Kinetic Modelling for a CO_2-H_2O-Plasma: a Vibrational Kinetics Study

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Abstract: A kinetic modelling study is performed to obtain greater understanding of the vibrational kinetics of a CO_2-H_2O plasma. For this purpose, an electron impact cross section set for water is created using a swarm-derived method. The CO_2 model of Kozak and Bogaerts [1] is extended by this cross section set, as well as additional chemistry and VT-reactions of H_2O.
Keywords: H_2O, cross sections, EEDF, CO_2-conversion, global model

1. General

According to the United Nations secretary general, António Guterres, climate change and global warming are the biggest threats to humanity. Therefore, great efforts need to be taken in order to keep the warming of the earth under 1.5°C as stated by the Paris agreement. One of the strategies can be the use of carbon capture and utilisation (CCU), of which CO_2-conversion is an example. For this purpose, plasma conversion is a promising method.

Due to the fact that CO_2 is rarely found in pure form and the fact that the addition of a secondary gas can be beneficial for the conversion, it is interesting to understand the influence of the different mixture components. For CO_2-gas, CH_4- and N_2-mixtures have already been studied extensively. However, a common but less studied gas mixture is CO_2-H_2O. For this mixture higher conversion rates have been reported by Chen et al. [2] in a MW-plasma. Nevertheless, no model for this gas mixture has been created yet. To close this gap, the CO_2 model of Kozak and Bogaerts [1] is extended with H_2O. Therefore, a new reaction set is created that focusses on the reactions between H_2O and CO_2 and its possible products, where H_2O plays the role of a collision partner. The focus is on the influence of H_2O on the CO_2 vibrational levels.

2. Method

a) H_2O Cross Section Set

In order to propose the cross sections for electron collisions with H_2O, which will be used for the modelling of CO_2-H_2O plasmas, it is important to introduce the concepts of consistent and complete sets. A set is considered complete when it is able to describe the main electronic processes responsible for momentum and energy losses, including those yielding changes in the number of electrons, such as ionization. On the other hand, a set is consistent when it is able to reproduce measured values of swarm parameters, when used as input data to evaluate the Electron Energy Distribution Function (EEDF) from a Boltzmann solver [3]. The Boltzmann solvers used in this work are described below.

A complete and consistent set of cross sections is often obtained adopting a swarm-based procedure [3]. It starts with the collection of a set of cross sections from the literature, whose magnitudes are then adjusted to improve the agreement between calculated and measured swarm data. Here it is important to mention that such procedure does not validate the cross section of each individual process nor it ensures the uniqueness of the whole cross section set. The main simulation tool used in this work for the calculation of swarm parameters and EEDF is BOLSIG+ [4]. This simulation tool is a free and user-friendly computer program for the numerical solution of the Boltzmann equation for electrons in weakly ionized gases in uniform electric fields.

b) H_2O-CO_2-model

The calculations are performed by the Fortran 90-module, called ZDPlasKin [5]. This is a zero-dimensional solver. The changes in concentration are only a function of time. Therefore, only the mass conservation equations for every particle and the Boltzmann equation are solved. The simulations follow the time evolution of species densities and gas temperature. The mass conservation equations for every particle are:

$$\frac{dn_s}{dt} = \sum_{j=1}^{jmax} Q_{sj} = \sum_{j=1}^{jmax} R_j \left[a_{sj}^R - a_{sj}^L \right], \quad (1)$$
$$R_j = k_j \prod_l n_l, \quad (2)$$

