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Nuclear Instruments and Methods in Physics Research A 580 (2007) 14–17
NUCLEAR INSTRUMENTS & METHODS IN PHYSICS RESEARCH Section A
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Integral and differential elastic collision cross-sections for low-energy Ar^+ ions with neutral Ar atoms

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Available online 10 May 2007

Abstract

Integral and differential elastic collision cross-sections for Ar^+ ions with neutral Ar atoms are calculated using modified Tang and Toennies ion–atom interaction potential models, TTIA and TTIA-wb, to describe experimental spectroscopic data for the Ar_2^+ molecular ion, and the phase shifts are calculated by the JWKB approximation. Results are presented for center-of-mass energies in the 1 meV to 10 eV range. In our calculations, the effects of the spin–orbit interaction are included through a semi-empirical model. The results obtained agree with the scarce data available in the scientific literature.

PACS: 25.60.D; 34.50; 34.50.−s; 61.18.Bn

Keywords: Elastic scattering; Symmetric charge transfer; Intermolecular potentials

1. Introduction

When a charged ion Ar^+ collides with an atom of the same species, Ar, in addition to elastic scattering we may have collisions with charge exchange:

$$Ar^+ + Ar \rightarrow Ar^+ + Ar$$

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In both processes, the total kinetic energy does not change and the resonant charge exchange has the effect of converting a collision with center-of-mass deflection angle Θ into one with a $\pi - \Theta$ angle.

The concept of symmetrical charge transfer or charge exchange in which the charge of the ion is transferred to the neutral atom during the collision is difficult to test in experiments. Experimental and theoretical data available in the literature for Ar^+ ions on Ar atoms scattering cross-sections are scarce.

2. Interaction potentials

When an atomic ion collides with an atom of the same element, the two nuclei have the same charge, and the field where the electrons move has in addition to the symmetry axis, a center of symmetry and the total wave functions must be either symmetric or antisymmetric with respect to the interchange of the coordinates of the two particles and give rise to a pair of potential curves of even (*gerade* (g)) and odd (*ungerade* (u)) symmetry [1]. The accurate calculation of collision cross-sections must take into account this pair, $V_g(r)$ and $V_u(r)$, of potential energy curves.

The Ar^+ ion due to the spin–orbit coupling of electronic angular momentum shows a spin–orbit splitting into a $^2P_{3/2}$ ground state and a $^2P_{1/2}$ metastable excited state.

In the interaction of Ar^+ ions with Ar atoms, neglecting the spin–orbit coupling, the ion is in a ^2P state and the atom in a ^1S state and the four lowest electronic states qof the molecular ion Ar_2^+ are designated [2] as $^2\sum_g^+$,

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doi:10.1016/j.nima.2007.05.012

$^2\sum_u^+$, $^2\prod_g$ and $^2\prod_u$, all of which separate to the same atomic state. When spin–orbit coupling is taken into account, the molecular ion Ar_2^+ has six low-lying molecular states—three doubly degenerate *gerade–ungerade* potential pairs. These are labeled, using the Hund's case (c) nomenclature as $I(1/2)_u$, $I(1/2)_g$, $I(3/2)_u$, $I(3/2)_g$, $II(1/2)_u$ and $II(1/2)_g$, where the values in parentheses represent the quantum number of the projection of the total electronic angular momentum onto the internuclear axis, Ω. The designations I and II refer to the states correlated with the first $Ar^+(^2P_{3/2})+Ar(^1S_0)$ and the second $Ar^+(^2P_{1/2})+Ar(^1S_0)$ dissociation limits, respectively.

In this work, we first calculate the potential energy curves for the $^2\sum_g^+$, $^2\sum_u^+$, $^2\prod_g$ and $^2\prod_u$ electronic states, neglecting the spin–orbit interaction, using modified Tang and Toennies interaction potential models (TTIA and TTIA-wb).

