BASIC DATA OF Ar^+ AND Ar_2^+ IONS IN ARGON GAS NEEDED TO OPTIMIZE LOW TEMPERATURE PLASMA JETS FOR BIOMEDICAL USES

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ABSTRACT

Collision cross sections and transport coefficients are calculated for Ar^+ and Ar_2^+ ions, in the ground and metastable states, colliding with gaseous Ar. These basic data are of great interest for a better understanding of physical and chemical properties of the plasma jet using argon as carrier gas. The needed collision cross sections were determined using a close coupling quantum method for the mono-atomic ion colliding with its parent gas. For the diatomic ion, a hybrid approach, mixing classical and quantum dynamics, and an "inverse" method, based on a simplified spherical potential, were used. The ion transport coefficients are calculated from the corresponding collision cross sections by using an optimized Monte Carlo code over a wide range of reduced electric field. Calculated transport coefficients are compared with available experimental data.

1. INTRODUCTION

The collision cross sections and transport data (reduced mobility, diffusion coefficients and reaction rates) are needed to optimize the features of many plasma devices devoted for instance to biomedical applications. More particularly, they can be used in electro-hydrodynamic and chemical models of the low temperature plasma jets to quantify and to tune the production of active species essential for biomedical applications (antitumor treatment, wound healing or blood coagulation [1]…). Many low temperature plasma devices are generated using helium carrier, due to the relatively low voltage required to ignite electrical discharge [2]. In this case, transport coefficients of He^+ and He_2^+ ions were already calculated in previous studies [3,4]. However, in order to generate plasma jet with different active species and also to anticipate the future shortage of helium world-wide production, it is interesting to investigate other carrier gases such as argon. In the case of electrical discharges using argon carrier gas at atmospheric pressure, the atomic Ar^+ and diatomic Ar_2^+ ions can significantly affect the physical and chemical properties of the low temperature plasma jet used in the biomedical field [5,6]. Transport coefficients in weakly ionized gases under action of an external electric field are closely related to electronic potential energy curves or surfaces and corresponding collision cross sections. In fact, Ar^+ and Ar_2^+ ions can be found in the plasma jet in two different states. A fraction of ions is in the ground state level where J=3/2 is the total (orbital + spin) angular momentum of the ion. This corresponds to 2 possible absolute values Ω = (1/2, 3/2) for the projection of this total angular momentum on a given axis. Atomic and diatomic ions in the ground state are respectively labelled $Ar^+(^2P_{3/2})$ and $Ar_2^+(I(1/2)_u)$. Another fraction is in the metastable state where J=1/2 and includes ions with Ω = 1/2 only. In this case, ions are labelled $Ar^+(^2P_{1/2})$ and $Ar_2^+(II(1/2)_u)$.

Following this introduction, section 2 is devoted to the mono-atomic ion Ar^+ [7]. The interaction potentials of Ar_2^+ with the inclusion of the spin-orbit interaction are first described. Then, the close coupling quantum calculation method [8] of collision cross sections is briefly described followed by the collision cross sections results, for ions in the ground $^2P_{3/2}$ and metastable $^2P_{1/2}$ states, calculated from several interaction potentials [9–11]. The ion transport coefficients are then

calculated using an optimized Monte Carlo code and are shown for the interaction potential which gives the best agreement with the experimental data. In section 3, ion transport coefficients of Ar_2^+ ions in Ar are calculated. The diatomics-in-molecules (DIM) model provides the Ar_3^+ interaction energy surfaces. Then, the molecular dynamics simulation, using classical trajectories which take into account vibrational and rotational motions, allows to calculate the momentum transfer cross-sections used for the ion transport coefficients calculation. Moreover, an "inverse" method, based on a simplified effective interaction potential, is also used for the collision cross section calculation. Monte Carlo ion transport coefficients are then calculated and a critical comparison between results obtained with the two calculation methods and available experimental data [12–14] is performed.