where n_s is the density of the species s, Q_{sj} is the source term for reaction j of the species s, a_{sj}^R and a_{sj}^L represent the stoichiometric coefficients on the right and left side, respectively, of species s for reaction j. R_j is the reaction rate and k_j the reaction rate coefficient. The reactor geometry used is a surfatron MW plasma, where the gas flow is moving through a cylindrical discharge tube (cooled by the reactor walls which are at room temperature) and is passing through a plasma region that is formed using microwaves guided perpendicular to the tube. An artefact of the 0D-model is that all variables are taken as uniform in the radial direction and diffusion and heat conduction are neglected along the reactor axis. By using the 0D approximation the reaction kinetics and gas flow along the reactor axis are described, creating a pseudo 0D-model [6]. Using the conservation of mass flow rate, the velocity of a volume in the tube can be calculated. Since velocity is related to time and position, the time-dependence can be converted into position-dependence. In this case the parameters are therefore expressed as a
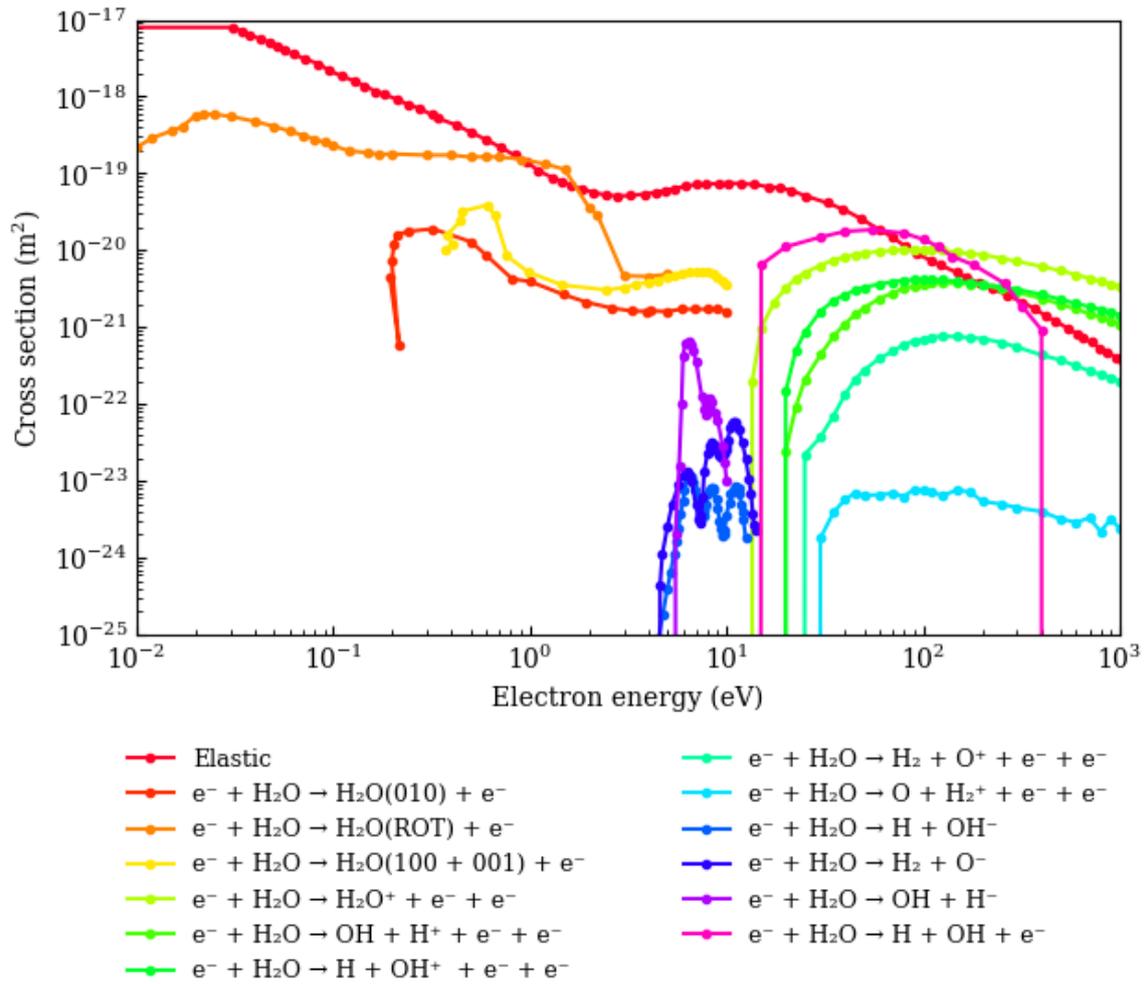
Fig. 1 H_2O Cross Section Set

function of the axial coordinate z. The model further considers a triangular power density profile [6].

As mentioned above, the code of Kozak and Bogaerts [1] is extended by electron impact cross sections of H_2O, as well as by the chemistry of H_2O-CO_2 [7], and by VT reactions [8]. Because of the high vibrational self-relaxation rates in H_2O (orders of magnitude faster than relaxation by collisions with other molecules) [9] and the lack of available data, no VV reactions of H_2O(-CO_2) were added. The vibrational-vibrational (VV) exchange (between molecules) leads to higher populations of higher vibrational levels, whereas on the other hand due to vibrational-translational (VT) exchanges, energy of the vibrational modes is lost to translations and the higher vibrational levels get more easily depopulated.

3. Creation of H_2O Cross Section Set

The swarm parameters are obtained from the LXCat database and Hasegawa et al. [10]. The swarm parameters calculated in this work are the (i) electron reduced mobility and (ii) effective ionization Townsend coefficient, represented by μN and α/N - η/N, respectively

As a start, the LXCat database was consulted. However the available sets were both far from perfect when compared to the experimentally measured swarm data from Hasegawa et al. [10]. When the sets are compared, we can conclude, from both reduced mobility and Townsend coefficient, that the Triniti [11] set provides better results. Consequently, the Triniti set was chosen as a base set. To further optimize the cross section set of Triniti, a literature survey was performed to find additional information about the most important cross sections.

