Optical detection of carbon monoxide for solar fuel production

Optical detection of carbon monoxide for solar fuel production:

Searching for ways to bring sunlight into our engines

Producing hydrocarbons from CO_2 by making use of renewable energies has great potential to satisfy the ever increasing global energy demand while at the same time being CO_2 neutral. The production process involves the dissociation CO_2 to CO, which is the most energy costly step and therefore needs to be optimised. Non-equilibrium plasma discharges have been shown to be promising candidates to achieve efficient conversion. To investigate the conversion efficiency, it is necessary to measure the amount of CO produced. For this purpose, a two-photon absorption laser induced fluorescence (TALIF) diagnostic system has been realized that can yield temporally and especially spatially resolved measurements. Thus, the dissociation processes in plasma discharges can be studied and optimised.

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Fossil fuels such as oil, coal or gas are the pillars of our modern energy supply, providing for about 80% of our global energy consumption [1]. However, they have two major disadvantages: First, these resources are limited; the depletion of oil and gas is predicted to happen within the next one hundred years [2]. The global energy demand is rising at the same time, driven by the industrial and economic progress of emerging countries all over the world. Second, the usage of fossil fuels for energy production results in the emission of carbon dioxide (CO_2), the greenhouse gas which is generally considered to be the main driver of global warming [3].

To tackle these challenges, a lot of research has been performed in the past decades to find and optimise new pathways to renewable and clean energy such as solar or wind power. These, however, come with challenges of their own: while sun and wind may be viewed as sources of 'unlimited' energy, their output is somewhat uncontrollable. Solar energy can only be harvested during the daytime, while wind has to be considered entirely erratic. To use the gained energy effectively, it is necessary to store surpluses and use them when sun and wind power fall short. Another issue is the transport of solar and wind energy from the production site to wherever it is needed. A prominent example is the idea proposed by the DESERTEC foundation to secure the energy production of the EU by setting up solar power plants in the Sahara desert [4]. All political implications aside, bringing this power from Africa to Europe remains the key challenge. This is where the so-called solar fuels come in – a new method to store and transport energy.

Solar fuels – Turning sunlight into value-added chemicals

Figure 1 shows the cycle of solar fuel production: the greenhouse gas CO_2 is collected and then dissociated to form carbon monoxide (CO). Electric energy from clean, sustainable sources powers the process and is converted into chemical energy stored within the CO. To make this chemical energy usable, the Fischer-Tropsch process is applied. This is an efficient chemical process used to turn carbon compounds, with the addition of water, into liquid hydrocarbons, i.e. fuels like gasoline or kerosene. These fuels can

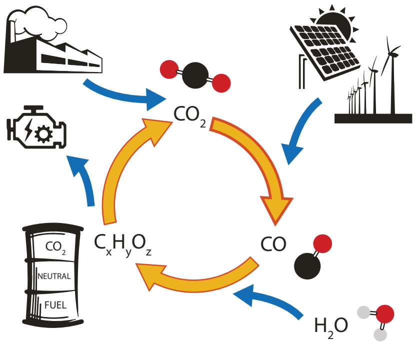

Figure 1 **The cycle of solar fuel production: CO_2 is dissociated into CO using renewable energies. Value-added hydrocarbons are made from this CO and water. These hydrocarbons can be used in conventional engines, where they are burnt to form CO_2 again. By reusing CO_2, the cycle is kept carbon neutral.**

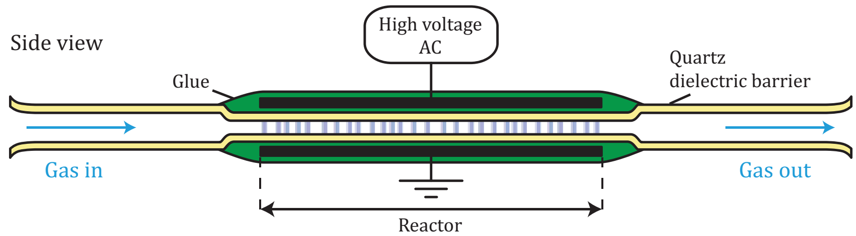

Figure 2 **Schematic depiction of a DBD reactor. Two electrodes are glued onto a quartz glass tube that serves as the dielectric. CO_2 gas can flow through the tube. When a voltage is applied, filamentary plasma discharges are formed between the electrodes.**

then be directly used in conventional engine systems as they are similar to classical fossil fuels. This way, the solar or wind energy gets stored in liquid fuels that are easy to transport and easy to use. There is no need to develop new engines, keeping the implementation costs low. Once the fuels are burned, they are turned into CO_2 again, which can be collected and used again to create more fuels – the cycle is closed and remains CO_2 neutral.