2. Ar^+ COLLISIONS WITH Ar

In order to calculate the ion transport coefficients for Ar^+ ions in Ar, several *ab initio* interaction potentials were considered [9–11]. At intermediate and short interatomic distances, the spin-orbit couplings are small compared to the electrostatic interactions. At long range, the electrostatic interactions vanish and spin-orbit interactions are dominant. In order to obtain potential curves with inclusion of the spin-orbit interaction, the semi-empirical Cohen-Schneider model [15] was used, inducing couplings between the states which have the same Ω and *g/u* symmetry. We then obtain 6 adiabatic interaction potential curves with inclusion of the spin-orbit interaction labelled $I(1/2)_{u,g}$, $I(3/2)_{u,g}$ and $II(1/2)_{u,g}$. I or II corresponds respectively to J = 3/2 or J = 1/2 asymptotically. Adiabatic interaction potential curves with inclusion of the spin-orbit interaction are displayed in figure 1.

As spin-orbit couplings exist only between states which have the same Ω and *g/u* symmetry, Ω is conserved during the collision. The global problem involving 6 potentials can be split into 2 separate simpler ones for each subspace Ω=1/2 and Ω =3/2. For Ω =3/2, the calculation involves only the 2 potential curves $I(3/2)_{u,g}$. In this case, only elastic and charge transfer can take place. For Ω=1/2, the 4 potentials curves $I(1/2)_{u,g}$ and $II(1/2)_{u,g}$ are involved : collision can induce both charge transfer and spin change. Assuming argon nuclei are distinguishable particles, integral $Q_0^{ij}(\varepsilon)$ and momentum transfer $Q_1^{ij}(\varepsilon)$ cross-sections from initial internal (charge + spin state) ion state i to final one j have been calculated as follows [3]:

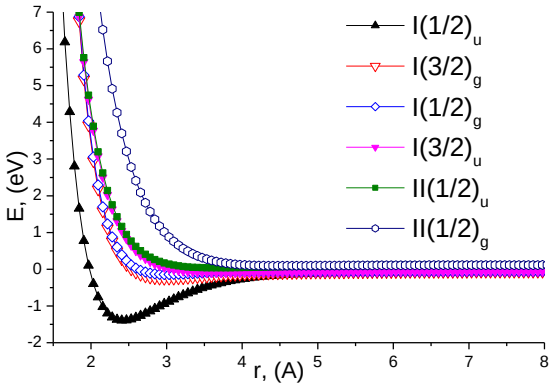

Fig. 1. Interaction potential curves with inclusion of the Spin-Orbit interaction for the six lowest electronic states of Ar_2^+.

$$Q_0^{ij}(\varepsilon) = \frac{\pi}{k_i^2}\sum_l (2l+1)\left|T_{ij}^l(\varepsilon)\right|^2 \qquad (2.1)$$

$$Q_1^{ij}(\varepsilon) = \frac{\pi}{k_i^2}\sum_l \{(2l+1)\left|T_{ij}^l(\varepsilon)\right|^2 - 2(l+1)Re\left[T_{ij}^l(\varepsilon)^* T_{ij}^{l+1}(\varepsilon)\right]\} \qquad (2.2)$$

