic transitions have been identified whose energies are close to the energies of vacancy formation in the shells intersecting in the collisions. Characteristic Auger-electron[4,6,8-13] and x-ray[14,15] lines have also been observed, corresponding to transitions in filling of the corresponding vacancies.

The very high resolution in study of inelastic study loss spectra, which is necessary for separation of the discrete energy loss lines and measurement of their natural widths, is provided by the method developed by us of simultaneous analysis of the kinetic energies of the two colliding particles with detection of these particles in coincidence[16]. This method has been used to obtain data on symmetric cases, i.e., on collisions of ions and atoms of identical elements: Ar^+–Ar[5] and Ne^+–Ne, Kr^+–Kr[7].

In the present work we have studied the inelastic energy loss and ionization for asymmetric cases, i.e., in collisions of different ions—He^+, N^+, Ne^+, Cl^+, and Ne with the same atom Ar. The range of incident particle initial energies T_0 was 25–48 keV, and of the scattering angles $\vartheta = 10$–$30°$. A brief report of the results obtained has been given previously[17].

II. EXPERIMENTAL RESULTS AND DISCUSSION

The energy loss spectra were investigated for occurrence of various processes of change of the charge states of the colliding particles:

$$A^{k+} + B \rightarrow A^{m+} + B^{n+} + (m+n-k)e$$

(brief designation k0mn). Part of the experimental data were obtained without use of the coincidence method by analysis of the angular, energy, and charge distributions of any one of the scattered particles. The information obtained in this case was less detailed. However, this method requires less time than measurement with the coincidence method. Therefore it was desirable to use it in study of the averaged characteristics of inelastic collisions: the probabilities for excitation of various inelastic energy loss lines, the average values of energy loss and charge of the scattered particles over a wide range of T_0 and ϑ. In analysis of the experimental data the angles ϑ (for fixed values of T_0) were compared with the distances of closest approach between the colliding particles r_0, calculated by Nikulin[18] for the Thomas-Fermi and Thomas-Fermi-Dirac potentials and the quantum-mechanical electron density distributions in the atoms.

For the pair He$^+$-Ar, right up to the smallest distance of closest approach studied in the present work, ~ 0.025 Å, i.e., a distance considerably less than the size of the L and K shells of Ar, a single energy loss line was observed which was due to inelastic processes in the outer shells of the interacting particles. The line energy corresponding to the peak of the distribution, for the He$^+$-Ar case increases smoothly with increasing initial energy T_0 and is practically independent of the scattering angle ϑ, amounting to 92 ± 8 eV (T_0 = 24.5 keV, ϑ = 20°) and 135 ± 15 eV (T_0 = 48 keV, ϑ = 30°).

For collisions of the heavier ions N$^+$, Ne$^+$, and Cl$^+$ with Ar, the dependence of the inelastic energy loss spectrum and the charge state of the scattered particles on the distance of closest approach has much in common with the similar dependences for collision of identical particles[1-7]. On reaching distances of closest approach corresponding to intersection of the inner electron shells, the inelastic energy loss spectrum consists of several lines Q_l (the index l, which is equal to I, II, and III, indicates the number of the line in the spectrum in the order of increasing energy loss). As can be seen from Fig. 1, the line energies $\bar{Q}_l$, averaged over all charge states of the scattered particles, depends only weakly on the approach distance. At the same time the probabilities of excitation of the various lines W_l are sharply redistributed in the region of intersection of the inner shells. For N$^+$-Ar and Ne$^+$—Ar collisions these variations are observed in the range $r_0 \sim 0.1$ Å, corresponding to intersection of the K shell of the incident ion and the L shell of Ar. In the case Cl$^+$-Ar, redistribution of the probabilities W_l occurs in the region $r_0 \sim 0.25$ Å, corresponding to intersection of the L shells of the two particles. As the result of this redistribution of probabilities, there is a sharp rise in the average inelastic energy

$$\bar{Q}(r_0)=\sum_l W_l(r_0)\bar{Q}_l(r_0).$$

There is also a rapid change of the average charge $\bar{n}$ of the Ar recoil ions in the case Ne$^+$-Ar and the average charge $\bar{m}$ of Cl ions in the case Cl$^+$-Ar. On the other hand, the average charge of the second particle in these collisions changes smoothly. We recall that in collisions of identical particles the charges of the two particles change in a step in the transition from excitation of one inelastic loss line to another.

Below we have given a more detailed discussion of the experimental results and their interpretation, separately for phenomena accompanying excitation of outer and inner electron shells of the colliding particles.

