Modelling Future Solar Fuels
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ABSTRACT
The conversion of CO\(_2\) into CO is an important process for the production of liquid fuels using renewable energy. This method also reduces the concentration of CO\(_2\) in our atmosphere. In this paper we report our findings on the development of modelling the Electron Energy Distribution Function (EEDF) in CO\(_2\) plasmas that follows from solving the Boltzmann equation. Ionization, which is needed to maintain a plasma, requires a high reduced electric field E/N. However, the most efficient way to dissociate CO\(_2\) using vibrational excitation requires low E/N. Our theoretical findings imply that the addition of Na has a positive impact on reducing the E/N.

Keywords
Boltzmann equation, EEDF, conversion of CO\(_2\), computational physics, solar fuels, Sodium.

INTRODUCTION
Recently the New York Times featured "Heat-Trapping Gas Passes Milestone, Raising Fears" [1], stating that the concentration of CO\(_2\) in the atmosphere reached a daily average of 400 ppm.\(^1\) The CO\(_2\) level in our atmosphere increased steadily during the past decades. To reduce the amount of CO\(_2\), different techniques can be used. The most widely used today is the Carbon Capture and Storage (CCS) where CO\(_2\) is captured and stored underground for an undetermined amount of time. Rather than storing CO\(_2\) and wasting valuable energy, it would be beneficial if the CO\(_2\) is used for the production of liquid fuels. This process is called Carbon Capture and Utilization (CCU). To further reduce CO\(_2\) emission, we can opt for renewable energy sources to produce these fuels as opposed to the many non-renewable energy sources being used today. This way we can try to achieve a CO\(_2\) neutral system. CO\(_2\) neutral systems have the advantage of solving three problems at once: no additional CO\(_2\) is emitted, energy is produced and when non-renewable energy supplies get depleted, CCU will still be operational. The process of making such fuels, called solar fuels\(^2\), could be combined with the current CO\(_2\) capture facilities. Renewable energy is mainly produced in remote areas, which makes liquid fuels exceptionally useful due to their high storage capacity and easy transportation methods. The problem of accessibility is also solved. During periods of time where more energy is being produced than consumed or the other way around, the energy can be stored as liquid fuels. This contributes to the uprisng interest in the production of solar fuels.

The conversion of CO\(_2\) into CO is one link in the chain to the production of solar fuels. Using plasma for the conversion results in a couple of complications. A high conversion rate is important to minimize the energy loss. To produce a CO\(_2\) plasma, the CO\(_2\) needs to be ionized. Apart from ionization, the CO\(_2\) molecules are also electronically and vibrationally excited. CO\(_2\) molecules that collide with another CO\(_2\) or with an electron, can dissociate into CO and O. Vibrational excitation plays an important role in the dissociation process and its efficiency peaks at lower energy levels. The ionization potential, however, is much higher and requires more energetic electrons, which is in contrast with the efficiency of the vibrational excitation. A high energy input also implies higher energy loss on energy inefficient processes such as electronic excitation. A possible solution is to split the ionization and the dissociation and let it take place at different times. We can then observe whether a time-dependent electric field has an influence or not. Another option is to add a gas with a low ionization potential to lower the energy required to maintain the plasma. We consider Sodium. To get a better understanding of the processes that take place and the influence of different parameters on the conversion rate, we look at the Electron Energy Distribution Function (EEDF). This distribution tells us how many electrons have a certain energy. To obtain this function, we need to solve the Boltzmann equation. This equation describes how electrons gain energy from an applied electric field and how they exchange energy due to collisions with the background gas. Solving this equation however is not as straightforward as we would like it to be.

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\(^1\) The concentration is measured in particles per million (ppm).

\(^2\) Solar fuels are defined as fuels produced by using renewable energy converting hydrogen or carbon dioxide to fuels which can be stored for later usage.
CO₂ MOLECULE

The dissociation of CO₂ is given by the following formula

\[ \text{CO}_2 \rightarrow \text{CO} + \frac{1}{2} \text{O}_2 \]

where ΔH is the enthalpy needed for dissociation. The structure of the CO₂ molecule is important, because it has an impact on the vibrational excitation that is being used. Because CO₂ is a linear diatomic molecule, we find 3 vibrational modes which can be found in Figure 1: the symmetric stretch mode (100), the bending mode, which is double degenerate (010) and the asymmetric stretch mode (001). These modes can be obtained by excitation due to electron-CO₂ collisions or by two CO₂ molecules that collide.