The molecular states $^2\sum_u^+$ and $^2\prod_g$ are bound by appreciable chemical forces, and for these molecular states we use the potential model TTIA based on universal damping functions for the dispersion coefficients, suggested by Tang and Toennies [3] for closed-shell systems, and modified by Siska [4] for the ion–atom interaction:

$$V(r) = A\,\exp(-br) - B\,\exp\left(\frac{-br}{2}\right) - \sum_{n=2}^{3} f_{2n}(r) C_{2n} r^{-2n}$$

and the damping function, $f_{2n}(r)$, is given by

$$f_{2n}(r) = 1 - \exp(-br)\sum_{k=0}^{2n}\frac{(br)^k}{k!}.$$

In this model, the three parameters, constants A, B and b, can be adjusted to reproduce spectroscopic data or *ab initio* calculations, using the well depth D_e, location of the minimum r_e and the zero crossing position σ of the interaction potential. The long-range behavior of the potential is reproduced by the dispersion coefficients, C_4 and C_6. The coefficient C_4 represents the ion-induced dipole interaction and the coefficient C_6 describes the van der Waals dispersion and the ion-induced quadrupole interaction, and these coefficients are calculated from dipole and quadrupole polarizabilities [1]. For the interaction of Ar^+ ions with Ar atoms, $C_4 = 11.8213\times10^{-40}\,\mathrm{eV\,m^4}$ and $C_6 = 41.6875\times10^{-60}\,\mathrm{eV\,m^6}$.

The molecular states $^2\sum_g^+$ and $^2\prod_u$ are weakly bound states, with small values of dissociation energy D_e (Table 1), essentially bound by long-range interaction and the short-range potential is basically exponentially repulsive. To describe satisfactorily these states we have modified the TTIA potential, adding a new exponential repulsive term, TTIA-wb:

$$V(r) = A\,\exp(-br) - B\,\exp\left(-\frac{br}{2}\right) + C\,\exp(-2br) - \sum_{n=2}^{3} f_{2n}(r) C_{2n} r^{-2n}.$$

Table 1
Parameters of the interaction potentials of the lowest electronic states of $ArAr^+$, without spin–orbit coupling

	States			
	$^2\sum_u^+$	$^2\prod_u$	$^2\sum_g^+$	$^2\prod_g$
D_e (eV)	1.3903[a]	0.0409[a]	0.0104[a]	0.1944[a]
r_e (10^{-10} m)	2.4221[a]	3.8049[a]	5.4059[a]	2.9962[a]
σ (10^{-10} m)	1.9799[b]	3.2469[b]	4.6432[b]	2.5742[b]
A (eV)	2886.4778	1862.4198	746.77763	6426.3915
B (eV)	106.83207	−1.0950271	0.3324593	31.356626
C (eV)	–	−4045.9842	777.45419	–
b (10^{+10} m^{-1})	3.1571857	2.9630838	2.1764265	3.5461148

[a]Experimental, from Ref. [5].
[b]Values derived from Ref. [5].

We have adjusted the three parameters A, B and b of the TTIA potential and the four parameters A, B, C and b of the TTIA-wb potential, to reproduce experimental high-resolution photoelectron spectroscopy data, dissociation energies D_e and equilibrium internuclear distances r_e, reported by Wüest and Merkt [5] for the $^2\sum_g^+$, $^2\sum_u^+$, $^2\prod_g$ and $^2\prod_u$ states of Ar_2^+ (Table 1).

The spin–orbit interactions mix configurations of the same Ω value and the same symmetry g/u. The three spin–orbit mixed interaction potentials pairs: $I(1/2)_u$, $I(1/2)_g$; $I(3/2)_u$, $I(3/2)_g$; and $II(1/2)_u$, $II(1/2)_g$, had been calculated from the potentials of the molecular states without spin–orbit coupling: $^2\sum_g^+$, $^2\sum_u^+$, $^2\prod_g$ and $^2\prod_u$, using the treatment of the spin–orbit interaction given by the Cohen and Schneider semi-empirical model [6].

The potential energy curves with spin–orbit coupling, thus obtained, are displayed in Fig. 1 and compared with the *ab initio* calculations of Gadea and Paidarová [7] and Ha et al. [8].

3. Collision cross-sections

In the collision of an atomic ion with an atom with identical nuclei, due to the possibility of its resonant charge transfer to the neutral atom, an interference takes place between the direct scattering of incident ion at angle Θ and resonant charge transfer scattering of the incident ion at angle $(\pi-\Theta)$. In this case, the theoretical quantum descriptions of the scattering must reflect the two physically different processes. The correct scattering amplitude is then a linear combination of the amplitudes $f(\Theta)$ and $f(\pi-\Theta)$, with the sign depending upon whether the nuclear potential is *gerade* or *ungerade* and whether the nuclei have integral spin or half-integral spin [1].