1. Excitation of Outer Electron Shells

It was shown previously[1,2,4-7] that the line with lowest energy (Q_I) observed in the loss spectra in deep collisions is due to excitation and ionization of the outer shells of the interacting particles. In Table I for the case of Ne$^+$-Ar, T_0 = 46 keV, ϑ = 13°, we have shown the values measured in the present work for the energy Q_I

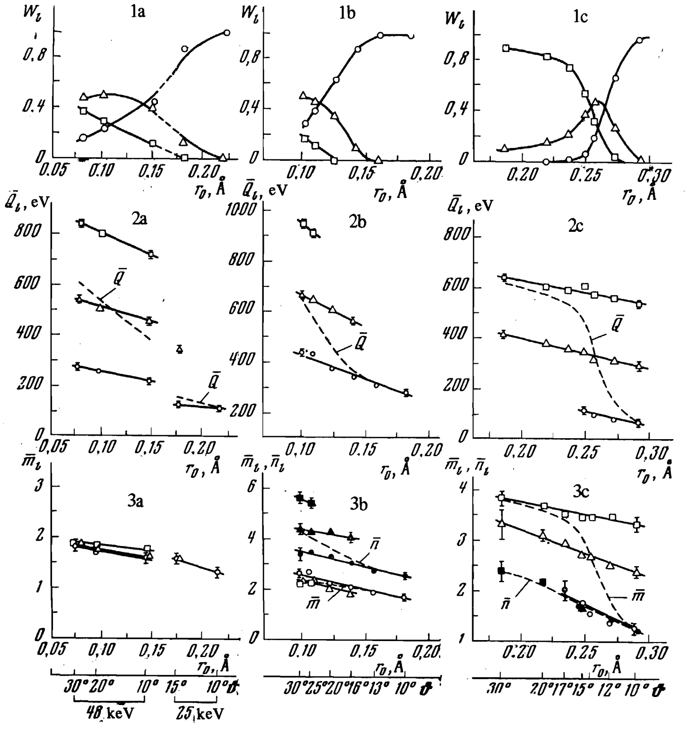

FIG. 1. Dependence on distance of closest approach r_0 between colliding particles: 1—relative probabilities W_l for excitation of various inelastic loss lines Q_l, 2—average energies $\bar{Q}_l$ of inelastic loss lines, 3—average charges of the scattered incident particle $\bar{m}_l$ (hollow symbols) and recoil particle $\bar{n}_l$ (solid symbols) in excitation of various loss lines. Plots a—N$^+$-Ar, T_0 = 25 and 48 keV; b—Ne$^+$-Ar, T_0 = 46 keV; c—Cl$^+$-Ar, T_0 = 25 keV. The points correspond to: ○, ●—l = I, △, ▲—l = II, □, ■—l = III.

Table I.

Process 10mm	Σ, eV	Q_I, eV	ΔQ_I, eV	Q_I^*, eV
1012	43	226±6	156±10	183
1021	57	266±8	182±10	209
1013	84	257±10	160±12	173
1022	85	291±6	146±6	206
1031	120	336±10	180±20	216
1023	125	323±6	158±8	198
1032	148	355±10	154±16	207
1033	189	383±10	153±18	194

*Here we define $\Sigma = \sum_m U_m + \Sigma_n U_n$.

and the width ΔQ_I of the first inelastic loss line, and also the excess inelastic energy

$$Q_I^* = Q_I - \sum_m U_m - \sum_n U_n$$

for occurrence of various processes of change of charge states of the colliding particles kOmn. The sums of the ionization potentials ΣU_m and ΣU_n are the expenditures of energy in ionization of the two particles, and the excess energy Q_I^* is the total kinetic energy of the electrons removed in the collision. It follows from Table I for the specific elementary process 10mn that the line energy appreciably exceeds the energy expended in ionization of the particles. This means that the number of excited electrons forming each of the autoionized states exceeds the number of electrons removed from the particles in decay of these states.

It is interesting to note that the average inelastic energy $\overline{Q}_I$ is distributed between expenditure in ionization and in energy carried away by electrons in a proportion which is practically independent of the structure of the interacting particles and the conditions of the collision: the energies T_0 and the distances of closest approach r_0. In fact, for the investigated pairs Ar^+-Ar[5], Ne^+-Ne, and Kr^+-Kr[7], and Ne^+-Ar and Cl^+-Ar the ratio is

$$\overline{Q}_I^* \Big/ \Big(\overline{\sum_m U_m} + \overline{\sum_n U_n}\Big) = 1.25 \pm 0.25.$$

From Table I it can also be seen that both the line width and the energy carried away by electrons do not increase with an increase in the number of electrons removed. This is apparently due to the fact that the ionization process in a specific collision event is not the result of a series of independent single-electron transitions, but necessarily occurs through the stage of formation of a common autoionized state. A similar picture was observed earlier also for symmetric pairs of colliding particles[1,5,7]. As we have shown previously[5,7], for description of the excitation and ionization of the outer shells under conditions of deep collisions it is extremely desirable to use a statistical approach.