![Figure 1: The three normal vibrational modes of CO₂.](image)

SOLVING THE BOLTZMANN EQUATION

The Boltzmann equation

The EEDF provides us with more information about the processes going on in a CO₂ plasma. To find the EEDF (F) we look at the Boltzmann equation (see Equation 1).

\[ \frac{\partial F}{\partial t} + v \cdot \nabla F + \frac{X}{m} \cdot \frac{\partial F}{\partial v} = \left( \frac{\partial F}{\partial t} \right) _c \]

(1)

X is the force acting on the particles and (\(\partial F/\partial t\)), is the time rate of change of F due to collisions. The term here still includes elastic collisions. The left hand side represents the total derivative of F in the phase space. In this approach we only consider a homogeneous plasma. Therefore we can eliminate the spatial derivatives, omitted in the next equation, [2]

\[ \frac{\min \frac{\partial F}{\partial t}}{2e} = \frac{1}{3} \frac{d}{du} \left( uE^2 \frac{\partial F}{\partial u} \right) - 2m \frac{d}{du} \left( \frac{u^2 N_u F}{u^2} \right) = \left( \frac{\partial F}{\partial t} \right) _{\text{exc}} \]

(2)

where \(m\) is the electron mass, \(e\) is the charge of an electron, \(M\) is the mass of a CO₂ atom, \(N\) is the gas density and \(E\) is the strength of the electric field which can be time-dependent. \(u\) is the electron energy in eV and \(Q_u\) is the total cross-section for momentum dissipation and depends on the energy \(u\). \(Q_0\) is the cross-section for momentum scattering for elastic collisions. \(Q_{\text{exc}}\) and \(Q_{\text{ion}}\) are the cross-sections for ionization and excitation (electronic and vibrational) of CO₂ molecules respectively. As can be seen in the Boltzmann equation after division by \(N\), the reduced electric field \(E/N\) is an important parameter. It determines the overall behaviour of the EEDF.

Discretization

In order to be able to solve the Boltzmann equation numerically, we have to discretize the space. The function \(F(u,t)\) is taken over an interval \([0, u_{\text{max}}]\). This interval is divided into discrete points which are given by \(u_i = \Delta u i\), where \(\Delta u\) is equal to \(u_{\text{max}}/(a-1)\) with \(a\) the number of grid-points chosen. \(A\) can then be defined as the size of the matrix \(A\). For the discretization of the Boltzmann equation, we use a second-order approximation. Using explicit iteration, we can find Equation 3 for the discretized Boltzmann equation.

\[ \frac{F_{\text{new}} - F_{\text{old}}}{\Delta t} = \frac{2e}{m} A \cdot F_{\text{old}} \]

(3)

The matrix \(A\) is a collection of different processes e.g. excitation and super-elastic collisions. For the boundary at zero energy we consider \((\partial F/\partial u)\) to be zero and for \(u_{\text{max}}\) the assumption that higher energies have negligible influence is made. The EEDF is also normalized after each iteration to make up for any electron loss.

Oscillating field

As mentioned before, we also consider an oscillating field. The EEDF will then contain an electric field that changes in time with frequency \(f\) given by \(E=E_0\sin(2\pi ft)\). Now, in addition to \(E/N\), the reduced frequency \(\omega/N\) also becomes a main parameter. When \(\omega/N\) is very high, the electrons do not have time to change the energy they gain from the electric field. This results in an EEDF independent of time and so the applied electric field appears as constant as given in Equation 4. When \(\omega/N\) is low, the EEDF will change in time.

\[ \langle E \rangle = \frac{1}{2} E_{\text{max}}^2 \]

(4)

Super-elastic collisions

Electrons also collide with vibrational excited molecules. The molecule can then fall back to the ground state. We call this a super-elastic collision. The amount of super-elastic collisions depends on the density of the vibrational excited molecules. This is also dependent on interactions between different CO₂ molecules.

\[ N_{\text{e}}(E) = \frac{g_v}{g_0} N_0 \cdot \exp \left( \frac{-E}{k_B T_\text{c}} \right) \]

(5)

The vibrational distribution function tells us how many CO₂ molecules are in which vibrational state. A first approximation of this distribution can be made by assuming thermal equilibrium and results in a Boltzmann distribution, as seen above in Equation 5, where we make sure to keep the degeneracy of the different vibrational modes in mind. We have to assume a vibrational temperature \(T_c\). To add these collisions into the Boltzmann equation, we also need cross-sections \(Q_{\text{el}}\) which depend on the cross-sections \(Q_{\text{exc}}\) for excitation.

RESULTS

Constant electric field

First we considered a constant electric field. We can see in the next two figures the results of these simulations. It is easily seen that for much higher \(E/N\), the EEDF has a much longer tail, which corresponds to more electrons with high energy and less electrons with low energy.

The rate coefficients given in the Figure 3, contain 3 of the excitation processes that have been considered. It illustrates that the rate coefficients for vibrational excitation (the three uppermost) do not vary as much as the rate coefficient for ionization (the lowest one) under the variation of the reduce electric field \(E/N\).
Oscillating field

$\omega/N$ is an important parameter for oscillating fields. In Figure 4 we can see the EEDF for an oscillating field. The EEDFs on the outside are from the oscillating field. On the bottom we can find the EEDF when the electric field reaches its minimum, while the uppermost is when the electric field reaches a maximum. The EEDF in the middle is for constant electric field given in Equation 4.

We intend to look at an oscillating field to see if we can enhance vibrational excitation and ionization at different times thus improving the conversion. In Figure 5 the ionization rate coefficient over the timespan of one cycle is given. The horizontal lines contain the rate coefficients for constant electric field and the mean taken over one cycle for oscillating field. For the vibrational excitation rate coefficients we find similar plots. However, it is clear that the rate coefficients do not differ a lot, making this method less useful. Therefore the addition of Sodium was explored.