To calculate the integral and differential collision cross-sections for Ar^+ ions with neutral Ar atoms, we carry out the procedure used in our previous study for the collision of Xe^+ ions with neutral Xe atoms [9].

Natural argon is a mixture of 0.3365% of ^{36}Ar ($I=0$), 0.0632% of ^{38}Ar ($I=0$) and 99.6003% of ^{40}Ar ($I=0$). Thus, in the collision of Ar^+ ions with Ar atoms, most of

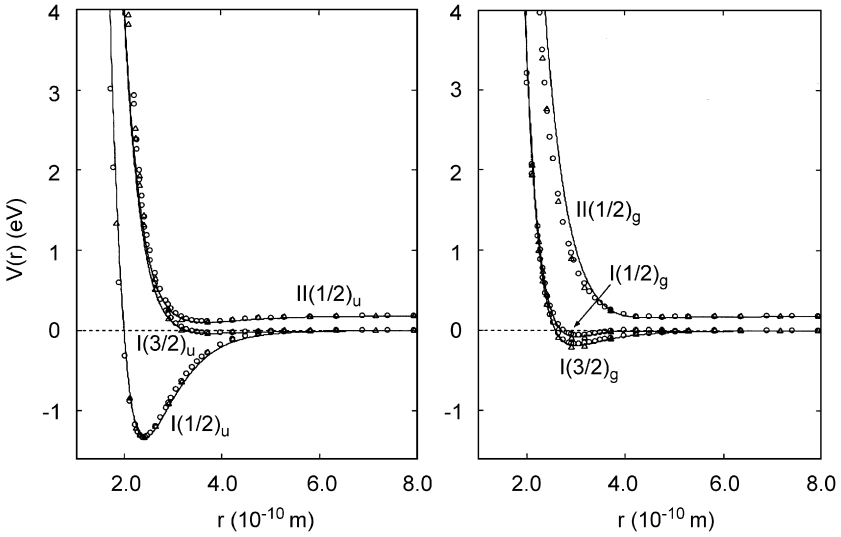

Fig. 1. Potential energy curves, with spin–orbit coupling, of the electronic states of $ArAr^+$: (—) this work (calculated from the parameters of Table 1 and using the spin–orbit interaction [6]); (△) Gadea and Paidarová [7] and (○) Ha et al. [8], *ab initio*.

the collisions will be between particles with identical nuclei with nuclear spin $I=0$, 99.2034%, and the remaining (0.7966%) will be between particles with distinguishable nuclei.

The differential cross-section $I_S(\Theta)$ for $^{A}Ar^+$ ions to be scattered by ^{A}Ar atoms, with identical nuclei with spin $I=0$, through the angle Θ into the solid angle $d\Omega$ is given by [1,9]

$$I_S(\Theta)=\tfrac{1}{4}|f^g(\Theta)+f^u(\Theta)+f^g(\pi-\Theta)-f^u(\pi-\Theta)|^2.$$

For the collision of $^{A1}Ar^+$ ions with ^{A2}Ar atoms, with distinguishable nuclei, the differential cross-section for the scattering of either of the ions through Θ, is

$$I_S(\Theta)=\tfrac{1}{4}|f^g(\Theta)+f^u(\Theta)|^2+\tfrac{1}{4}|f^g(\pi-\Theta)-f^u(\pi-\Theta)|^2.$$

The integral elastic cross-section Q_S is obtained by integrating $I_S(\Theta)$ over the whole space.

The differential cross-section for charge exchange $I_{CT}(\Theta)$ is given by [9]

$$I_{CT}(\Theta)=\tfrac{1}{4}|f^g(\pi-\Theta)-f^u(\pi-\Theta)|^2.$$

Integrating the differential cross-section $I_{CT}(\Theta)$ over all angles we obtain the integral cross-section for charge exchange:

$$Q_{CT}=\frac{\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\sin^2(\eta_l^g-\eta_l^u).$$

The phase shifts, η_l^g and η_l^u, for the calculation of scattering amplitudes $f^g(\Theta)$, $f^g(\pi-\Theta)$, $f^u(\Theta)$ and $f^u(\pi-\Theta)$, were calculated using the JWKB approximation [10], as before [9].

The differential elastic scattering $I_S(\varepsilon,\Theta)$ cross-sections have been calculated for each one of the g–u pairs of the electronic states, $\{I(1/2)_u, I(1/2)_g\}$, $\{I(3/2)_u, I(3/2)_g\}$ and $\{II(1/2)_u, II(1/2)_g\}$.

