Single- and double-electron transfer reactions of ground and metastable state Ar^{2+} ions

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Abstract. Electron transfer cross sections have been measured for reactions of Ar^{2+} ions with Ar, N_2 , O_2 , CO, CO_2 , CH_4 and C_2H_6 . Time-of-flight techniques have been used to measure both fast neutral Ar^0 and fast Ar^+ products from single- and double-electron transfer processes involving Ar^{2+} ions with 4.0 to 7.0 keV impact energies. Incident Ar^{2+} ions have been produced by controlled electron impact ionisation of argon atoms. Reactions have been examined as a function of ionising electron energy and cross sections determined for ground state $\text{Ar}^{2+}(^3\text{P})$ ions. Charge transfer cross sections have been determined to be in the range of $3 \times 10^{-16} \text{ cm}^2$ for the systems examined. Double-electron transfer cross sections are the same order of magnitude as those measured for the corresponding single-electron transfer reactions. The state distribution of our reactant ion beam has been estimated and electron transfer cross sections obtained for single- and double-electron transfer reactions of metastable Ar^{2+} ions. The magnitudes of electron transfer cross sections in individual systems are similar for both ground and metastable state Ar^{2+} reactions.

1. Introduction

Reactions of multicharged ions have received attention from investigators pursuing the development of experimental and theoretical collision physics as well as from groups examining the influence of these reactions in: the operation of energy efficient fusion plasmas; the description of astrophysical plasmas; and the production of short wavelength lasers. Much of the research work involving multicharged ions has been directed toward the measurement of total cross sections for single and multi-electron transfer processes (Janev and Presnyakov 1981). Total cross sections for electron transfer can be quite large for reactions involving multicharged ions and the products can be highly excited. Product ion state distributions from single-electron transfer reactions of doubly-charged ions have been obtained recently by optical spectroscopic methods (Barrett and Leventhal 1981, Matsumoto *et al* 1982, Kadota *et al* 1982) and by techniques involving translational spectroscopy (Kamber *et al* 1982). Several investigations have been carried out to examine the effects of incident ion states on electron transfer reactions of thermal energy ions (Johnsen and Biondi 1978a, b, 1979, Smith *et al* 1979). Electronic state selection of thermal energy reactant ions has been achieved by taking advantage of different ion-state reactivities with various drift-tube carrier gases which served to deplete certain incident ion states prior to reaction with target gases. Although thermal reactions of doubly-charged ions have

been shown to depend strongly on the incident ion state, little work has been done to examine the effect of incident ion electronic states on reactions at keV incident ion energies. It is the purpose of this paper to report results of an investigation to determine one- and two-electron transfer cross sections in collisions of 4–7 keV ground and metastable state Ar^{2+} ions with various molecules.

2. Experimental

Time-of-flight techniques have been employed to measure fast neutral and ionic products resulting from electron transfer reactions. The apparatus and techniques have been described and used previously to obtain cross sections for formation of fast neutral products from electron transfer reactions of singly-charged ions (Moran and Wilcox 1978). In brief, reactant Ar^{2+} ions have been produced by controlled electron impact ionisation of high-purity argon gas. Ionising electrons have been emitted from a directly-heated thorium oxide filament and accelerated into the ion source by a voltage controllable from 2 to 100 V. The electron beam intensity has been kept constant during each measurement by means of a regulated filament current supply having an electron trap filament current feedback loop. Several plates with holes and an external magnet have been used to collimate the electron beam and ensure passage of a well-defined electron beam through the ion source. The absolute energy of the electron beam has been determined from applied voltages and checked by measurement of known ionisation energies of several rare gases and diatomic molecules. The electron-beam energy has been monitored during each experiment by measurement of the Ar^{2+} ionisation energy.

Reactant Ar^{2+} ions produced in the ion source have been drawn out of the ion source by a fast rising pulse and then accelerated to terminal velocities. The fully accelerated ion beam next entered a static gas collision region where electron transfer reactions have taken place. The pressures of high-purity target gas molecules introduced into the collision region have been continuously monitored by an ion gauge. This gauge has been baffled to prevent transport of charged species from the gauge into the collision region. The ion gauge has been calibrated against a capacitance manometer, the accuracy of which has been checked by a cooled McLeod gauge with data corrected for thermal transpiration.

