Effect of gas temperature on CO_2^+ ion transport in CO_2

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Abstract

The effect of gas temperature on the transport of the CO_2^+ ion in its parent gas CO_2 is studied. For this purpose, a Monte Carlo solution technique of the ion transport equation developed in the past by the authors, which was formally proved to provide the exact solution of the transport equation, is used. The study is performed first by benchmarking against experimental data and another Monte Carlo code, using cross sections from literature and then changing the gas temperature. The solution is characterized through its moments such as reduced mobility, coefficients of its expansion in Legendre polynomials and three-dimensional ion velocity distribution function. It is shown that the gas temperature has a significant effect on all these quantities. This finding has important consequences for plasma modeling which are discussed.

Keywords: CO_2^+ ion, ion transport, test particle Monte Carlo, gas temperature

Introduction

In recent years, there has been a great effort in the realization of computer models for the simulation of plasma reactors and concepts for the activation of the CO_2 molecule, a molecule otherwise rather inert, in order to make it chemically reactive and in this way reuse it, for example in the production of fuels or chemicals with high added value [1 - 3]. This with the aim of creating a carbon-closed economy and positively impacting the problem of climate change due to anthropogenic greenhouse gases [4 - 7]. Computer models designed for this purpose achieve ever-increasing levels of accuracy and refinement, particularly as regards the study of the kinetics of the neutral CO_2 molecule, including the fundamental role of vibrational levels [8 - 11]. Great progress is also being made regarding the kinetics and transport of free electrons, and the chemical kinetics itself [12 - 14]. In this context, compared to other aspects of the CO_2 plasma, ion transport has received less attention, even though ion transport quantities have an important role in plasma kinetics. For example, in gliding arc plasma models [15] the continuity equation for ions requires an accurate knowledge of the ion mobility, which enters into the expression of the ion flux. The charged particles number density is then employed into the self-consistent calculation of the electric field. Consequently, the mobility of the main ions, including of course CO_2^+, affects, in multiphysical plasma models, not only the ion density itself, but also the results for the electric field and, through its effect on plasma resistivity, the plasma temperature. Now, since most CO_2 plasma sources are characterized by strong temperature variation and temperature gradients (e. g. strong gas cooling like in the case of supersonic expansion [2, 16] and strong gas heating like in the case of tangential gas injection with microwave heating [6, 7, 17, 18]), one would expect that the mobility of CO_2^+ in its parent gas and CO_2-bearing gas mixtures had been carefully characterized in the past. Surprisingly, this is not the case, and most recent papers [15] still include the effect of the gas temperature by using the approximate, phenomenological approach of McDaniel and Mason [19]. Consequently, present models of CO_2 plasmas based on macroscopic approaches, and including a description of ion transport, are wanting of an improvement from this point of view. Experiments under wide temperature ranges are presently unavailable, leaving up-to-date theory as an alternative. Accurate calculations of the ion mobility can be performed by accurate solution of the corresponding transport

equation, using either deterministic or stochastic methods. This is why the CO_2^+ ion transport in a plasma composed essentially of CO_2 is an excellent case study for new investigations.

In this work, a rigorous and exact solution of the transport equation for ions in parent gas based on the Monte Carlo (MC) method is applied to this case study, using a method which was developed and thoroughly tested by the authors of the present work in other case studies [20 - 23]. An interesting aspect of the method that is applied here is that, not only it takes into account in a complete way the gas temperature, also by evaluating exactly its effect on the collision frequency, but, in the past, a demonstration has been formulated which shows from a strictly mathematical point of view the equivalence of the method to the exact solution of the transport equation [20]. We can therefore be sure that there are no ambiguities, approximations or other filters in the connection between cross sections and macroscopic results.

Numerical method

Details of the method have been provided in previous publications [20, 24]. The starting point is the Boltzmann equation for ions transport in the integral form:

$$f(t) = e^{-\alpha_{\max} t} f_0 + \alpha_{\max} e^{-\alpha_{\max} t} \int_0^t A(t') e^{\alpha_{\max} t'} f(t') dt', \quad (1)$$

where $f(t)$ is the ions phase space distribution as a function of time, f_0 its value for $t = 0$. The operator A is defined as

$$Af = f(\mathbf{v}) \left[1 - \frac{n(\mathbf{r})}{\alpha_{\max}} \int |\mathbf{v} - \mathbf{V}| \, \sigma_{\text{tot}}(|\mathbf{v} - \mathbf{V}|) F(\mathbf{V}) d^3V \right]$$

