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Transport coefficients for He^+ ions in mixtures He/CF_4: modeling laboratory and astrophysical plasmas

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Abstract. A complete set of cross sections for helium ions in a mixture of helium and carbon tetrafluoride is recommended. The transport properties for He^+ions in He/CF_4 mixtures required to model the discharge containing the mentioned ions were calculated by the Monte Carlo method at a temperature of T = 300 K. In this paper we give the drift velocity, characteristic energy, reduced mobility and specially rate coefficients for low and moderately reduced electric fields E /N (E-electric field, N-gas density) and accounting for non-conservative collisions. This paper is dedicated to the presentation of the set for He^+ions scattering cross-sections in CF_4 which is estimated using available experimental data for exothermic charge transfer cross-sections producing CF_3^+ and CF_2^+ions and endothermic charge transfer cross-section producing CF^+, C^+ and F^+ions. The aim of this paper is to determine how the addition of a percentage for He in He/CF_4 mixtures affects the separation of bulk and flux transport parameters for He^+ions.

Key words: He^+ – He/CF_4 mixtures – Monte Carlo simulations – cross sections – transport coefficients

1. Introduction

He-CF_4 mixtures are used in gaseous electronic multipliers for various imaging purposes (X-rays, charged particles, thermal neutrons and dark matter detection) (Fraga et al., 2003; Kaboth et al., 2008). After hydrogen, which makes up about 90% of the cosmos, helium is the second most abundant element (about 9%).

We notice the importance of obtained results as atomic and molecular data which are input parameters for modeling of various environments. Low temperature can change the state of metals, gases, liquids and solids, cause damage to organisms depending on length of exposure, and change the functionality of mechanized processes. Electron multiplication bursts affect the production of various ions that can affect the time distribution of detected particles (Bošnjaković, 2016). The experimental transport coefficients required as input data for He^+ion transport models in He are existing (Viehland et al., 2017;

Basurto et al., 2000; Helm, 1977; Stefansson et al., 1988; Viehland & Mason, 1995). Only bulk values in CF_4 of transport coefficients can be experimentally determined (Robson, 1991). Due to significant particle losses in He^+ in CF_4, the experimental transport coefficients were not measured. Although some experimental points for the cross sections of He^+ion scattering in CF_4 were obtained by (Fisher et al., 1990). A complete set of cross-sections for this system with more details is given in the paper (Nikitović et al., 2017). Quantum-mechanical calculation of a certain cross-section is a required task that requires knowledge of the surface potential energy of ions and molecules to be constructed from the structure of the reactants. Less intensive computational methods, such as the Denpoh-Nanbu theory (Denpoh & Nanbu, 1998; Nikitović et al., 2014; Petrović et al., 2007), require knowledge of thermodynamic formation data and are applicable to a range of molecules. Although thermodynamic formation data are known in this case, such an approach is difficult to apply, since the reaction does not take place via the excited ($HeCF_4^+$ *) complex but via the excited CF_4^+ (CF_4^+ *) states. It is also more appropriate to select the limit energies for the reaction products from the energy thresholds of the CF_4^+ state (Motohashi et al., 2005) than from the enthalpies of formation.

Ion charge transfer reactions with molecules are important elementary processes in modeling kinetics in all types of plasma. In many cases, it is known that the cross section for these reactions represents the most important part of the set of cross section. From the observation of the line spectra of excited F atoms obtained by spectrometric measurements (Motohashi et al., 2005) in CF_4, it can be concluded that the charge transfer reaction is the dominant process in collisions with inert gas ions. This argument seems to be enough to ignore other possible reactions. The aim of this paper is to report on a topic important for both basic studies and application. We estimated the set of cross sections for He^+ in He/CF_4 using existing experimental data (Viehland et al., 2017; Basurto et al., 2000; Helm, 1977; Stefansson et al., 1988; Viehland & Mason, 1995). In the next section, we will discuss the compilation of existing data and establish one possible set of cross-sections. We will then describe the calculation of transport parameters and finally discuss our results. The coefficients of velocity, flux and bulk reduced mobilities, calculated from flux and bulk drift velocities by Monte Carlo simulation are significantly different in the region of moderate E/N.

