

# Vibrational kinetics of CO<sub>2</sub> in non-thermal plasma

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**Abstract:** In this abstract we present results on a diagnostic study of the vibrational kinetics of CO<sub>2</sub> molecules in a non-thermal plasma. Time-resolved Fourier Transform absorption spectroscopy and spontaneous Raman scattering is used to obtain information about the ro-vibrational density distributions in the electronic ground state of CO<sub>2</sub> in a pulsed glow discharge. During the active part of the plasma pulse a clear non-equilibrium is observed between the rotational and the  $\nu_3$ , and the  $(\nu_1, \nu_2)$  and  $\nu_3$  vibrational density distributions.

**Keywords:** CO<sub>2</sub> dissociation, glow discharge, vibrational excitation, infrared absorption, Raman spectroscopy

## 1. Introduction

The fraction of energy used world wide originating from renewable resources is increasing steadily. At the end of 2016 the renewable energy share of global electricity production was estimated at 24.5%,[1] while five years earlier, at the end of 2011 the share was estimated at 20.3%.[2] Meanwhile, our society is build on the consumption of fossil fuels to, e.g., produce heat in household boilers or stoves, mechanical work in vehicle engines, or electrical energy in power plants. The output of renewable sources is predominantly in the form of electrical energy and therefore it is necessary to advance the implementation of an electricity-based society. That this transition is already in progress, becomes clear from e.g. the upcoming popularity of electric cars [1] and the recent agreement of the Dutch government to remove natural gas connections from existing houses and to build new houses connectionless. [3] However, the mere replacement of fossil-fuel based equipment with their electrical counterparts is not sufficient, as one of the bigger challenges inherent to an increasing share of renewable energy is the intermittency problem.[4]

The intermittency problem for day-to-day energy demand is visualized well in Fig. 1. Here the net production of solar and wind power is shown in Germany for the month of August 2017, together with the electrical power demand.[5] Day and night cycles are clearly visible from the drop in demand when the evening falls, though the demand decreases rarely below 60% of the maximum. On the other hand, solar energy is only produced during daytime, and the amount of wind energy varies strongly over the full month. Additionally, there is a seasonal imbalance: significantly more solar energy is produced during long summer days than during the darker winter, while in winter there is an increased electrical energy demand. Assuming that the energy production and consumption in Germany is representative for other

countries, it should be clear that when renewable energy sources should become predominant in the total energy production, we need a solution to match short- and long-term production and demand.

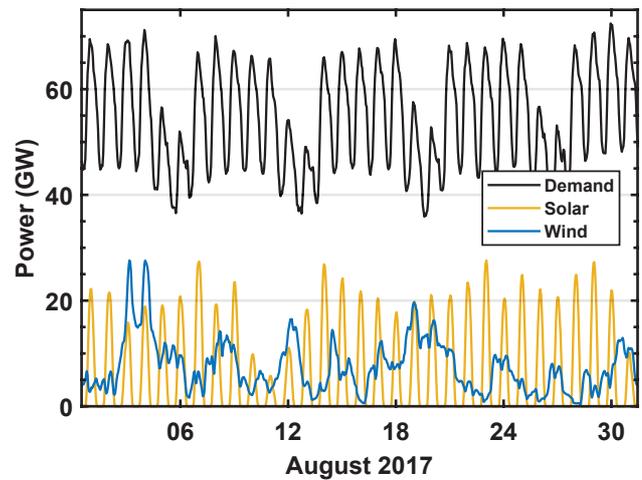


Fig.1. German day-to-day energy demand in August 2017

This solution consists of the storage of an energy surplus during peak production, which then can be addressed when the demand cannot be met. A noteworthy and very efficient method do accomplish this, is pumped hydroelectric storage (PHS) where the energy is stored in the potential energy of water by simply pumping it to a higher-up reservoir and releasing it through turbines when the energy is needed. Efficiencies of this technique can even be greater than 80%.[6] PHS is being used at many locations around the earth, but the amount of water and/or height difference that is needed to make this a viable option for solving the intermittency problem makes this not a very practical solution for every location.

