DYNAMICS OF LOW-ENERGY CHARGE-TRANSFER PROCESSES: $Ar^{2+} + He \rightarrow Ar^+ + He^+ AT eV$ COLLISION ENERGIES

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The dynamics of the single-charge-transfer processes between $Ar^{2+}({}^{3}P, {}^{1}D)$ and $He({}^{1}S)$ were studied in a crossed-beam experiment in the collision-energy range 0.5–1.6 eV. Scattering diagrams of the Ar^{+} product show a significant difference in the relative differential cross section distributions for processes with Ar^{2+} in the ${}^{3}P$ and ${}^{1}D$ states. This behaviour may be accounted for by assuming that the non-adiabatic transition occurs predominantly either before or after the system reaches the classical turning point. Ratios ${}^{3}P/{}^{1}D$ of the total cross sections of the two processes were estimated to be 0.32 and 0.83 at collision energies of 0.53 eV and 1.62 eV, respectively.

1. Introduction

Single-charge-transfer processes between doubly charged ions and atoms or molecules,

$$A^{2+} + B \to A^{+} + B^{+},$$
 (1)

belong to the group of charge-transfer processes between multiply charged ions and neutrals widely studied especially at keV collision energies. Coulomb repulsion between products is the dominant feature of the product-channel potential; its combination with the ion—induced-dipole interaction potential between reactants usually leads to a shift of the crossing region to fairly large internuclear separations. Systems of this type have been investigated by the translational spectroscopy method in the keV collision-energy region to obtain information on total cross sections, on reactant and/or product states, and possibly on important avoided crossings, transition probabilities and shapes of potential energy curves near these crossing regions [1-4].

Data on processes (1) at low (eV or sub-eV) collision energies are much less abundant and have concerned only total cross section measurements from beam [4,5] and swarm (SIFT or SIFT-drift) experiments [6-8], or a combination of these with spectro-

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scopic studies [9]. However, more detailed data are much needed: the non-adiabatic transitions in this low-collision-energy range should be predominantly induced by rotational (Coriolis) coupling [10-12]. The role of this coupling as well as of the entranceand exit-channel potentials in promoting various stateto-state processes and in determining the distribution of the differential cross section is of prime importance for a better understanding of the collisional dynamics of these processes.

In this paper we report a crossed-beam study of the charge-transfer process

$$Ar^{2+} + He \rightarrow Ar^{+} + He^{+}$$
(2)

at collision energies of 0.5-1.6 eV (c.m.), where the abovementioned effects ought to play a significant role [13]. The scattering study made it possible not only to resolve relative contributions of various electronic states of the reactant ion, but also to obtain angular, state-resolved information (relative differential cross sections for different reactant states) which had not previously been available for these processes.

Under the conditions of our experiments (electronimpact ionization of Ar at low pressures), the reactant beam contained the ground $({}^{3}P)$ and the two metastable (¹D, ¹S) states of Ar^{2+} . The states can be expected to be formed in their statistical ratio [9], i.e. ³P: ¹D: ¹S = 9:5:1. The energetics of the respective processes (calculated for the lowest spin-orbit states) are [14]

$$Ar^{2+}(^{3}P) + He(^{1}S) → Ar^{+}(^{2}P) + He^{+}(^{2}S),$$

--ΔH_R = 3.00 eV, (2a)
$$Ar^{2+}(^{1}D) + He(^{1}S) → Ar^{+}(^{2}P) + He^{+}(^{2}S),$$

-ΔH_R = 4.74 eV, (2b)

Ar²⁺(¹S) + He(¹S) → Ar⁺(²P) + He⁺(²S),

$$-\Delta H_{\rm R} = 7.12 \text{ eV}.$$
 (2c)

Other states of the spin-orbit multiplets of reactants and products $(Ar^{2+} and Ar^{+})$ could participate, but their role was not resolved in this study. Excited electronic states of the products lie at least 13.5 eV higher than the reported product ground states, and could not be formed in experiments at collision energies below 2 eV.

2. Experimental

Experiments were carried out on the crossed-beam apparatus EVA II, used in the usual arrangement [15]. The Ar²⁺ beam was produced by 150 eV electron impact on argon gas at about 10^{-2} Pa in the ionization chamber. Ions were extracted, mass analyzed at about 100 eV, and decelerated to the desired energy. The resulting beam had an energy and angular spread of 0.2 eV and 1° (fwhm), respectively, and its intensity at the scattering center was approximately 10^{-10} A. The ion beam was crossed perpendicularly with a thermal beam of He atoms (angular 3pread of 10° fwhm). Reactant and product ions were detected by means of a 0.4 X 1.0 mm² detection slit, energy analyzed by a stopping potential energy analyzer, mass anayzed, and detected by a rultiplier. Modulation of the He beam and lock-in derection techniques were used to deal with background problems. The angular resolution of the experiments was approximately ±1° in the lab coordinate system.