2. Cross section sets

Our goal in this section will be to establish a set of cross sections because only the set of cross sections contains relevant information for calculating the transport properties of the selected ion in a given gas. In our chosen case, the general knowledge of the total cross-section indicates that at low energies they

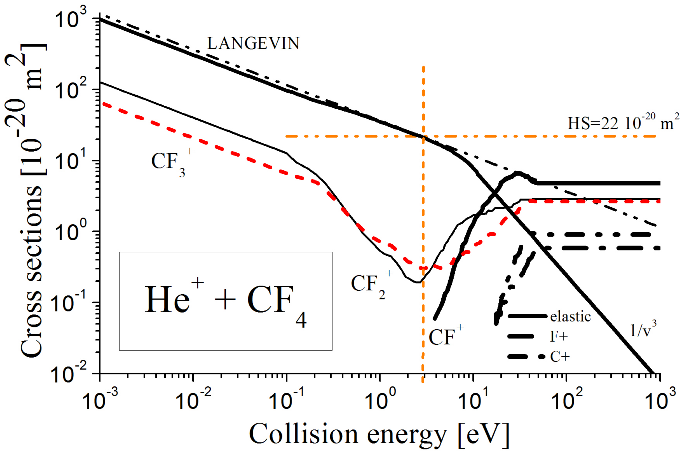

Figure 1.: Cross section set for He^+ + CF_4.

would be affected by attractive long-range forces, while at high energies they would be affected by repulsive forces.

For low energies, when the interaction potential is very close to the induced dipole potential, it can be assumed that the total cross section of the moment transfer is $\sigma_{mt} = 1.105\ \sigma_L$ where σ_L is the Langevin cross section (McDaniel et al., 1970). The Langevin cross section was determined using the average gas polarizability. The average polarizability of CF_4 is poorly determined (Fisher et al., 1990) and can lead to deviations in the calculated ion mobility in CF_4 (Stojanović et al., 2014; Georgieva et al., 2003). As a consequence, this would affect the prediction of plasma parameters in modeling. The value of 3.86 10-30 m3 used by Stojanović et al. (2014) who found an excellent agreement between the experimental and the calculated reduced mobility of CF_3^+ions in CF_4.

From measurements of exothermic cross sections Fisher et al. (1990) for the production of CF_2^+ and CF_3^+ from $He^+ + CF_4$ it can be concluded that the scattering is appropriate to describe with induced polarization potential up to 0.2 eV. Thus, assuming that charge transfer reactions are the dominant interaction, a cross section of elastic moment transmission can be obtained by deduction of experimental reactive cross sections (Fisher et al., 1990) from the assumed total moment transfer.

Extrapolation of the behavior of the cross section of the transmission of elastic moment outside the Langevin point of intersection to the cross section of the soft sphere (Fisher et al., 1990) was done by smooth connection with the trend $1/v^3$ (Krstić & Schultz, 2009; Raspopović et al., 2015) where v is the center-velocity of mass (see Figure 1). Extrapolation is performed in the energy

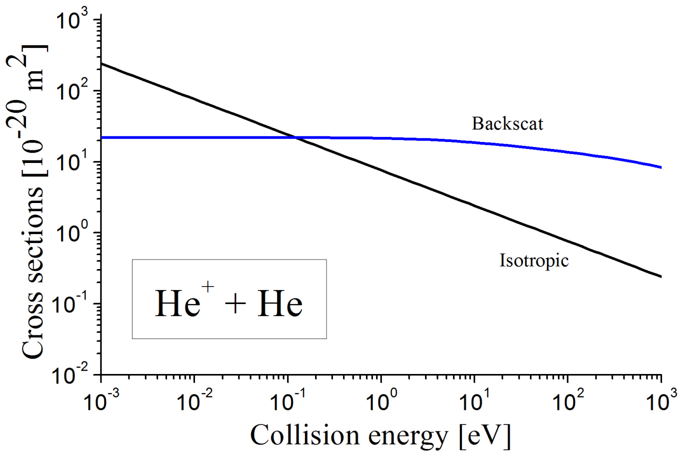

Figure 2.: Cross section set for He$^+$ + He.