The first step was replacing the Triniti values that showed a small energy range, with cross sections that show a larger range of availability. The next step was to replace the effective cross sections by elastic cross sections. An important focus of this work was on finding the right rotational cross sections for water due to their importance.

For polar molecules, rotational excitation is the dominant process in low energy collisions. Moreover, at energies below the vibrational threshold, the only inelastic process is rotational excitation, and thus the rotational transition plays a significant role in slowing down electrons in a molecular gas [12]. Water, in general, exhibits large

(a) 14.04 cm

(b) 14.67 cm

(c) 15.31 cm

(d) 16.93 cm
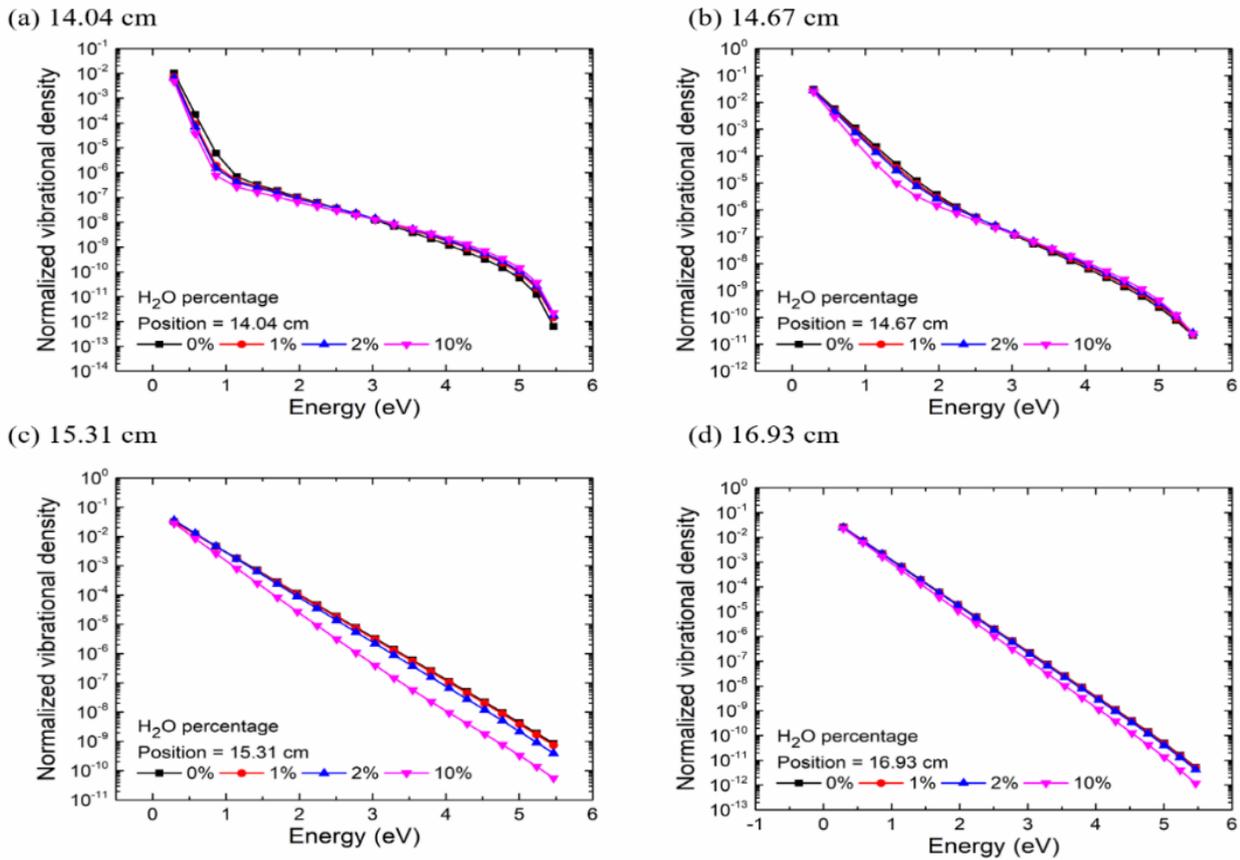
Fig. 2 VDFs calculated with the 0D model, for pure CO_2 and 1, 2 and 10% of H_2O addition, at different positions in the plasma tube (see text) – beginning of the plasma at 14.04 cm (a), inside the plasma at 14.67 cm (b) and at 15.31 cm (c), just outside the plasma at 16.93 (d). The x-axis represents the asymmetric vibrational levels, therefore the ground level is not added.

rotational total cross sections, since it is a polar molecule and therefore interacts strongly with low energy electrons.

However, obtaining rotational cross sections experimentally can be troublesome. This happens because the rotational levels of water lie very close together and electron beam experiments do not have enough resolution to resolve each rotational state [13]. In addition, swarm experiments can give very accurate cross sections for the sum of all overlapping reactions, but only estimates of partial cross sections can be obtained. If partial cross sections come into play, the use of computational methods is of big help.