Because of kinematic reasons, the Ar⁺ product

ions were measured, although the signals of He⁺ could be detected also. Several scans of lab angular distributions of Ar^+ were combined with a series of stopping potential curves (3–6 curves at each of about 10 lab scattering angles) to provide a basis for the construction of scattering diagrams of Ar^+ in the usual way [16].

3. Results and discussion

Examples of scattering diagrams of Ar⁺ resulting from the charge-transfer process (2) are shown in figs. la and lb for collision energies T = 0.53 and 1.62 eV. Contours show the normalized Cartesian probability $P_{\rm C}$ [16,17]. The cross marks the most probable position of the tip of the velocity vector of the center of mass. Circles designated ³P, ¹D and ¹S show the loci of the c.m. velocity of the Ar⁺ product, corresponding to the exoergicities of processes (2a), (2b) and (2c), respectively. It can be seen that the Cartesian probability distribution of scattered Ar⁺ forms two concentric ridges closely following the two inner circles (³P and ¹D). The circle of the ¹S state lies practically outside of the scattering diagrams. Therefore, we can connect the inner and outer ridge with the formation of Ar⁺ in processes (2a) and (2b), respectively. Although the population of the ${}^{1}S$ state in the Ar²⁺ beam is presumably smaller than that of the ¹D state (statistically 1/5), it appears that the cross section of process (2c) is considerably smaller than that of process (2b), as the ¹S circle in the scattering diagrams lies outside of the Ar⁺ distribution. This conclusion is consistent with the results of SIFT [7] and drift [8] experiments, where the total cross section of process (2c) was found to be smaller by two to four [8] orders of magnitude than the cross section of (2a) or (2b).

Fig. 2 shows the product relative translational energy distributions, P(T'), for the two collision energies; P(T') was obtained from the scattering diagrams using the usual procedure [16,17]:

$$P(T') \approx u \int_{0}^{\pi} P_{C}(u_{1}, u_{2}, u_{3}) \sin \vartheta \, \mathrm{d}\vartheta, \qquad (3)$$

where P_{C} is the Cartesian probability, u is the magnitude of the Ar⁺ c.m. velocity and u_1, u_2, u_3 are its



Fig. 1. Scattering diagrams of Ar^+ : (a) collision energy T = 0.53 eV, (b) T = 1.62 eV. The circles represent loci of Ar^+ c.m. velocities, as expected for the single-charge transfer from Ar^{2+} in the ³P, ¹D and ¹S states, respectively.



Fig. 2. Product relative translational energy distribution, P(T'), as derived from the scattering diagrams in fig. 1. The arrows show the product relative translational energies for the charge transfer from Ar^{2+} in the ³P, ¹D and ¹S states, respectively.

Cartesian components, and ϑ is the c.m. scattering angle. The distributions show two peaks, corresponding to the energy release connected with processes (2a) and (2b). The peaks are less resolved than in the scattering diagrams, as by the integration procedure one incorporates all inaccuracies of the experiments, spreads in beams, etc. We believe that the tailing of the P(T') curves beyond the arrow ¹S is due to experimental inaccuracy rather than to a real contribution of process (2c).

By evaluating the integral

$$\int_{u} \int_{\vartheta} u^2 P_{\rm C}(u_1, u_2, u_3) \sin \vartheta \, \mathrm{d}\vartheta \, \mathrm{d}u \tag{4}$$

separately over the Ar⁺ c.m. velocity ranges 0 < u $< u_{\rm B}$ and $u_{\rm B} < u < \infty$, one can evaluate contributions of the two reactant states of Ar²⁺, ³P and ¹D, to the total probability of forming the products. The boundary value $u_{\rm B}$ of the Ar⁺ c.m. velocity was estimated by averaging the positions of the minima between the two forward peaks in the scattering diagrams. The ratio of these two contributions is then proportional to the ratio of the total cross sections of processes (2a) and (2b), $\sigma_{tot}({}^{3}P)/\sigma_{tot}({}^{1}D)$. The proportionality factor, when keeping other parameters constant, is the ratio of abundances of the two states in the primary beam. Assuming this ratio to be approximately equal to the statistical ratio of their formation, ${}^{3}P$: ${}^{1}D = 2:1$, we obtain for $\sigma_{tot}({}^{3}P)/\sigma_{tot}({}^{1}D)$ the value 0.32 at T = 0.53 eV and 0.83 at T = 1.62 eV [‡].

