Collision cross-sections and reduced mobility of He_2^+ ions colliding with He for optimization of low temperature plasma sources for biomedical uses

A. Chicheportiche[1], M. Benhenni[1], M. Yousfi[1], B. Lepetit[2], R. Kalus[3], F.X. Gadea[4]

[1] *LAPLACE, UMR CNRS 5213, Université de Toulouse, 118 route de Narbonne, Toulouse, France*
[2] *IRSAMC, LCAR, UMR CNRS 5589, Université de Toulouse, 118 route de Narbonne, Toulouse, France*
[3] *Centre of Excellence IT4 Innovations & Department of Applied Mathematics, VSB – Technical University of Ostrava, 17. listopadu 15/2172, 708 33 Ostrava - Poruba, Czech Republic*
[4] *IRSAMC, LCPQ, UMR CNRS 5626, Université de Toulouse, 118 route de Narbonne, Toulouse, France*
chicheportiche@laplace.univ-tlse.fr

Calculated collision cross-sections and transport coefficients are presented for the He_2^+/He interaction system. Momentum transfer cross-sections required for ion mobility are determined from quantum, semi-classical (JWKB) and classical approaches using a DIM He_3^+ interaction potential. The corresponding cross-sections are then used in an optimized Monte Carlo code to calculate the ion transport coefficients over a wide range of reduced electric field *E/N*. Moreover, a rigid core potential model for the ion-neutral system is also used to determine the elastic momentum transfer cross-section using the JWKB approximation. Reduced mobilities are compared with available experimental data. Such ion transport data will be used in electro-hydrodynamic and chemical kinetic models of the low temperature plasma jet to quantify and to tune the active species production for a better use in biomedical applications.

1. Introduction

The ion swarm data (reduced mobility, diffusion coefficients and reaction rates) are needed to optimize the features of many plasma devices devoted for instance to biomedical applications. They can more particularly be used in electro-hydrodynamic and chemical models of the low temperature plasma jets to quantify and to tune the production of active species production for a better use in medical field (antitumor treatment, wound healing, blood coagulation…). The interested reader can for instance see ref. [1] and the references given therein. In the case of electrical discharges using helium carrier gas at atmospheric pressure, the diatomic ion He_2^+ can significantly affect the physical and chemical properties of the low temperature plasma jet used in biomedical field [2].

In fact, after the formation of atomic ions He^+ and metastable He* by impacts with energetic electrons of the discharge, He_2^+ molecular ions can be generated in our atmospheric pressure devices following three-body or two-body reactions [3]:

$$He^+ + 2He \rightarrow He_2^+ + He$$
$$He^* + 2He \rightarrow He_2^* + He$$
$$e + He_2^* \rightarrow He_2^+ + 2e$$
$$He^* + He^* \rightarrow He_2^+ + e$$
$$He_2^* + He_2^* \rightarrow He_2^+ + e + 2He$$

In weakly ionized gases under action of an external electric field, transport coefficients are closely related to the ion–neutral interaction potentials and the corresponding collision cross-sections. In this work, the ion transport data of He_2^+ ions in He, for which there are some available experimental data at low reduced electric field *E/N*, are calculated from the momentum transfer cross-sections [4] using an optimized Monte Carlo simulation over a wide range of *E/N* [5].

Elastic and inelastic momentum transfer cross-sections have been first calculated by using a quantum method where the Infinite Order Sudden Approximation (IOSA) is made to deal with vibration and rotation of the He_2^+ molecule colliding with He atoms [6]. A semi-classical Jeffreys-Wentzel-Kramers-Brillouin (JWKB) calculation with the same approximation [7] has then been done to obtain the elastic momentum transfer cross-section using only the electronic ground state of the DIM He_3^+ interaction potential [8]. A molecular dynamics simulation using classical trajectories which take into account vibrational and rotational motions was also used to calculate the elastic momentum transfer cross-section. Finally, an "inverse" method based on the experimental reduced mobility results [9] at low electric field *E/N* provided the elastic momentum transfer cross-section also. A comparative analysis of the calculated ion transport coefficients obtained by the different methods will be presented and compared to available experimental data [9].

