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 Ar₂⁺ 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.

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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 ↔ Ar⁺+Ar

Ar⁺+Ar ↔ Ar+Ar⁺.

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 π−Θ 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, Vₔ(r) and Vu(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 ²P₃/₂ ground state and a ²P₃/₂ 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 of the molecular ion Ar₂⁺ are designated [2] as ²Σ⁺, ⁴Σ⁺, ²Π, and ⁴Π.
potential is reproduced by the dispersion coefficients, the interaction potential. The long-range behavior of the and the damping function, II(1/2)g, where the values in parentheses represent the

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

The molecular states $2\Sigma_u^+$ and $2\Pi_g$ 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 $\sigma$ 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, $C_4 = 11.8213 \times 10^{-40}$ eV m$^4$ and $C_6 = 41.6875 \times 10^{-60}$ eV m$^6$.

The molecular states $2\Sigma_u^+$ and $2\Pi_g$ 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>
<thead>
<tr>
<th>States</th>
<th>$2\Sigma_u^+$</th>
<th>$2\Pi_u$</th>
<th>$2\Sigma_u^+$</th>
<th>$2\Pi_u$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_e$ (eV)</td>
<td>1.3903$^a$</td>
<td>0.0409$^a$</td>
<td>0.0104$^a$</td>
<td>0.1944$^a$</td>
</tr>
<tr>
<td>$r_e$ (10$^{-10}$ m)</td>
<td>2.4221$^a$</td>
<td>3.8049$^a$</td>
<td>5.4059$^a$</td>
<td>2.9962$^a$</td>
</tr>
<tr>
<td>$\sigma$ (10$^{-10}$ m)</td>
<td>1.9799$^b$</td>
<td>3.2469$^b$</td>
<td>4.6432$^b$</td>
<td>2.5742$^b$</td>
</tr>
<tr>
<td>$A$ (eV)</td>
<td>2886.4778</td>
<td>1862.4198</td>
<td>746.7763</td>
<td>6426.3915</td>
</tr>
<tr>
<td>$B$ (eV)</td>
<td>106.83207</td>
<td>-1.0950271</td>
<td>0.3324593</td>
<td>31.356626</td>
</tr>
<tr>
<td>$C$ (eV)</td>
<td>-4045.9842</td>
<td>777.45419</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$b$ (10$^{-10}$ m$^{-1}$)</td>
<td>3.151785</td>
<td>2.960838</td>
<td>2.176425</td>
<td>3.5461148</td>
</tr>
</tbody>
</table>

$^a$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 $2\Sigma_u^+$, $2\Sigma_u^+$, $2\Pi_g$ and $2\Pi_u$ states of Ar$_2^+$ (Table 1).

The spin–orbit interactions mix configurations of the same $\Omega$ value and the same symmetry $g/u$. The three spin–orbit mixed interaction potential pairs: I(1/2)$_u$, I(1/2)$_g$, I(3/2)$_u$, I(3/2)$_g$, II(1/2)$_u$, II(1/2)$_g$, had been calculated from the potentials of the molecular states without spin–orbit coupling: $2\Sigma_u^+$, $2\Sigma_u^+$, $2\Pi_g$ and $2\Pi_u$, 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 Paidaróva [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 $\theta$ 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
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 $^{\Lambda}$Ar$^+$ ions to be scattered by $^{\Lambda}$Ar atoms, with identical nuclei with spin $I = 0$, through the angle $\Theta$ into the solid angle $d\Omega$ is given by [1,9]

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

For the collision of $^{\Lambda_1}$Ar$^+$ ions with $^{\Lambda_2}$Ar atoms, with distinguishable nuclei, the differential cross-section for the scattering of either of the ions through $\Theta$, is

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

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]

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

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

The differential elastic scattering $I_S(e, \Theta)$ 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}.

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 $V_{II}^{g,u}(1/2)$ and $V_{II}^{g,u}(3/2)$ 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 $V_{II}^{g,u}(1/2)$.

In Fig. 2 we plot results of the calculated differential elastic collision cross-sections for Ar$^+$ ions, in the state $^2P_{1/2}$, with Ar as a function of the center-of-mass scattering angle $\Theta$ for collision energies $\epsilon$ of 0.01 and 1 eV, calculated from the pair of electronic states {II(1/2)u, II(1/2)g}.

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
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.

References