An interesting experimental fact has been noted in study of the charge distributions of the scattered particles under conditions of excitation of the line Q_I. It had been shown earlier[1,2,4] that in collisions of identical particles the two collision partners are ionized identically, i.e., the charge distributions $P_I(m)$ and $P_I(n)$ and the average charges of the two particles $\overline{m}_I$ and $\overline{n}_I$ are identical. In collisions of the unlike particles Ne^+-Ar and Cl^+-Ar the charge distributions of the particles are different, but with high accuracy the average expenditure of energy in ionization of each of the particles is the same:

$$\overline{\sum U_m} = \overline{\sum U_n}$$

and the average ionization potentials of the ions produced are identical: $\overline{U}_m = \overline{U}_n$. (The quantities $\overline{\Sigma U}$ and $\overline{U}$ were determined as the average values for the distributions $P_I(m)$ and $P_I(n)$.) The latter equality means that on the average electrons are removed from the two particles with binding energies which are less than some value which is identical for the two particles. The existence of a binding energy level common for the two particles provides a basis for assuming that ionization of the outer shells occurs in the collision process while the atomic particles are still interacting with each other.

2. Excitation of Inner Electron Shells

The appearance in the loss spectra of the lines Q_{II} and Q_{III} is due to excitation of the inner shells of the colliding particles. As has been noted previously[5,7], each of the lines Q_{II} and Q_{III} can be considered to be the result of superposition of two processes: the excitations of the outer and inner shells, i.e., excitation of the line Q_I and respectively one (Q_{I-II}) or two (Q_{I-II} and Q_{II-III}) levels. For the pairs studied we determined the energies $\overline{Q}_{l-l'}$ and the widths $\Delta\overline{Q}_{l-l'}$ of these levels, and also the ionization of the particles $\overline{m}_{l-l'}$ and $\overline{n}_{l-l'}$ due to their excitation. Here it was assumed that the excitation of the inner shells does not affect the excitation and ionization processes in the outer shells, i.e., the quantities discussed were defined as

$$\overline{Q}_{l-l'} = \overline{Q}_{l'} - \overline{Q}_l, \quad \Delta\overline{Q}_{l-l'} = (\Delta\overline{Q}_{l'}^{\,2} - \Delta\overline{Q}_l^{\,2})^{1/2},$$
$$\overline{m}_{l-l'} = \overline{m}_{l'} - \overline{m}_l.$$

The characteristic values of these quantities are given in Table II.

A. Vacancy Formation

The results of the present work are in agreement with this assumption that the cause of appearance of the lines Q_{II} and Q_{III} is the formation of respectively one or two vacancies in the inner shells. This is indicated by the closeness of the energies of the identified levels $\overline{Q}_{I-II}$ and $\overline{Q}_{II-III}$ to the binding energies E_{bi} in the corresponding shells. Thus, in Ne^+-Ar collisions the levels $\overline{Q}_{I-II}$ = 225 eV and $\overline{Q}_{II-III}$ = 270 eV are excited, whose energies are close to the binding energy of $L_{2,3}$ electrons in Ar (Table II).

From Table II it follows that one or both vacancies are formed in that one of the interacting shells for which the binding energy is less. This is obvious for N^+-Ar and Ne^+-Ar collisions, since the binding energy for the K shells of N and Ne are substantially greater than the energy of the observed levels $\overline{Q}_{l-l'}$. It is difficult to draw this conclusion for the case Cl^+-Ar on the basis of comparison of the energies of the levels and the binding energies of $L_{2,3}$ electrons in the Cl and Ar atoms, but, as will be shown in the next section, it is substantiated by the data on particle ionization. The conclusion that the electron binding energy has a decisive influence on the place of vacancy formation is in agreement also with the experimental results obtained by Fastrup, Hermann, and Smith[6].

Table II.