Incident Ar^{2+} and fast Ar^+ , Ar^0 products from electron transfer reactions proceeded through a 1 m drift region and have been collected on the cathode of a gated electron multiplier. The final 0.2 m segment of drift region has been insulated from the first segment so that it has been possible to retard the ions as they passed from the first drift region to the second. In the absence of a retarding voltage on the second drift region, the reactant Ar^{2+} and fast Ar^+ , Ar^0 products have approximately equal arrival times at the collector; an arrival time characteristic of m/e 20 u ions. However, application of a deceleration voltage to the second drift region gave the reactant Ar^{2+} a longer arrival time than the fast Ar^+ products without affecting the Ar^0 arrival time. In this mode of operation, three separate peaks have been obtained in the time-of-flight spectrum. These peaks correspond to; reactant Ar^{2+} ions, fast Ar^+ , and Ar^0 products from the reactions

(2)

Secondary electron emission coefficients of the cathode, determined using standard techniques (Hayden and Utterback 1964), have been found to be approximately equivalent for Ar^+ and Ar^0 . Equal emission coefficients have resulted in equivalent collection efficiencies for both Ar^0 and Ar^+ fast products over the kinetic energy range of our experiments.

Two-electron transfer processes in $\text{Ar}^{2+} + \text{Ar}$ reactions have been extensively studied at low keV kinetic energies. The cross sections obtained in previous investigations are illustrated in figure 1. These data from different groups are in moderate accord with each other. The full curve from 4 to 7 keV energy represents an average of the cross sections. We have chosen to measure relative cross sections in our present investigation and have put our data on an absolute basis using the average value (line) of cross sections measured previously in the 4–7 keV ion impact energy range.

Figure 1. Total charge transfer cross sections (10^{-16} cm^2) for production of fast neutral Ar^0 as a function of reactant ion kinetic energy (keV) in $\text{Ar}^{2+} + \text{Ar}$ interactions. Experimental data given in this figure are from: $\circ$, Cosby and Moran (1972); $\triangle$, Kaneko *et al* (1981); $\blacktriangle$, Hasted and Hussain (1964); $\square$, Latypov *et al* (1969); $\blacksquare$, McGowan and Kerwin (1967).

3. Results and discussion

3.1. Reaction energetics

The minimum energy required to produce $\text{Ar}^{2+} (^3\text{P}_J)$ ions from electron impact ionisation of ground-state $\text{Ar} (^1\text{S}_0)$ atoms is 43.39 eV whereas the corresponding energy to

form $\text{Ar}^+(^2\text{P}_J)$ ions is 15.76 eV (Moore 1949). The large energy difference between single- and double-ionisation energies results in a large energy defect, ΔE , for the single-electron transfer reactions

involving ground-state species. The magnitude of this energy defect is reduced for reactions producing excited-state products. Energy defects for the various $\text{Ar}^+(n, l, J)$ products are illustrated in figure 2 for reactions involving $\text{Ar}^{2+}(^3\text{P}_J, ^1\text{D}_2 \text{ and } ^1\text{S}_0)$ reactant ions. The metastable $\text{Ar}^{2+}(^1\text{D}_2 \text{ and } ^1\text{S}_0)$ states are present in the reactant ion beam and their relative abundances are discussed in § 3.2. The high density of product ion states gives rise to a near continuum of endothermic product channels.

Figure 2. Energy defects (eV) for the reactions $\text{Ar}^{2+}(\text{X}) + \text{Ar}(^1\text{S}_0) \rightarrow \text{Ar}^+(n, l, J) + \text{Ar}^+(n', l', J')$ where $\text{X} = ^3\text{P}_J, ^1\text{D}_2, ^1\text{S}_0$.

The potential energy of the incident $\text{Ar}^{2+}(^3\text{P}_J) + \text{Ar}(^1\text{S}_0)$ reactant channel follows the ion-induced dipole interaction

$$V = -2e^2\alpha(\text{Ar})/R^4 \quad (4)$$

where α is the polarisability of the target $\text{Ar}(^1\text{S}_0)$ atoms. The various $\text{Ar}^+(n, l, J) + \text{Ar}^+(n', l', J')$ product channels have been described in terms of a combination of Coulomb repulsive and ion-induced dipole attractive potentials of the form suggested by Kamber *et al* (1982)

$$V = e^2/R - e^2(\alpha(\text{Ar}^+) + \alpha(\text{Ar}^+))/2R^4 - \Delta E \quad (5)$$

where α is the polarisability of Ar^+ products and ΔE is the energy defect of individual

product channels. These approximate potential energy curves for incoming reactants and outgoing products of single-electron transfer reactions are shown in figure 3 by chain and full curves respectively. Diabatic transitions between the reactant and exothermic product channels are possible at an internuclear separation of approximately 1.7×10^{-8} cm. Two-electron transfer product channels which form $\text{Ar}^{2+}({}^1\text{D}_2$ and ${}^1\text{S}_0$ states) are shown by the broken curves. Although these channels are forbidden as products by the Wigner spin-conservation rule ($\Delta S = 0$), they are illustrated as possible product channels since this rule is not strictly obeyed in collisions of the heavier rare-gas systems (Kamber *et al* 1982, Moore 1974).