Addition of Sodium

The addition of a gas with a low ionization potential could lower the possible $E/N$ used for the conversion of CO$_2$. CO$_2$ has an ionization potential of 13.3 eV which is rather high and unfortunately when ionization is possible, also electronic excitation is present. Electronic excitation is a way to dissociation that we want to avoid as much as possible since it is less energy efficient than using vibrational excitation. In Figure 6, the ratio between the ionization rate coefficients of CO$_2$ and Na is given. Na has an ionization potential of 5.14 eV. We added an amount of Na that corresponds to a fraction of the density of CO$_2$ in the groundstate. We can conclude that the addition of Na has a positive effect on the ionization degree of the plasma. However, we need to keep in mind that this approach only added the ionization process for Na, whereas other processes that might influence the behaviour of the EEDF are left out. Note that for low $E/N$, the addition of 1% Na also starts to modify the EEDF, as is visible from the difference with lower concentrations.

Addition of super-elastic collisions

The addition of super-elastic collisions brings electrons with low energy back to higher energies. Electrons with a high energy are more likely to be excited electronically and therefore reduce the energy efficiency of the conversion. When we assume thermal equilibrium as a first approximation, a vibrational temperature $T_v$ is assumed (see Equation 5). Figure 7 the effect of the vibrational...
temperature on the EEDF is presented. When we consider a temperature \( T_e \) of zero eV, we know that, using the explained approximation, we will get the same EEDF as for considering no super-elastic collisions. This is indeed the case. The EEDF for \( T_e = 0.1 \text{eV} \) is almost the same as the EEDF we get when considering no super-elastic collisions. However, the distribution of the vibrational modes is more complex than this. A \( \text{CO}_2 \) molecule collides with other \( \text{CO}_2 \) molecules as well and such collisions can change the distribution.

![Image of EEDF for super-elastic collisions](image)

Figure 7: EEDF for super-elastic collisions for \( T_e = 0.1 \text{eV} \) and for \( T_e = 1.0 \text{eV} \) with \( E/N = 70 \text{Td} \).

**Vibrational distribution function**

By adding the super-elastic collisions and approximating \( T_e \) as \( T_e = 2m_{\text{ion}}/3 \), as in thermodynamic equilibrium, we implicitly assume that no molecules are dissociated. However, the distribution function of the vibrational modes is also dependent on the heavy particle collisions and so we added a simple model, adapted from [3], that describes the redistribution of the vibrational distribution function. The model assumes the electron density \( n_e \). Such a vibrational distribution can be found in Figure 8. Just as we expected, the asymmetric stretch, which can be found around 0.27 eV, has a peak. The considered model can also be replaced by the Fokker-Planck equation.[4]

![Image of Vibrational distribution function for 50 Td](image)

Figure 8: Vibrational distribution function for 50 Td.

**CONCLUSION**

The Boltzmann equation describes how electrons move in the energy space in time. Solving this equation results in the EEDF that tells us more about the different processes going on. To convert \( \text{CO}_2 \) into CO using plasma we want low \( EN \) to optimize the dissociation by using vibrational excitation, but also higher \( EN \) to maintain plasma.

We considered excitation and ionization and looked at the rate coefficients. The ionization coefficient varies much more under variation of the reduced electric field than the vibrational rate coefficients. Adding an oscillating field resulted in a slightly higher ionization rate, but this increase is rather low. For this reason, we considered the addition of Sodium. It turned out that this addition, even in the order of a promille of the concentration of \( \text{CO}_2 \), made a difference in the total ionization rate coefficients.

Adding super-elastic collisions has an impact on the EEDF. It puts electrons with low energy back to higher energy and this leads to less efficient conversion. The first approximation, assuming thermal equilibrium, assumed no heavy particle collisions. These collisions, however, also affect the EEDF and are considered in a model for the vibrational distribution. The vibrational distribution function shows a clear peak around the asymmetrical stretch.

The model used to determine the vibrational distribution function can also be substituted with a model described by Fridman: the Fokker-Planck equation. Solving this equation then results in a continuous vibrational distribution function. The addition of the Fokker-Planck equation requires a lot more time and hasn’t been added to the model yet.

**ROLE OF THE STUDENT**

At DIFFER (Dutch Institute for Fundamental Energy Research) the Solar Fuels group recently started constructing an experimental set-up for the conversion of \( \text{CO}_2 \) into CO. They brought forth the topic of the research that Christine Verbeke performed during her Honours-bachelor research under the supervision of prof. dr. W.J. Goedheer. She made a first version of the program that solves the Boltzmann equation for the conversion of \( \text{CO}_2 \) into CO that can provide the Solar Fuel group with more information for their experiments. The program will be adapted in the future to keep up with the new ideas and proposals of the Solar Fuels group. During the past year, Christine Verbeke processed the data and discussed the results with her supervisor from time to time. She held several presentations to keep the group members up to date and also presented a poster at the annual Plasma Physics conference in Lunteren. At the end, she wrote a report of which this paper is a shorter version.

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**REFERENCES**