Collision	T_0, keV	Interacting shells	$l-l'$	$\bar{Q}_{l-l'}$, eV	$\Delta\bar{Q}_{l-l'}$, eV	$\bar{m}_{l-l'}$	$\bar{n}_{l-l'}$	E_{bi}, eV
N^+—Ar	48	K(N)—L(Ar)	I—II	250±10	75±30	0,05±0,15	—	K(N)—400
			II—III	290±10	90±30	0,10±0,15	—	
Ne^+—Ar	46	K(Ne)—L(Ar)	I—II	225±15	70±35	—0,30±0,10	1,0±0,3	K(Ne)—870
			II—III	270±25	70±35	—0,10±0,15	1,1±0,3	
Cl^+—Ar	25	L(Cl)—L(Ar)	I—II	225±10	60±15	1,10±0,10	0±0,2	$L_{2,3}$(Cl)—200
			II—III	255±10	60±30	0,75±0,15	0±0,2	
Ar^+—Ar[5]	26	L(Ar)—L(Ar)	I—II	260±10	65±15	0,7±0,1	0,7±0,1	$L_{2,3}$(Ar)—250
			II—III	270±10	65±15	0,7±0,1	0,7±0,1	

As the results of the present experiment show, formation of one or both vacancies in one of the interacting particles occurs with comparable probability. For example, for N^+-Ar collisions with $r_0 = 0.8$ Å (Fig. 1), the probabilities turn out to be $W_{II} \sim 0.5$ and $W_{III} \sim 0.4$. We can assume that in the case of collisions of identical particles the two vacancies also occur with appreciable probability in one of the partners. This assumption is confirmed by the results of our previous work[19], in which we studied the correlation between the scattered-particle charge states for Ar^+-Ar collisions. It was found that in excitation of the line Q_I there is practically no correlation. At the same time there is a correlation for the lines Q_{II} and Q_{III}, the correlation being greater for the line Q_{II}. The correlation arising in collisions of identical particles in excitation of the line Q_{II} is evidently due to the fact that in this case only one vacancy is formed, i.e., one of the partners is selected. Correspondingly, in excitation of the line Q_{III} only an asymmetric distribution of the two vacancies (2-0 or 0-2) between the collision partners can result in appearance of a correlation, and the symmetric distribution of vacancies (1-1) does not produce a correlation. By comparing the correlation values for excitation of different loss lines, we can quantitatively evaluate the probability for formation of the two vacancies in one particle. This probability turned out to be extremely high:

$$0.8^{+0.2}_{-0.3}.$$

The possibility of formation of two L vacancies in one of the atoms is indicated also by the experimental results from study of the electron energy spectra arising in Ar^+-Ar collisions[12]. Ogurtsov, Flaks, and Avakyan have observed electrons with an energy corresponding to the Auger process LL-MMM in which the energy of the transition of two M electrons to an L vacancy is transferred to one emitted electron. However, evaluation of the cross section for appearance of two L vacancies is not possible from their data, since it is not known in what ratio the two vacancies are filled as the result of one LL-MMM or two ordinary L-MM Auger processes.

B. Ionization of Particles in Excitation of Vacancies

Excitation of levels $Q_{l-l'}$ is accompanied by removal of some additional number of electrons $\bar{m}_{l-l'}$ and $\bar{n}_{l-l'}$ from the colliding particles. As has been noted by us earlier[7], in collisions of identical particles the total number of electrons $\bar{m}_{l-l'}$ and $\bar{n}_{l-l'}$ turns out to be close to the number of electrons leaving an isolated atom on filling of a vacancy as the result of Auger transitions. From Table II it follows that in collisions of unlike particles the average number of electrons removed in filling of a vacancy is also close to this same value. However, in contrast to symmetric collisions, in which the two particles are ionized identically, i.e., $\bar{m}_{l-l'}$ is always equal to $\bar{n}_{l-l'}$, in asymmetric cases that one of the particles is ionized in which the vacancy is produced.

In Cl^+-Ar collisions the chlorine atom is ionized ($\bar{m}_{l-l'} \approx 1$, while $\bar{n}_{l-l'} \approx 0$). This means that even for close binding energies in the interacting shells the vacancy is produced preferentially in that one of the shells in which the binding energy is smaller. It is interesting to note that in Ne^+-Ar and Ne-Ar collisions the average charge of neon decreases somewhat in the transition from excitation of the line Q_I to excitation of Q_{II} and from Q_{II} to Q_{III} (see Table II and Fig. 1). This means that the assumption that the excitation processes in the outer and inner shells are independent is only approximate.