$$+ \frac{n(\mathbf{r})}{\alpha_{\max}} \int |\mathbf{v}' - \mathbf{V}| \, \sigma(|\mathbf{v}' - \mathbf{V}|, \Omega) f(\mathbf{v}') F(\mathbf{V}) \, d\Omega d^3v', \quad (2)$$

where $n(\mathbf{r})$ is the number density of the background gas, $F(\mathbf{V})$ the phase space distribution of neutrals, $\mathbf{r}$ the ions position vector, $\mathbf{v}$ and $\mathbf{V}$ are the ion and neutral velocity vector (primed quantities refer to post-collision, unprimed to pre-collision velocities), respectively, σ the differential cross section, σ_{tot} the total cross section, Ω is the solid angle between the vectors $\mathbf{v}' - \mathbf{V}$ and $\mathbf{v} - \mathbf{V}'$; finally, $\alpha_{\max}$ is the maximum collision frequency given by

$$\alpha_{\max} = \max_{\mathbf{r},\mathbf{v},\mathbf{V}} n(\mathbf{r})|\mathbf{v}-\mathbf{V}|\sigma_{\mathrm{tot}}(|\mathbf{v}-\mathbf{V}|). \quad (3)$$

Note that, in equation (1), dt' is a total differential, therefore integration with respect to t implies changes is position $\mathbf{r}(\mathrm{t})$ and velocity $\mathbf{v}(\mathrm{t})$. In the calculation of the maximum in the above formula, a numerical parameter v_{max} is set for the magnitude of the vectors $\mathbf{v}$ and $\mathbf{V}$. The value of v_{max} is easily selected large enough to avoid any numerical effect on the results.

The formal solution of equation (1) is

$$f(t) = e^{-\alpha_{\max} t}\left[\sum_{n=0}^{\infty} \alpha_{\max}^{n} \int_{\omega_n} A(t_n)\dots A(t_1) d^n t\right] f_0, \quad (4)$$

where we indicate by ω_n the n-dimensional manifold given by

$$\omega_n = (\{t_1,\dots,t_n\}, 0 < t_1 < t_2 < \dots < t_n < t). \quad (5)$$

When integrals in Eq. (4) are calculated by the standard MC method and $f(t)$ is a distribution,

$$f(t) = (\int \rho(\mathbf{r}) d^3 r/N) \sum_{i=1}^{N} \delta(\mathbf{r}-\mathbf{r}_i(t))\delta(\mathbf{v}-\mathbf{v}_i(t)), \quad (6)$$

where $\rho(\mathbf{r})$ the number density of ions and N is the number of simulated particles, it is found that the ion-neutral collision times are given by the formula

$$t_{i+1} = t_i - \alpha_{\max}^{-1} \ln \eta_i$$

$$t_n \le t < t_{n+1}, \quad (7)$$

where $\{\eta_i\}_{1\le i\le n}$, $0 < \eta_i \le 1$ is a collection of random numbers with individual distributions $p_i(\eta_i) = 1$ and, after a suitable collision partner is generated out of the (three-dimensional) thermal distribution of velocities, the effect of the collision has to be calculated with a probability

$$p = \frac{n(\mathbf{r})|\mathbf{v}-\mathbf{V}|\sigma_{\mathrm{tot}}(|\mathbf{v}-\mathbf{V}|)}{\alpha_{\max}}, \quad (8)$$

while with a probability $1-p$ no collision occurs (null collision).

The reduced mobility K_0 is calculated from the shift of the center of gravity of the ion distribution (Eq. (6)) using the formula

$$K_0 = \frac{\mathrm{v}_d}{E}\frac{p(\mathrm{Torr})}{760}\frac{273.16}{T(\mathrm{K})} = \frac{1}{269\ \mathrm{cm}^{-3}}\frac{\mathrm{v}_d(\mathrm{cm/s})}{(E/n)(\mathrm{Td})}, \quad (9)$$

where, v_d is the drift velocity, E the electric field, p the gas pressure, T the gas temperature, E/n the reduced electric field.

The coefficients of the Legendre polynomials are, then, determined from the following expansion of Eq. (6) [21]:

$$f = f_0(\varepsilon) + f_1(\varepsilon)P_1(cos\theta) + f_2(\varepsilon)P_2(cos\theta) + \cdots$$

$$f_l\left(\varepsilon + \frac{\Delta\varepsilon}{2}\right) = \frac{2l+1}{2}\frac{1}{N\Delta\varepsilon}\int_0^\pi P_l(cos\theta)f(\varepsilon, cos\theta)sin\theta d\theta, \quad (10)$$

where θ is the angle between the velocity vector and the direction of the electric field vector and $\Delta\varepsilon$ the energy bin size for the discretized energy grid used to sample the distribution function.