2. Interaction potentials

As part of that work, the three lowest electronic states of He_2^+/He interaction system are described by

DIM (Diatomic In Molecules) potentials and couplings [8]. Since it is well known that pure DIM models do not work well for helium cations larger than dimer due to an insufficient inclusion of three-body interactions, the authors of ref. [8] developed an effective model employing some empirical modifications of the diatomic inputs to the DIM methodology to partially remove this defect. In the framework of the IOS approximation (for quantum and semi-classical calculations) the vibrational and rotational motions of the diatomic are frozen, and the anisotropy of the atom-molecule interaction is taken into account by a simple average over the approach angle φ. Figure 1 displays an overview on the adiabatic electronic ground state for He_2^+/He interaction system versus internuclear distance between He and He_2^+ for a fixed distance r_{eq} = 2.1 a.u. (equilibrium one) between the two atoms of the diatomic ion, and also versus the angle φ between He^+-He internuclear axis and the axis between the He_2^+ centre of mass and He atom.

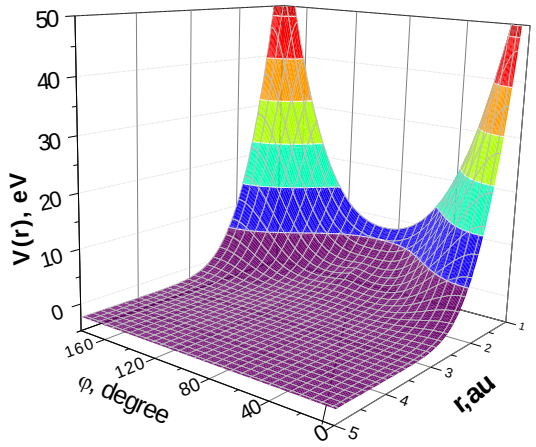

Fig. 1. Adiabatic electronic ground state of He_3^+ with r_{eq}=2.1 a.u.

3. Momentum transfer cross-sections

3.1. Quantum calculation

The scattering matrix $T^l_{ij}(\varepsilon,\varphi)$ for the angular momentum l at collision energy ε for the approach angle φ, from initial state i to final one j, is calculated from the 3 coupled potential curves $V_1(r,\varphi)$, $V_2(r,\varphi)$ and $V_3(r,\varphi)$ [10]. The scattering matrix is then used to calculate elastic and inelastic momentum transfer cross-sections $Q_1^{ij}(\varepsilon,\varphi)$ from the following [4]:

$$Q_1^{ij}(\varepsilon,\varphi) = \frac{\pi}{k_i^2}\sum_l \{(2l+1)\left|T^l_{ij}(\varepsilon,\varphi)\right|^2 - 2(l+1)Re\left[T^l_{ij}(\varepsilon,\varphi)^* T^{l+1}_{ij}(\varepsilon,\varphi)\right]\} \quad (1)$$

where k_i is the initial wave vector.

The momentum transfer cross-sections $Q_1^{ij}(\varepsilon)$ are then obtained by an integration over solid angle which corresponds here to a simple average of $Q_1^{ij}(\varepsilon,\varphi)$ over the approach angle φ.

Elastic and inelastic momentum transfer cross-sections are then used in an optimized Monte Carlo code [5] instead of the differential cross-sections to take into account the anisotropy of collisions [4].