C. Widths of Levels Associated with Vacancy Formation

Excitation of autoionized states associated with vacancy formation in the inner shells of the interacting particles leads to an increase of the natural widths of the loss lines ΔQ_{II} and ΔQ_{III} in comparison with the width of the first line ΔQ_I. As can be seen from Table II, the widths measured in the present work $\Delta\bar{Q}_{l-l'}$ of levels corresponding to formation of L vacancies in Cl and Ar atoms are on the average 70 eV, i.e., they turn out to be close to the values of $\Delta\bar{Q}_{l-l'}$ for the pair Ar^+-Ar[5].

One of the factors leading to appearance of intrinsic widths of the levels $Q_{l-l'}$ is the ambiguity in the energy for vacancy formation ΔE_{vac}. This is due to the dependence of the binding energy of an inner electron on the state of the outer shells of the colliding particles, and also to the possibility of a transition of an internal electron to one of the free discrete levels or to the continuum.

To evaluate the quantity ΔE_{vac} we used the calculations of Larkins[20] of the binding energy of $L_{2,3}$ electrons in the atom and ion of Ar with various numbers of electrons removed from the outer shell. It was assumed that occurrence of $L_{2,3}$ vacancies occurs in Ar ions with various charges, formed in excitation of the outer shells. The experimental probabilities for the various charge states of Ar in excitation of the first inelastic loss line Q_I for Ar⁺-Ar collisions, $T_0 = 26$ keV, $\vartheta = 15°$, are: $P_I(0) = 0.06$, $P_I(1) = 0.35$, $P_I(2) = 0.48$; $P_I(3) = 0.11$. From this it was determined that the width of the distribution ΔE_{vac} at half-height is ~ 35 eV, which is a factor of two smaller than the intrinsic widths of the levels, and the peak of the distribution corresponds to $E_{vac} \approx 276$ eV, which, on the other hand, is greater than the experimental value $\overline{Q}_{I-II}$ (see Table II). The distribution of E_{vac}, taking into account the possibility of relocation of the $L_{2,3}$ electron not only into the continuum but also into one of the vacant discrete levels, was obtained on the assumption that the relocation of an inner electron to any part of the energy interval from the lowest vacant level to the edge of the continuum was equally probable. The width of this distribution is also ~ 35 eV, and the peak is displaced toward lower energies, $E_{vac} \approx 255$ eV. Thus, the effect of different states of the outer shells on the energy for vacancy formation cannot completely explain the observed level widths $\Delta\overline{Q}_{l-l'}$.

The appreciable width $\Delta\overline{Q}_{l-l'}$ can be due to filling of vacancies before separation of the particles. In this case, as was noted previously for Ar⁺-Ar collisions[5], the width is determined by the dependence of the probability and energy of the transition between the terms of the system on the internuclear distance.

D. Lifetime of Vacancies in Internal Shells and Correlation of Final Charge States of the Particles

The experimental results which have been set forth in the two preceding sections B and C provide indirect information on the time of filling of the internal vacancies. The preferential removal of electrons, observed in the filling of vacancies, from that particle in which the vacancy was produced provides a basis for the assumption that the filling occurs after the collision. On the other hand, to explain the widths of the lines we are forced to assume that the autoionized states can also decay before separation of the particles.

The probability of filling of vacancies before and after the particle separation can be evaluated from the data on correlation of the final charge states of the particles[19], which have already been utilized above in section A. Since, in excitation of the line Q_{II}, an L vacancy is formed in one of interacting particles, and the filling of the vacancy is accompanied by removal of some additional number of electrons $(m + n)_{I-II}$, then naturally as a result of this ionization a correlation can arise between the charges of the scattered particles.

If vacancy filling occurs in the collision process before or simultaneously with the ionization of the outer shells, then it is reasonable to assume that there will be no correlation in excitation of the line Q_{II} in this case (as for the line Q_I). It is known that in the absence of correlations the equality $p'_{II}(m, n) = P_{II}(m)P_{II}(n)$ should be observed, where $p_{II}(m, n)$ is the probability of occurrence of the elementary process 10mn in excitation of the loss line Q_{II}, and $P_{II}(m)$ and $P_{II}(n)$ are the experimental probability values, which are

$$P_{II}(1) = 0.09, P_{II}(2) = 0.37,$$
$$P_{II}(3) = 0.41, P_{II}(4) = 0.12, P_{II}(5) = 0.01.$$

In this case the correlation ratio η'_{II} (as was done previously[19] we have used the quantity η to estimate the degree of correlation) is zero.