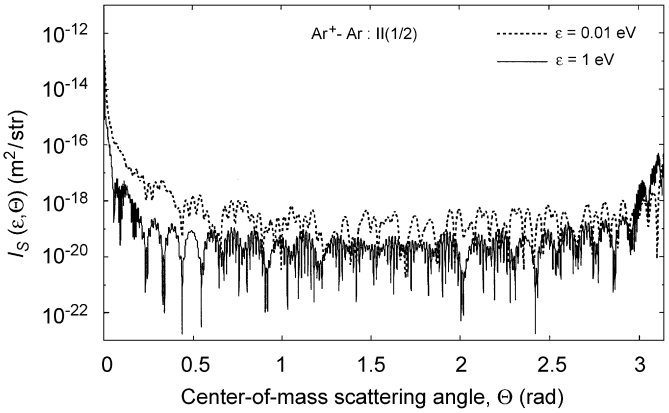

Fig. 2. Elastic differential cross-sections $I_S(\varepsilon,\Theta)$ of Ar^+ ions, in the state $^2P_{1/2}$, with Ar as a function of the center-of-mass scattering angle Θ for collision energies ε of 0.01 and 1 eV, calculated from the pair of electronic states $\{II(1/2)_u, II(1/2)_g\}$.

The cross-sections for scattering of the ground state $^2P_{3/2}$ ions were calculated from the two g–u pairs of the potential energy curves $V^{g,u}_{I(1/2)}$ and $V^{g,u}_{I(3/2)}$, assuming a statistical distribution of Ar^+ spin–orbit states. The cross-section for scattering of the metastable excited state $^2P_{1/2}$ ions is calculated from the pair of the potential energy curves $V^{g,u}_{II(1/2)}$.

In Fig. 2 we plot results of the calculated differential elastic collision cross-sections for Ar^+ ions, in the metastable state $^2P_{1/2}$, with Ar atoms. The results of integral cross-sections for Ar^+ in Ar are presented in Fig. 3.

The available cross-sections in the scientific literature for ion transport at small energies are mostly based on determination of the ion mobility and subsequent calculation of the momentum transfer cross-section. For Ar^+ in Ar the best-available experimental data include the

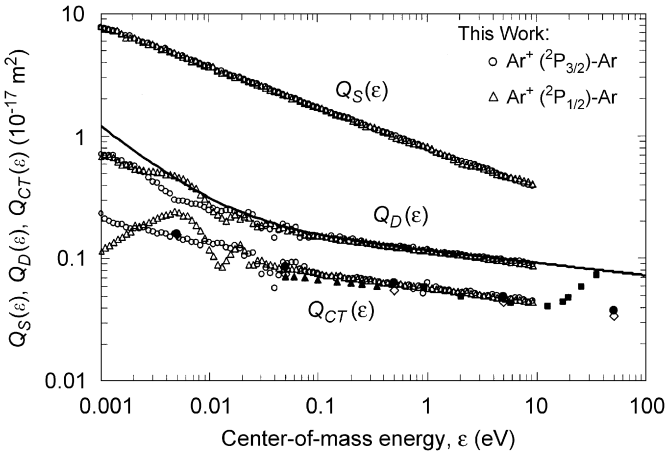

Fig. 3. Integral elastic scattering cross-section $Q_S(\varepsilon)$, charge transfer cross-section $Q_{CT}(\varepsilon)$ and diffusion (or momentum transfer) cross-section $Q_D(\varepsilon)$ for Ar^+ ions with Ar. Calculated in this work: (○) Ar^+ (ion state $^2P_{3/2}$) and (△) Ar^+ (ion state $^2P_{1/2}$); (—) Phelps [11]; (▲) Hegerberg et al. [12] (experimental); (■) Rao et al. [13] (experimental); (●) state $^2P_{3/2}$ and (◇) state $^2P_{1/2}$, Pullins et al. [14].

mobility measurements of Hegerberg et al. [12], and the translational kinetic-energy distributions of Rao et al. [13].

4. Conclusions

We have calculated integral and differential elastic scattering cross-sections for Ar^+ ions with Ar atoms, at center-of-mass energies from 0.001 to 10 eV, which agree with the scarce data available.

Acknowledgments

This work was supported by FEDER through Project POCI/FP/FNU/63430/2005 from Fundação para a Ciência e para a Tecnologia—Portugal.

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