where $T^l_{ij}(\varepsilon)$ is the scattering collision matrix (dimension 2x2 for the Ω=3/2 subspace and dimension 4x4 for the Ω=1/2 one) at collision energy ε for the collision angular momentum l and k_i is the initial wave vector. As we are in fact in presence of undistinguishable particles, elastic and charge transfer processes for each spin state transition are combined to provide a single symmetrized cross-section. Finally, collision cross-sections for each internal energy level $^2P_{3/2}$ or $^2P_{1/2}$ were obtained by averaging over Ω. Figure 2 display the symmetrized and averaged momentum transfer $Q_{1sym}(\varepsilon)$ cross sections calculated from Gadéa and Paidarová's interaction potentials [10] for $^2P_{3/2}$ and $^2P_{1/2}$. The momentum transfer cross-section, obtained by Phelps [16] using a "Langevin" polarization scattering method, is also plotted for comparison. However, Phelps doesn't give doesn't give cross section values for energies below 0.1 eV absolutely needed for transport coefficients calculation at low electric fields E/N. In figure 2, it is noteworthy that, at low energy, $Q_{1sym}(^2P_{1/2}) < Q_{1sym}(^2P_{3/2})$ which would lead to reduced mobility $K_0(^2P_{1/2}) > K_0(^2P_{3/2})$ at low E/N. However, at high energy collision cross sections are quite similar.

Ion transport coefficients, for each internal energy level, were then calculated from corresponding symmetrized differential cross sections using an optimized Monte Carlo code [17]. Reduced mobility data and diffusion coefficients, calculated from Gadéa and Paidarová's interaction potentials which give the best

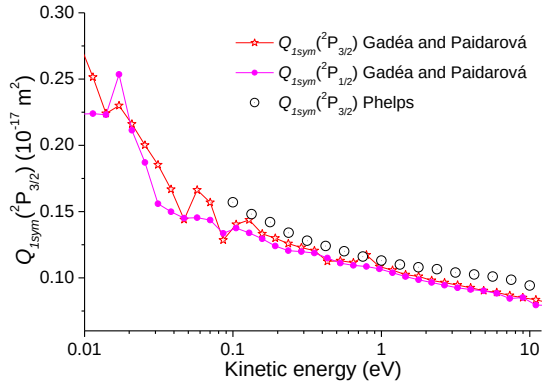

Fig. 2. Calculated symmetrized momentum transfer cross sections $Q_{1sym}(\varepsilon)$ for Ar^+ ions in the $^2P_{3/2}$ and $^2P_{1/2}$ states.

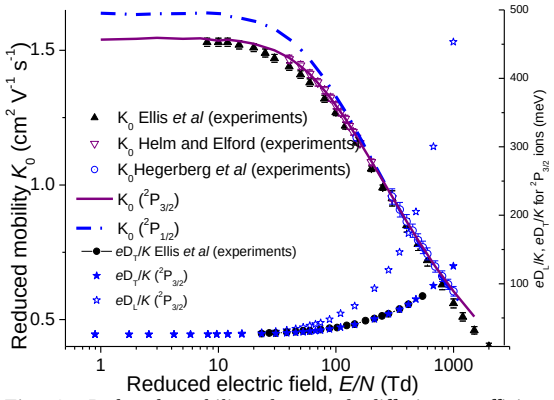

Fig. 3. Reduced mobility data and diffusion coefficients calculated via a close-coupling quantum method from the Gadéa and Paidarová's interaction potentials compared with various experimental results [12–14].

agreement with experimental mobility results [12–14], are plotted in figure 3. We see an excellent agreement between experimental mobility data and the calculated ones for the $^2P_{3/2}$ state. A mean relative error lower than 0.2% from Helm and Hegerberg experimental results was obtained. Moreover, transversal diffusion coefficients were obtained within the ±5% experimental errors bars.

3. Ar_2^+ COLLISIONS WITH Ar

As part of this work, the electronic states of Ar_2^+/Ar interaction system have been described by diatomics-in-molecules (DIM) potentials and couplings. In short, the DIM method enables us to decompose the electronic Hamiltonian of clusters into a sum of atomic and diatomic contributions [18].