The correlation will be maximal if the filling of the vacancy occurs after the separation of the particles, when the ionization processes in the outer shells are already completed. The probabilities $p''_{II}(m, n)$ in this case can be calculated by modeling if we proceed from the assumption, which is in good agreement with experiment, that formation of inner vacancies does not appreciably affect the distribution of the number of electrons removed, which is characteristic of the first loss line Q_I:

$$p''_{II}(m, n) = a_1[0.5P_I(m-1)P_I(n) + 0.5P_I(m)P_I(n-1)] + a_2[0.5P_I(m-2)P_I(n) + 0.5P_I(m)P_I(n-2)],$$

where a_1 and a_2 are the probabilities of removing one and two electrons in filling of the vacancy (the probabilities a_0, a_3, and a_4 are negligibly small). If in determination of $p''_{II}(m, n)$ we make use of the experimental values

$$P_I(1) = 0.28,\quad P_I(2) = 0.52,\quad P_I(3) = 0.20,\quad a_1 = 0.65,\quad a_2 = 0.35$$

the correlation ratio turns out to be $\eta''_{II} = 0.45$, which is appreciably greater than the experimental value $\eta_{II} = 0.28$.[19]

The real probabilities $p_{II}(m, n)$ were represented in the form of a sum:

$$p_{II}(m, n) = kp_{II}'(m, n) + (1 - k)p_{II}''(m, n),$$

where k is the probability of filling the vacancy before the separation of the particles. Equality of the theoretical and experimental values of the correlation ratio is achieved for $k = 0.4$. This means that within the framework of the assumptions made the filling of inner vacancies occurs with comparable probabilities during and after the collision.

E. Comparison of the Results Obtained for Inelastic Energy Loss Spectra and the Electron and X-ray Spectra

A number of experimenters[9,11,14,15,21] have measured the cross sections for Auger electron emission σ_{Aug} and x-ray emission σ_{rad} arising on filling of vacancies in inner shells as a function of the initial collision energy for a number of pairs of colliding particles. Figure 2 shows these functions for Ar⁺-Ar collisions. The cross sections σ_{Aug} and σ_{rad} were obtained in the study of spectra corresponding respectively to the total yield of electrons and photons, i.e., to collisions with all possible impact parameters p. From experiments on inelastic energy loss, in turn, the cross sections for vacancy formation σ_{vac} can be calculated for a fixed energy T_0 according to the formula

$$\sigma_{vac} \approx \sigma_{II} + 2\sigma_{III} = 2\pi \int_0^\infty W_{II}(p)p\,dp + 4\pi \int_0^\infty W_{III}(p)p\,dp,$$

where σ_{II} and σ_{III} are the cross sections for excitation of the loss lines Q_{II} and Q_{III} (the factor 2 takes into account that in excitation of the line Q_{III} two vacancies are produced in each collision event), $W_{II}(p)$ and $W_{III}(p)$ are the probabilities of excitation of the lines as a function of the impact parameter p, which is uniquely related to the distance of closest approach r_0. In Fig. 2 we have shown the experimental functions $W_l(r_0)$ necessary

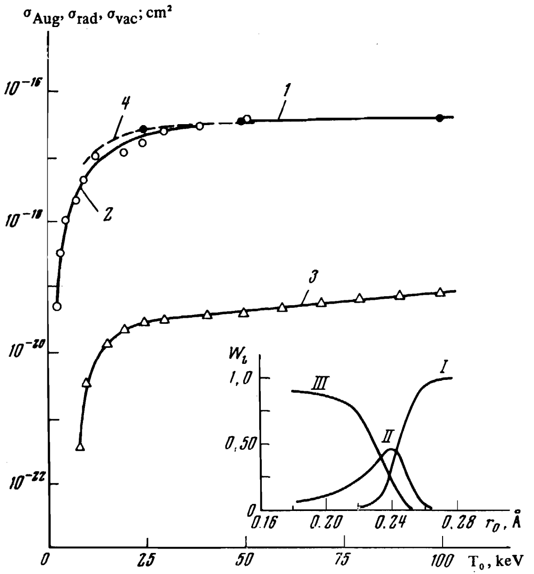

FIG. 2. Cross sections for formation of $L_{2,3}$ vacancies, σ_{vac}, emission of electrons, σ_{Aug}, and x rays, σ_{rad}, occurring on filling of $L_{2,3}$ vacancies, as a function of initial energy T_0 in Ar^+-Ar collisions: 1—σ_{Aug} from ref. 11, 2—σ_{Aug} from ref. 21, 3—σ_{rad} from ref. 15; 4—σ_{vac}. Below at the right are shown relative probabilities for excitation of inelastic energy loss lines Q_l for different distances of closest approach r_0 for Ar^+-Ar collisions, T_0 = 26 keV: I—W_I, II—W_{II}—W_{III}.

for calculation of σ_{vac} for an initial energy T_0 = 26 keV, the shape of these dependences being practically constant over the energy range studied, 10—50 keV. Formation of some additional number of vacancies which evidently occurs at approach distances less than ~ 0.1 Å,[2] cannot change the cross-section σ_{vac} appreciably, in view of the smallness of the corresponding cross sections.