The most energy costly step and so the bottleneck of this cycle is the dissociation of CO_2 into CO. To make the cycle energy efficient, this step must be optimised as much as possible. Energy efficiency also means cost efficiency and thus plays a major role in the financial aspect: in order to convince the energy industry to switch to a new technique, it has to be cheaper than the established ones.

Non-equilibrium plasma discharges – a pathway to efficient CO_2 conversion

One promising pathway to achieve efficient CO_2 conversion is the application of non-equilibrium plasma discharges as they open up chemical pathways that might otherwise remain unattainable. The particles (electrons, ions, neutral atoms and molecules etc.) in these discharges are not in thermal equilibrium: due to their light mass, the electrons pick up a lot of kinetic energy, while the plasma bulk remains cold. In recent years, two kinds of discharges have been studied in particular, both with their own advantages and disadvantages.

One is the dielectric barrier discharge (DBD) as shown in figure 2: two electrodes separated by a dielectric (quartz glass in this case), with a gap for a gas flow in between. When a voltage is applied, filamentary electric sparks spanning across the gap start creating a plasma. Parts of the CO_2 gas flowing through the discharge gap are then dissociated into CO. This type of discharge has been chosen for two main reasons: firstly, it can be run at atmospheric pressures, keeping the investment cost low as no expensive vacuum pumps are needed. Secondly, as this type of discharge was invented over 150 years ago, its properties are well known making it a suitable system for research. However, in experiments, DBDs have exhibited one major drawback: the gas conversion and energy efficiency amount up to only a few percent [5]. While suitable for fundamental research, for the time being, DBDs do not appear to be the way to achieve CO_2 conversion on a large scale.

The search for a more promising plasma source has led to so-called microwave discharges. For that purpose, an electromagnetic microwave is used to couple power into the CO_2, creating a plasma where CO is produced. Unlike DBDs, however, these discharges are operated at sub-atmospheric pressures in the order of a few hundred mbar, requiring some vacuum equipment like a simple rotary pump. Simulations have predicted a gas conversion rate of up to 80% and an energy efficiency of about 20% for these discharges – significantly higher than in the DBD [6]. First experiments have been performed to verify the predicted trend and have achieved conversion rates up to 30% [7]. Based on the model, it is assumed that the main driver of CO_2 dissociation in the discharge is the vibrational excitation of CO_2 molecules [6].

Two-photon absorption laser-induced fluorescence on CO

Pinpointing the mechanisms and conditions that lead to efficient CO_2 dissociation is the scientific key question. Optical diagnostic techniques are one way to obtain information about what is happening in the plasma. We are using a method called two-photon absorption laser-induced fluorescence (TALIF) to detect the produced CO. It makes use of the phenomenon of fluorescence, where atoms (or in our case molecules) are excited by light of one certain wavelength to emit light of a different wavelength. This phenomenon can be observed for example with UV black lights that make certain dyes or body paint 'glow in the dark'. The same happens in our experiment: UV light coming from a laser gets absorbed by the CO, which then emits light in the visible range of blue to green colour; our measured TALIF spectrum of CO is given in figure 5 and is in good agreement with literature [8]. The amount of emit-

TALIF on CO – theory and experiment

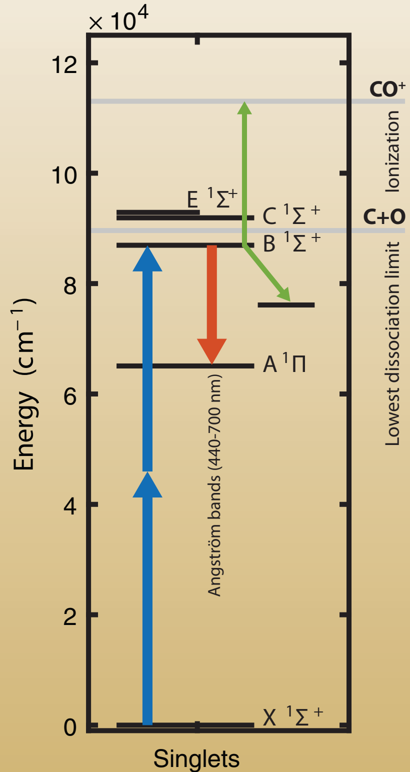

Figure 3 The excitation scheme of CO. Two photons of 230 nm excite the molecule from the electronic ground state to the second excited state. From there, it relaxes to the first excited state emitting light at 400-700 nm.