In this paper, we will consider the hypothesis of isotropic scattering (based on the momentum transfer cross section). The reason to do this is that the isotropic scattering hypothesis with the momentum transfer cross section in [25] is known to reproduce accurately the experiments at low temperature: unfortunately, no other detailed set of cross sections has such a good performance compared to experiment for the CO_2^+/CO_2 case. Having more information, it is not difficult at all to include anisotropy in our model. What we do is to solve exactly the isotropic problem in a thermal gas, and we will connect results with previous modeling studies [25] based on the same hypothesis and data.

To summarize, the method described above is a null collision test particle MC method which takes into account the thermal distribution of target particles.

Results

The code using the method described in the previous section was used with the following numerical parameters: number of particles: 10^5 up to 10 Td, to reduce statistical noise, then 2×10^4, maximum energy: 500 eV with 2×10^5 energy bins for cross sections interpolation. The sample time is 10^{-5} s, results are averaged over 10 sample times, once steady state is reached, which takes about 200 sample times. Cross sections for CO_2^+/CO_2 elastic momentum transfer and charge transfer were taken from [25].

In Fig. 1, a comparison of the results for the reduced mobility as a function of the reduced electric field with experimental results in [26, 27] and MC results from [25], where the same cross sections were used, is shown. The agreement between the two computational codes is excellent, with very small systematic deviations (up to 3%) for lower E/n values, confirming that both MC methods with use of the cross sections proposed by [25] are capturing the microphysics of ion/molecule scattering at the nominal temperature of 300 K. However, as always in swarm analysis, the validation of the cross section responsible for this good performance is a tricky point: the cross section is the solution of an inverse problem and therefore in some way it includes also the effect of the thermal distribution of neutral molecules in the experiments. As it will be elaborated further in the rest of this paper, an extension of the inversion procedure to a wide range of gas temperature should lead to more accurate cross sections than those used today, should the gas temperature have a significant effect on the ion transport. Results by our MC method which, as mentioned, solves the complete form of the transport equation including the thermal distribution of neutrals, show this is the case. In Fig. 2 we show results of our calculations for different values of the gas temperature in a reasonable range for several applications of this specific system. A significant effect on the reduced mobility is observed for almost any value of E/n and it is particularly strong for E/n values less than 100 Td, with variations spanning a range of about 30% when the temperature is varied in the range 300 - 600 K and analogously in the range 600 -1000 K. A discussion of the consequence of this effect on the value of the swarm cross sections of this test case will be provided later, while, assuming that cross sections in [25], that, in any case, are the only ones available in literature, are valid for a quantitative discussion of the temperature effect, we show now a more detailed analysis of such effect.

As it is well known, an accurate characterization of the details of the solution of the transport equation can be obtained by expanding such solution into Legendre polynomials. Of course, our MC approach is solving this equation making no simplifications and requires no special analytical pretreatment of the solution, therefore, as shown in our previous paper [21], the expansion of the 2D solution is performed a posteriori and it is not functional to the solution process itself which means that our results for Legendre polynomials coefficients of any order are exact although higher orders coefficients tend to be affected by statistical (not systematic) errors. In Fig. 3, results are reported for several coefficients of the expansion as a function of

the ion energy, for a gas temperature of 300 K and several E/n values. The comparison of the corresponding figures at the 3 different gas temperatures (Fig. 4 and Fig. 5) shows that the effect of this last parameter on the solution is not only quite strong, but also subtle on the shape of the velocity distribution. In fact, the relative contribution of higher coefficients is different in the different cases, for example, at 10 Td and 300 K the 3rd coefficient has much higher values than the subsequent two at low ion energy, whereas this is no more true at 600 K and 1000 K. Also, the relative trends of the first and second coefficient are altered by the temperature effect at the relatively high E/n value of 100 Td. These results suggest that the change in gas temperature is having an effect on the trend of the three-dimensional distribution. In order to catch a global, more insightful although less quantitative view of such effect, we have reported the solution obtained with our MC in a series of contour plots of the ion velocity distribution function (IVDF) as a function of the longitudinal v_x and transversal $\mathrm{v}_t = (\mathrm{v}_\mathrm{y}^2 + \mathrm{v}_\mathrm{z}^2)^{1/2}$ ion speed components. The distribution f is normalized in such a way that