Where electricity can directly be used to charge batteries or to create hydrogen by the electrolysis of water, the work presented here involves the development of a method to utilize electrical energy for the creation of hydrocarbon fuels from their core raw material, CO<sub>2</sub>. The dissociation of CO<sub>2</sub> is a key part in this process. In this process CO<sub>2</sub> is initially harvested from an external source, such as the exhausts of factories. Then, electrical energy surpluses of renewable sources are used to reduce CO<sub>2</sub> to CO. In the next step, (a source of) hydrogen is added to create a syngas mixture, which is further converted to hydrocarbons, or solar fuels by the Fischer-Tropsch process. The Fischer-Tropsch process is a common method in industry to create liquid hydrocarbons from syngas (yet often created from e.g. coal or natural gas). [7] The combustion of solar fuels returns the initial CO<sub>2</sub> and releases the renewable energy that is used to create it. In the ideal case, a CO<sub>2</sub>-neutral energy cycle is created.

It should be noted that this cycle works most efficiently if the CO<sub>2</sub> does not leave the system and is reused for the next cycle. It is appealing to use solar fuels in vehicles as airplanes and cargo ships where batteries are not a serious option due to their weight, but then the produced CO<sub>2</sub> is generally emitted in the open air. In this case, the energy cost of harvesting new CO<sub>2</sub> should be added to the overall efficiency of the storage and consumption procedure, which is not yet very favorable. [8] However, in the long term, this might still be a solution for enabling the use of these vehicles when fossil fuels are no longer an option. Until then the main application of this cycle would be in a dedicated plant, presumably close to the renewable energy source, where the solar energy is converted to solar fuel during the day, and back to electricity at night, as well as seasonal storage to match supply and demand in summer and winter.

The reduction of CO<sub>2</sub> to CO is energy expensive, and is therefore a key step within the solar fuel cycle: an efficient dissociation is essential for an efficient cycle. A preferred dissociation method, which is finding much attention, makes use of the non-thermal nature of plasma, or ionized gas. Exploiting this phenomenon, the most efficient method to reduce CO<sub>2</sub> to CO is in literature proposed to be by selectively exciting the asymmetric stretch vibration of CO<sub>2</sub>, designated as  $\nu_3$ . In this so-called vibrational ladder-climbing process, the distance between CO and O becomes ever larger, after which at 5.5 eV dissociation happens without significant heat formation.

## 2. Diagnostics and plasma source

In this abstract we discuss the development of two diagnostics to increase our current level of understanding of the vibrational kinetics within CO<sub>2</sub> discharges, with the intention to ultimately contribute to a controlled and efficient dissociation process. The diagnostic techniques are (1) time resolved *in situ* Fourier transform infrared (FTIR) spectroscopy and (2) spatiotemporally resolved *in situ* rotational Raman spectroscopy. The resulting line-of-

sight averaged transmittance spectra of (1) are recorded with a spectral resolution of 0.2 cm<sup>-1</sup> and a temporal resolution of 10 μs to be able to track the evolution of different (pulsed) plasmas. Additionally, an analysis algorithm has been developed to be able to compute the transmittance through a non-thermal medium of CO<sub>2</sub>, CO, and O<sub>2</sub>. The parameters of interest that are acquired from analysis are:  $T_{rot}$ , the rotational temperature;  $T_3$ , the temperature of the asymmetric stretch vibration of CO<sub>2</sub>;  $T_{1,2}$ , the combined temperature of the other two CO<sub>2</sub> vibrations;  $T_{CO}$ , the vibrational temperature of CO; the conversion of CO<sub>2</sub> to CO (i.e. the number densities of both molecules).

