

Benchmarking of Monte Carlo Flux simulations of electrons in CO₂

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Abstract. Electron velocity distribution functions (EVDFs) in CO₂ obtained by means of the Monte Carlo Flux (MCF) method are compared with results from two-term and multi-term Boltzmann solvers. The MCF method provides detailed calculations of the EVDF through a highly efficient variance reduction technique. Benchmark calculations of Legendre polynomial coefficients of the EVDF expansion are reported for a wide range of reduced electric fields (E/N), showing excellent agreement with multi-term solutions. Rate coefficients of inelastic processes calculated from two-term Boltzmann solvers differ significantly, up to 70%, from MCF and multi-term solutions, due to the anisotropy of the EVDF. An extension of the method to consider the thermal distribution of the background gas is also presented. This extension, together with an accurate description of the population of rotationally and vibrationally excited states, provides excellent agreement with measured transport

coefficients at low E/N . A good agreement is obtained at moderate E/N between experimental values of dissociation rate coefficients and MCF calculations after careful consideration and analysis of several cross sections data sets.

Keywords: Monte Carlo Flux, CO₂, electron velocity distribution function, benchmarking

1. Introduction

The investigation of electron kinetics and transport in CO₂ is an important topic, since collisions of free electrons with CO₂ molecules are fundamental for the excitation of internal degrees of freedom and electronic states, dissociation and ionization of the molecule [1]. Initial studies on this topic focused on the description of laser kinetics [2–4] and plasma activation of small molecules, such as CO₂ [5, 6]. More recently, renewed interest on the topic has been mainly motivated by a possible application to carbon capture and utilization [7–9]. In terms of numerical investigations of electron kinetics, CO₂ is considered a complex gas due to the presence of a broad Ramsauer minimum in the elastic momentum transfer cross section, together with evenly distributed electron energy loss processes due to vibrational or electronic excitations. In the pioneering work of Nighan [10], emphasis has been given to the evaluation of the Electron Energy Distribution Function (EEDF) that exhibits deviations from the Boltzmann one, upon application of an external and homogeneous electric field.

Detailed information about past and present advances in the solution of the electron Boltzmann Equation (EBE) can be found in [11–14]. A common approach for the solution of the EBE is the expansion of the Electron Velocity Distribution Function (EVDF) in spherical harmonics for the angular dependence of the velocity space. Instead of the full spherical harmonics representation, an expansion in Legendre polynomials can be applied in cases of rotational symmetry of the distribution function around the direction of the electric field. A considerable simplification is often obtained by

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4 assuming that the EVDF is well represented by the first two terms in the expansion.
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6 This is referred in literature as two-term approximation [15]. Recently, progress in the
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8 modelling and understanding of CO₂ plasmas has been made by several groups using
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10 the two-term approach. The kinetics of CO₂ dissociation kinetics has been studied
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12 by Bogaerts and co-authors [16–18]. In those models, the effects of several chemical
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14 processes are taken into account in a 0D approach, by means of the codes ZDPlasKin [19]
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16 or GLOBAL_KIN [20, 21]. In particular, in ZDPlasKin, rate coefficients of electron
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18 impact processes are computed with the two-term solver BOLSIG+ [22, 23]. A detailed
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20 investigation of electron kinetics has been performed by the Bari group [24, 25] with the
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22 use of native codes that couple a time resolved solution of the two-term EBE with the
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24 description of vibrational and chemical kinetics. Efforts in coupling a solution of the
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26 two-term EBE with the rate equations for vibrational and chemical kinetics have been
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28 carried out also by the Lisbon group, with particular emphasis on the comparison with
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30 experimental analysis of glow discharges [26, 27]. In addition, a complete set of cross
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32 sections has been proposed by the Lisbon group [28] and optimized for the calculation
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34 of flux transport coefficients in swarm analysis with the two-term solver LoKI-B, that
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36 has been recently released as an open source code [29, 30]. However, the two-term
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38 approximation obtained by an expansion in Legendre polynomials is not applicable in
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40 absence of rotational symmetry in the velocity space [31]. In addition, the anisotropy
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42 of the distribution is enhanced if inelastic processes give a significant contribution to
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44 electron energy losses [32]. The two-term approach can be extended to higher orders in
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46 the expansion, giving rise to multi-term Boltzmann solvers, that are typically applied
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48 to accurate calculations of electron transport coefficients [13]. Another motivation for
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50 accurate solutions of the EBE is the calculation of transport coefficients (bulk and flux)
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52 that have been investigated in the framework of swarm analysis experiments [33, 34].
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54 Such multi-term solvers are known to overcome the small anisotropy assumption implicit
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56 in the two-term approach. An example of open source code that is based on a multi-
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58 term expansion in Legendre polynomials of the EVDF is MultiBolt [35, 36]. Multi-term
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solutions of the EBE to the CO₂ case have been performed by Loffhagen [37] for the study of spatial and temporal relaxation of the EVDF. In addition, the group at James Cook University has considered the effect of magnetic fields on electron transport [11,38], pointing out the necessity of a full spherical harmonics expansion in cases of absence of rotational symmetry in the velocity space. A comparison of different methods to calculate electron swarm coefficients has been presented in Segur et al. [39] and, more recently, in Vass et al. [40] for a wide range of reduced electric fields (E/N), this last using the IST-Lisbon set of cross sections [28]. Monte Carlo (MC) methods can also be applied for solving the charged particles transport problem [41,42], especially in conditions of strong anisotropy of the distribution function in the velocity space or when spatially dependent quantities are needed [15]. Since the MC method is mainly based on the description of electron history from collision to collision, it is of easier implementation than a multi-term solver. Moreover, the method is equivalent to an infinite expansion in spherical harmonics [43]. Recently, electron impact rate coefficients for vibrational excitation of CO₂ gas molecules have been calculated using an MC method by Vojnović et al. [44], in the presence of DC electric and magnetic fields. In general, application of particle based methods is favoured in plasmas due to the complexity of these last. As an example, a recent work has proposed to study the splitting of CO₂ in a plasma-enhanced catalysis system by means of a 1D Particle-In-Cell with Monte Carlo Collisions (PIC/MCC) code [45]. An example of code based on MC and used for calculation of electron transport properties is Magboltz, that was developed by Biagi [46,47]. Considerable effort has been devoted to benchmarking Boltzmann solvers and MC codes for electrons. In particular, notable is the work of Braglia and Romanó [48] on the calculations of electron transport coefficients in CO₂. An extended comparison, including also multi-term calculations, has been published subsequently by Braglia, Wilhelm and Winkler [49], highlighting the inadequacy of the two-term approach for the case of a spatially homogeneous system under the application of a constant electric field. In spite of the excellent agreement between MC and Boltzmann

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5 six-term calculations, in [49] the difficulties of obtaining accurate MC calculations of
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7 excitation rates, particularly when they are sensitive to the tail of the distribution,
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9 are also pointed out. This is mainly due to stochastic fluctuations in the computed
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11 EEDFs that affect the accuracy of MC results. Furthermore, MC calculations may
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13 require considerable computational time, due to the high number of electron collisions
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15 that have to be simulated before steady-state is attained. Moreover, being the method
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17 intrinsically time-dependent, it can suffer from a problem of multiple time scales that
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19 range from the inverse of the momentum relaxation frequency to the inverse of the
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21 energy relaxation frequency. The ratio of the two time scales, for the case of electron
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23 transport, is of the order of the electron to heavy particle mass ratio m/M [1].

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25 Acceleration of the convergence and improvement of MC efficiency and accuracy
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27 can be obtained by means of variance reduction techniques (VRTs) [50, 51]. Those
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29 techniques are usually employed in MC to reduce the statistical error in the calculation of
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31 macroscopic quantities by using different statistical weights for the simulated particles.
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33 An example of VRT is the Monte Carlo Flux (MCF). The MCF method has been
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35 originally proposed by Schaefer and Hui [52] for studying the electron transport
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37 problem and applied afterwards mainly by Longo and Capitelli [15, 53]. In the MCF
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39 method, while collisional events are still based on a MC description, a reduction of the
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41 computational time is obtained by employing an efficient VRT. Moreover, the problem
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43 of strongly different timescales is solved by the use of a deterministic Markov chain
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45 for the time evolution. However, as the method has generally been overlooked, it
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47 was never benchmarked against solutions of the EBE under the simplest stationary
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49 and homogeneous conditions for molecular gases. The present work is an extension
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51 of previous studies, like [49], focusing here on a systematic comparison of different
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53 numerical methods to describe electrons in CO₂. A Fortran version of MCF has
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55 been recently implemented and benchmarked for electrons in Argon by the present
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57 authors [54]. This reconsideration is in the perspective of an integration of MCF
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59 in 0D/1D codes describing the interplay between electrons and chemical kinetics in
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5 plasmas.