The new cross section set obtained by the above described procedure (figure 1) is mostly based on the cross sections found in the LXCat database and the vibrational cross sections of Seng and Lindler [14]. It consists of 13 processes that are the most important for our 0D model: (i) one elastic [15], (ii) three attachment [11], [12], (iii) five ionization [12], and (iv) four excitation cross sections (including vibrational and rotational) [11], [14].

4. Results of the 0D model for CO₂-H₂O

Figure 2 shows the vibrational distribution functions (VDFs) of CO_2, calculated with the model, for 0%, 1%, 2% and 10% of water, and for different positions along the discharge tube. Note that the plasma itself is found from ~13.5 cm to ~16.5 cm. It can be noticed that most VDFs

are thermalized (i.e. they show a Boltzmann distribution) after ~15 cm (which is still in the plasma). At 14.04 cm and 14.67 cm, it can be noticed at first that the lower vibrational levels (up to v = 9, which corresponds to an energy of 2.51 eV) are slightly quenched in the plasma upon H_2O addition (see figure 2(a, b)). However, the higher populated levels show a slight increase in population. This effect disappears further along the tube, and thus further in the plasma. Additionally, thermalized curves are obtained. These results partially correspond to our expectations, since water is predicted to quench the vibrational levels, but a greater effect was expected. In addition, the slight increase in densities of the higher vibrational levels was not expected.

Although the limited number of papers on CO_2-H_2O-plasmas available show mostly a strong quenching, Chen et al. [2] reported a higher CO_2 conversion in their experiments, which can help us understand the results. A possible explanation is a cooling effect caused by H_2O addition. Indeed, a drop in average gas temperature in the plasma region was calculated in our model, from 2269 K for pure CO_2 to 1976 K for 10% H_2O. Higher temperatures reduce the population of CO_2 vibrational levels (due to the increase of the VT reaction rate coefficients) [2], and therefore in this case a cooling effect has a positive outcome. At the same time, an increase in the average electron temperature with an increasing concentration of H_2O (from ~0.94 eV for pure CO_2 to ~1.80 eV for 10%

H_2O) was predicted by the model, which in this case is beneficial for the higher vibrational excitation of CO_2 [2]. The fact that the higher vibrational levels are depopulated again further along the tube upon H_2O addition (see figure 2(c, d) can be attributed to the lower T_e, and faster decrease in electron temperature compared to the gas temperature. Moreover, the rate coefficients for quenching are dependent on the gas temperature. Therefore, the quenching increases more slowly than the electron temperature and will therefore need more time to become a more important mechanism, explaining the increased population of the higher vibrational levels in the beginning of the plasma. Towards the end of the plasma, thermalisation can be observed, which results in lower electron temperature, and thus the quenching becomes more dominant. When the gas leaves the plasma, again the electron temperature drops faster than the gas temperature, which makes the quenching process more prominent.

Additionally, the increased concentration of H_2O creates changes in the EEDF. The different EEDF can also (partially) explain the intensification of the results mentioned above. Note that, due to the complexity of the plasma, more factors can come into play, which might be overlooked at this time. On the other hand, due to the small changes that occur (as seen mostly in 1% and 2% of H_2O), the results might also depend on uncertainties of the calculations. In general, it can be suggested that, when the quenching becomes the dominant process, further in the plasma, the expected quenching occurs.

The hypotheses stated above, i.e., influence of the gas and electron temperature, and electron energy distribution (calculated with inclusion of the newly provided cross sections of H_2O), can be tested by (i) running simulations with a constant temperature (gas and/or electron), and (ii) removing the electron impact reactions of water from the model. This type of simulations is planned for the near future.

5. Conclusion

A kinetic modelling study was performed to obtain physical insight into the vibrational kinetics of a CO_2-H_2O-mixture. As a first step, a cross section set for H_2O electron impact reactions was created, using a swarm-based method and an extensive literature study. This resulted in a new cross section set containing 13 reactions, i.e., one elastic, three attachment, five ionization, and four excitation cross sections. Secondly, the 0D model was used to calculate the normalized vibrational densities of the CO_2 asymmetric vibrational levels, for pure CO_2, 1%, 2% and 10% of water. The results showed an overall decrease in densities of the lower asymmetric vibrational levels, which was expected. However, the decrease was not so prominent. Additionally, a small increase in vibrational densities of the higher vibrational levels (v > 10) was noticed in the beginning of the plasma. Different hypotheses can be made to account for these results, including (i) a lower gas temperature and (ii) a higher electron temperature, that favour the (higher)

vibrational population, as well as (iii) changes in the EEDF due to addition of cross sections for water.

7. References
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