Figure 3. Potential energy curves for $\text{Ar}^{2+}({}^3\text{P}_J) + \text{Ar}({}^1\text{S}_0)$ interactions as a function of internuclear distance. The reactant channel is given by the chain curve. Possible product channels for two-electron transfer are given by the broken curves and the chain curve for the resonant reaction. The full curves represent single-electron transfer channels which have $\text{Ar}^+(n, l, J) + \text{Ar}^+(n', l', J')$ products.

A total of nine resonant and near-resonant two-electron transfer reaction channels are available for the $\text{Ar}^{2+}({}^3\text{P}_J)$ state where J equals 2, 1 and 0. Only one resonant channel exists for the two-electron transfer processes involving $\text{Ar}^{2+}({}^1\text{D}_2)$ ions. Likewise there is only one resonant channel for the two-electron transfer reactions of $\text{Ar}^{2+}({}^1\text{S}_0)$ ions.

It has been suggested (Salzborn and Müller 1980) that the observed total cross section for one-electron charge transfer in reaction (3) occurs by means of the exothermic channel. Single-electron transfer rate coefficients for reactions of doubly-charged ions with rare-gas atoms have been measured at thermal energies by Smith

et al (1980). They interpreted their data on the basis of a curve-crossing model and showed that when reactant curves cross exothermic single-electron transfer product curves in the $2\text{--}7 \times 10^{-8}$ cm internuclear distance range there is a high probability for single-electron transfer. In addition to the exothermic product channel crossings invoked to explain the thermal energy data, endothermic channel crossings at small internuclear distances must also be considered for keV incident ion energies. Energy analysis of Ar^+ products from reaction (3) carried out by Ast *et al* (1975) indicates that endothermic channels dominate reactive scattering in the forward direction. Their data are reproduced by the full curve in figure 4. Energy defects for all possible reaction channels have been computed for reactant Ar^{2+} ions in the $^3\text{P}_J$, $^1\text{D}_2$ and $^1\text{S}_0$ states. The number of reaction channels having energy defects within 0.1 eV of each other has been tabulated and the total weighted sum plotted as a function of energy defect. This sum, obtained by a 9:5:1 weighting of the respective $^3\text{P}_J$, $^1\text{D}_2$ and $^1\text{S}_0$ state reaction channels, is represented by the full vertical lines at 0.1 eV increments in figure 4. The experimental curve extends over a wide range of energy defects and indicates that a large number of possible product channels are involved in reaction (3). The maximum in the curve suggests a high probability for endothermic reactions having energy defects ranging from -5 to -9 eV.

Replacement of target atoms by molecules increases the number of possible product channels significantly. This is illustrated in figure 5 where potential energy curves for the reactions

Figure 4. Fast Ar^+ product ion kinetic energy distribution measured by Ast *et al* (1975) is displayed by the full curve. Energy defects for various $\text{Ar}^+ + \text{Ar}^+$ product channels are summed together and displayed as vertical lines in 0.1 eV energy increments. These defects for various $\text{Ar}^+ + \text{Ar}^+$ product channels are weighted according to the statistical population of Ar^{2+} ion states ($^3\text{P}_J$, $^1\text{D}_2$, $^1\text{S}_0$) in the reactant ion beam.

Figure 5. Potential energy curves for $\text{Ar}^{2+}(^3P_J) + \text{N}_2(X^1\Sigma_g^+, v=J=0)$ interactions as a function of ion-molecule separation distance. The reactant channel is given by the curve with full circles. Broken lines represent single-electron transfer channels which have $\text{Ar}^+ + \text{N}_2^+(v=J=0)$ products in the designated states. The full lines on the right-hand side of the figure illustrate the square of vibrational overlaps for vertical $\text{N}_2(X^1\Sigma_g^+, v=J=0) \rightarrow \text{N}_2^+(X, A, B, C, D, v)$ and $\text{N}_2^{2+}(v)$ Franck-Condon transitions. Full curves represent the two-electron transfer channels.