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7 In particular, considering electron transport in gases, often the cold gas
8 approximation is used, assuming a fixed background of target particles at rest. However,
9 this approximation is not valid for low reduced electric fields (E/N), when the mean
10 electron energy is comparable with the thermal energy of the background gas. Extension
11 of the Boltzmann transport equation to consider energy exchange in elastic collision
12 due to the thermal motions of molecules in a DC electric field has been originally
13 considered by Davydov. This correction term in the elastic operator, also called
14 Davydov-Boltzmann term [13], can be derived by an analysis of the linear EBE under
15 assumption of conservative collisions, expansion of the distribution function in the first
16 order and thermal equilibrium of the background gas molecules [55] or by considering
17 the analogy with a Fokker-Planck formulation [56]. In this work, the MCF method
18 is extended to consider the contribution of finite gas temperature of the background
19 gas by means of an exact Test Particle Monte Carlo technique [57]. This extension
20 allows one to study gas kinetics effects of electron transport at low E/N . Moreover,
21 considering the specific case of CO_2 , inconsistencies arising in neglecting the population
22 of internal degrees of freedom, while including effects of finite gas temperature, are
23 highlighted. Beside the scope of this work, another interesting application where MCF
24 can be advantageous compared with other EBE solvers, is in near-runaway conditions.
25 In fact, MCF can provide fast and accurate calculations of EVDFs at high E/N .
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44 The paper is organized as follows. In Section 2, a description of the numerical
45 method is introduced. Section 3.1 presents results of benchmarked calculations of
46 EEDFs and anisotropic components of the EVDF, over a wide range of E/N . The
47 Boltzmann solvers BOLSIG+ [23] and MultiBolt [35], using a two-term and ten-term
48 expansion in Legendre polynomial, respectively, are used for benchmarking. Particular
49 emphasis is given to the accuracy of calculation of chemical rate coefficients of inelastic
50 processes. In Section 3.2, an upgrade of the MCF method, with the technique that
51 takes into account the thermal velocity distribution of the background gas, is presented.
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In Section 3.3, effects of gas kinetics and population of rotationally and vibrationally excited states are analyzed for electrons in CO₂. The importance of considering accurate descriptions of excited states population is also emphasized. In Section 3.4, the use of Biagi cross sections is tested for calculation of transport coefficients and electron impact dissociation rate coefficients and compared with experimental measurements.

2. Numerical method

The numerical method has been described in detail in [54]. Here we report the main characteristics of the method and code implementation and the new features added in the present work. The case of a spatially homogeneous system, in the presence of an external DC electric field applied along the \mathbf{z} -direction is considered. The MCF method [52] is used for calculation of EVDFs in pure CO₂. In MCF calculations, the velocity space is partitioned into a finite number of cells of size $\Delta\mathbf{v}$ in the \mathbf{v} -direction. Hence the electron velocity distribution is obtained as a distribution defined in a discrete space. Usually, under condition of spherical symmetry around the direction of the electric field, such as in the present work, a 2D discretization in energy and $\cos\theta$ is sufficient for a characterization of the velocity distribution function. Furthermore, this description allows one to rewrite the electron transport problem in the following form [15]:

$$n_i(t + \Delta t) = \sum_j (q_{ji}(\Delta t) n_j(t)) - n_i(t) \sum_j q_{ij}(\Delta t), \quad (1)$$

where $n_i(t)$ is the number of electrons in the i -th cell at time t , $q_{ji}(\Delta t)$ is the conditional transition probability of electrons moving from the i -th to the j -th cell in velocity space within the time interval Δt . In order to have an accurate description of the collisional transport in velocity space, Δt is assumed to have values that ensure enough “mixing” of the velocity components due to scattering events, such that:

$$\tau_m < \Delta t \ll \tau_e, \quad (2)$$

where τ_m is the momentum relaxation time and τ_ϵ is the energy relaxation time. In this way, the linear Boltzmann equation for electrons can be described as a discrete Markov process where the time evolution of the system depends only on the knowledge of accurate transition probabilities [58]. In MCF, these last are calculated with short time MC simulations that track electron trajectories from the initial to the final cell that is reached after Δt . Moreover, the electron motion is followed for a time typically much shorter than the relaxation time of the distribution function (Eq. (2)). This makes MCF much more computationally efficient than a conventional MC method.

The numerical implementation of MCF has been performed in Fortran and it includes three main modules that are called in the following order:

- Discretization module: This module is responsible for reading and parsing the MCF input data. In fact, the code requires as input collisional cross sections in LXCat format [59]. In addition, numerical parameters such as energy bin size ($\Delta\epsilon$), maximum energy (ϵ_{max}), number of $\cos\theta$ bins ($n_{\cos\theta}$) and number of electrons per cell (n_p) are required. Cross sections are interpolated in the energy range $[0, \epsilon_{max}]$ using a piecewise linear interpolation. The EVDF and quantities averaged over it are calculated for different physical parameters, such as reduced electric field (E/N), initial gas composition and gas temperature (T_{gas}) that, in this work, are assumed to be constant.
- Monte Carlo module: In this module, transition probabilities are calculated with MC simulations that take into account an exact description of collision statistics with the modified time step approach [42], where each particle contributes to the statistical sampling of transition probabilities [52]. The calculation is initiated by inserting in each cell a uniform distribution of n_p electrons, whose trajectory is traced for a time interval Δt . The time interval is estimated using the criterion in [54]. This heuristic procedure has been proven to give values of Δt that satisfy condition (2). Pseudo-random numbers from a Fortran implementation of the Mersenne Twister algorithm [60, 61] are used to compute the time between

subsequent collisions and the type of collision with the null-collision method [62]. Depending on the nature of the collision, random numbers are also used to compute the electron energy and direction after the scattering [42, 63]. Effects of non-conservative collisions are included using a dynamic list of particles, as described in [54].

As a difference with respect to [54], two different treatments for the electron velocity distribution of the background gas are considered. If the cold gas approximation is used, the background of CO₂ molecules is considered at rest. In this case, the collision frequency for an electron of velocity \mathbf{v} is calculated as

$$\nu(v) = N\sigma(v)v, \quad (3)$$

where N is the gas number density, $\sigma(v)$ is the collisional cross section for electron-molecule scattering and v is the electron speed. Equation (3) is usually a good approximation to describe electron transport in gases because of the large electron to heavy particles mass difference and the high electron to neutral temperature ratio, but it may become inadequate at low values of reduced electric field, such that the mean electron energy becomes comparable with the thermal energy of the gas. For this reason, the effect of a finite temperature of the background gas is taken into account following a procedure introduced in [57]. According to this treatment, for each electron collision, the velocity of the neutral background gas \mathbf{u} is sampled from a Maxwell-Boltzmann distribution function at T_{gas} . In this way, the electron collision frequency can be written in the exact form, depending on the electron-neutral relative velocity [64]:

$$\nu(v) = N \int \sigma(|\mathbf{v} - \mathbf{u}|) |\mathbf{v} - \mathbf{u}| F(\mathbf{u}) d\mathbf{u}, \quad (4)$$

where $F(\mathbf{u})$ is the distribution of the CO₂ molecules at T_{gas} . The von Neumann rejection technique is used to sample the velocity components of the vector \mathbf{u} .

- Markov chain module: In this module, transition probabilities from MC simulations

are stored in the form of a matrix. If time dependent quantities are sought, equation (1) is solved iteratively in the form of a matrix equation. As an alternative, the steady-state solution is retrieved by solving an eigenvalue problem using the DGEEV subroutine of the LAPACK 3.8.0 library [65].

As output, MCF provides time-dependent or steady-state EVDFs which are used for the computation of Legendre polynomial coefficients, chemical rate coefficients and transport coefficients.

3. Results

Electron impact cross sections with CO₂ molecules are taken from the Biagi database [66], that includes 92 different collision processes. This set of cross sections set has been recently transcribed from the code Magboltz v11.6 [47] and carefully checked by comparing Boltzmann and MC calculations [66]. In particular, the dataset provides an elastic momentum transfer cross section that takes into account the contribution from the ground vibrational state CO₂($\nu_1\nu_2\nu_3 = 000$) (where ν_1 , ν_2 and ν_3 are the vibrational quantum number of the symmetric stretching, bending and asymmetric stretching mode, respectively), including rotational states and vibrational bending mode in thermal equilibrium at 293.15 K. The elastic momentum transfer cross section for the vibrational bending mode is tabulated separately and available in the same database. Such a cross section takes into account the contribution of the first level of the bending mode (CO₂(010)), together with two low-lying vibrational levels (CO₂(020) and CO₂(030+110)). For electron energies below 5 eV, inelastic processes are dominated by electron impact vibrational excitation of CO₂(000) that is described by a set of 14 processes. In particular, the following processes are included:

- Vibrational excitation of CO₂(000) to bending mode levels with thresholds 0.083, 0.159 and 0.251 eV, corresponding to the states CO₂(010), CO₂(020) and CO₂(030+110).

- Vibrational excitation of $\text{CO}_2(000)$ to the first vibrational level of the symmetric stretching mode with threshold 0.172 eV (i.e. $\text{CO}_2(100)$).
- Vibrational excitation of $\text{CO}_2(000)$ to the first vibrational level of the asymmetric stretching mode with threshold 0.291 eV (i.e. $\text{CO}_2(001)$).

In addition to the processes above, electron impact excitations to vibrational states with a threshold up to 2.5 eV are taken into account. For higher electron energies, other inelastic conservative processes are described by 79 reactions that include electron impact excitation and dissociation. Cross sections for those processes are derived mainly from the analysis of photoabsorption in CO_2 [67]. This technique gives cross sections for levels that are coupled with the ground electronic state through dipole excitations [68]. Non-dipole allowed transitions are called triplet excitations and related cross sections are optimized in Magboltz [47] to reproduce the measured Townsend ionization coefficient [68]. In particular, for electron energies between 6 and 12 eV, the following processes contribute to electron impact dissociation of CO_2 :

- Dipole allowed transitions to singlet states leading to dissociation of CO_2 into CO and O, described by 10 different processes with thresholds ranging from 6.50 to 8.75 eV.
- Dissociative excitation via CO_2 triplet state with threshold 8.89 eV.
- A second group of dipole transitions to singlet states leading to dissociation of CO_2 into CO and O, described by 6 different processes with thresholds ranging from 8.90 to 10.15 eV.
- Dissociative excitation with threshold 11.05 eV.
- Dissociative excitation via sum of triplets with a threshold of 11.30 eV.

Electron impact dissociation of CO_2 is also considered at energies above 13.7 eV, which is the ionization energy of CO_2 into CO_2^+ . In particular, the following processes are included:

- Dipole allowed transitions leading to dissociation, that are separated from ionization processes based on the average of many measurements of the ionization efficiency [67, 68], described by 25 different processes with thresholds ranging from 13.78 to 19.75 eV.
- Dissociative excitation via sum of triplets with a threshold of 25 eV.