$$\int f \, d\mathrm{v}_t d\mathrm{v}_x = N \tag{11}$$

therefore ions appear to accumulate in a toroidal region surrounding the v_x axis. Results are reported in Figs. 6-9. In Fig. 6, where the electric field is particularly low, our plots display essentially an equilibrium distribution, quite isotropic at the gas temperature. No surprise, therefore, that the distribution keeps this isotropy at higher temperatures, although ions are strongly redistributed. Much subtle, as it was suggested by the previous analysis, is the effect produced by gas temperature at intermediate and even high E/n values, when, as clearly shown in Figs. 8 and 9, the increase of temperature leads to a less conspicuous beam-like behavior in the direction of the electric field and produces a sort of transversal wing. All previous results confirm that the effect of gas temperature on ion transport is non negligible, non-trivial and its effect on integrated modeling of the plasma is to be taken into account, using calculation methods which include the thermal distribution of neutral particles not only in the energy redistribution after the collision, but also in the evaluation of collision frequency in the most rigorous way. Nevertheless, this good practice, at the moment, to our knowledge, is not followed in the inverse process which is used to calculate most of the cross sections for plasma modeling.

Conclusions

A study of CO_2^+ ion transport in its parent gas has been performed by solving the Boltzmann equation with a thermal velocity distribution of neutrals in the collision term, using an exact MC method. Benchmarking has been performed using the best available cross sections, but allowing for a gas temperature variation in a large range.

What is highlighted is that the temperature of the gas has a significant effect on the transport properties of the ion and on the shape of the three-dimensional velocity distribution that determines these properties. This message is quite general and will not be altered by improving cross sections, although details in results may change. It is therefore necessary to draw the appropriate conclusions regarding the need to integrate the determination of gas temperature in the transport of ions in future multi-modular models of CO_2 plasmas, and also the need to use more accurate methods than the ones used so far for the determination of this effect in calculations related to ions transport in CO_2 but also in other systems.

As a further conclusion of our work, it appears that, in the determination of cross sections from inversion of transport data, a better practice to establish details of the cross sections specially at low energy is to perform experiments and calculations at several gas temperatures. In spite of the importance of CO_2^+ transport in CO_2 as a test case, however, this approach is applied to calculations for the first time here: experiments are therefore much sought.

Acknowledgments

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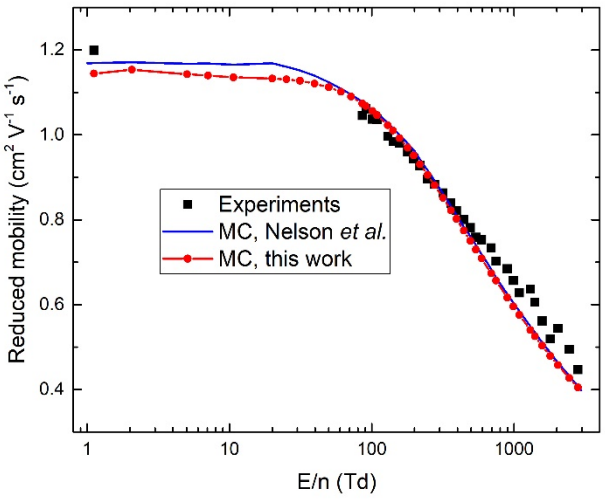

Fig. 1 Reduced mobility of CO_2^+ in CO_2 as a function of the reduced electric field: Results of this work are compared with MC results from Nelson *et al.* [23] and experimental results (from [24] at about 1 Td and from [25] for E/n values higher than about 80 Td).

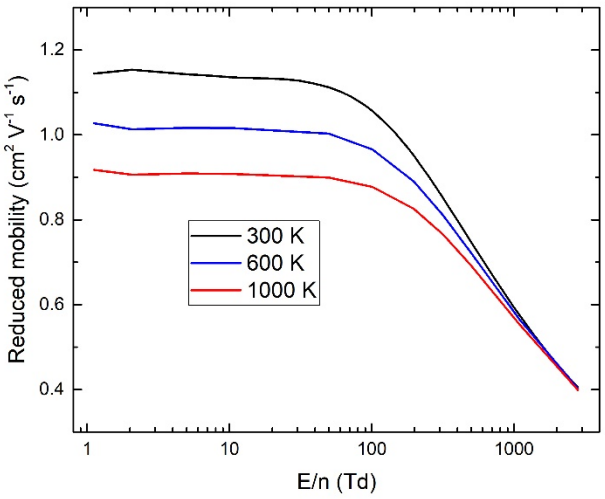

Fig. 2 Reduced mobility of CO_2^+ in CO_2 as a function of the reduced electric field for three different values for the gas temperature.