are given as a function of ion-molecule separation distance R . The potential energies for the various reaction channels at $R = \infty$ are illustrated by the horizontal lines on the right side of this figure. The broken curves represent potential energies for single-electron transfer channels in which $v=0$ N_2^+ ions in the $X^2\Sigma_g^+$, $A^2\Pi_u$, $B^2\Sigma_u^+$, $D^2\Pi_g$ and $C^2\Sigma_u^+$ states are considered products. The lengths of the horizontal lines are proportional to Franck-Condon factors for electron removal from $\text{N}_2(X^1\Sigma_g^+, v=0)$ molecules in vertical transitions (Lofthus and Krupenie 1977). The overlaps for the $D^2\Pi_g$ state are negligible at lower v and only become appreciable at high v and are not illustrated. Neuschäfer *et al* (1979) have observed optical emissions from low-energy $\text{Ar}^{2+} + \text{N}_2$ collisions which they attribute to spontaneous radiative decay from the $\text{N}_2^+(D^2\Pi_g)$ product state.

Two-electron transfer channels forming N_2^{2+} ions are given by the full curves in figure 5. The curve with asymptotic potential energy of -0.69 was computed using

the 42.7 eV N_2^{2+} ionisation energy measured by Agee *et al* (1981) while the curve with ΔE at 0.27 eV was obtained from laser photodissociation experiments of Cosby *et al* (1983). Diabatic transitions from the $Ar^{2+} + N_2$ curve to various $Ar^+ + N_2^+$ curves are possible at distances of several Ångströms. These latter curves cross the $Ar + N_2^{2+}$ curves which can ultimately lead to two-electron transfer. The N_2^{2+} state examined by Cosby *et al* (1983) most likely has a $^1\Sigma_g^+$ designation. Production of this state would be spin forbidden in $Ar^{2+}(^3P_J) + N_2(X^1\Sigma_g^+, v=0)$ collisions but, as noted previously the Wigner rules may not be strictly applicable for heavy particle collisions.

The corresponding energies ($-\Delta E$), at infinite internuclear separation distance, for reactions (1) and (2) involving molecular O_2 , CO, CO_2 , CH_4 and C_2H_6 systems are given in figure 6 by horizontal lines. Franck-Condon factors for forming various v' levels of the singly-charged product diatomic and triatomic ions from the $v''=0$ levels of the respective target molecules are given by the lengths of the horizontal lines. Broken curves indicate dissociation limits of the product ions. Franck-Condon factor envelopes for the polyatomic alkanes, obtained from photoion-photoelectron experiments and documented by Hedrick and Moran (1976), are given by the shaded areas. Energetic onsets for formation of doubly-charged ions are denoted by the

Figure 6. Energies (eV) for electron transfer reactions of $Ar^{2+}(^3P_J)$ ions with neutral species Y ($Y = O_2$, CO, CO_2 , CH_4 and C_2H_6). Franck-Condon factors for O_2 , CO and CO_2 are represented by the length of the horizontal lines. The CH_4 and C_2H_6 Franck-Condon factors are represented by shaded areas.

curves with full circles. Doubly charged ionisation energies for O_2 , CO and CO_2 have been taken from the compilation of Agee *et al* (1981). The 35.1 eV vertical transition energy for forming CH_4^{2+} was taken from the work of Hanner and Moran (1981) who noted that this molecular ion is initially formed on a repulsive portion of the potential energy curve and undergoes spontaneous dissociation into single charged fragments. The minimum energies (Jones *et al* 1982) to form stable doubly-charged ions in the C_2H_6 system are: 30.3 eV for $\text{C}_2\text{H}_4^{2+}$; 31.4 eV for $\text{C}_2\text{H}_5^{2+}$ and 34.5 eV for $\text{C}_2\text{H}_3^{2+}$.