Ionization processes of CO₂ to different singly-charged and multiply-charged ions (CO₂⁺ ($\tilde{A}^2\Pi_u$), CO₂⁺ ($\tilde{B}^2\Sigma_u^+$), CO₂²⁺, O⁺, O²⁺, CO⁺, C⁺, C²⁺, ionization to Carbon K-shell, ionization to Oxygen K-shell) are also included in the set. Moreover, dissociative attachment of CO₂ into CO and O⁻ is considered.

It should be noted that other sets of electron scattering cross sections in CO₂ are available in LXCat. In particular, the IST-Lisbon database includes a comprehensive set of cross sections that are optimized for the calculation of swarm transport coefficients from the solution of a two-term homogeneous EBE [28]. However, in this work, for the sake of numerical benchmarking and consistency with the MC approach implemented, the Biagi database has been preferred since it provides a complete set of cross sections to be used for solving the EBE under multi-term expansion or MC calculations. It is worth noting that, at the moment, there are large discrepancies between cross sections for electron kinetics in CO₂ of different datasets. Those discrepancies involve particularly the description of electronic excitation and dissociation processes [69]. In this respect, this work also aims to assess the validity of Biagi cross sections for describing electron kinetics in CO₂ in Monte Carlo (or multi-term) codes.

An example of temporal evolution of the EEDF in CO₂ obtained with the Biagi cross sections is shown in Fig. 1. Calculations were performed with MCF at a constant reduced electric field of 50 Td, assuming a fixed gas composition of pure CO₂ at $N = 7.24 \times 10^{22} \text{ m}^{-3}$ (collapsed in the CO₂(000) level). As regards numerical parameters, the energy domain is discretized with $\Delta\epsilon = 0.1 \text{ eV}$ and $\epsilon_{max} = 20 \text{ eV}$. The simulation is initiated by placing $n_p = 10^5$ electrons per cell that are used for the calculation of transition probabilities within the time interval $\Delta t = 1.8 \times 10^{-9} \text{ s}$. The time resolved

EEDF is computed by an iterative application of equation (1) to an initial Boltzmann distribution of electrons at 300 K, until reaching steady-state at around 1.8×10^{-7} s.

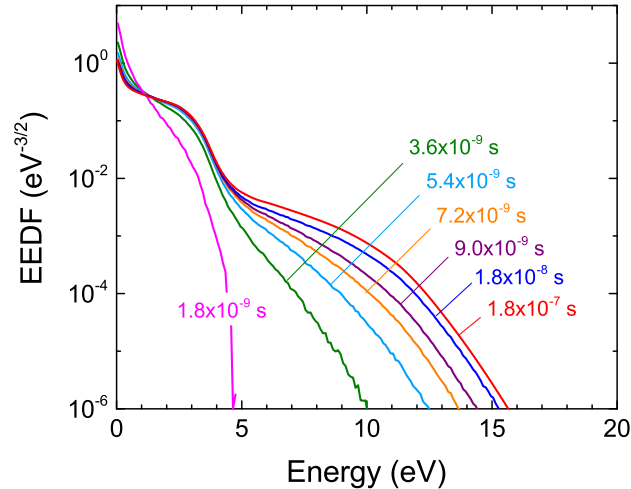


Figure 1: Time evolution of the EEDF in CO_2 under a constant reduced electric field of 50 Td and gas number density of $7.24 \times 10^{22} \text{ m}^{-3}$. A time step of $\Delta t = 1.8 \times 10^{-9}$ s is used in MCF calculations of transition probabilities.

It is worth noting that in the energy range between 1.0 and 5.0 eV, steady-state is established after only 5.4×10^{-9} s, that is about a factor 10 less than for the lower energies portion ($\epsilon < 1.0$ eV) and the tail of the distribution ($\epsilon > 4.0$ eV). This reflects the differences between energy and momentum relaxation frequencies in each energy range. When steady-state is reached, a tail appears in the EEDF starting from around 7 eV following a drop in the distribution. This feature is typical of molecular gases with high vibrational cross sections [1]. In fact, those inelastic processes act as a sharp barrier that electrons have to overcome to reach higher energies. In addition to that, as mentioned before, several different inelastic processes involving mainly electron impact dissociation of CO_2 are present in the energy region between 6.5 and 8.75 eV. The CPU time for MCF simulations for these conditions, including calculations of transition probabilities and time resolved EEDFs, is about 1 min with an Intel Fortran compiler on an Intel Xeon CPU E5-2637 v3 @ 2.50 GHz processor. In MCF, most of the CPU time is spent on calculation of transition probabilities, whereas the solution of the deterministic

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problem is typically very fast (of the order of a few milliseconds, depending on the size of the matrix). In total, the CPU time from MCF calculations is about a factor 3 higher than the one from steady-state solutions with the multi-term solver MultiBolt [35] with similar accuracy in rate coefficient calculations, as shown in more details later in this Section.

In the following subsection emphasis is given to benchmark calculations of Legendre polynomial coefficients and chemical rate coefficients from MCF and Boltzmann solvers using the two-term (BOLSIG+ [23]) and ten-term (MultiBolt [35]) expansion in Legendre polynomials. The benchmark is limited to steady-state conditions. Two different case studies are considered, corresponding to moderate and high E/N . For the sake of codes benchmarking, the following assumptions have been included:

- An invariant chemical composition of pure CO₂ as a background gas is considered. In this gas, the population is collapsed in the CO₂(000) state. In this way, CO₂ is modelled as an ideal gas, where the population of internal states at a finite gas temperature is neglected. Even if the first vibrational levels of the ground state can be largely populated already at room temperature, this strong assumption is made for the sake of numerical benchmarking with other solvers (i.e. MultiBolt), that do not include options for population of excited states. Extension of the model by considering finite gas temperature is discussed in Section 3.2. Moreover, the effect of inclusion of population of internal energy levels is shown in Section 3.3.
- The gas is weakly ionized, such that the effect of self-collisions of electrons can be neglected (in the spirit of the linear Boltzmann equation).
- An homogeneous and time-independent electric field is considered, such that non-local effects of electron kinetics can be neglected.
- All elastic and inelastic scattering collisions are treated as isotropic. Although anisotropic scattering may have important effects on electron transport at high E/N , detailed collision dynamics is not included in the Boltzmann solvers used for benchmarking.

3.1. Cold gas approximation

The MCF method is applied to the case of electrons in CO₂ by calculating the EVDF under the cold gas approximation, in steady-state and homogeneous conditions. Results of MCF are benchmarked in the range $E/N = 20 - 1000$ Td against the codes BOLSIG+ [23] and MultiBolt [35] for the calculation of the first three Legendre polynomial coefficients. At low E/N values, benchmarking with the two-term solver is very good as expected (not shown). The validity of the widely used two-term approximation is verified for the calculation of chemical rate coefficients of inelastic processes such as vibrational excitation and CO₂ dissociation.

3.1.1. Moderate reduced electric fields: $E/N = 20 - 100$ Td

MCF calculations are performed with the following numerical parameters: $\Delta\epsilon = 0.1$ eV, $\epsilon_{max} = 20$ eV, $n_{\cos\theta} = 50$ and $n_p = 10^4$. In particular, a discretization in $\cos\theta$ is needed for computing higher order Legendre polynomial coefficients, whereas setting $n_{\cos\theta} = 1$ is sufficient for the representation of the isotropic part of the distribution. Default numerical parameters are used in the two-term Boltzmann solver BOLSIG+ (precision = 10^{-10} , convergence = 10^{-5} , number of iterations = 2000 and 100 energy intervals). The MultiBolt solver was used in the hydrodynamic regime, under a ten-term expansion in Legendre polynomials of the velocity distribution function with default parameters (convergence error in mean energy = 10^{-6} , maximum number of iterations = 2000, energy remap = 1, number of energy intervals = 1000). In Fig. 2, it can be noticed that the EEDFs obtained with MCF and MultiBolt present significant deviations with respect to the ones calculated with BOLSIG+. This is particularly visible in the tail of the distributions, for $E/N < 80$ Td.

The discrepancy in results from the two-term approach is mainly due to the presence of a pronounced Ramsauer minimum in the elastic momentum transfer cross sections in the energy range of interest. Due to the high number of vibrational excitation processes, the collision frequency of inelastic processes reaches values comparable with the one of

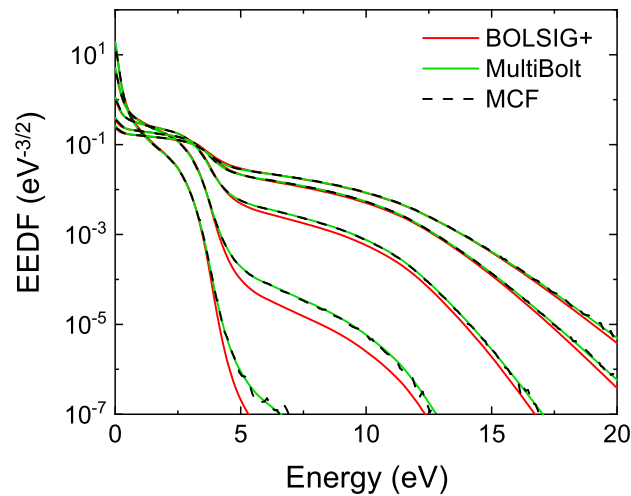


Figure 2: Zeroth order Legendre polynomial coefficient calculated with MCF, BOLSIG+ (two-term solver) and MultiBolt (ten-term solver) in CO_2 at different values of constant reduced electric field. From left to right: 20, 30, 50, 80 and 100 Td.

elastic processes. Hence, the small energy variation assumption implicit in the two-term approach is not valid [31]. Calculations of f_1 and f_2 (Fig. 3), for the same values of E/N , show that the two Legendre polynomial coefficients have absolute values similar to the corresponding EEDFs. The strong coupling between the first three coefficients of the expansion is another explanation for the discrepancies in results from the two-term approach. Moreover, comparing MCF results of Fig. 2 with Figs. 3a and 3b, it is possible to notice that higher order Legendre polynomial coefficients present slightly higher stochastic fluctuations in the tail of the distribution. This is due to the fact that, in MC methods, Legendre polynomial coefficients are calculated from the n -particle distribution function, where each of the n simulated electrons contributes as a term weighted by the respective Legendre polynomial [70]. For this reason, anisotropic components of the distribution suffer from lower counting statistics compared to the isotropic one.