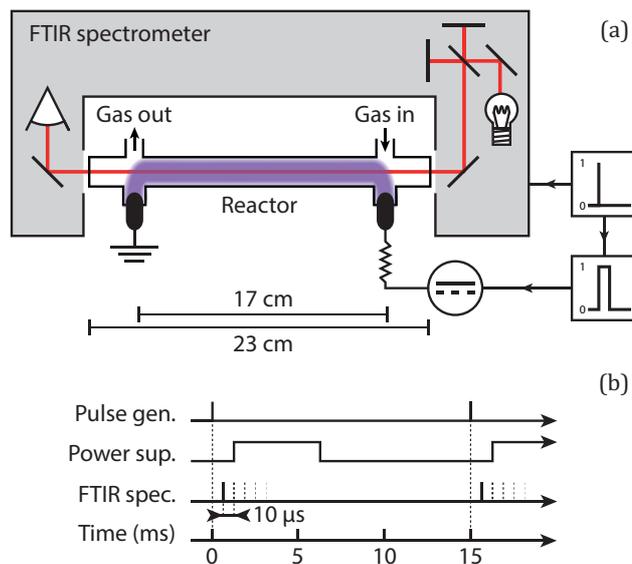


Fig. 1. The FTIR setup (a) and timing sequence (b) for time resolved measurements in the pulsed glow discharge

For diagnostic (2) a laser setup is built, employing a 100Hz Nd:YAG laser which is frequency doubled to 532 nm, and an algorithm is developed to measure and analyse spatiotemporally resolved (100x100x100 μm<sup>3</sup>, 10ns resolution) pure rotational Raman spectra. Before Raman scattered light can be recorded, the intense Rayleigh scattered light has to be rejected which is done by implementing a volume Bragg grating (VBG) as an ultra-narrow-band notch filter (OD 3 to 4, 7 cm<sup>-1</sup> full-width at half-maximum). [9] The parameters of interest that result from analysis are the rotational temperature, the number densities of CO<sub>2</sub>, CO, and O<sub>2</sub>, accompanied by an indication of the vibrational temperatures of CO<sub>2</sub>. The latter is acquired through the nuclear degeneracy of CO<sub>2</sub> which is dependent on the vibrational state of the molecule, and which is expressed in the ratio between even and odd numbered scattering peaks.

The plasma under study is a CO<sub>2</sub> glow discharge, operated at pressures between 1.3 mbar and 6.7 mbar with a plasma current between 10 mA and 50 mA. The motivation of studying a glow discharge is its homogeneity (useful for line-of-sight measurements), its

capability of vibrational excitation (known from the CO<sub>2</sub> laser community), and its suitability to be numerically modeled (good for extended analysis and model validation). The vibrational kinetics have been studied by pulsing the plasma with a typical pulse cycle of 5-10 ms on-off. Note that the residence time of the gas in the order of seconds is much larger than the cycle period, hence the gas composition at the start of every pulse is a combination of CO<sub>2</sub> and its dissociation products from previous pulses: CO, O<sub>2</sub>, and possibly O.

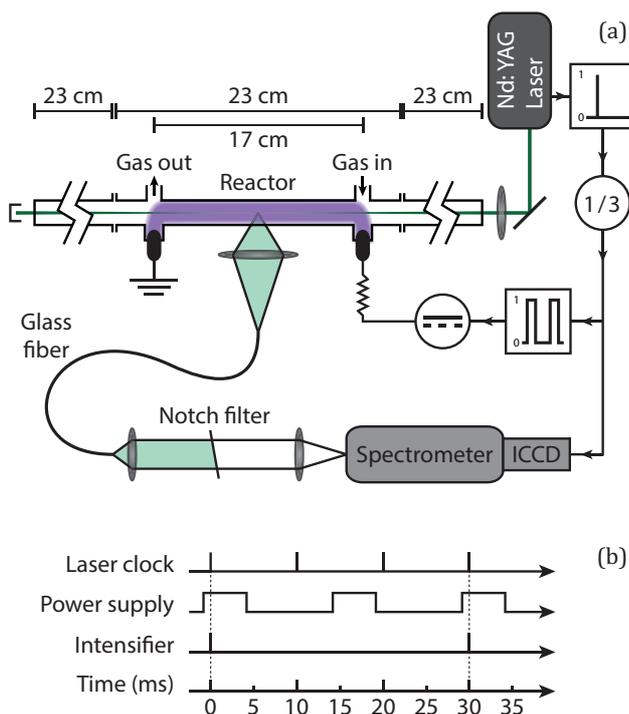


Fig. 2. The laser setup (a) and timing sequence (b) for spatiotemporally resolved Raman measurements