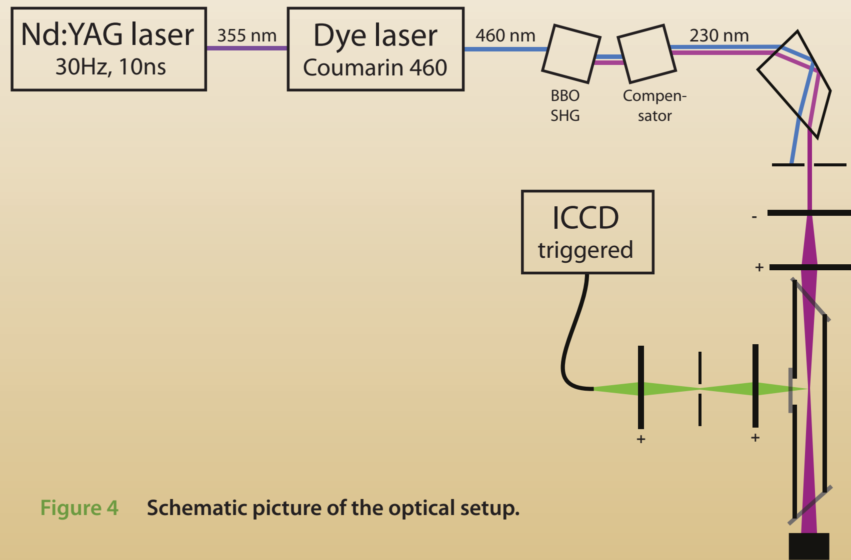

Figure 4 Schematic picture of the optical setup.

In order to obtain fluorescence emission from CO molecules, they must be excited to higher energy levels. Figure 3 shows the excitation scheme applied in this experiment: the molecules get excited from the ground state $X^1\Sigma^+$ to the second excited state $B^1\Sigma^+$. In the case of TALIF, two photons are absorbed (2 × 230 nm in this case) instead of one as in conventional laser-induced fluorescence (LIF); this is a way to reach higher energies than would otherwise be difficult or even impossible to achieve with the available laser systems. After excitation, the molecules relax to the first excited state $A^1\Pi$, emitting a photon in the so-called Ångstrom band of 400-750 nm (red arrow) that is subsequently detected. The TALIF signal intensity is directly proportional to the number density of CO molecules in the ground state. The molecules in the excited state may also lose their energy, e.g. due to collisions, without emitting fluorescence, this effect is called quenching (green arrows).

The optical setup of the experiment used to realise TALIF is depicted in figure 4: a frequency-tripled Nd:YAG laser is used to pump a dye laser. To achieve the necessary 230 nm the light emitted by the Coumarin 460 dye at 460 nm is doubled by a BBO crystal. A Pellin-Broca prism is used to separate the 230 nm photons from the remaining 460 nm. The laser beam is then focused into a reference cell or plasma reactor. The induced fluorescence is detected at a 90° angle to the laser beam; it is focused onto an optical fibre that is connected to a triggered ICCD camera and a spectrograph. In this way the fluorescence spectrum can be recorded and evaluated.

ted light (integrated over the peaks) gives information about how much CO has been produced. In this way, the conversion efficiency of the plasma discharge can be studied with high resolution in space (the spatial resolution is defined by the size of the laser spot) as well as in time (the pulse rate of the laser defines the temporal resolution). It is also possible to spread the laser beam into a sheet of laser light to collect two-dimensional information from the measurements.