Total chemical rate coefficients for the vibrational excitation of $\text{CO}_2(000)$ to $\text{CO}_2(010)$, $\text{CO}_2(020)$ and $\text{CO}_2(110 + 030)$ and for electron impact dissociation are calculated with MCF and BOLSIG+ and compared to results from MultiBolt. Results

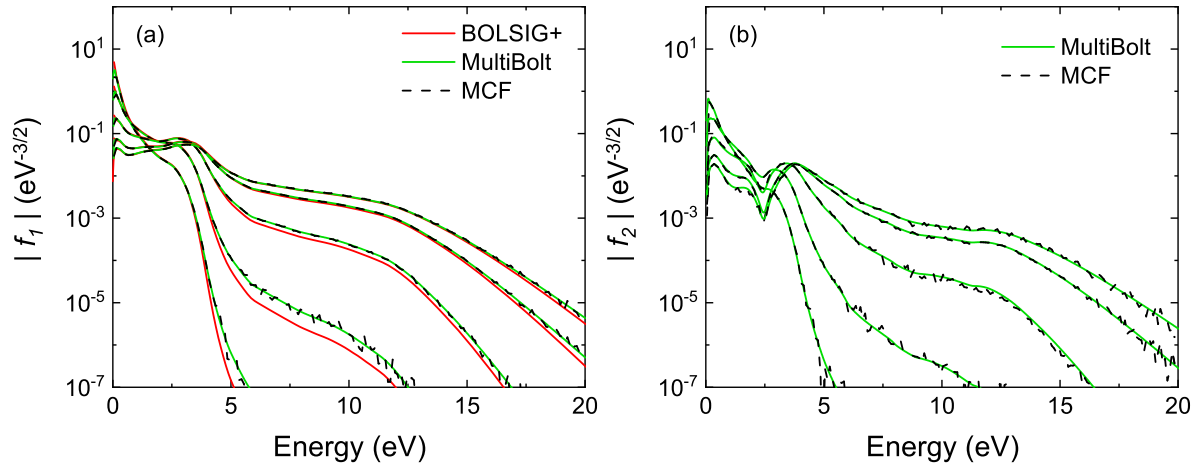


Figure 3: (a) First order and (b) second order Legendre polynomial coefficients calculated with MCF, BOLSIG+ (two-term solver) and MultiBolt (ten-term solver) at different constant reduced electric fields in CO_2 . From left to right: 20, 30, 50, 80 and 100 Td. Calculations of f_2 are compared to results from MultiBolt only, since BOLSIG+ solutions are truncated at the first order.

are shown in Fig. 4a and 4b, respectively. Since vibrational excitation processes have a low energy threshold, deviation in the rate coefficients of the two-term solver BOLSIG+ is within 5%, whereas MCF results are within 1% compared with MultiBolt (Fig. 4a). Rate coefficients of inelastic processes that have threshold near the tail of the distribution are more sensitive to departures of the EEDF from the multi-term solution. This is shown in Fig. 4b for the electron impact dissociation processes. In this case, the relative difference with multi-term calculations can exceed 70%, whereas MCF deviations are within 3%. Discrepancies between MCF results and MultiBolt calculations are mainly due to the different energy grids in the two codes and to the presence of small stochastic fluctuations in the EEDFs from MCF, that can be reduced by increasing the number of simulated particles. As regards rate coefficients of inelastic processes, similar results were obtained by Braglia and co-authors [48] when comparing a conventional MC with a two-term solver. In particular, they pointed out the inadequacy of the two-term approach for

calculation of certain rate coefficients, like electronic excitations, in a range of reduced electric fields from 10 to 100 Td. In their work, using a different set of electron impact cross sections, the error from a two-term solution was up to 40% for the rate coefficient of electronic excitation with threshold 7.0 eV at $E/N = 40$ Td.

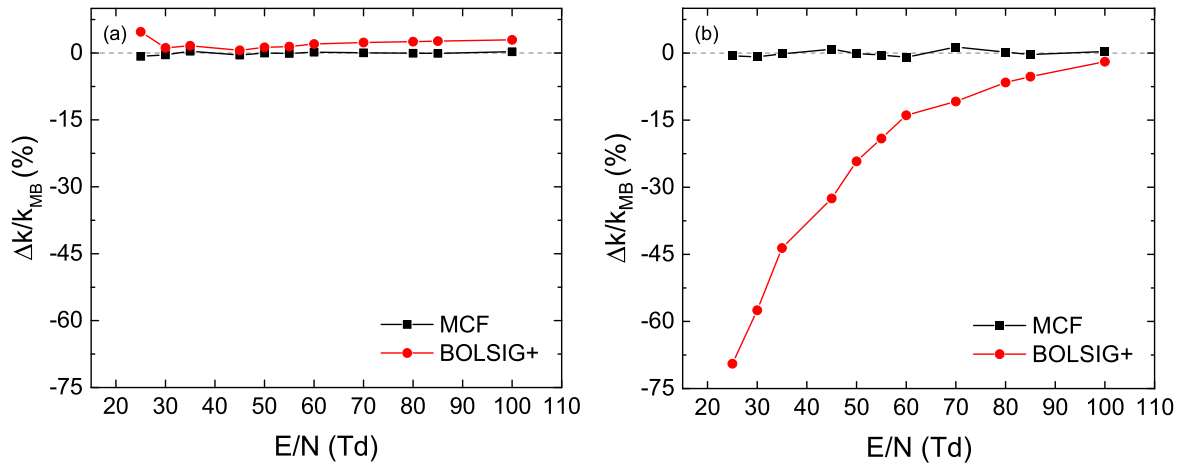


Figure 4: Relative difference (in percent) of total rate coefficients in CO_2 of (a) vibrational excitation $\text{CO}_2(000) \rightarrow \text{CO}_2(010)$, $\text{CO}_2(020)$ and $\text{CO}_2(110 + 030)$ and (b) electron impact dissociation to CO and O calculated from MCF and BOLSIG+ (two-term solver) with respect to MultiBolt calculations (ten-term solver), at different reduced electric fields.

3.1.2. High reduced electric fields: $E/N = 400 - 1000$ Td

In this section we study electron transport at high E/N . As already mentioned, for benchmarking purposes, collision dynamics of elastic and inelastic processes is assumed to be isotropic in velocity space. This choice is dictated by the fact that none of the other two Boltzmann solvers include options for anisotropic scattering. However, anisotropic collision dynamics is particularly important at high E/N , since it can have an impact on the EVDF shape and on the average quantities calculated from it [71]. Moreover, equal energy sharing between the primary and secondary electron is assumed in ionization events. In this case, a more correct treatment of energy sharing should include single differential cross sections [63, 72]. As an alternative, when the energy of

the incident electron is just above the ionization threshold, a good approximation in MC models is to distribute randomly the energy remaining, after subtracting the ionization energy, between the primary and secondary electron with a uniform distribution. Future investigations will focus on more advanced treatment of collision dynamics at high E/N . In this case, the numerical parameters used in MCF are: $\Delta\epsilon = 0.3$ eV, $\epsilon_{max} = 120$ eV, $n_{\cos\theta} = 50$ and $n_p = 10^4$. The same numerical parameters as in previous case studies are used for BOLSIG+ and MultiBolt. Results for EEDFs calculated at 400, 600 and 1000 Td are shown in Fig. 5.

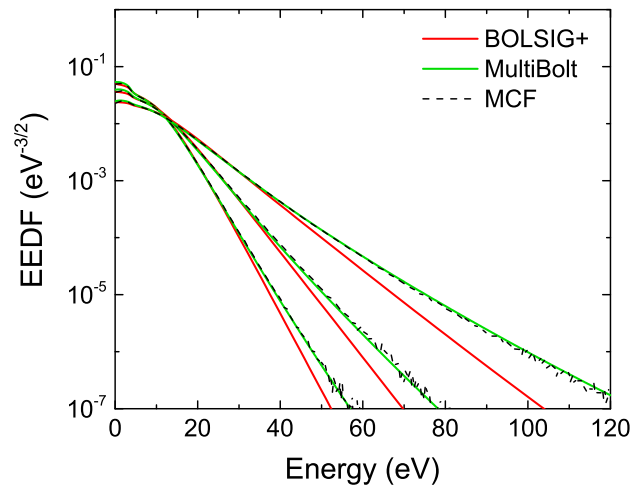


Figure 5: Zeroth order Legendre polynomial coefficient calculated with MCF, BOLSIG+ (two-term solver) and MultiBolt (ten-term solver) in CO_2 at different values of constant reduced electric field. From left to right: 400, 600 and 1000 Td.

Large deviations from a two-term solution can be noticed in the EEDF calculations (Fig. 5). This is mostly due to the presence of electronic excitation and ionization processes that are dominant for energies above 30 eV. Moreover, at such high energies, the electron motion is driven by the presence of strong electric fields that sets a preferential direction in velocity space. In those conditions, the first and second Legendre polynomial coefficients for energies above 30 eV are even higher than the corresponding isotropic component, as shown in Fig. 6. The discrepancies between two-term solutions and the ones obtained with the other methods affect the calculation of flux transport

coefficients, such as reduced mobility and components of the diffusion tensor (not shown).