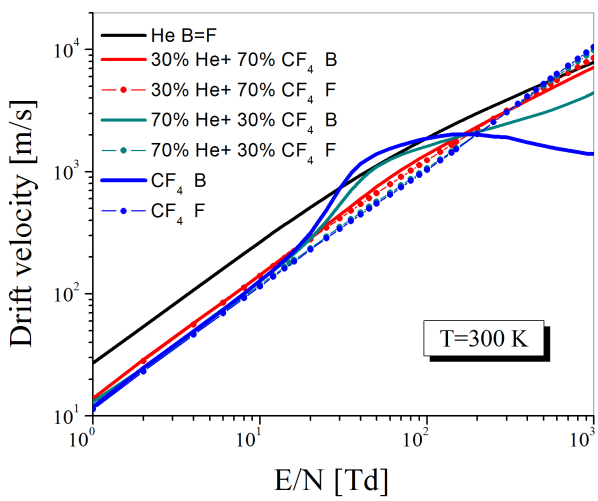

Figure 3.: Drift velocity for He$^+$ in He/CF$_4$ mixtures as a function of E/N.

region where a repulsive interaction is expected to occur, which is estimated to be above about 3 eV. Finally, all exothermic and endothermic cross-sections of Fisher et al. (1990). Reactive cross sections were approximated by constant values at all kinetic energies of ions above 50 eV using data for the production ratio between the observed ions as proposed in (Parker & El-Ashhab, 1983).

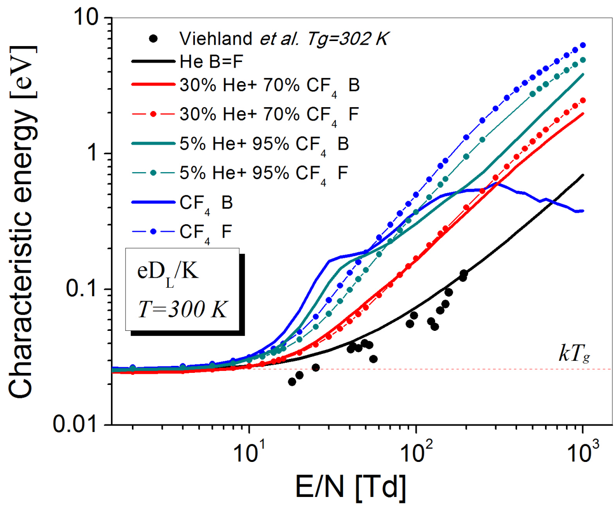

Figure 4.: Longitudinal characteristic energy for He^+ in He/CF_4 mixtures as a function of E/N.

It was found that different extrapolations (short dot-dashed or dashed line in Figure 1) of unusual low energy behavior observed by cross-sectional measurement led to CF_2^+ formation (where exothermic reaction behavior is expected regardless of, He^+ spin state) have negligible impact on mobility. In the case of the system, He^+ on He, the Phelps sections taken from the database were used for (Phelps, 2011). The section consists of two components: Isotropic and Backscat is given in Figure 2.

3. Transport parameters

Transport properties needed for modeling CF_4 discharges containing He^+ions are calculated by the Monte Carlo method. A code that properly takes into account thermal collisions was used (Ristivojevic & Petrović, 2012). It has passed all relevant benchmarks Fisher et al. (1990) and was tested in our work on several types of charged particles (Petrović et al., 2007; de Urquijo et al., 2013).