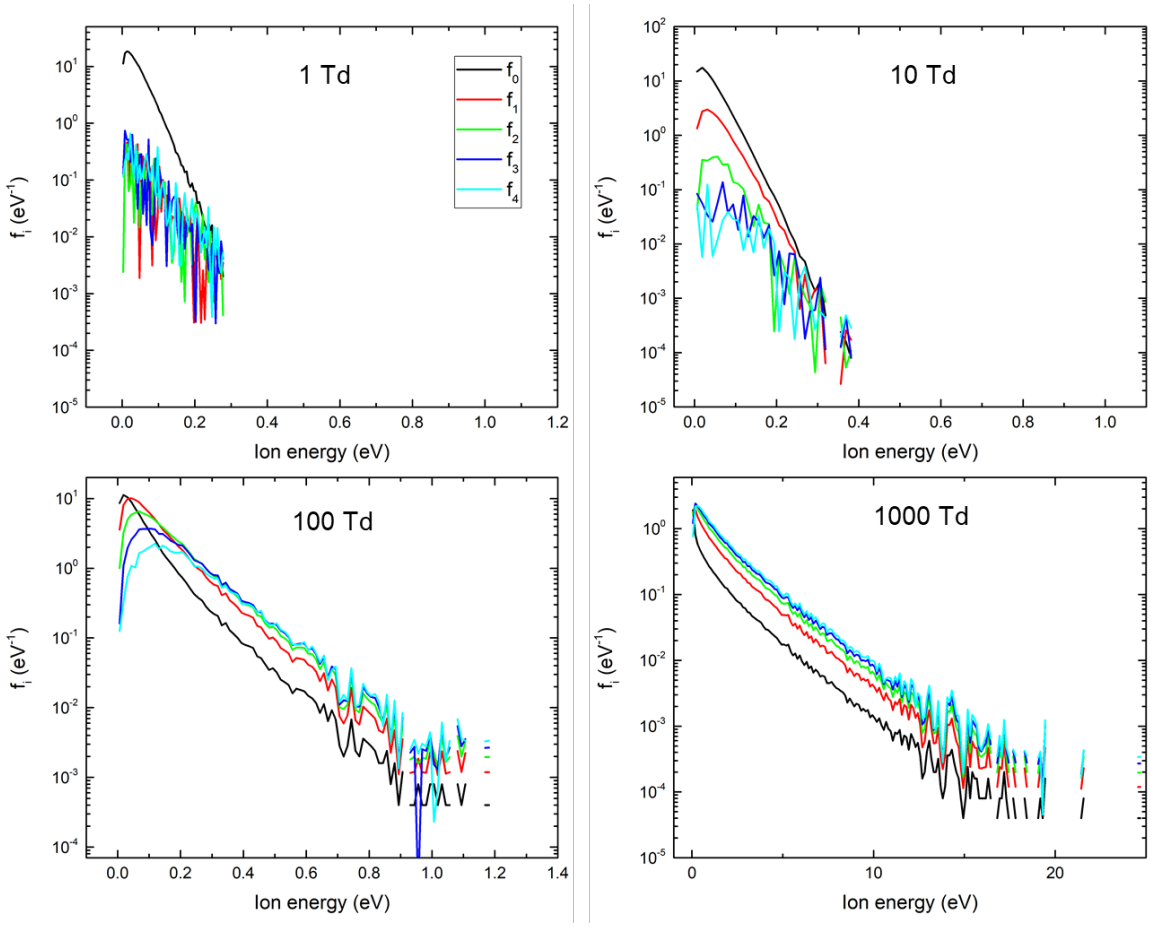

Fig. 3 Legendre polynomials expansion coefficients for a gas temperature of 300 K and different values of the reduced electric field.