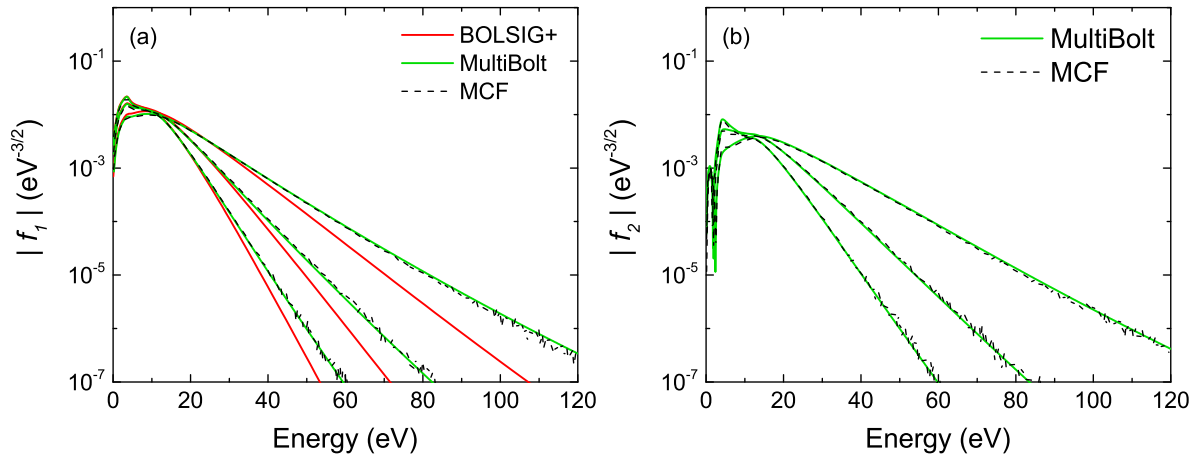


Figure 6: (a) First order and (b) second order Legendre polynomial coefficients calculated from MCF, BOLSIG+ (two-term solver) and MultiBolt (ten-term solver) at different constant reduced electric fields in CO_2 . From left to right: 400, 600 and 1000 Td. Calculation of f_2 are compared with MultiBolt only, since BOLSIG+ solutions are truncated at the first order.

However, such deviations for distributions calculated with the two-term approximation do not impact considerably the calculation of chemical rate coefficients of inelastic processes. An example is shown in Fig. 7 for the same inelastic processes of excitation to bending mode levels and electron impact dissociation as in the previous section. It can be noted that BOLSIG+ calculations present relative errors within 5%, whereas MCF results are within 2%, mainly because of effects of the numerical discretization of the energy domain.

3.2. Finite gas temperature of the background gas

The MCF model described in [54] has been upgraded to consider effects of finite gas temperature of the background gas on the EVDF. In this section, the focus is on low values of reduced electric fields, such that the mean electron energy is comparable with

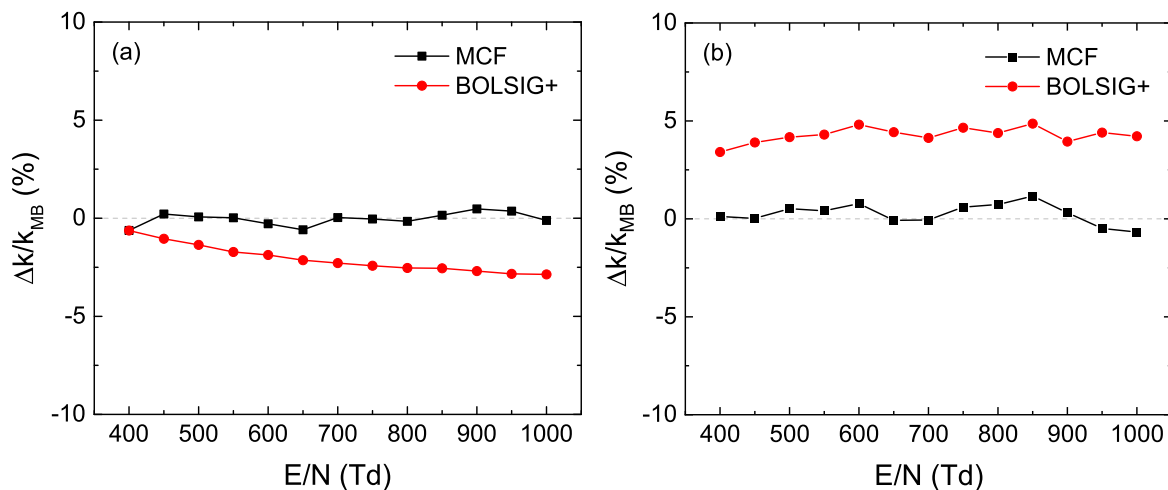


Figure 7: Relative difference (in percent) of total rate coefficients in CO_2 of (a) vibrational excitation $\text{CO}_2(000) \rightarrow \text{CO}_2(010)$, $\text{CO}_2(020)$ and $\text{CO}_2(110 + 030)$ and (b) electron impact dissociation to CO and O calculated from MCF and BOLSIG+ (two-term solver) with respect to MultiBolt calculations (ten-term solver), at different reduced electric fields.

the thermal energy of the background gas. In this context, MCF results are compared with BOLSIG+, that includes a Boltzmann-Davydov term in the elastic operator. It is important to notice that in this subsection, the population of vibrational and rotational levels of CO_2 ground state is neglected. In this way, the background gas is treated as an ideal one, where the gas temperature has only effects in energy exchanges between neutral molecules and electrons in elastic collisions. Reduced electric fields between 0.5 and 1.5 Td are considered, together with gas temperatures between 300 and 1000 K. The partial dissociation of the gas which occurs at the highest temperature has also been neglected. As regards the MCF code, the Test Particle Monte Carlo method described in [57] has been implemented. The scattering is treated in the centre-of-mass frame and requires cross sections in the same reference frame. Conversion of cross sections from the laboratory to the centre-of-mass frame depends on the thermal energy of the target particles [73]. In this case, however, the difference between cross sections in the two reference frames is negligible, due to the low electron-to-molecule mass ratio. As

described in [57], in case of elastic collisions, the relative velocity vector is randomly rotated isotropically in velocity space. In case of inelastic collisions, the relative velocity is updated taking into account the energy loss involved in the process.

MCF calculations are performed with the following numerical parameters: $\Delta\epsilon = 0.002$ eV, $\epsilon_{max} = 0.25$ eV, $n_{\cos\theta} = 1$ and $n_p = 10^4$. Default numerical parameters are used in the two-term Boltzmann solver BOLSIG+ (precision = 10^{-10} , convergence = 10^{-5} , number of iterations = 2000 and 100 energy intervals). Since MultiBolt does not have an option for the description of finite gas temperature effects, it was not used for benchmarking in this section. An example of EEDFs calculated at $T_{gas} = 0$ (cold gas), 500 and 1000 K is shown in Fig. 8a for a constant E/N of 0.5 Td. As expected, the finite gas temperature enhances the tail of the EEDF due to the transfer of energy from neutral target particles to electrons. The first Legendre polynomial coefficients are shown in Fig. 8b, where it can be noted that the effect of the gas temperature is similar to the one for f_0 .

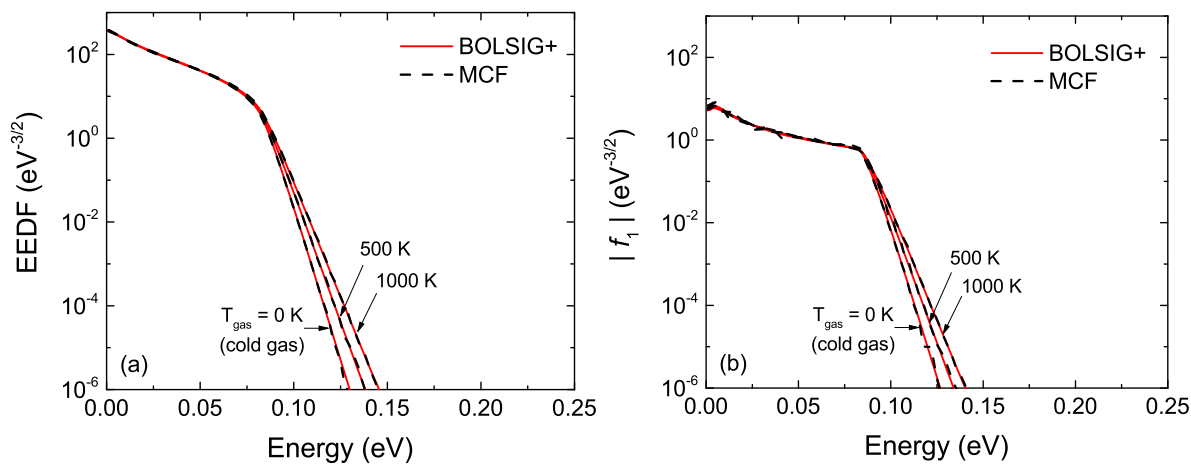


Figure 8: (a) Zeroth and (b) first order Legendre polynomial coefficients calculated with MCF and BOLSIG+ at 0.5 Td for different gas temperatures in CO_2 . Calculation at $T_{gas} = 0$ corresponds to frozen background gas (cold gas), whereas results at $T_{gas} = 500$ or 1000 K include finite gas temperatures.