3.2. Semi-classical calculation

In the case of the JWKB approximation, only the elastic momentum transfer cross-section $Q_1^{11}(\varepsilon,\varphi)$ has been calculated from the following well-known formula:

$$Q_1^{11}(\varepsilon,\varphi) = \frac{4\pi}{k^2}\sum_l (l+1)\, sin^2(\,\delta_{l+1}^{\varepsilon,\varphi} - \delta_l^{\varepsilon,\varphi}\,) \quad (2)$$

Phase-shifts $\delta_l^{\varepsilon,\varphi}$ were obtained from the ground electronic state $V_1(r,\varphi)$ of He_3^+ interaction potential [8] as the following [7]:

$$\delta_l^{\varepsilon,\varphi} = \left(l+\frac{1}{2}\right)\frac{\pi}{2} - k\, r_0^{\varphi} + \int_{r_0^{\varphi}}^{\infty}\left(\sqrt{k^2 - \frac{2\,\mu\, V_1(r,\varphi)}{\hbar^2} - \frac{(l+\frac{1}{2})^2}{r^2}\,k}\right)dr \quad (3)$$

where k is the wave vector, r the internuclear distance between He and He_2^+ centre-of-mass for a fixed r_{eq} distance, μ the reduced mass, $\hbar$ the reduced Planck constant and r_0^{φ} represents the distance of closest approach for $V_1(r,\varphi)$.

Elastic momentum transfer cross-section $Q_1^{11}(\varepsilon,\varphi)$ was obtained as previously by a simple average of $Q_1^{11}(\varepsilon,\varphi)$ over the approach angle φ.

3.3. Classical calculation

The classical trajectory approach has been used with bunches of He_2^+/He collision trajectories starting from appropriately chosen initial conditions, integrated numerically, and finally used in momentum transfer cross-section evaluations.

The He_2^+/He collision complex has been treated semi-classically [11], i.e., classical equations of motion have been used for nuclei,

$$\dot{q}_i = \frac{p_i}{m},\quad \dot{p}_i = \left\langle \chi\left| -\frac{\partial \hat{H}}{\partial q_i}\right|\chi\right\rangle \quad (4)$$

where q_i, $\dot{q}_i$ and p_i are respectively centre-of-mass coordinates, velocities and momenta of the nuclear sub-system $(i = 1, \ldots, 3N-3)$, χ is current

electronic state, and $\hat{H}$ is the electronic Hamiltonian, and quantum Schrödinger equation,

$$ih\frac{\partial|\chi\rangle}{\partial t} = \hat{H}|\chi\rangle \qquad (5)$$

has been used for electrons. Eqs. (4) and (5) have been integrated numerically using a fourth-order Runge-Kutta algorithm with the integration step ranging between t_{int} = 0.04 fs and t_{int} = 0.1 fs.

The initial conditions for the present task consist of the initial nuclear coordinates, velocities and electronic state of He_2^+, and the initial coordinates and velocity of the impacting neutral atom.

Totally 20,000 – 40,000 trajectories have been employed for each particular collision energy to get converged values of the momentum transfer cross-section. More trajectories are required for lower energies.

All the classical calculations have been performed using our MULTIDYN code package [12].

3.4. "Inverse" method

The elastic momentum cross-section $Q_1^{11}(\varepsilon)$ was also calculated from a semi-classical JWKB approximation by using a core potential model [13]. This model is well adapted for a polyatomic ion interacting with polar and non-polar molecules. A (12-4) core potential was used in order to obtain a good agreement between measured mobility and calculated one. This (12-4) core potential $V_{core}(r)$ is given by:

$$V_{core}(r) = \frac{\varepsilon_w}{2}\left\{\left(\frac{r_m - a}{r - a}\right)^{12} - 3\left(\frac{r_m - a}{r - a}\right)^{4}\right\} \qquad (6)$$

where ε_w is the potential well depth, r_m the position of the minimum potential energy and r the internuclear distance. The parameter a describes the shift induced by the ion on the neutral atom, of the centre-of-mass from the charge centre.

In this method, that we call the "inverse" method, the potential parameters were adjusted until a good agreement was found between calculated and measured mobility values over a reduced electric field range [9]. Then, from this fitted momentum transfer cross-section, mobility calculations (cf. figure 2) were extended to a higher *E/N* range.

Comparative analysis between the different momentum transfer cross-sections $Q_1^{ij}(\varepsilon)$ obtained in this work will be shown during the conference.