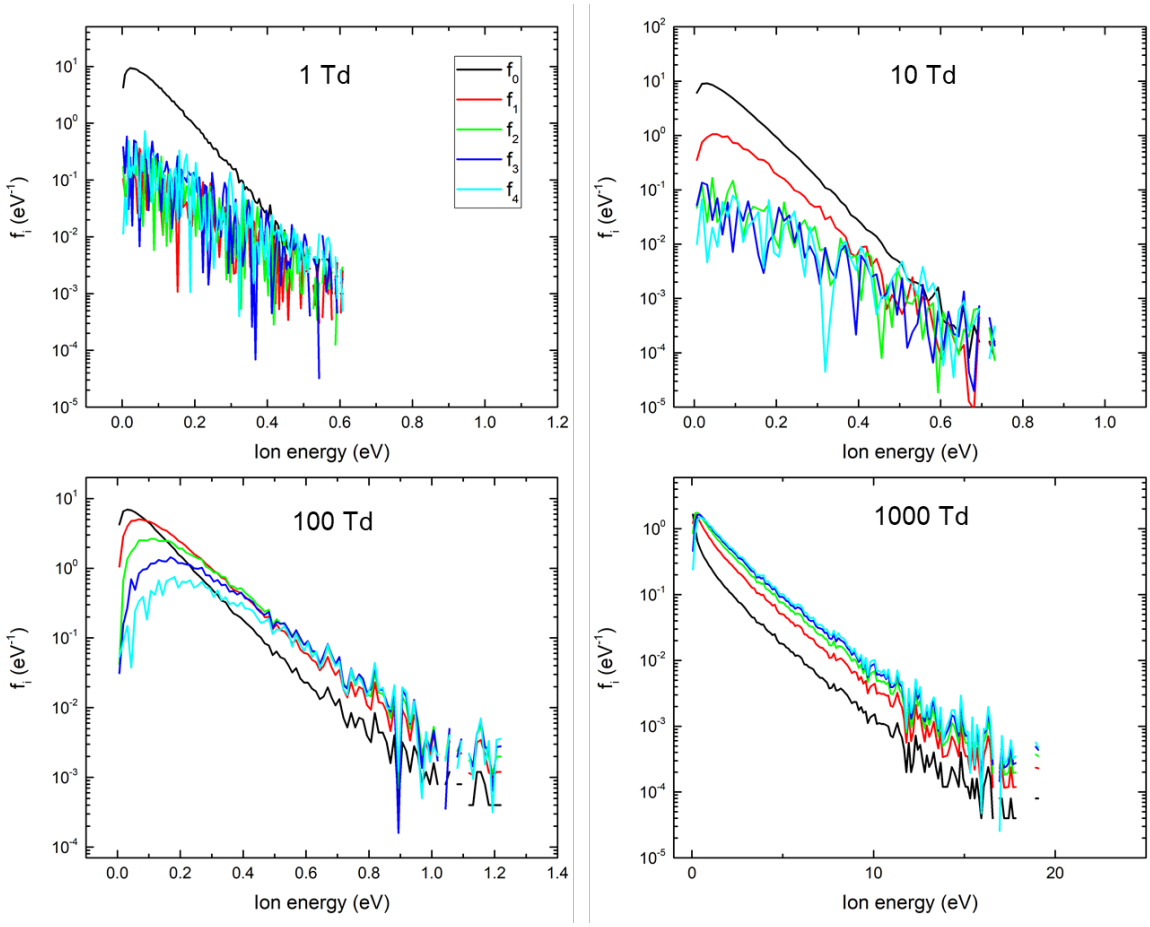

Fig. 4 Legendre polynomials expansion coefficients for a gas temperature of 600 K and different values of the reduced electric field.