However, there is one major challenge to deal with: so-called quenching effects. Quenching is a collective term for all kinds of effects that take the energy from the excited molecule before it can emit the fluorescence; these effects are often caused by collisions with other particles but ionisation or dissociation also play a role. This means that higher pres-

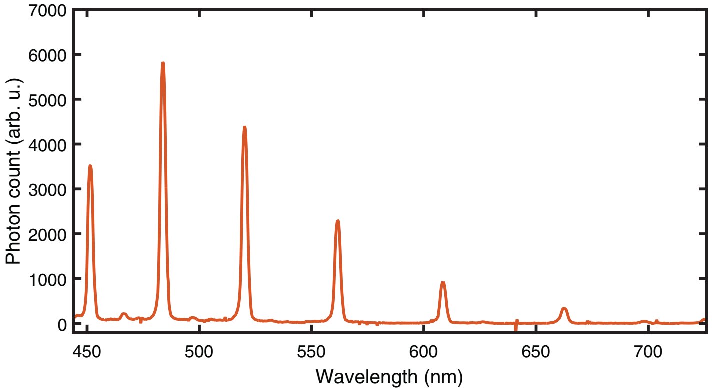

Figure 5 Measured TALIF spectrum of CO.

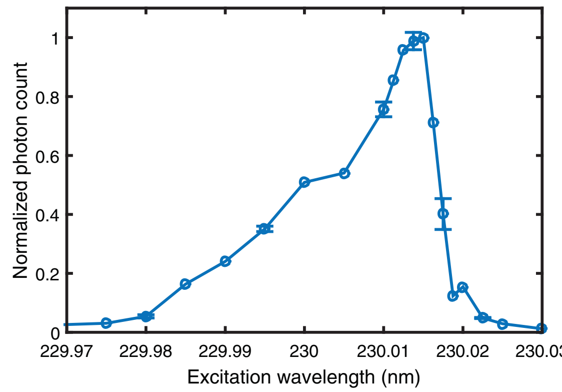

Figure 6 Total CO fluorescence emission plotted against the excitation wavelength. The optimum excitation wavelength was found to be 230.015 nm. All measurements were in pure CO at a pressure of 100 mbar.

sures, and so higher collision frequencies between particles in the plasma, raise the quenching rate; lower pressures can therefore be favourable for the application of laser-induced fluorescence.

The quenching rates in an experiment are not constant, they depend for example on the different species in the gas and their partial pressures. It is very challenging to quantify these effects and thus to quantify the TALIF signal. That is why laser-induced fluorescence is rather used for relative than absolute measurements of species densities. In our experiment, we plan to use infrared laser absorption spectroscopy to help us quantify the TALIF signal.

Characterisation of the system

In order to fully understand the fluorescence spectrum, it needs to be characterised for different experimental conditions. The first step is to find the optimum excitation wavelength for the laser. For this, a wavelength scan is performed with our tuneable dye laser on a reference cell filled with 100 mbar of pure CO. The fluorescence intensity is recorded and plotted against the laser wavelength as shown in figure 6. The optimum laser wavelength was found at 230.015 nm and is in good agreement with literature [8]. Using this wavelength, the next step is to investigate the pressure range in which a reasonable TALIF signal can be obtained. Two 'competing' effects make up the pressure dependence of the TALIF signal intensity: obviously, if more molecules are present (i.e. high number density), more fluorescence will be emitted; the fluorescence intensity increases linearly with the number density. On the other hand, a higher number density also means higher pressure and more collisions within the gas. The excited molecules are being quenched without emitting the desired fluorescence; this effect decreases the signal exponentially. The combination of both effects can be observed in figure 7 where the total intensity is plotted against the CO pressure in the reference cell: for pressures below ~250 mbar, the signal increases with pressure, while for higher pressures, the quenching becomes dominant and the TALIF signal starts to decrease. However, in further experiments it has been observed, that collisions between CO and CO_2 (which would be the predominant case in a DBD) cause far weaker quenching, leading to higher TALIF signals that are easier to detect.