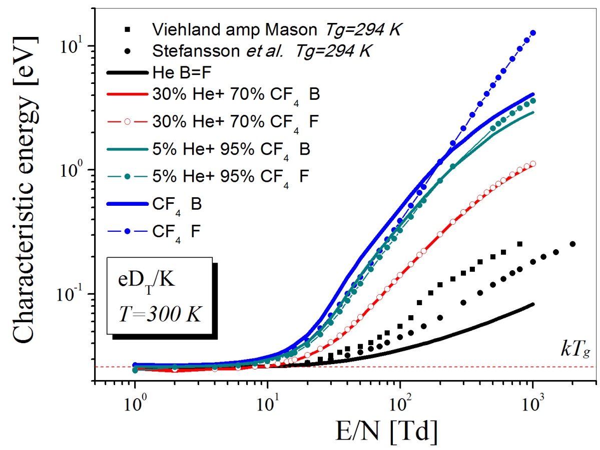

Figure 5.: Transversal characteristic energy for He$^+$ in He/CF_4 mixtures as a function of E/N.

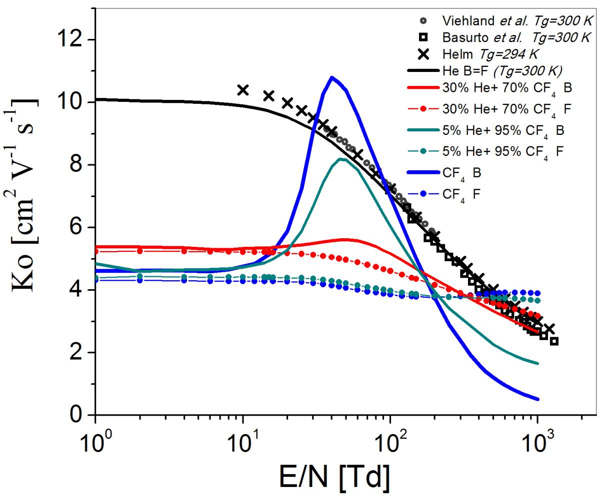

Figure 6.: The bulk and flux reduced mobility for He$^+$ in He/CF_4 mixtures as a function of E/N.

Swarm parameters of He^+ in He/CF_4 mixtures for a temperature of T=300 K are presented.

The calculated transport parameters are the mean energy, characteristic energy, drift velocity, diffusion coefficients, ionization and attachment coefficients and chemical reaction coefficients for ions (Petrović et al., 2009). The excitation coefficients are also measured but seldom used in modeling. Note that these transport parameters are the only information present in the literature up to now and there are no published experimental data for the transport coefficients of He^+ in He/CF_4 mixtures. The transport parameters of He^+ions swarm in neutral gases He and CF_4, as well as in mixtures were calculated: (1) 5% He + 95% CF_4 (2) 30% He + 70% CF_4 and (3) 70% He + 30% CF_4.

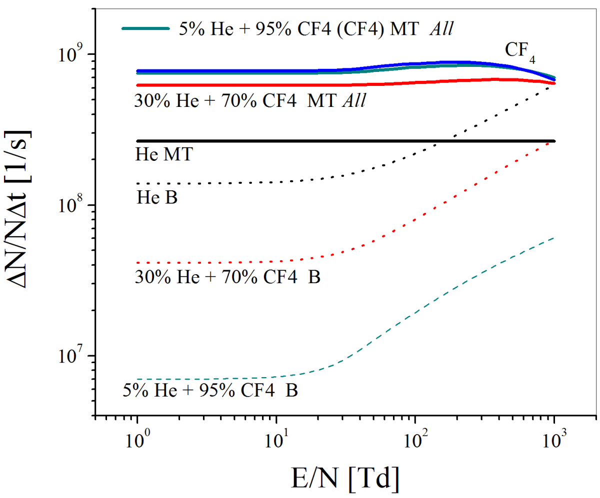

Figure 7.: Rate coefficients for He^+ in He/CF_4 mixtures as a function of E/N: momentum transfer.