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5 It should be considered that, due to the necessity of sampling velocity components
6 of the colliding partners, this MCF extension is more computationally expensive. In
7 fact, while EEDF calculations with a frozen background gas require about 1 minute
8 only, having a finite T_{gas} leads to calculations that are about 3 times longer, mainly
9 because of the generation of additional random numbers for sampling the velocity
10 components of the molecules. An improvement in MCF computational performances
11 can be achieved, for example, by employing high performance computing techniques,
12 such as parallelization or multi-threading.
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20 Effects of finite gas temperature of the background gas can also be appreciated
21 by comparing rate coefficients of inelastic processes at low E/N . In Fig. 9, total rate
22 coefficients for the vibrational excitation processes to bending mode levels ($\text{CO}_2(000)$
23 $\rightarrow \text{CO}_2(010)$, $\text{CO}_2(020)$ and $\text{CO}_2(110 + 030)$) are calculated at different T_{gas} from 300
24 to 1000 K, in a range of E/N from 0.5 to 1.5 Td and compared with results of MCF
25 obtained with the cold gas approximation. The relative difference of MCF results with
26 respect to cold gas calculations at $T_{gas} = 0$ K increases at lower values of E/N and
27 exceeds 80% for $T_{gas} = 1000$ K at 0.5 Td.
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38 *3.3. Effect of gas kinetics and inclusion of population of excited states*

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40 Until now, for numerical benchmarking purposes, the CO_2 system has been modelled as
41 an ideal gas, where the population of excited states has been neglected by assuming that
42 vibrational states of the ground electronic state are collapsed into the $\text{CO}_2(000)$ state. In
43 particular, for the CO_2 case, this assumption breaks down already at room temperature,
44 where the first vibrationally excited levels (e.g. $\text{CO}_2(010)$) can be significantly populated
45 [28]. Here we compare results from the previous section with calculations that include
46 population of excited states. In this section, electron transport at low E/N is studied,
47 where the population of the first six low-energy vibrational levels of the CO_2 ground
48 electronic state has been considered. In particular, together with the ground vibrational
49 state $\text{CO}_2(000)$, we consider:
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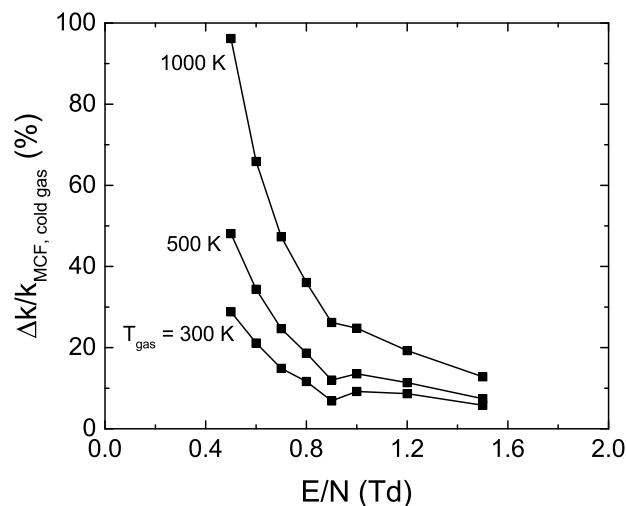


Figure 9: Relative difference (in percent) of MCF total chemical rate coefficients for vibrational excitations ($\text{CO}_2(000) \rightarrow \text{CO}_2(010)$, $\text{CO}_2(020)$ and $\text{CO}_2(110+030)$) obtained at $T_{\text{gas}} = 300, 500$ and 1000 K, with respect to MCF results obtained under cold gas assumption, as a function of the reduced electric field.

- The first vibrational level of the asymmetric stretching mode ($\text{CO}_2(001)$).
- The first vibrational level of the symmetric stretching mode ($\text{CO}_2(100)$).
- The first three effective vibrational levels of the bending mode (i.e. $\text{CO}_2(010)$, $\text{CO}_2(020)$ and $\text{CO}_2(030 + 110)$ with degeneracy equal to 2, 3 and 6, respectively. The last one presents Fermi resonance between symmetric stretching and bending mode levels.

In this way, the CO_2 molecule is assumed to be a truncated system composed by six vibrational levels of the ground electronic state, that can be populated by electron impact vibrational excitation and de-populated through superelastic collisions. Cross sections for superelastic processes are calculated by assuming micro-reversibility, with the Klein-Rosseland formula [15]. In order to correctly describe the CO_2 molecule using a MC method and the Biagi database and to compare results with different methods, the set of cross sections requires a specific treatment. In this respect, it is important to notice that the elastic momentum transfer cross section of the Biagi database takes into account

the contribution of the ground electronic state, rotational states and vibrational bending mode in thermal equilibrium at a fixed $T_0 = 293.15$ K. Since we want to populate the aforementioned vibrational states according to a Boltzmann distribution at a generic vibrational temperature T_{vibr} , a change in the elastic momentum transfer cross sections for $T_{vibr} \neq T_0$ has to be taken into account. In this work, the following formula is used, according to the Magboltz source code v11.3 [47]:

$$(\sigma_{el}(\epsilon))_{T_{vibr}} = \frac{1 - \xi_{bend}}{\alpha_{ground}} [(\sigma_{el}(\epsilon))_{T_0} - \alpha_{bend}\sigma_{bend}(\epsilon)] + \xi_{bend}\sigma_{bend}(\epsilon), \quad (5)$$

where $(\sigma_{el}(\epsilon))_{T_{vibr}}$, $(\sigma_{el}(\epsilon))_{T_0}$ and $\sigma_{bend}(\epsilon)$ are the cross section of elastic momentum transfer calculated at T_{vibr} , the cross section provided in the Biagi database of LXCat [66] (at T_0) and the cross section of elastic momentum transfer of the bending mode (that is tabulated separately in LXCat [66]), respectively. The term ξ_{bend} is the fractional population of the bending mode levels (i.e. $\text{CO}_2(010)$, $\text{CO}_2(020)$ and $\text{CO}_2(030 + 110)$) calculated at T_{vibr} , whereas α_{bend} is the fractional population of the bending mode levels at T_0 and α_{ground} is the fractional population of the other vibrational levels of the ground electronic state (i.e. $\alpha_{ground} = 1 - \alpha_{bend}$). Note that, in case $T_{vibr} = T_0$, the calculated elastic momentum transfer cross section is equal to the one reported in the Biagi database of LXCat (i.e. $(\sigma_{el}(\epsilon))_{T_{vibr}} = (\sigma_{el}(\epsilon))_{T_0}$). The elastic momentum transfer cross section from the Biagi database ($(\sigma_{el}(\epsilon))_{T_0}$) is reported in Fig. 10, together with the one calculated at $T_{vibr} = 1000$ K ($(\sigma_{el}(\epsilon))_{T_{vibr}}$) and the one of the bending mode levels ($\sigma_{bend}(\epsilon)$). In the energy range between 0.1 and 5.0 eV, the cross section obtained at $T_{vibr} = 1000$ K is higher than the corresponding one at $T_0 = 293.15$ K. This is due to the fact that, at higher vibrational temperatures, the fractional population of bending mode levels is higher than the one at room temperature, thus the calculated cross section is closer to the one for bending mode levels. The increase in the elastic momentum transfer cross section in CO_2 with increasing population of vibrational states has been investigated experimentally by Buckman and co-authors [74] and inconsistencies arising by neglecting this effect have been noted by Haddad and Elford [75], for the calculations

of electron drift velocities in CO₂ at different gas temperatures.

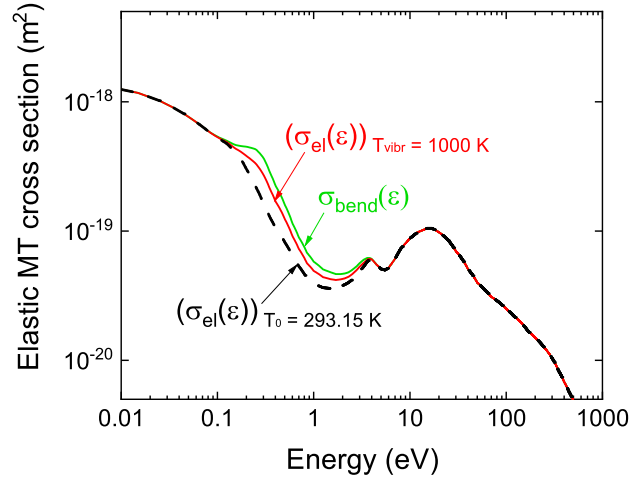


Figure 10: Elastic momentum transfer cross sections of CO₂ considering the contribution of the bending mode levels ($\sigma_{bend}(\epsilon)$), for electron impact with molecules in the ground electronic state at $T_{vibr} = 1000$ K ($(\sigma_{el}(\epsilon))_{T_{vibr}}$) and for electron impact with molecules in the ground electronic state provided in the Biagi database of LXCat ($(\sigma_{el}(\epsilon))_{T_0}$) for thermal equilibrium at $T_0 = 293.15$ K.

In order to be consistent with the elastic momentum transfer cross section used in the present work, rotational excitation and de-excitation processes must be taken into account. At present, the Biagi database of LXCat does not include rotational cross sections. However, those processes are included in the Magboltz source code v11.3 [47]. Rotational excitation and de-excitation cross sections were calculated considering electric quadrupole transitions that are characterized by a difference between initial and final rotational quantum numbers of $\Delta J = \pm 2$ [76]. Cross sections in [76] are valid for low energy electrons, since the principal contribution comes from large distances of the incoming electrons from the molecules. For energies greater than about 6.0 eV, an artificial Born decay of $1/\epsilon$ in the cross sections has been introduced, as in the Magboltz source code [47]. In the present work, 31 rotational states of the CO₂ ground state (i.e. even values of J from 0 to 60) are considered and they are populated according to a Boltzmann distribution at temperature $T_{rot} \neq T_0$. Using the formulas for cross sections

for rotational excitations $\sigma_{J,J+2}(\epsilon)$ and de-excitations $\sigma_{J,J-2}(\epsilon)$, it is possible to subtract their contribution from the elastic momentum transfer cross section $(\sigma_{el}(\epsilon))_{T_{vibr}}$ (defined in Eq. 5) as

$$(\sigma_{el}(\epsilon))_{T_{vibr}, T_{rot}} = (\sigma_{el}(\epsilon))_{T_{vibr}} - \sum_J [\xi_J^{exc} \sigma_{J,J+2}(\epsilon) + \xi_J^{de-exc} \sigma_{J,J-2}(\epsilon)], \quad (6)$$

where $(\sigma_{el}(\epsilon))_{T_{vibr}, T_{rot}}$ is the elastic momentum transfer cross section obtained by considering the contribution of the population of bending mode levels at T_{vibr} and by subtracting the contribution of the inelastic rotational cross sections. The terms ξ_J^{exc} and ξ_J^{de-exc} are the fractional populations at T_{rot} of the rotational states considered in rotational excitations and de-excitations, respectively. We note that, for the present conditions, effects of rotational excitations and de-excitations are negligible compared to vibrational energy losses, in agreement with [77].