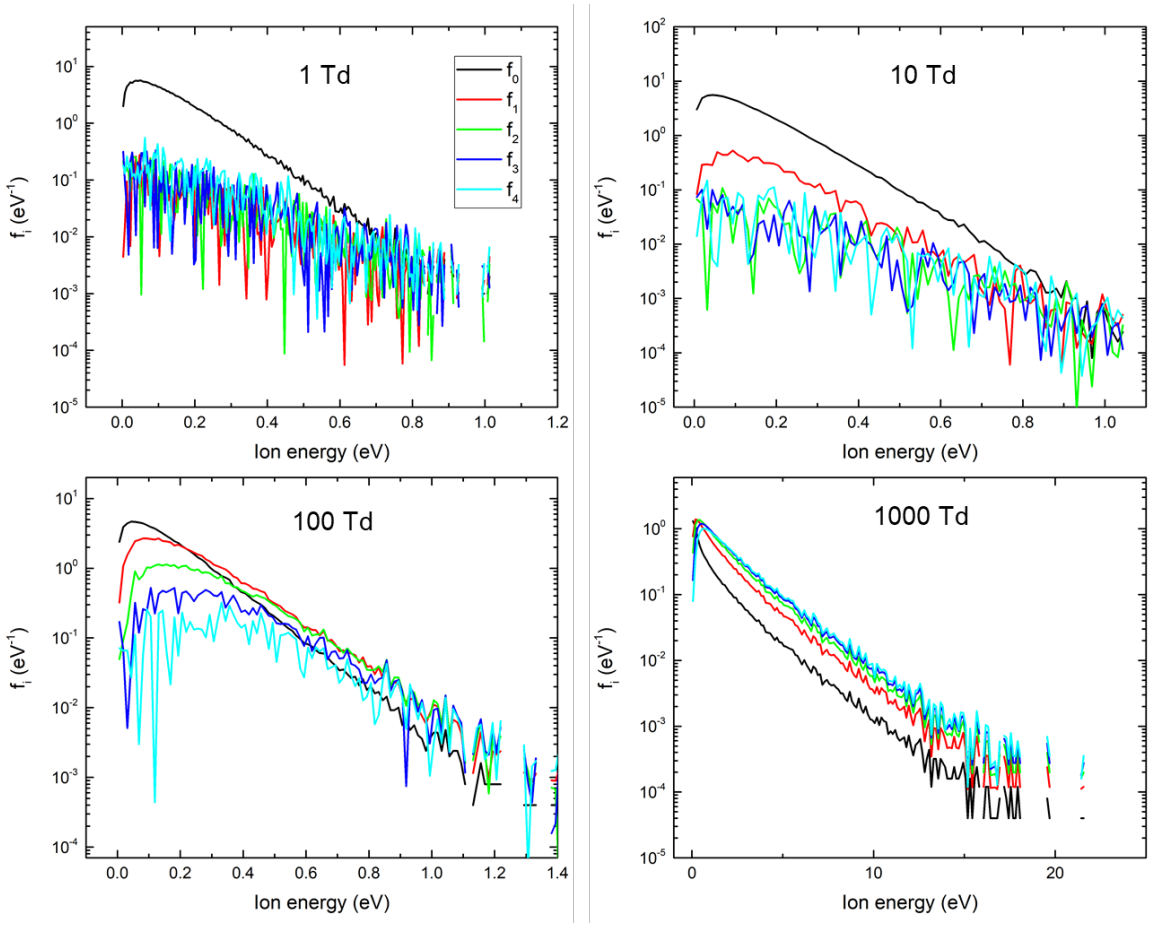

Fig. 5 Legendre polynomials expansion coefficients for a gas temperature of 1000 K and different values of the reduced electric field.

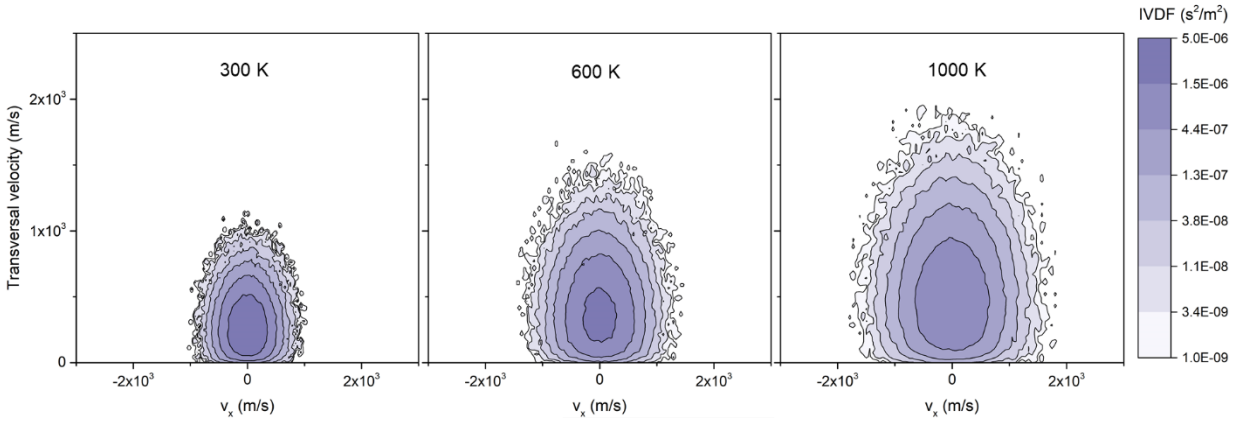

Fig. 6 CO_2^+ velocity distribution as a function of velocity components parallel and transversal to the electric field, for a reduced electric field of 1 Td and different values for the gas temperature.