The flux and bulk drift velocities (Robson et al., 2005; Ness & Robson, 1986; Nikitović et al., 2018; Nikitović & Raspopović, 2021) for He^+ in He/CF_4 mixtures as a function of E/N are given in Figure 3. The drift velocities obtained by the Monte Carlo simulation are calculated in real space (bulk) and in velocity space (flux) values which are obtained as $d<x>/dt$ and $<v>$, respectively. At low energies, at E/N<200 Td due to intense formation of CF_3^+ and CF_2^+ions in charge transfer reactions instead of He^+ions, the center of mass of the swarm moves forward, so that the bulk velocity is greater than the flux. With further increase E/N>200 Td when the high-energy ions from the distribution function increasingly have non-conservative collisions in which the CF^+, C^+ and F^+ be-

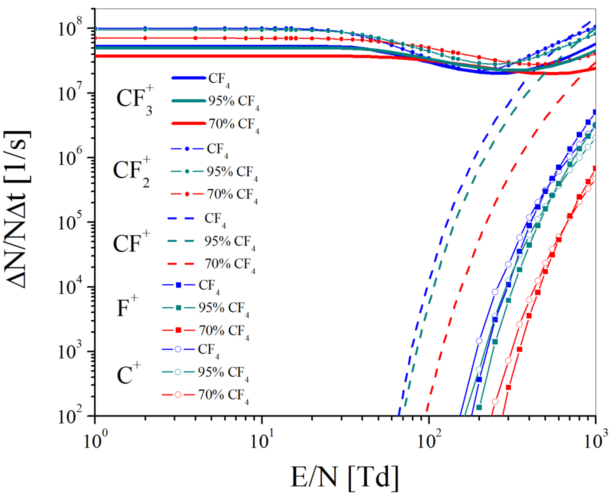

Figure 8.: Rate coefficients for He$^+$ in He/CF_4 mixtures as a function of E/N: production reactions.

coming He$^+$ions disappear, shifting the center of mass of the swarm backward, resulting in a bulk velocity less than the flux.

In Figure 4 we present the characteristic energies (diffusion coefficient normalized to mobility D/K in units of eV) determined in the direction of the electric field. Figure 4) are shown that with increasing percentage of CF_4 molecules in the mixture with He there is an increase in bulk and flux values of longitudinal characteristic energy, except in the case of balk values of eDL/K at CF_4 concentrations higher than 95% for E/N>40 Td. Already 5% He$^+$ions in a mixture with CF_4 significantly reduces the differences between balk and flux values of longitudinal characteristic energy, and in a mixture with 30% He these differences are still noticeable. Figure 4) also includes the experimentally measured values of eDL/K by Viehland et al. (2017) for the system He$^+$ + He (black symbols).

The transversal characteristic energy also increases with increasing percentage of He/CF_4 mixtures (Figure 5). Smaller differences between balk and flux values are in transversal compared to longitudinal characteristic energy. With 30% He in the mixture there is no difference between bulk and eDT/K flux. In Figure 5) the experimentally measured values of eDT/K by Stefansson et al. (1988) and Viehland & Mason (1995) for the system He$^+$ + He (black symbols).

Reduced mobility for He$^+$ions in CF_4 as a function of E/N (E-electric field strength, N-gas number density) compared with bulk and flux values is shown in Figure 6. Significant peak in the bulk reduced mobility is obtained as a result of difference in energy dependence of elastic and exothermic cross sections (Nikitović et al., 2019) . Let us remind the reader that the bulk drift velocity ($W = d < x > /dt$) is reaction corrected flux drift velocity ($w =< v >$): $W = w + S$, where S is the term representing a measure of the effect of reactions on the drift velocity. Difference between bulk and flux reduced mobilities is a consequence of energy dependent reactions. We found that the cross section leading to formation of CF_2^+ (where irrespective of the He^+ spin state exothermic behavior of reaction is expected) are negligible on mobility.