Detecting CO for solar fuel production

First measurements on CO_2 conversion in a plasma discharge have been

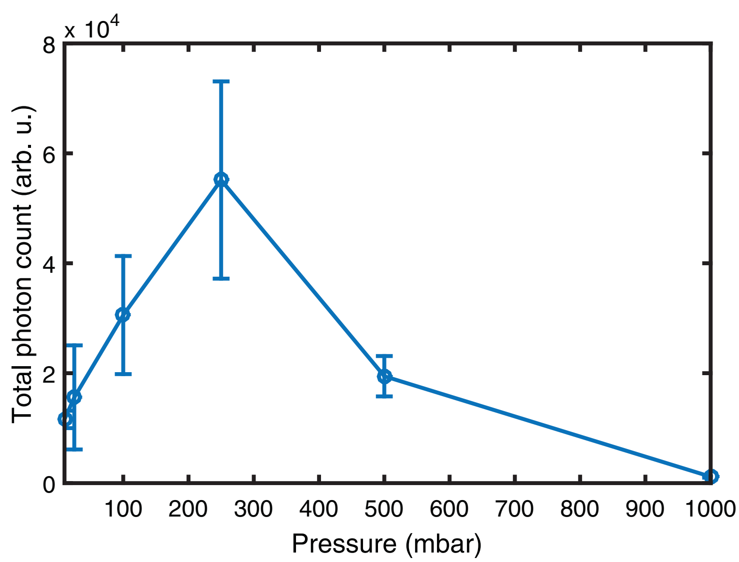

Figure 7 Total CO fluorescence emission plotted against the CO pressure.

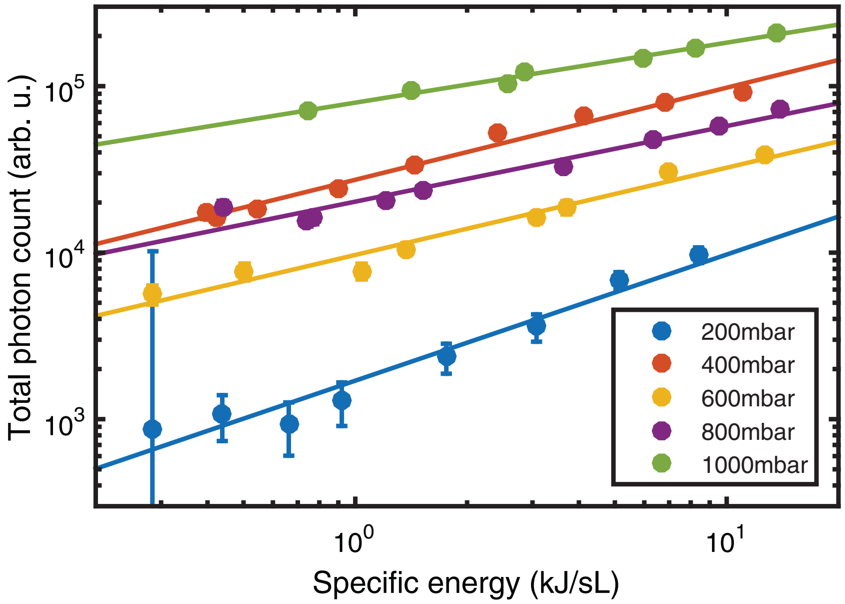

Figure 8 **Total CO fluorescence emission of a DBD plotted against the specific energy input (i.e. the energy input per molecule) for different pressures. The working gas for the discharge was CO_2, all detected CO is a product of the dissociation process.**

performed. For this, a similar DBD as depicted in figure 2 has been used. Measurements were taken for different pressures (200-1000 mbar) and different powers. The results are shown in figure 8, where the total photon count (a measure for the number density of produced CO) is plotted against the specific energy input (i.e. the energy input per molecule) in kilojoule per standard litre on a log-log scale. It is shown that the CO production increases with the energy input. As it is difficult to quantify the TALIF signal, it is not possible to obtain a conversion efficiency from this measurement. However, previous measurements under similar conditions have shown a conversion efficiency of 1% or below.

The aim of this experiment was to see if the TALIF diagnostic is suitable for solar fuel research. The linear trend on a log-log scale that can be seen in figure 8 is in agreement with our expectations from previous experiments [5], showing that it can be used to study the CO production. The effects of quenching, however, cannot be neglected: the slopes of the linear fits in the graph should be about the same, but they decrease with increasing pressure. The fluorescence signal is lost due to quenching.

Conclusions

CO_2 can be converted to CO by using non-equilibrium plasma discharges. To do this efficiently, it is important to understand the various physical and chemical processes happening in the plasma. To study these processes and their individual influence, a TALIF diagnostic system has been realised and tested. First measurements show that it is suitable for solar fuel research, but also that quenching effects have to be characterised and taken into account. Future measurements will help understanding how to efficiently dissociate CO_2 into CO so the process can be used to store and transport surpluses of clean wind and solar energy in the form of fuel.

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