### 3. Results

FTIR and Raman measurements show that  $T_3$  and  $T_{CO}$  rapidly increase within the first ms of the discharge for several hundreds of Kelvin, after which they stabilize during the remainder of the pulse.  $T_{rot}$  slowly increases with tens of Kelvin during the discharge, reaching higher values for larger pressures and currents.  $T_{1,2}$  follows the same trend as  $T_{rot}$ , exceeding it with a few tens of Kelvin. In the afterglow, the vibrational temperatures decay to the rotational temperature, which in turn slowly decays to initial value. During the whole cycle, the temperatures are ordered as  $T_{CO} \geq T_3 \geq T_{1,2} \geq T_{rot}$ . With rotational Raman spectroscopy (2) it is shown that apart from a longitudinal homogeneity in temperatures, the glow discharge is very homogeneous in gas composition as well, despite using pure CO<sub>2</sub> as initial gas. It is argued that the homogeneity is caused by gas mixing, stimulated by diffusion as well as expansion and contraction throughout the plasma cycle. The demonstrated homogeneity directly justifies the

assumption made for FTIR analysis, of a uniform line-of-sight of absorption. Within the conditions under study, the exponential decay rate of  $T_3$  to  $T_{rot}$  in the afterglow is purely a function of  $T_{rot}$ . Pressure and gas composition (varying fractions of CO, O<sub>2</sub>, and (presumably) O) do not appear to play an important.

In the active discharge, the dependence of  $T_3$  elevation over  $T_{rot}$  on pressure and current is studied for constant  $T_{rot}$ . It is found that for constant current, the elevation scales inversely to pressure, while at constant pressure, an increasing current showed an increase of  $T_3$ . However, the latter relation is difficult to quantify, as there is a strong relation between current and CO concentration, while CO is shown to have a strong stimulating effect on  $T_3$ . [10, 11] For the majority of the active discharge period the elevation of  $T_3$  above  $T_{rot}$  decreases significantly for increasing pressure. Nonetheless, no clear relation is observed between CO concentration and pressure. Therefore, a relation between  $T_3$  elevation and CO formation could not be confirmed. [11] Nonetheless, promising conversion peaks in the near afterglow are observed. A future study can reveal whether this is related to non-thermal ladder-climbing, which is a known effect in e.g. the afterglow of N<sub>2</sub> discharges.

### 4. Conclusions

The combined results provide ample experimental foundation to expand our knowledge on CO<sub>2</sub> vibrations and dissociation, especially through comparison with numerical models. Through a collaboration of the experimental groups in Paris (LPP, Guaitella) and Eindhoven (PMP, Engeln), and the modeling group of Guerra in Lisbon, over the past few years, progress has been made on the modeling of the non-equilibrium kinetics in pure CO<sub>2</sub> plasma [12, 13]. In the further development of the models interactions between CO<sub>2</sub>, CO, O<sub>2</sub>, O, and de-excitation at the reactor wall will be included.

Not discussed in this abstract, but the versatility of the developed Raman laser setup has been demonstrated on a pulsed kHz driven He jet in open air and reported on in [14]. It is shown that the VBG notch filter works satisfactorily for the crucial rejection of Rayleigh scattering for Thomson spectroscopy, too. The scattering analysis algorithm is extended with Thomson theory, to acquire electron densities and temperatures.

### 4. Acknowledgements

This work is partly supported by NWO, under project numbers 713.013.003 and 15325, and partly by LABEX Plas@par receiving financial aid managed by the Agence Nationale de la Recherche under the reference ANR-11-IDEX-0004-02.

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