Calculation of σ_{vac} can be carried out with a good approximation also by means of the simplified formula $\sigma_{vac} = 2\pi p^2_{crit}$[11], assuming that the probability of vacancy formation increases in a step at a critical approach distance $r_{crit} \approx 0.24$ Å.

As can be seen from Fig. 2, beginning with a certain energy, a sharp rise is observed in all three cross sections σ_{vac}, σ_{Aug}, and σ_{rad}, which is a consequence of existence of a threshold value of the internuclear distance, on reaching which the formation of vacancies in the inner shells becomes possible. In Fig. 2 one is struck by the fact that the cross sections σ_{vac} and σ_{Aug} are almost completely identical. As can be seen from the figure, the mean decay channel of autoionized states with a vacancy in an inner shell is Auger transitions. It should be noted also that the widths of the Auger peaks in the electron spectra arising in Ar^+-Ar collisions[11,13] and Ne^+-Ar collisions[11] are in agreement with the widths $\Delta Q_{l-l'}$ of the levels identified in ref. 5 and in the present work. The relation between the appearance of a discrete structure in the inelastic energy loss spectra and appearance of Auger electrons is confirmed also by the results of Thomson et al.[13], who showed that the threshold distances of closest approach for these two processes are identical.

Thus, we can conclude that there is agreement between the results of three groups of experiments on the excitation and decay of autoionized states associated with formation of inner vacancies in atomic collisions.

F. The Mechanism of Vacancy Formation

As has been noted above, for the pair He^+-Ar no excitation was observed of loss lines associated with vacancy formation in the inner shells of Ar, up to closest approach distances less than the dimensions of the L and K shells of Ar. According to our data, the cross section for production of L vacancies in Ar for this pair for T_0 = 48 keV is less than 2×10^{-19} cm². In contrast to He^+-Ar collisions, formation of L vacancies in Ar in collisions of N^+, Ne^+, and Ar^+ ions with Ar atoms occurs with a probability close to unity just as the inner shells of the interacting particles intersect. For this reason the cross sections for vacancy production turn out to be one to two orders of magnitude higher and for the same initial energy are respectively 4.0×10^{-18}, 3.5×10^{-18}, and 3.0×10^{-17} cm². A number of studies[8-11,14,15] have shown that the cross sections for emission of Auger electrons and photons arising on filling of L vacancies in Ar in H^+-Ar and He^+-Ar collisions are several orders of magnitude smaller than in the case of heavy-particle collisions for equal relative collision energies. This effect indicates a difference in the excitation mechanisms in collisions of the simplest ions and of many-electron ions with Ar atoms.

It is well known that ionization of inner shells of particles in collisions with participation of a proton or α particle occurs as the result of the direct Coulomb interaction between the incident particle and the electron of the corresponding shell. The experimental data are in good agreement with the theoretical calculations for this interaction[9]. In collisions involving many-electron atomic particles the formation of vacancies is due to electronic transitions on crossing of the terms of the quasimolecule arising at the moment of collision. This mechanism of vacancy formation as applied to deep collisions of atomic particles has been discussed by Fano and Lichten[22]. In view of the complexity of the calculation of the complete terms of the quasimolecule, these authors analyze the energy states of the individual electrons, obtained in terms of the molecular orbital approximation, as a function of the internuclear distance r. In the limiting cases r → ∞ and r → 0 the electronic levels of the quasimolecule (molecular orbitals) coincide with the levels of the isolated atoms and the combined atom. One of the principal assumptions of Fano and Lichten[22] is that the behavior of the molecular orbitals in the intermediate region of internuclear distances is adiabatic, as the result of which intersection occurs of orbitals formed from atomic levels belonging to the various electron shells.

The model of Fano and Lichten[22] has successfully explained the formation of vacancies in Ar^+-Ar and Ne^+-Ne collisions and, as was shown in ref. 7, has permitted interpretation of the experimental results for Kr^+-Kr collisions. An additional achievement of the model is the explanation of the formation of only two $L_{2,3}$ vacancies in Ar^+-Ar collisions in the region of closest approach distances r_0 ~ 0.24 Å. According to the Fano and Lichten model the formation of $L_{2,3}$ vacancies at these distances is due to the advance of the $4f\sigma$

orbital, which contains two electrons. As shown in the present work, the two vacancies can arise in one of the partners with a high probability. In the absence of the model it would be difficult to explain why, in spite of the symmetry of the system, in the case where two vacancies are formed in one atom, absolutely no vacancies are formed in the second atom, i.e., formation of three or four vacancies in a single collision is not observed.