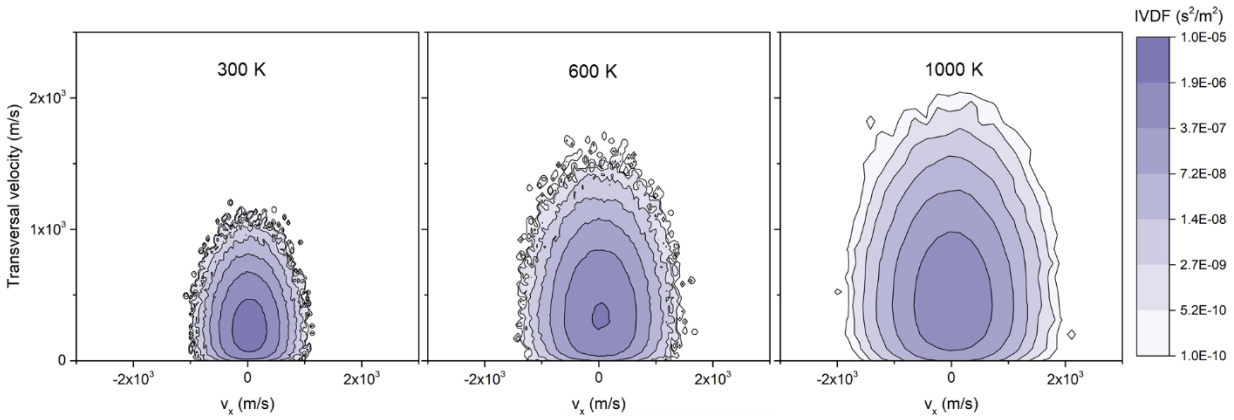

Fig. 7 CO_2^+ velocity distribution as a function of velocity components parallel and transversal to the electric field, for a reduced electric field of 10 Td and different values for the gas temperature.

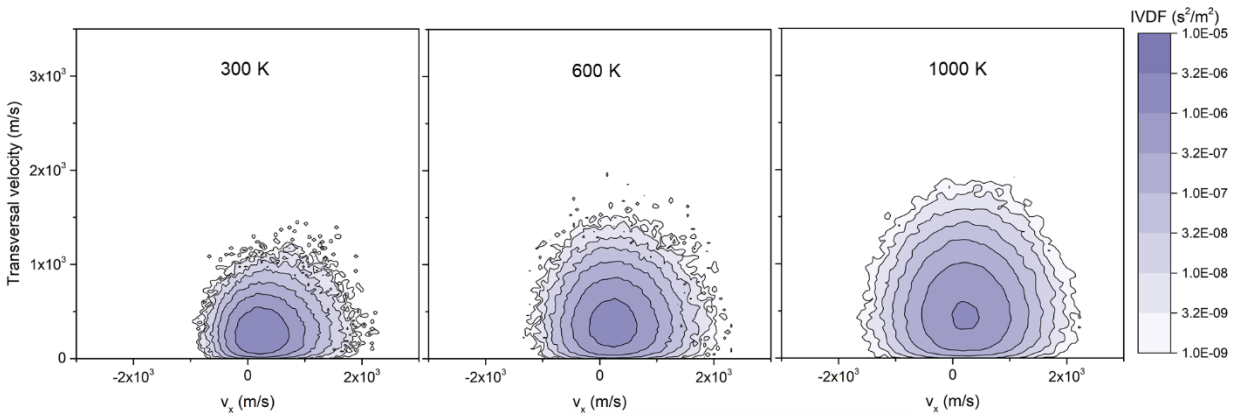

Fig. 8 CO_2^+ velocity distribution as a function of velocity components parallel and transversal to the electric field, for a reduced electric field of 100 Td and different values for the gas temperature.

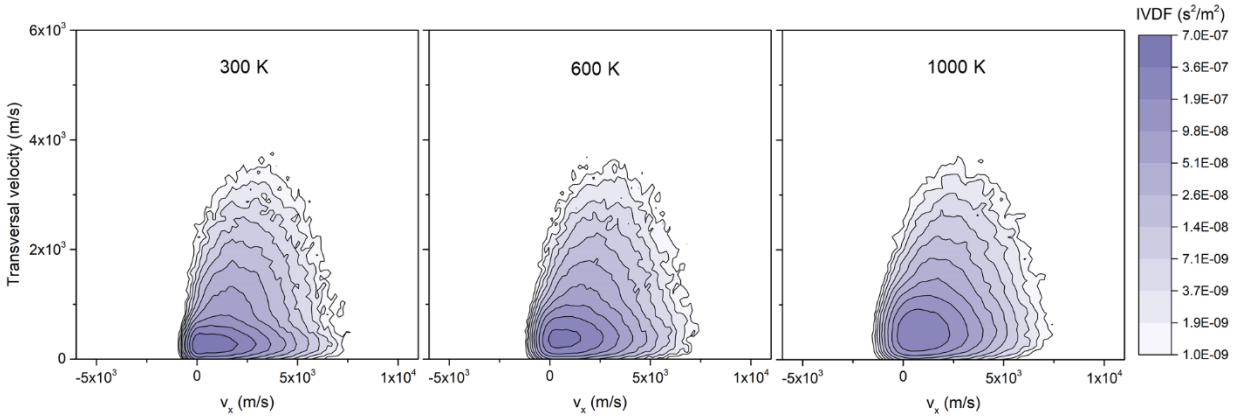

Fig. 9 CO_2^+ velocity distribution as a function of velocity components parallel and transversal to the electric field, for a reduced electric field of 1000 Td and different values for the gas temperature.