Mobility of He^+ + CF_4 depending on E/N has a pronounced maximum at about 40 Td, while mobility of He^+ + He does not; has a plateau at low E/N that immediately declines as a result of pronounced backs cat interaction. At low E/N higher values of Ko for the He^+ + He system than those for He^+ + CF_4 are due to less the reduced mass of the ion neutral pair. At low E/N balk values for Ko are higher than flux values as a consequence of low-energy capture of He^+ions by CF_4 molecules in an exothermic reaction in which CF_3^+ion is formed. At large E/N flux values are higher than the balk values due to higher ion capture at high energies than at lower ones. With increasing He concentration in the mixture, the differences between bulk and flux values are significantly reduced. For a mixture of 30% He + 70% CF_4 these differences can be clearly seen only in the region of about 40 Td. In Figure 6 the experimentally measured values of Ko by Viehland et al. (2017), Basurto et al. (2000) and Helm (1977) for the system He^+ + He (black symbols).

In Figures 7 and 8 we show rate coefficients for elastic momentum transfer and for all reactive processes as a function of E/N. The rate coefficients as final output of our calculations is needed as input in fluid equations for description of ion transport in He/CF_4 mixtures. The rate coefficients for all reactions presented in the cross-section sets are significantly different than one that should be obtained with cross sections obtained from statistical theories such are those obtained by Denpoh-Nanbu theory (Denpoh & Nanbu, 1998).

4. Conclusion

In this paper we have determined the cross section of elastic moment transport as a function of energy for He^+ scattering on CF_4 that can be used in modeling He^+ transport in He/CF_4 mixtures. We used the data for a simple theoretical cross-section of the transmission of the total moment and obtained the cross-section of the transmission of the elastic moment by deduction of all experimentally obtained cross-sections of the charge transfer. In doing so, we assumed that the measured cross-sections of the charge transfer were collisions with the highest probability. Thus, in this paper, we have estimated the set of cross sections for He^+ions in He/CF_4 that can be used as an independent input in modeling He^+ion transport. This estimation was performed using measured cross-sections of charge transfer.

Since, according to our knowledge, there is no direct information in the literature on how the mobility of high recombination energy ions, such as He^+ions, behave in He/CF_4 mixtures, we calculated transport parameters using the Monte Carlo simulation method (Nikitović et al., 2014; Nikitović et al., 2016, 2019).

In this work, we obtained and considered data on longitudinal and transversal characteristic energy, bulk and flux reduced mobility and rate coefficients. Data on swarm coefficients for positive and negative ions are required for hybrid and fluid codes (White et al., 2014) and the current focus on liquids or liquids in rare gas mixtures dictates the need to produce data compatible with these models. Given the current interest in liquid and / or liquid models in mixtures with rare gases, data on swarm coefficients for positive and negative ions for hybrid and fluid codes are needed. Atmospheric and near-atmospheric pressure glow discharges generated in both pure helium and helium-air mixtures have been studied using a plasma chemistry code originally developed for simulations of electron-beam-produced air plasmas.

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References

Basurto, E., de Urquijo, J., Alvarez, I., & Cisneros, C., Mobility of He^+, Ne^+, Ar^+, $N^+{}_2$, $O^+{}_2$, and $CO^+{}_2$ in their parent gas. 2000, *Phys. Rev. E*, **61**, 3053, DOI: 10.1103/PhysRevE.61.3053

Bošnjaković, D., Ph Dissertation. 2016, *Faculty of Electrical Engineering, University of Belgrade, Belgrade, Serbia*

de Urquijo, J., Jovanović, J. V., Bekstein, A., Stojanović, V., & Petrović, Z. L., Ion mobilities and transport cross sections of daughter negative ions in N_2O and N_2O-N_2 mixtures. 2013, *Plasma Sources Sci. Technol.*, **22**, 025004, DOI: 10.1088/0963-0252/22/2/025004