In order to investigate the effect of population of energy levels of the CO₂ ground electronic state on EEDF calculations, MCF simulations have been performed. Results are shown in Fig. 11 for a constant $E/N = 0.5$ Td. The same numerical parameters as in the previous subsection were used. In particular, Fig. 11 shows a comparison of the EEDF obtained under cold gas assumption (in which the gas temperature, rotational and vibrational temperature are set to zero) with the one obtained by setting higher temperatures. First of all, as noticed in the previous subsection, by setting $T_{gas} = 500$ K ($\neq T_0$) and $T_{rot} = T_{vibr} = 0$, effects of gas kinetics are included by considering the energy exchange with the hot target molecules. However, this approach neglects the contribution of excited states of the ground electronic state. Moreover, we notice that this approach is inconsistent with the use of the elastic momentum transfer cross section from the Biagi database, that takes into account ground electronic state, bending mode and rotational contribution in thermal equilibrium at 293.15 K. In Fig. 11, results of EEDFs obtained at $T_{gas} = T_{rot} = T_{vibr} = 300$ K and $T_{gas} = T_{rot} = T_{vibr} = 500$ K are also shown, in which vibrational and rotational states are populated according to a Boltzmann distribution at T_{vibr} and T_{rot} , respectively.

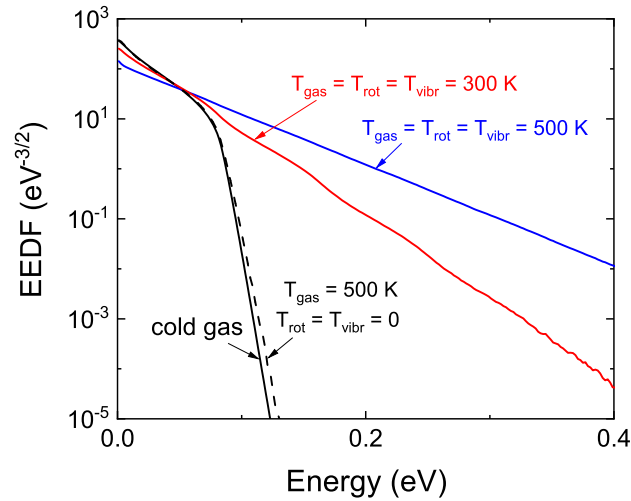


Figure 11: Electron energy distribution functions in CO_2 at 0.5 Td considering cold gas assumption with frozen background and neglecting population of excited states; hot background of CO_2 molecules at $T_{gas} = 500$ K neglecting population of excited states ($T_{rot} = T_{vibr} = 0$) and hot background at $T_{gas} = 300$ K (500 K) and Boltzmann population of rotationally and vibrationally excited states at $T_{rot} = T_{vibr} = 300$ K (500 K).

As it can be noticed, the EEDFs obtained in these conditions present an higher tail. This is mostly due to the presence of superelastic vibrational collisions, in conditions where the electron temperature is comparable with T_{vibr} . A secondary cause of differences between calculations at 300 and 500 K is due to the fact that higher temperatures lead to an increase of the elastic momentum transfer cross section in the energy range of interest (from Eq.(5) and (6)), thus leading to a higher elastic collision frequency with respect to the inelastic one.

3.4. Comparison with experimental results

The characteristic energy (i.e. the ratio between transversal diffusion coefficient and mobility) from BOLSIG+ [23] and MCF, using the Biagi dataset of cross sections [66] is compared. Results are shown in Fig. 12, together with experimental values from the Dutton database of LXCat [78] at $T_{gas} = 195$ and 300 K. As expected,

BOLSIG+ and MCF results with a frozen background (cold gas) deviate from the experimental values for $E/N \leq 0.2$ Td, where the mean electron energy becomes comparable with the thermal energy of the background gas. Moreover, BOLSIG+ results including a Davydov-Boltzmann correction at 300 K deviate from experimental values at the same T_{gas} and $E/N < 5$ eV, as well. As opposed to BOLSIG+ calculations, in MCF the elastic momentum transfer cross section is modified using Eq.(5) and (6), that consider population of the vibrational and rotational states of the ground electronic state, according to a Boltzmann distribution at T_{gas} , as explained in the previous subsection. Moreover, superelastic collisions are taken into account. With this treatment, experimental values for the characteristic energy are reproduced by MCF with an error within 3%. With this comparison, the importance of considering an accurate description of excited states at low E/N , together with a thermal background, is emphasized. The inclusion of those states has an effect on the EEDF through superelastic collisions and should be consistent with the choice of the elastic momentum transfer cross section used in the calculations.

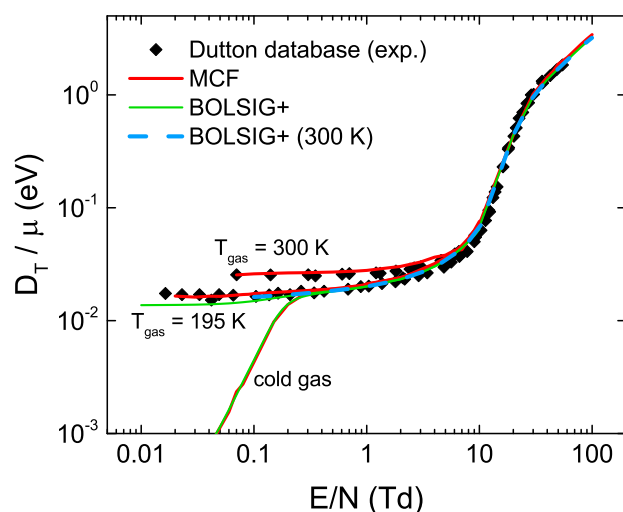


Figure 12: Measured characteristic energies in CO_2 [78] and calculated values from BOLSIG+ [23] and MCF, considering cold gas approximation or finite gas temperatures.

MCF and BOLSIG+ [23] calculations of reduced mobilities (μN) using Biagi cross sections set are compared with experimental measurements from LXCat databases

[78–82]. Results are shown in Fig.13 for $0.01 < E/N < 100$ Td at 300 K. Results from MCF and BOLSIG+ show an agreement with experimental data within 2%. A similar agreement, between measurements and calculations of bulk drift velocities, is found by Vass and co-authors [40], using the IST-Lisbon cross sections set [28] in Monte Carlo and multi-term solvers. However, it is important to notice that there are fundamental differences between the Biagi and the IST-Lisbon datasets. In particular, on the one hand, the Biagi elastic momentum transfer cross section and total cross section (given by the sum of elastic and inelastic contributions) are in good agreement with experimental measurements [83,84], within 3%. On the other hand, the IST-Lisbon elastic momentum transfer cross section is calculated from an effective cross section, by subtraction of the inelastic contributions (weighted by the fractional population of each state) [28]. At 300 K, differences are found between the two datasets, leading to an IST-Lisbon elastic momentum transfer cross section higher than the Biagi one for energies above 3 eV. Another important difference between the two datasets lies in the description of the inelastic processes with thresholds above 6 eV. In fact, the Biagi set includes several cross sections for dipole-allowed and triplet excitations, as mentioned in Section 3, whereas the IST-Lisbon set includes two different processes with threshold of 7 and 10.5 eV, as in the Phelps database [85]. Further work is needed to understand the differences between those cross sections sets and their impact on calculations of other swarm parameters, such as the bulk longitudinal diffusion coefficient multiplied by the gas number density $D_L N$, that presents large deviations between experimental measurements and calculations for E/N greater than 100 Td using the currently available cross sections sets [40].

In addition, Biagi cross sections are optimized taking into account superelastic collisions from vibrational and rotational states of the ground electronic state. The importance of those collisions for accurate calculations of swarm data is shown in Fig.13, where BOLSIG+ calculations of μN are also presented without superelastic process. In particular, for $0.01 < E/N < 1$ Td, the difference between BOLSIG+ results obtained

by neglecting contributions of superelastic processes and MCF, that intrinsically includes them, is up to 7%. A similar effect of the superelastic collisions on the EVDF and on electron swarm parameters has been highlighted for other polyatomic molecules [86].

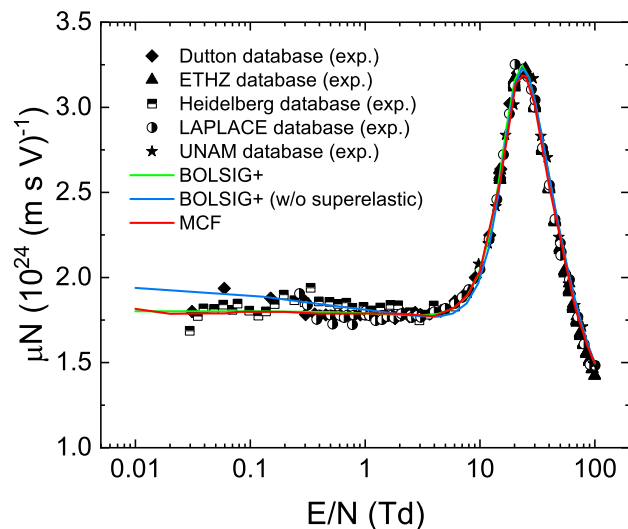


Figure 13: Measured reduced mobilities in CO_2 [78–82] and calculated values from MCF and BOLSIG+ [23] at 300 K.