3.2. Reactant ion-beam state distribution

Requisite for determination of charge transfer cross sections for different Ar^{2+} electronic states is the assessment of the incident ion-state distribution. Energies of various Ar^{2+} states have been tabulated (Moore 1949) and transition probabilities listed (Wiese *et al* 1969) for spontaneous radiative transitions of Ar^{2+} states. The energies to form the ground $\text{Ar}^{2+}(^3\text{P}_J)$ state and lower metastable $\text{Ar}^{2+}(^1\text{D}_2)$ and $\text{Ar}^{2+}(^1\text{S}_0)$ states are 43.4, 45.1 and 47.5 eV respectively. The lifetime of the $\text{Ar}^{2+}(^1\text{D}_2)$ state with respect to radiative $^1\text{D} \rightarrow ^3\text{P}$ transitions is approximately 9s while the $\text{Ar}^{2+}(^1\text{S}_0)$ state has an approximate radiative lifetime of 0.1 s in $^1\text{S} \rightarrow ^1\text{D}$, ^3P transitions. These lifetimes are sufficiently long for the $^1\text{D}_2$ and $^1\text{S}_0$ states to be present in our reactant ion beam. Evidence for the production of these states in electron impact ionisation as well as their abundances and reactivities in different experimental systems are discussed below.

Low-energy non-resonant charge transfer cross sections for Ar^{2+} -He reactions were observed by Maier and Stewart (1978) to increase as Ar^{2+} energies were lowered to several tenths of an electron volt, and these workers suggested this increase was probably caused by reactions involving metastable Ar^{2+} ions in their incident ion beam.

Johnsen and Biondi (1978a, b) used a drift-tube mass spectrometric apparatus to measure mobilities and thermal rate constants for Ar^{2+} -rare-gas interactions. They measured varying mobilities for a given reactant ion-atom system and indicated that different mobility groups resulted from reactions of different Ar^{2+} electronic states which they associated with the $^3\text{P}_J$, $^1\text{D}_2$ and $^1\text{S}_0$ states. Neuschäfer *et al* (1979) used a flow-drift-tube apparatus to measure the thermal $\text{Ar}^{2+}(^3\text{P}_J)$ and $\text{Ar}^{2+}(^1\text{S}_0)$ charge transfer reactions with nitrogen molecules. They suggest that reactant Ar^{2+} ions are formed in the $^3\text{P}_J$, $^1\text{D}_2$ and $^1\text{S}_0$ states in the statistical ratio of 9:5:1 by electron impact ionisation of argon gas. Störi *et al* (1979) used the same flow-drift-tube apparatus to determine thermal charge transfer rate constants for reactions of $\text{Ar}^{2+}(^3\text{P}_J)$ and $\text{Ar}^{2+}(^1\text{S}_0)$ ions with diatomic and polyatomic molecules. Smith *et al* (1979, 1980) employed a selected ion flow tube to measure rate coefficients for reactions of $\text{Ar}^{2+}(^3\text{P}_J)$ and $\text{Ar}^{2+}(^1\text{S}_0)$ states with a number of atoms and molecules at thermal energies. Holzscheiter and Church (1981) examined the reactions of Ar^{2+} with N_2 at very low pressures using a stored-ion technique. In this latter work, reactant ions were produced by electron impact ionisation and stored for several seconds in an ion trap, a time interval long enough to permit radiative decay of the $\text{Ar}^{2+}(^1\text{S}_0)$ state but short compared with the $\text{Ar}^{2+}(^1\text{D}_2)$ radiative lifetime. Thus, they were able to selectively measure the $\text{Ar}^{2+}(^1\text{D}_2)$ - N_2 reactions without interferences from $\text{Ar}^{2+}(^1\text{S}_0)$ state ions.

Kamber *et al* (1982) measured both the elastic and inelastic differential Ar^{2+} -Ne charge transfer cross sections at 0.54 keV. Their zero-angle energy-loss spectra for single-electron transfer processes illustrated transitions involving both ground $\text{Ar}^{2+}(^3\text{P}_J)$ and metastable $\text{Ar}^{2+}(^1\text{D}_2)$ states in the reactant ion beam.

Matsumoto *et al* (1982) used an elegant optical attenuation technique to determine the fraction of metastable $\text{Ar}^{2+} (^1\text{D}_2)$ state in an Ar^{2+} ion beam produced by electron impact ionisation. They extended the beam attenuation method of Turner *et al* (1968) to the attenuation of specific emission lines from excited Ar^{*+} charge transfer products in Ar^{2+} -Na reactions. Combining the beam and optical attenuation methods, Matsumoto *et al* (1982) determined the $^1\text{D}_2$ state abundance to be 0.29 ± 0.16 which is in harmony with abundances estimated from statistical weights of the $\text{Ar}^{2+} (^3\text{P}_J, ^1\text{D}_2$ and $^1\text{S}_0)$ states. Thus, we have assumed our Ar^{2+} reactant ions to be primarily in the $^3\text{P}_J$, $^1\text{D}_2$ and $^1\text{S}_0$ states with relative abundances of 0.60, 0.33 and 0.07 respectively.

