Strong violation of adiabaticity in slow atomic collisions

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Transitions are observed between nonintersecting terms of a system of colliding particles, the distance between which is ~200 eV. The transition probabilities greatly exceed the probabilities estimated on the basis of the existing theoretical models.

Collisions of many-electron atoms and ions at velocities lower than the orbital velocities of the electrons are successfully described on the basis of the adiabatic approximation. The interaction of the atomic particles is adiabatic at low values of the non-adiabaticity parameter $\xi = \hbar v / a \Delta E(R) \ll 1$, where $\Delta E(R)$ is the energy of the transition between the terms of the quasi-molecule at an internuclear distance R, v is the velocity of the nuclei, and a is the characteristic collision length. Transitions between terms occur at $\xi \gtrsim 1$, which usually corresponds to the intersection or approach of the terms. In our study we observed transitions that occur with noticeable probability at rather small values of the nonadiabaticity parameter $\xi \approx 0.1 - 0.01$.

We investigated collisions in which nitrogen, oxygen, and argon atoms and ions take part, in the energy interval $E_0 = 10-50$ keV, i.e., at relative velocities $v_0 = (4-8) \times 10^7$ cm/sec. We investigated the energy spectra $d^2\sigma/d\Omega\, dE_e$ of the secondary electron produced in the collisions. The electron emission angle was 125° relative to the direction of the primary beam. The energy resolution of the analyzer was 4%. The cross sections were calibrated against the absolute data of[1] for Ar^+–Ar collisions at 50 keV.

Some of the obtained spectra are shown in Fig. 1. The intense peak at $E_e = 180$ eV corresponds to Auger electrons that occur when $2p$-vacancies are filled in Ar. The peak at $E_e = 340$ eV is due to transitions to the $1s$ level in N. In collisions in which oxygen molecules and atoms take part, the picture is essentially the same as in the case of nitrogen.

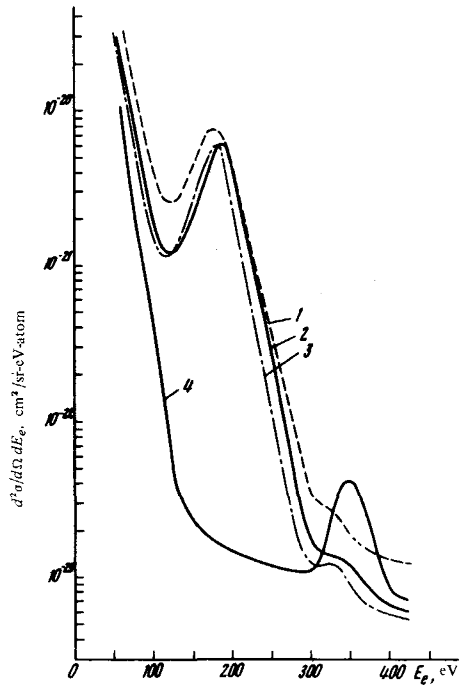

FIG. 1. Energy spectra of knocked-out electrons: 1-N^+-Ar, 50 keV; 2-N_2^+-Ar, 50 keV; 3-N^+-Ar, 17.3 keV; 4-N^+-N_2, 17.3 keV.

The interpretation of the transitions of the internal electrons is presently based principally on an analysis of correlation diagrams of molecular orbitals. The cor-

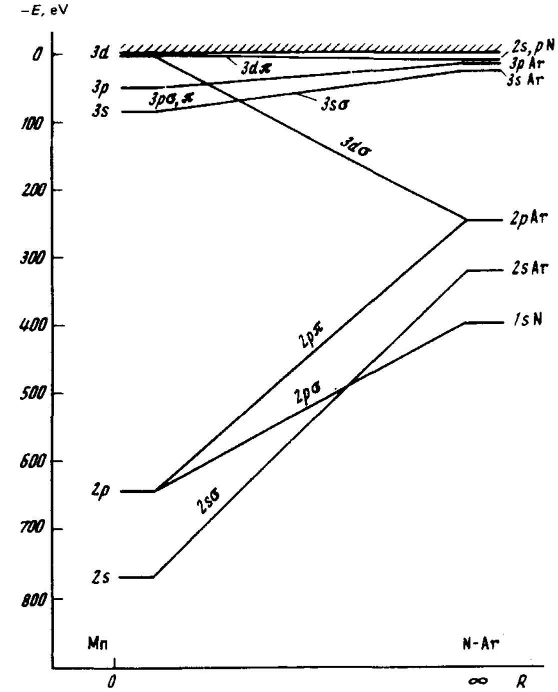

FIG. 2. Correlation diagram of N-Ar molecular-orbital system.