The most interesting result of the study is a marked difference between the angular distribution of Ar⁺ formed by processes (2a) and (2b). From the scattering diagram at T = 0.53 eV (fig. 1a), it can be seen that the inner ridge of the scattered Ar⁺ (process (2a), reaction with $Ar^{2+}({}^{3}P)$) is strongly peaked forwards with respect to the direction of the incoming Ar^{2+} : in addition, there is a very weak maximum in the backward direction. On the other hand, the outer ridge (process (2b), reaction with $Ar^{2+}(^{1}D)$) shows a pronounced sideways peaking, with an additional weaker peak in the forward direction. At T = 1.62 eV, the strong forward peaking of Ar^+ from process (2a) remains practically unchanged. However, the scattering of Ar^+ from $Ar^{2+}(^1D)$ changes considerably: the forward maximum substantially increases, while the sideways-scattered portion shifts more in the forward direction, forming an outer ridge, slowly decreasing towards $\vartheta = 90^{\circ}$. The shift from the sideways peak forwards is a gradual process, as indicated by other scattering diagrams at collision energies between 0.5 and 1.6 eV.

The angular changes of the scattering can be seen even better in terms of c.m. angular distributions (i.e. relative differential cross sections), $P(\vartheta)$, evaluated from the scattering diagrams separately for the reactant states ³P and ¹D by means of the formula [16, 17]

$$P(\vartheta) = \int u^2 P_{\rm C}(u_1, u_2, u_3) \,\mathrm{d}u \tag{5}$$

integrating up to $u_{\rm B}$ and beyond it, in a similar man-

[‡] We have no independent way of determining the actual relative abundance of the two states in the beam. Therefore, we relate our results to the expected statistical ratio of their formation, being aware that we do not consider contributions of cascading from higher states. However, our cross section ratio at 0.53 eV obtained in this way agrees well with the ratio of rate coefficients of these two states (0.35) from drift measurements [8].



Fig. 3. c.m. angular distributions (relative differential cross sections) of the Ar^+ product, as derived from the scattering diagrams in fig. 1.

ner to eq. (4). The results are given in fig. 3. At T = 0.53 eV, there is a steep forward peak of Ar^+ from the reaction with $\operatorname{Ar}^{2+}({}^{3}\mathrm{P})$, and a pronounced sideways peak at $\vartheta = 90^{\circ}$ with a distinct forward contribution from the reaction with $\operatorname{Ar}^{2+}({}^{1}\mathrm{D})$. At T = 1.62 eV, the latter process leads to a shift of the sideways peak to smaller scattering angles, peaking at $\vartheta = 60^{\circ}$, and to an increase of the forwards-scattered fraction.

Trajectory calculations on this system have been carried out using a simplified model. The model assumes a Coulomb repulsion (R^{-1}) potential between the products and an ion-induced-dipole attractive potential (R^{-4}) between the reactants which is cut off by a hard-sphere potential at the internuclear distance 2.0 Å (where the well depth has a reasonable value of 0.5 eV). The electronic structure of the system was not considered; it was merely assumed that in the vicinity of the crossing point, R_{cr} , an unspecified non-adiabatic transition occurs from the reactant to the product potential energy curve. The first aim was to decide if there was a difference in angular scattering depending on whether the transition occured on the way "in" or "out" during the collision



Fig. 4. Classical model of the charge-transfer processes (2a, 2b): the ion-induced-dipole potential V_{ID} and the Coulomb potential V_C acting between reactants and products, respectively, are plotted against the internuclear distance R. A hard-sphere repulsion V_{HS} defines the distance of closest approach R_{HS} . The curved arrows show pathways a and b (see :ext).

(pathways (a) or (b), fig. 4). Preliminary results show clearly that pathway (a) results in a pronounced sideways peaking of scattered Ar^+ , which shifts forwards with increasing collision energy in the range studied. On the other hand, pathway (b) leads to a strongly forward-peaked scattering. It appears, therefore, that the difference in the angular distribution of Ar^+ may depend significantly on whether a non-adiabatic transition occurs predominantly on the incoming branch of the trajectory before the classical turning point is reached (pathway (a), fig. 4) or on the outgoing branch when the system recedes from the turning point (pathway (b)).

However, as a full theoretical description requires using in addition a realistic form of the ion—induceddipole potential and a detailed treatment of the nonadiabatic transitions, we refrain from drawing definite conclusions from the preliminary trajectory calculations and leave this to our forthcoming paper.

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