A small fraction (2–4%) of the Ar^{2+} ions in our reactant beam may occupy higher excited states. Varga and Winter (1978) found evidence of these higher metastable states in their measurements of yields and energy distributions of secondary electrons ejected by Ar^{2+} impact on a clean polycrystalline tungsten target. The secondary electron yield was found to be sensitive to a high-lying metastable component in the Ar^{2+} beam produced above 50 eV. An increase in the secondary electron yield in the 60–70 eV ionising electron energy range provided evidence of metastable $\text{Ar}^{2+} (3\text{d } ^5\text{D}^o \text{ and } 3\text{d } ^3\text{F}^o)$ states which have appearance energies of 61.4 and 66.5 eV respectively. The abundance of these higher metastable states was estimated to be 1.8 to 3.8% of the total number of ions in an Ar^{2+} beam produced by 80 eV electron impact ionisation of Ar. Our examination of one- and two-electron transfer cross sections as a function of electron energy used to form the reactant Ar^{2+} beam gave no evidence for the presence of these higher metastable states in our reactant ion beam.

3.3. Cross sections for $\text{Ar}^{2+} (^3\text{P})$ and Ar^{2+} (metastable) reactant ions

Total cross sections for one- and two-electron transfers in the collisions of Ar^{2+} with a variety of target species have been determined for reactant ions formed by 90 eV

Table 1. Total charge transfer cross sections for the reaction $\text{Ar}^{2+}(\text{all states}) + \text{Y} \rightarrow \text{Ar}^0 + \text{Y}^{2+}$.

Ion kinetic energy (eV)	Cross sections (10^{-16} cm^2)					
	Y = O ₂	N ₂	CO	CO ₂	CH ₄	C ₂ H ₆
7000	1.3	1.8	2.6	5.6	1.3	4.0
6800	1.2	1.8	2.5	5.3	0.9	4.2
6600	1.2	1.8	2.4	5.2	0.9	4.4
6400	1.2	1.8	2.2	5.1	0.9	4.4
6200	1.3	1.8	2.3	4.7	1.0	4.5
6000	1.3	1.7	2.2	4.9	0.9	4.5
5800	1.2	1.8	2.1	4.5	1.0	4.5
5600	1.1	1.8	2.1	4.4	1.1	4.5
5400	1.1	1.7	2.0	4.2	1.0	4.6
5200	1.1	1.8	2.0	4.1	1.2	5.1
5000	1.4	1.8	1.9	3.7	1.3	5.3
4800	0.8	1.3	1.9	3.6	0.9	4.7
4600	1.0	1.5	2.1	3.8	1.2	5.1
4400	1.0	1.4	2.1	3.7	1.1	5.0
4200	1.1	1.1	2.2	3.5	1.3	5.2
4000	1.5	1.5	2.3	3.5	2.1	6.4

Table 2. Total charge transfer cross sections for the reaction $\text{Ar}^{2+}(\text{all states}) + \text{Y} \rightarrow \text{Ar}^+ + \text{Y}^+$.

Ion kinetic energy (eV)	Cross sections (10^{-16} cm^2)					
	$\text{Y} = \text{O}_2$	N_2	CO	CO_2	CH_4	C_2H_6
7000	2.3	1.8	1.8	1.9	1.6	3.3
6800	2.3	1.7	1.9	1.8	1.6	3.3
6600	2.3	1.8	1.9	1.9	1.7	3.4
6400	2.2	1.8	1.7	1.8	1.7	3.6
6200	2.3	1.8	1.8	1.7	1.8	3.5
6000	2.3	1.8	1.7	1.8	1.7	3.6
5800	2.3	1.8	1.8	1.8	1.8	3.6
5600	2.3	1.9	1.8	1.7	1.9	3.8
5400	2.3	1.9	1.8	1.7	2.0	4.1
5200	2.4	2.0	1.8	1.7	2.1	4.5
5000	2.4	2.0	1.7	1.6	2.2	4.6
4800	2.5	2.1	1.8	1.5	2.1	4.6
4600	2.5	2.1	1.6	1.5	2.2	5.2
4400	2.6	2.3	1.7	1.4	2.2	5.1
4200	2.2	2.0	1.5	1.2	2.0	4.5
4000	1.7	1.6	1.2	1.2	1.9	3.9

Figure 7. Relative cross section for $\text{keV Ar}^{2+} + \text{Y} \rightarrow \text{Ar}^0 + (\text{Y})^{2+}$ charge transfer reactions forming fast Ar^0 as a function of electron energy used to produce the reactant beam of Ar^{2+} ions. Results for different reactant systems with $\text{Y} = \text{Ar}, \text{CO}_2$ and CH_4 are given in the respective upper, middle and lower portions of this figure.