To calculate momentum transfer collision cross sections of $Ar_2^+(I(1/2)_u)$ and $Ar_2^+(II(1/2)_u)$ ions, a classical trajectory approach has been used with bunches of Ar_2^+/Ar collision trajectories starting from appropriately chosen initial conditions and numerically integrated [4]. The Ar_2^+/Ar collision complex has been treated semi-classically, i.e., classical equations of motion have been used for nuclei and quantum Schrödinger equation for electrons. We then obtain two collision cross sections for each internal energy level of the ion: one elastic, non-elastic and electronic excitation processes and another for the three body dissociation (Ar_2^+ + Ar → Ar^+ + Ar + Ar). In addition, a semi-classical JWKB approximation [19] using an isotropic core potential model [4] has been also used to obtain the elastic momentum cross-section. In this method, that we call the "inverse" method, an effective potential is adjusted until a good agreement is found between calculated and measured mobility values over a given reduced electric field range. Noteworthy, this method doesn't allow to calculate cross sections for different internal levels of the ion but gives an effective, state-averaged cross section. This state-averaged momentum transfer cross section has subsequently been used to extend the calculated ion transport coefficients to higher *E/N*.

Figure 4 shows, in arbitrary units, the obtained hybrid momentum transfer cross sections for electronically $(I(1/2)_u)$ and rotation-vibrationally ground-state Ar_2^+ ions colliding with Ar along with the one obtained from the effective "inverse" method. It is noteworthy that collision cross sections obtained with the two methods are quite close. Mobilities calculated with the "inverse" method could be obtained within the experimental error bars except at high *E/N* (cf. figure 5), which is probably due to the neglect of inelastic processes with this method. On the other hand, hybrid mobilities of Ar_2^+ ions in the ground state show a relative deviation varying between 4% and 15% from the experimental results. Thus, it seems from these preliminary results that either vibrationally excited Ar_2^+ or the metastable $II(1/2)_u$ state of the ionic diatom have to be

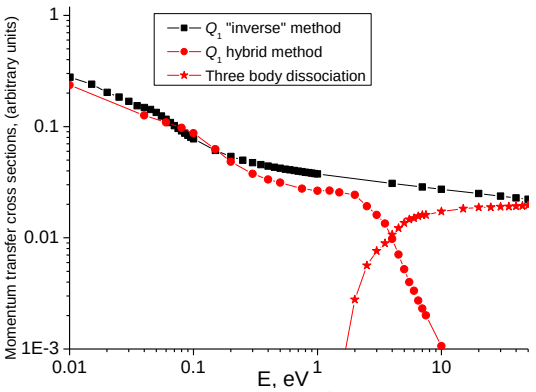

Fig. 4. Hybrid collision cross sections for elastic, non-elastic and electronic excitations obtained for electronically and rotation-vibrationally ground-state Ar_2^+, and for the three body dissociation for ions in the ground state compared to the one obtained with a potential core model ("inverse" method).

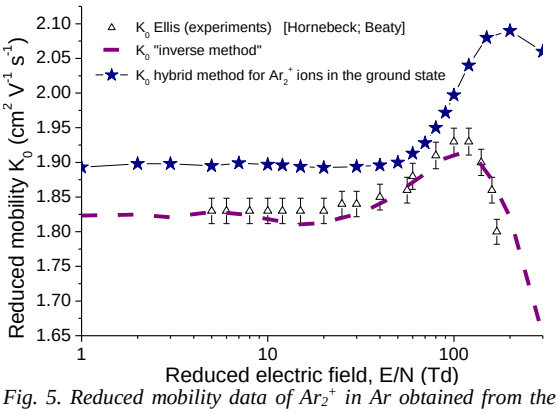

Fig. 5. Reduced mobility data of Ar_2^+ in Ar obtained from the "inverse" method and from the hybrid cross sections calculated for ions in the electronic and rotation-vibrational ground state. Experimental data are also shown for comparison.

considered to correctly model the experimental mobility data. Thus, the final mobility, calculated from an adequate combination of ground and metastable states ion mobilities and the mobilities obtained for vibrationally excited dimer, will be shown during the conference. Calculated longitudinal and transversal diffusion characteristic energies for Ar_2^+ ions in Ar will be presented also.

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