Denpoh, K. & Nanbu, K., Self-consistent particle simulation of radio-frequency CF_4 discharge with implementation of all ion-neutral reactive collisions. 1998, *J. Vac. Sci. Technol. A*, **16**, 1201, DOI: 10.1116/1.581259

Fisher, E. R., Weber, M. E., & Armentrout, P. B., Dissociative charge transfer reactions of Ar^+, Ne^+, and He^+ with CF_4 from thermal to 50 eV. 1990, *J. Chem. Phys.*, **92**, 2296, DOI: 10.1063/1.457969

Fraga, M. M. F. R., Fraga, F. A. F., Fetal, S. T. G., et al., The GEM scintillation in He-CF_4, Ar-CF_4, Ar-TEA and Xe-TEA mixtures. 2003, *Nucl. Instrum. Meth. in Phys. Res. A*, **504**, 88, DOI: 10.1016/S0168-9002(03)00758-7

Georgieva, V., Bogaerts, A., & Gijbels, R., Particle-in-cell/Monte Carlo simulation of a capacitively coupled radio frequency Ar/CF_4 discharge: Effect of gas composition. 2003, *J. Appl. Phys.*, **93**, 2369, DOI: 10.1063/1.1542920

Helm, H., The cross section for symmetric charge exchange of He^+ in He at energies between 0.3 and 8 eV. 1977, *J. Phys. B*, **10**, 3683, DOI: 10.1088/0022-3700/10/18/025

Kaboth, A., Monroe, J., Ahlen, S., et al., A measurement of photon production in electron avalanches in CF $_4$. 2008, *Nucl. Instrum. Meth. in Phys. Res. A*, **592**, 63, DOI: 10.1016/j.nima.2008.03.120

Krstić, P. S. & Schultz, D. R., Elastic and related transport cross sections for singly charged ion-atom scattering of light metals (Li, Be, B) and hydrogen. 2009, *J. Phys. B: At. Mol. Opt. Phys.*, **42**, 065207, DOI: 10.1088/0953-4075/42/6/065207

McDaniel, E. W., Cermak, V., & Ferguson, E. E. 1970, *Ion-molecule reactions*

Motohashi, K., Takahashi, T., Takahashi, N., & Tsurubuchi, S., Emission cross sections in low-energy collisions between He^+, Ne^+ ions and CF_4 molecule. 2005, *J. Phys. B: At. Mol. Opt. Phys.*, **38**, 3339, DOI: 10.1088/0953-4075/38/18/005

Ness, K. F. & Robson, R. E., Velocity distribution function and transport coefficients of electron swarms in gases. II. Moment equations and applications. 1986, *Phys. Rev. A*, **34**, 2185, DOI: 10.1103/PhysRevA.34.2185

Nikitović, Ž., Raspopović, Z., Stojanović, V., & Jovanović, J., Transport parameters of F- ions in Ar/BF3 mixtures. 2014, *EPL*, **108**, 35004, DOI: 10.1209/0295-5075/108/35004

Nikitović, Ž. D. & Raspopović, Z. M., Rate coefficients for Ar^+ in Ar/BF_3 mixtures. 2021, *Eur. Phys. J. D*, **75**, 118, DOI: 10.1140/epjd/s10053-021-00061-3

Nikitović, Ž. D., Raspopović, Z. M., & Stojanović, V. D., Reduced mobility of He^+ in CF_4. 2017, *Plasma Sources Sci. Technol.*, **26**, 044004, DOI: 10.1088/1361-6595/aa61db

Nikitović, Ž. D., Raspopović, Z. M., & Stojanović, V. D., Cross sections set and transport coefficients for Ar^+ in Ar/CF_4 mixtures. 2018, *Eur. Phys. J. D*, **72**, 168, DOI: 10.1140/epjd/e2018-90059-1