Figure 8. Relative cross sections for keV $\text{Ar}^{2+} + \text{Y} \rightarrow \text{Ar}^+ + (\text{Y})^+$ charge transfer reactions forming Ar^+ as a function of electron energy used to produce the reactant beam of Ar^{2+} ions. Results for different reactant systems with $\text{Y} = \text{Ar}$, CO_2 and CH_4 are given in the respective upper, middle and lower portions of this figure.

electron impact ionisation. Cross sections for two-electron transfer reactions of 4.000 to 7.000 keV Ar^{2+} ions with O_2 , N_2 , CO , CO_2 , CH_4 and C_2H_6 are given in table 1. Several features are evident from the data in this table: (i) the two-electron transfer cross sections are approximately constant from 4 to 7 keV ion energies; (ii) cross sections measured in each of the systems are of the same order of magnitude and range from 0.8 to $6.4 \times 10^{-16} \text{ cm}^2$.

Single-electron transfer total cross sections for reactions of Ar^{2+} with O_2 , N_2 , CO , CO_2 , CH_4 and C_2H_6 are given in table 2. These one-electron transfer cross sections show little variation with ion kinetic energy and cross sections range from 1.2 to $5.2 \times 10^{-16} \text{ cm}^2$ in the different systems. The magnitudes of one- and two-electron transfer cross sections are somewhat similar and the ratios of double- to single-electron transfer cross sections, averaged over the 4–7 keV incident ion kinetic energies, are 0.52, 0.88, 1.27, 2.66, 0.60, 1.20 for the respective O_2 , N_2 , CO , CO_2 , CH_4 , C_2H_6 systems.

The influences of excited states in the reactant ion beam are illustrated in figure 7 where relative two-electron transfer cross sections are presented as a function of electron energy used to produce the reactant ions. A similar presentation of relative single-electron transfer cross sections as a function of ionising electron energy is given in figure 8. The energetic onsets for forming ground state $^3\text{P}_2$ and metastable $^1\text{D}_2$, $^1\text{S}_0$ Ar^{2+} reactant ion states are indicated by arrows on the bottom of this figure.

Figure 9. Charge transfer cross sections (10^{-16} cm^2) for production of fast neutral product Ar^0 as a function of reactant ion kinetic energy (keV) in $\text{Ar}^{2+} (^3\text{P}_2 \text{ ground state}) + \text{Y}$ interactions. The target gas Y used in each collision system is listed on the right-hand side of the figure.

Increases in relative cross sections for both the $\text{Ar}^{2+} + \text{Ar}$ and $\text{Ar}^{2+} + \text{CO}_2$ reactions are observed in figures 7 and 8 as the Ar^{2+} excited-state population is raised by increasing the energy of the ionising electrons. Cross sections, $\sigma(^3\text{P})$, for reactions of ground-state $\text{Ar}^{2+} (^3\text{P})$ ions have been determined from data taken below the energy threshold for forming $\text{Ar}^{2+} (^1\text{D}_2)$ ions. Cross sections for two-electron transfer in $\text{Ar}^{2+} (^3\text{P})$ ground-state reactions are illustrated in figure 9 for the different collision systems. The corresponding single-electron transfer cross sections for $\text{Ar}^{2+} (^3\text{P})$ ion reactions are presented in figure 10 as a function of incident ion kinetic energy.

The ratios of ^3P state cross sections to total cross section σ_{T} (all states) for reactions of Ar^{2+} ions produced by 80 eV electron impact ionisation are given in table 3. In each collision system the ratio values of (ground state/all states) cross sections are similar for both the one- and two-electron transfer processes. Both thermal energy rate coefficients (Smith *et al* 1979) and the keV electron transfer cross sections, measured in the present investigation, for $\text{Ar}^{2+} - (\text{N}_2, \text{O}_2, \text{CO}_2)$ systems are slightly larger for reactions involving excited-state ions than for ground-state $\text{Ar}^{2+} (^3\text{P})$ ions. Although one- and two-electron transfer cross sections are approximately equal at keV energies, the single- and double-electron transfer channels are not observed as competitive parallel processes in molecular systems at thermal energies. Exothermic/thermoneutral double electron transfer processes dominate the thermal energy $\text{Ar}^{2+} (^3\text{P} \text{ and } ^1\text{S}) - (\text{N}_2, \text{O}_2, \text{CO}_2)$ reactions and lead to the formation of doubly-charged

Figure 10. Charge transfer cross sections (10^{-16} cm^2) for production of fast product Ar^+ as a function of reactant ion kinetic energy (keV) in $\text{Ar}^{2+} (^3\text{P}_2 \text{ ground state}) + \text{Y}$ interactions. The target gas Y used in each collision system is listed on the right-hand side of the figure.