Electron impact rate coefficients have also been calculated using Biagi cross sections [66] and compared with recent measurements by Morillo-Candas and co-authors [69]. In [69], dissociation rate coefficients are measured in a pulsed DC glow discharge at moderate values of E/N (i.e. $45 \text{ Td} < E/N < 110 \text{ Td}$) and compared with other measurements by Corvin and Corrigan [87]. Moreover, in the same work, experimental results are compared with results from BOLSIG+ [22], where EEDFs are obtained from a solution of the two-term Boltzmann equation using the IST-Lisbon cross sections set [28] and rate coefficients are calculated from several sets of cross sections from literature. Morillo-Candas and co-authors [69] recommend the use of Polak and Slovetsky cross sections [88] for calculations of electron impact dissociation rate coefficients in CO_2 , in the E/N range investigated. In this work, EEDFs are calculated using cross sections of the Biagi database [66], while dissociation rate coefficients are calculated using both Polak and Slovetsky [88] and Biagi [66] cross sections. These last were not considered

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4 in [69]. In Fig.14, total dissociation rate coefficients obtained with BOLSIG+ and
5 MCF at $T_{gas} = 300$ K are compared with experimental results of Morillo-Candas and
6 co-authors [69] and Corvin and Corrigan [87]. In the calculations, it is assumed that
7 vibrational and rotational states are populated according to a Boltzmann distribution
8 at T_{gas} . Since there are uncertainties on the measurements of Corvin and Corrigan
9 [87] given by the total pressure change and the determination of gaseous dissociation
10 products in the experiment, we focus on the comparison of our numerical results with
11 measurements of Morillo-Candas and co-authors [69]. Moreover, for all E/N values,
12 large discrepancies between calculations and experimental measurements of Corvin and
13 Carrigan [87] are found. The measurements of [87] are also significantly different
14 than the ones of Morillo-Candas and co-authors and, in [69], possible causes of this
15 discrepancy are pointed out. Overall, the agreement between measurements of Morillo-
16 Candas and calculations using Biagi cross sections is relatively good up to around 60
17 Td, while, for higher E/N values, results of the calculations are systematically higher
18 than the same measurements.
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34 MCF results suggest that the main dissociation channel, in this E/N range,
35 is through triplet excitation with thresholds of 8.89 eV and 11.30 eV. A smaller
36 contribution is given by dipole-allowed transitions with thresholds between 6.5 – 8.75
37 eV and 8.9 – 10.15 eV. For $E/N < 70$ Td, deviations between MCF and BOLSIG+
38 results exceed 60%, due to the anisotropy of the EVDF. Moreover, it is worth noting that
39 BOLSIG+ results are obtained with a modified input file of cross sections that takes into
40 account superelastic collisions between vibrational states and the population fractions
41 of those excited states and the same modified input file is used in MCF. Instead, if the
42 file downloaded from LXCat is used in BOLSIG+ without purposely modifying it, larger
43 discrepancies between MCF and BOLSIG+ are found due to the different treatment of
44 the excited states population (not shown).
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56 In Fig. 14, calculations using the cross sections of Polak and Slovetsky [88] are
57 also shown. In those calculations, EEDFs are obtained from MCF and BOLSIG+
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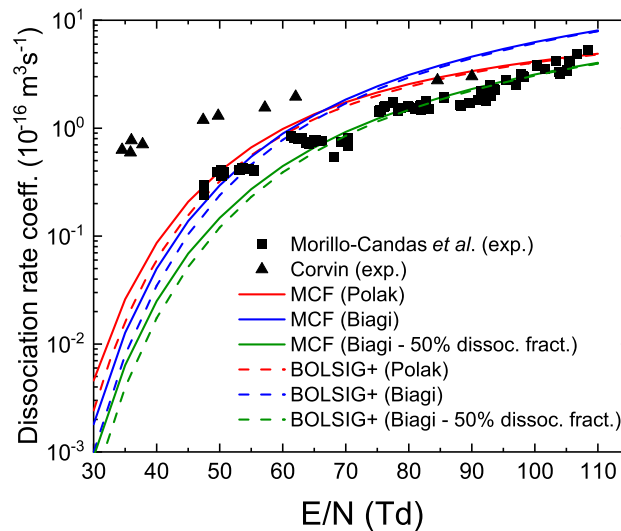


Figure 14: Electron impact dissociation rate coefficients measured [69,87] and calculated with MCF and BOLSIG+ [22] as a function of reduced electric field.

using only cross sections from the Biagi database, whereas the Polak and Slovetsky cross section is used for computation of rate coefficients. MCF and BOLSIG+ results obtained with Polak and Slovetsky cross sections at $E/N > 70$ Td are relatively closer to experimental data of Morillo-Candas and co-authors, than the ones calculated with Biagi cross sections.

Different sources of uncertainties could affect the results. First of all, in calculations of dissociation rate coefficients with Biagi cross sections, excitation to singlet and triplets states between 6 and 12 eV is assumed to be fully dissociative. An analysis of photoabsorption spectra suggests that those excitations are related to fast processes, like dissociation [68]. However, the dissociation fraction of those states is unknown. Moreover, excited states in molecules have a decay path which can also occur through vibrational relaxation and this can lead to a dissociation fraction below 100% [68]. In Fig. 14, MCF and BOLSIG+ calculations with Biagi cross sections, assuming a dissociation fraction of 50% from states having energies between 6 and 12 eV, is shown. This dissociation fraction is chosen to approximately match calculations at 300 K and experimental measurements at $E/N > 60$ Td. For lower E/N values, discrepancies

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4 between MCF calculations and measurements of Morillo-Candas and co-authors [69] are
5 found, while a better agreement is obtained with calculations at higher gas temperatures
6 of about 700 K and by assuming the same value of dissociation fraction (not shown).
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8 Further investigation is needed in order to accurately estimate the CO₂ dissociation
9 fraction via dipole-allowed and triplet excitations. New calculations of electron impact
10 cross sections, like the ones in [89], are very much sought, since measurements of those
11 cross sections usually present large uncertainties.
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18 In addition, it is important to mention that measurements in [69] have been
19 performed in conditions of gas temperatures between 300 and 700 K [90]. In particular,
20 results with $E/N < 60$ Td are obtained at higher current and pressure and thus at
21 higher gas temperatures [90]. This fact may explain the discrepancies between MCF
22 calculations with Biagi cross sections at 300 K and 50% dissociation fraction and
23 measurements in that range of E/N . Indeed, following the results of Fig. 11, rate
24 coefficients are expected to increase with T_{gas} . Moreover, as regards gas composition, in
25 experiments small fractions of dissociation products are formed [69] and those can have
26 a large impact in EEDF calculations, as shown in [91]. For this reason, and in order
27 to better estimate a correct value of dissociation fraction, experiments and calculations
28 performed at different controlled gas temperatures are highly sought after. From the
29 results of this analysis we conclude that, given the overall good agreement between
30 measurements and calculations, without the introduction of an additional dissociation
31 fraction, cross sections of Polak and Slovetsky [88] are preferred for calculations of the
32 electron impact dissociation rate coefficients, in this E/N range, as pointed out already
33 in [69].
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51 **4. Conclusions**

52 In this work, the MCF method has been benchmarked against two-term and multi-term
53 solutions of the EBE for calculations of EVDFs in CO₂, using the Biagi dataset of cross
54 sections [66]. MCF results have been obtained by means of a fully native code developed
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4 by the authors [54]. The study of the CO₂ molecule is particularly challenging, due to the
5 presence of a broad Ramsauer minimum in the elastic momentum transfer cross sections
6 and evenly distributed energy losses due to vibrational excitations. In this framework,
7 MCF can potentially be considered as a reference method, faster than conventional MC
8 approaches, for benchmarking popular Boltzmann solvers that are based on the two-
9 term approximation, with the caveat that, as we have shown, each method must operate
10 with its most appropriate optimized set of cross sections.
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18 The accuracy of MCF, with respect to the ten-term Boltzmann solver MultiBolt
19 [35], has been assessed through calculations of EVDFs and of chemical rate coefficients
20 for vibrational excitation and dissociation mechanisms, finding an excellent agreement.
21 As expected, large deviations from results obtained with the two-term solver BOLSIG+
22 [23] have been found at moderate E/N (between 20 and 80 Td) for calculations of rate
23 coefficients that are strongly sensitive to the tail of the distribution. This result shows
24 the importance of the choice of data and methods to describe electron kinetics in plasma
25 chemistry models that use these coefficients.
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34 Subsequently, the MCF method has been upgraded to include the effect of the finite
35 gas temperature of the background gas. This makes MCF more reliable for calculations
36 at low E/N , where the cold gas approximation does not apply and thermal gas effects
37 have an impact on the calculation of chemical rate coefficients and swarm parameters.
38 Results of MCF including finite gas temperature have been benchmarked against results
39 of BOLSIG+ [23], that includes a Davydov-Boltzmann correction in the elastic operator,
40 showing excellent agreement at low fields.
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48 Furthermore, we have extended the model to include the population of vibrational
49 and rotational states of the ground electronic state. In this way, CO₂ molecules
50 are modelled as a real gas, instead of having their population collapsed into the
51 CO₂(000) state. The inclusion of the population has an effect not only on superelastic
52 collisions, but also on the elastic momentum transfer cross sections. It is important
53 to notice that the detailed description of excited states and superelastic collisions is
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not explicitly presented in the cross sections set that is available in LXCat. However, their inclusion is fundamental for reproducing experimental transport coefficients at low E/N with high accuracy. In addition, the Biagi cross sections set has been used for calculations of electron impact dissociation rate coefficients, showing good agreement with recent measurements [69], using the Polak and Slovetsky [88] cross sections for calculations of dissociation rate coefficients. The use of the Biagi cross sections set, that includes a detailed description of electron energy loss mechanisms, opens up possibilities for comparison with other cross sections sets. The need for dedicated experiments performed at different gas temperatures, to assess the influence of temperature and validate the results and hypotheses of models, has been highlighted.

The model will be extended to simulate electron distribution functions in time-dependent and space-dependent electric fields and to test anisotropic scattering in collision dynamics.

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