Nikitović, Ž. D., Raspopović, Z. M., & Stojanović, V. D., Reduced mobility of Ar^+ in Ar/BF_3mixtures. 2019, *EPL*, **128**, 15001, DOI: 10.1209/0295-5075/128/15001

Nikitović, Ž. D., Stojanović, V. D., & Raspopović, Z. M., Modeling elastic momentum transfer cross-sections from mobility data. 2016, *EPL*, **114**, 25001, DOI: 10.1209/0295-5075/114/25001

Parker, J. E. & El-Ashhab, F. S. M., Charge-transfer reactions of carbon tetrafluoride. 1983, *Int.J. Mass Spectrom. Ion. Phys.*, **47**, 159, DOI: 10.1016/0020-7381(83)87160-5

Petrović, Z. L., Dujko, S., Marić, D., & Malović, G., ž Nikitović, O Šašić, J Jovanović, V Stojanović, and M Radmilović-Radjenović. Measurement and interpretation of swarm parameters and their application in plasma modelling. 2009, *J. Phys. D: Appl. Phys.*, **42**, 194002, DOI: 10.1088/0022-3727/42/19/194002

Petrović, Z. L., Raspopović, Z. M., Stojanović, V. D., et al., Data and modeling of negative ion transport in gases of interest for production of integrated circuits and nanotechnologies. 2007, *J. Appl. Surf. Sci.*, **253**, 6619, DOI: 10.1016/j.apsusc.2007.02.005

Phelps, A. 2011, database, https://nl.lxcat.net/cache/62710de742cec/, [Online; accessed 19-July-2022]

Raspopović, Z., Stojanović, V., & Nikitović, Ž., Effect of exothermic reactions on the mobility of Ar^+ in CF_4. 2015, *EPL*, **111**, 45001, DOI: 10.1209/0295-5075/111/45001

Ristivojevic, Z. & Petrović, Z. L., A Monte Carlo simulation of ion transport at finite temperatures. 2012, *Plasma Sources Sci. Technol.*, **21**, 035001, DOI: 10.1088/0963-0252/21/3/035001

Robson, R. E., Transport phenomena in the presence of reactions: Definition and measurement of transport coefficients. 1991, *Aust. J. Phys.*, **44**, 685, DOI: 10.1071/PH910685

Robson, R. E., White, R. D., & Petrović, Z. L., Colloquium: Physically based fluid modeling of collisionally dominated low-temperature plasmas. 2005, *Rev. Mod. Phys.*, **77**, 1303, DOI: 10.1103/RevModPhys.77.1303

Stefansson, T., Berge, T., Lausund, R., & Skullerud, H. R., Measurements of transport coefficients for lithium ions in argon and helium ions in helium with a drift-tube mass spectrometer. 1988, *J. Phys. D*, **21**, 1359, DOI: 10.1088/0022-3727/21/9/008

Stojanović, V., Raspopović, Z., Jovanović, J. V., de Urquijo, J., & Petrović, Z. L., Mobility of positive ions in CF_4. 2014, in Journal of Physics Conference Series, Vol. **514**, *J. Phys.:Conf. Series*, 012059

Viehland, L. A., Lutfullaeva, A., Dashdorj, J., & Johnsen, R., Accurate gaseous ion mobility measurements. 2017, *International Journal for Ion Mobility Spectrometry*, **20**, 95, DOI: 10.1007/s12127-017-0220-0

Viehland, L. A. & Mason, E. A., Transport Properties of Gaseous Ions over a Wide Energy Range, Part IV. 1995, *At. Data. Nucl. Data Tables*, **60**, 37, DOI: 10.1006/adnd.1995.1004

White, R., Tattersall, W., Boyle, G., et al., Low-energy electron and positron transport in gases and soft-condensed systems of biological relevance. 2014, *Appl. Radiat. Isot.*, **83**, 77, DOI: https://doi.org/10.1016/j.apradiso.2013.01.008