Table 3. Relative ratio of the ground-state cross section ($\sigma_g(^3\text{P})$) to the total cross section ($\sigma_T(\text{all states})$) for the reactions:

Y	$\sigma_g(^3\text{P})/\sigma_T(\text{all states})$	
	Reaction (a)	Reaction (b)
Ar	0.92	0.85
O_2	0.50	0.60
N_2	0.98	1.0
CO	0.94	0.90
CO_2	0.77	0.72
CH_4	1.55	1.22
C_2H_6	1.00	1.00

molecular ions which spontaneously decompose into single-charged fragments. The data in table 3 show that factors which lead to increases in single-electron transfer cross sections at keV energies also lead to increases in double-electron transfer cross sections. This association is not surprising since single- and double-electron transfer product channels are coupled to one another through diabatic transitions between potential curves for the single-electron transfer exothermic product channels and

curves for the double-electron transfer channels. For example, the $\text{Ar}^{2+}(^3\text{P}) + \text{Ar}(^1\text{S})$ reactant curve in figure 3 crosses the $\text{Ar}^{2+}(^2\text{P}) + \text{Ar}^{2+}(^2\text{P})$ product curve at 1.7×10^{-8} cm which in turn crosses the $\text{Ar}(^1\text{S}) + \text{Ar}^{2+}(^1\text{D})$ curve at 1.6×10^{-8} cm. The argon system is unique from all the others examined in this investigation since resonant two-electron transfer processes are possible. Curve crossings between one- and two-electron transfer product channels are indicated in the $\text{Ar}^{2+}(^3\text{P}) + \text{N}_2(\text{X } ^1\Sigma_g)$ reaction shown in figure 5. Multiple curve crossings can also couple the one- and two-electron transfer channels in the other polyatomic systems illustrated in figure 6.

Cross sections, $\sigma(\text{excited states})$, for reactions of Ar^{2+} metastable states have been determined from the relation

$$\sigma(\text{excited states}) = (\sigma_T(\text{all states}) - f_g \sigma(^3\text{P})) / f_{\text{exc}} \quad (8)$$

where $\sigma(^3\text{P})$ is the cross section involving ground-state ions and $\sigma_T(\text{all states})$ is the total measured cross section for reactions of Ar^{2+} ions with a ^3P , $^1\text{D}_2$, $^1\text{S}_0$ state distribution characteristic of 90 eV electron impact ionisation. The fraction (0.40) of the ion beam in these metastable states is denoted as f_{exc} and the fraction (0.60) in the ^3P ground state is represented by f_g . Two-electron transfer cross sections involving excited-state ions were determined from equation (8) at various incident ion energies and the results are presented in figure 11. Single-electron transfer cross sections for excited-state Ar^{2+} ions were determined from equation (8) and the results are shown

Figure 11. Charge transfer cross sections (10^{-16} cm^2) for production of fast neutral Ar^0 as a function of reactant ion kinetic energy (keV) in $\text{Ar}^{2+}(^1\text{D}_2, ^1\text{S}_0 \text{ excited states}) + \text{Y}$ interactions. The target gas Y used in each collision system is listed on the right-hand side of the figure.

in figure 12 as a function of ion kinetic energy for the different collision systems. Cross sections for excited-state reactions are in the range of 1 to $7 \times 10^{-16} \text{ cm}^2$. In general, excited-state cross sections for single- and double-electron transfer processes in individual systems are similar in magnitude and can be attributed in part to favourable curve crossings between the reactant and exothermic single-electron transfer channels which in turn cross those for the double-electron transfer channels.

Figure 12. Charge transfer cross sections (10^{-16} cm^2) for production of fast product Ar^+ as a function of reactant ion kinetic energy (keV) in $\text{Ar}^{2+} (^1\text{D}_2, ^1\text{S}_0 \text{ excited state}) + \text{Y}$ interactions. The target gas Y used in each collision system is listed on the right-hand side of the figure.

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