The rules for construction of correlation diagrams relating the levels of isolated and combined atoms have been discussed for asymmetric systems by Gershteĭn and Krivchenkov[23] and by Barat and Lichten[24]. As an illustration we have shown in Fig. 3 a correlation diagram for the Ne-Ar system, constructed on the basis of these rules. Analysis of the diagram for Ne-Ar and the diagrams constructed for other pairs shows that the conclusion of the present work, that the binding energy of the electrons has a decisive influence on which of the shells a vacancy is produced in, is in agreement with the Fano and Lichten model[22]. In particular, in the Ne-Ar system, as can be seen from Fig. 3, formation of just $L_{2,3}$ vacancies should occur in Ar, as the result of advance of the 3dσ orbital.

The high probability of L-vacancy formation in the Cl atom on achievement of the threshold distances of closest approach in Cl$^+$-Ar collisions (Fig. 1) is due, as in the case Ar$^+$-Ar, to advance of the 4fσ orbital, which crosses several upper unfilled levels. At the same time the appearance of a high probability for production of L vacancies in Ar, observed in N$^+$-Ar collisions and in particular in Ne-Ar and Ne$^+$-Ar collisions, requires special consideration. As can be seen from Fig. 3, the 3dσ orbital in the limit of the combined atom merges with the 3dπ and 3dδ orbitals. If we limit ourselves to discussion of interaction of only these orbitals, then the electronic transitions between them can be produced by a perturbation resulting from rotation of the internuclear axis in the collision process. Under these conditions transitions are possible from the 3dσ orbital to the 3dπ orbital, and from 3dπ to 3dδ, while transitions from 3dσ to 3dδ are forbidden by the selection rules of Fano and Lichten[22]. However, the 3dπ orbital is formed from the 2p level of Ne, in which there is only one vacancy in the case of Ne$^+$-Ar, while in the case Ne-Ar there is no vacancy at all, which should lead, as in the case of Ne$^+$-Ne, to a low probability for formation of inner vacancies[4,22]. Nevertheless the high probability of vacancy formation in Ne-Ar and Ne$^+$-Ar collisions in comparison with Ne$^+$-Ne collisions can be explained if we assume the possibility of cascade transitions (first the 3dπ orbital is vacated by $\pi \rightarrow \delta$ transitions and in this way the possibility arises for $\sigma \rightarrow \pi$ transitions). The probability of transitions between two levels of different symmetry, induced by rotation of the internuclear axis, can be close to unity, as has been shown by Russek[25].

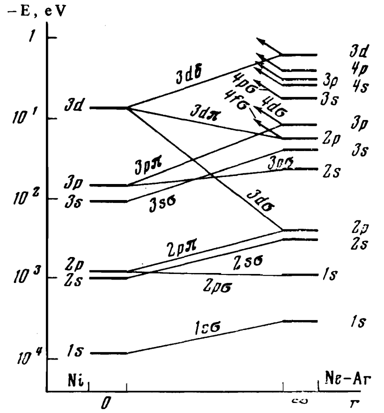

FIG. 3. Correlation diagram for molecular orbitals of the Ne-Ar system.

However, for the velocities and closest approach distances studied by us, there is evidently a more general reason for the high probability of vacancy formation—the interaction of a large number of levels. As is well known, the perturbation which produces transitions between orbitals as the result of rotation of the internuclear axis has a magnitude $\sim \hbar\omega$, where ω is the angular velocity of rotation of the internuclear axis. Expressing ω in terms of the velocity of relative motion of the particles V_0, the impact parameter p, and the distance of closest approach r_0, and substituting the numerical values of these quantities, we obtain $\hbar\omega = \hbar V_0 p/r_0^2 \approx 30$–$40$ eV. This means that it is actually necessary to take into account the possibility of transitions between the 3dσ orbital and a number of unfilled electron shells located above the 3d level of Ni, since they all lie in a narrow energy interval (E_{bi} for 3d electrons in Ni is only 8 eV). Inclusion of the interaction of many levels permits us to understand also the experimentally observed absence of any dependence of the L-vacancy formation probability in N$^+$-Ne and Ne$^+$-Ar collisions on the presence or absence of vacancies in the 3dπ orbital, since this determines the probability of only one of several possible transitions.

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