4. Calculated reduced mobility

Reduced mobilities have been then calculated by using an optimized Monte Carlo code [5] from the different momentum transfer cross-sections $Q_1^{ij}(\varepsilon)$ [4] obtained in the previous section. Preliminary calculated reduced mobility results are presented in figure 2.

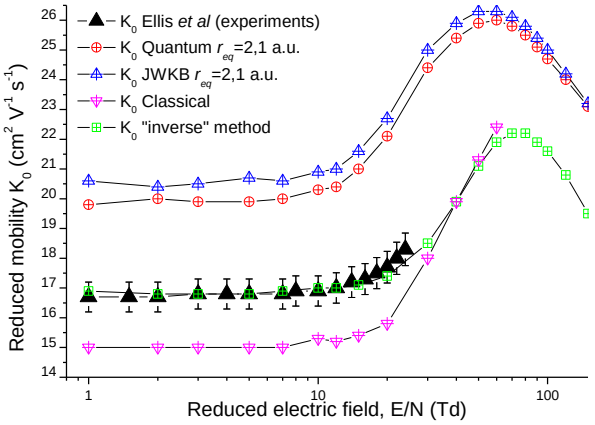

Fig. 2. Reduced mobility calculated with quantum (red circles) and semi-classical (blue triangles) methods with r_{eq} = 2.1 a.u., with a classical method (pink triangles) and finally with the "inverse" method (green squares).

We see that the "inverse" method gives the best agreement with experimental results [9]. The physical meaning of the potential (12-4) core used in this method will be discussed during the conference.

However, molecular dynamics calculation gives mobility results with about 10% error at low electric fields. Classical trajectories indeed suggest that the He_2^+ bond distance is significantly modified during collision. On the other hand, classical mobilities are lower than measured ones, presumably due to too large computed cross-sections. This is a consequence of the existence of strong quantum effects in the present light molecular system.

The difference between computed quantum results and experimental ones can be attributed to the reduced dimensionality approximation within the IOSA framework. Study of the influence of the equilibrium distance on mobility results will be presented during the conference.

Finally, it is noteworthy that the JWKB method, which is not including inelastic processes, doesn't give results significantly different from the quantum method. The influence of inelastic processes on mobility results will be shown during the conference.

References

[1] M. Yousfi, N. Merbahi, A. Pathak, O.Eichwald, Fund Clin Pharm **28** (2013)

[2] M. Laroussi, IEEE Trans on Plasma Science **37** (2009) 714

[3] Y Sakiyama and D B Graves J. Phys. D: Appl. Phys. **39** (2006) 3451–3456

[4] A. Chicheportiche, B. Lepetit, M. Benhenni, F. X. Gadea, J. Phys. B: At. Mol. Opt. Phys. **46** (2013) 065201

[5] M. Yousfi, A. Hennad, O. Eichwald, J. Appl. Phys. **84** (1998) 107-114

[6] G. A. Parker and R. T. Pack, J. Chem. Phys. **68** (1978) 1585

[7] R. J. Munn, E. A. Mason, F. J. Smith, J. Chem. Phys. **41** (1964) 3978

[8] F. Calvo, F.Y. Naumkin and D.J. Wales, J. Chem. Phys. **135** (2011) 124308

[9] H. W. Ellis, R. Y. Pai, E. W. McDaniel, E. A. Mason, L. A. Viehland, Atomic and Nucl. Data Tables **17** (1976) 177–210

[10] M. Child, Molecular collision theory, N.Y.: Dover Publications (1996)

[11] I. Janeček, D. Hrivňák, R. Kalus, and F. X. Gadéa, J. Chem. Phys **125** (2006) 104315

[12] http://moldyn.vsb.cz/index.php/software-menu/2-uncategorised/5-multidyn

[13] E.A. Mason, H. O'Hara and F.J Smith, J. Phys. B: At. Mol. Phys. **5** (1972) 169