relation diagram for the N-Ar pair is shown in Fig. 2. The formation of a $2p$-vacancy in Ar in N^+-Ar and Ar^+-N_2 collisions is due to the emergence of the $3d\sigma$ orbital and its interaction with the upper unfilled molecular orbitals. The formation of the $1s$ vacancy in N^+-N_2 collisions, according to the correlation diagram for symmetrical systems, is attributed to transitions between the $2p\sigma$ orbital and the unfilled $2p\pi$ orbital, which come close together as $R \to 0$. The diagram of Fig. 2, however, cannot explain the formation of a $1s$ vacancy in N in N^+-Ar collisions. In accordance with the diagram, the $1s$-vacancy could be produced as a result of $2p\sigma - 2p\pi$ or $2p\sigma - 2s\sigma$ transitions, but the orbitals $2p\pi$ and $2s\sigma$ are filled, and the indicated transitions are impossible.

It is impossible to attribute the observed transition to direct knock-out of the $1s$ electrons of the N atoms by Ar. The cross section σ_i of such a process can be estimated by using the universal relation for the ionization cross sections of atomic K shells,[2] namely $\sigma_i \approx Z^2 f(v^2/U_k)$ where U_k is the K-electron binding energy and Z is the effective charge of the ionizing particle. At low velocities, this estimate usually gives too high a value of the cross section. For the case of N^+-Ar at 17.3 keV, even if we assume that $Z_{Ar} = 16$, we obtain $\sigma_i \approx 2.2 \times 10^{-23}$ cm^2. Experiment, on the other hand, yields the much larger value $\sigma(1s) \approx 1.0 \times 10^{-21}$ cm^2, and in addition, as the energy changes from 17.3 to 50 keV the cross section ($1s$) increases by approximately 2.5 times, whereas the direct ionization cross section σ_i in the investigated energy region is proportional to E_0^4.[2]

It becomes necessary to assume that the reason for the formation of the $1s$ vacancy is the strong nonadiabatic coupling of the $2p\sigma$ orbital with the upper free levels, or even with the continuum. A possible way of

Pair	N^+ - Ar			N_2^+ - Ar		Ar^+- N_2	O^+ - Ar		O_2^+-Ar
E_0, keV	17,3	25	50	34,6	50	50	25	50	50
$\frac{\sigma(1s)}{\sigma(2p)} 10^4$	3.4±1.3	5.0±0.6	5.3±0,6	4.7±0.6	4.2±0.5	4.9±0.5	1.6±0,6	2.7±0.8	1.7±0.6

formation of the $1s$ vacancy is the two-step process. It is known[3] that when the atoms come close together to small internuclear distances, one or two vacancies are produced on the $3d\sigma$ orbital, with high probability, as a result of the emergence of this orbital. When the particles move apart, these vacancies can go over from the $3d\sigma$ to the $2p\sigma$ orbital, if the coupling between the orbitals is strong enough.

The main measurement results are listed in the table. If the proposed explanation is valid, then the ratio $\sigma(1/s)/\sigma(2p)$ of the cross section of formation of a $1s$-vacancy in N to the cross section of formation of a $2p$-vacancy in Ar is a direct measure of the probability of the $2p\sigma - 3d\sigma$ transitions.

Although the considered $2p\sigma - 3d\sigma$ transition is energywise most favored of all the possible ones, its energy changes, as R varies from ∞ to 0, from 280 to 720 eV in the O-Ar case and from 150 to 650 eV in the N-Ar case. At the same time, the nonadiabatic perturbation $\hbar v/a$ in the investigated conditions amounts to ~10 eV. Estimates of the maximum transition probability, made in accordance with[4], yield values that are smaller by several orders of magnitude than the experimental ones, and lead to an exponential dependence of the probability on the velocity, which is likewise not observed in experiment. The strong disparity between the experimental data and the estimates show that in the cases investigated by us the interaction between the terms differs significantly from that usually assumed to describe transitions between nonintersecting terms.

In collisions of Ar with N_2 and O_2 molecules, the formation of $1s$ vacancies is possible also as a result of the "carom" effect,[5] i.e., as a result of two successive collisions of the Ar atoms with the N or O atoms. Whereas in the first collision, as a result of the emergence of the $3d\sigma$ orbital, a $2p$-vacancy is produced in the Ar, in the second collision this vacancy can go over into the $1s$ level of N or O via a $2p\sigma - 2p\pi$ transition. However, as seen from the table, the ratios $\sigma(1s)/\sigma(2p)$ measured at equal velocities are practically the same for atoms and molecules. This means that in the investigated cases the contribution of the "carom" effect does not exceed the measurement errors, and the mechanism of formation of the $1s$ vacancies observed in the present study is predominant.

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