Vibrational excitation kinetics of CO_2 in a pulsed glow discharge

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Excitation of the asymmetric stretch vibrational mode of CO_2 is believed to be crucial for an efficient plasma assisted dissociation of CO_2 to CO. Using time-resolved *in situ* Fourier Transform Infrared spectroscopy we gain insight in the vibrational dynamics of CO_2 in a pulsed glow discharge (5/10 ms on/off). FTIR measurements in a discharge at 5 mbar and 50 mA reveal excitation of the asymmetric stretch mode of CO_2, showing a vibrational temperature of 913 K versus a rotational temperature of 437 K, at 0.5 ms after plasma-on. Rotational temperatures measured using spatially and time-resolved rotational Raman spectroscopy correspond well to the FTIR results and show no significant temperature changes over the longitudinal axis of the reactor.

1. CO_2 reduction for renewable energy storage

Efficient reduction of CO_2 to CO is a key step in the process of storing renewable energy in the form of hydrocarbon fuels. This dissociation process is believed to be most efficient when selectively exciting the asymmetric stretch mode of CO_2. We study the vibrational dynamics of CO_2 by performing *in situ* Fourier Transform Infrared (FTIR) spectroscopy, as well as rotational Raman spectroscopy on a pulsed glow discharge. Since the discharge mechanisms of such a plasma are well known, a glow discharge is particularly suitable for a fundamental study on vibrational energy levels.

2. Setup and analysis for vibrational kinetics

The cylindrical plasma reactor (23 cm length, 2 cm diameter) is operated under flowing conditions (7.4 sccm CO_2) in the millibar range, with a pulsed 10–50 mA plasma current at 5/10 ms on/off. To study the vibrational dynamics by IR absorption, the reactor is positioned inside the sample compartment of an FTIR spectrometer (Bruker, Vertex 70). The step-scan operation mode allows the recording of spectra with a temporal resolution of 10 µs, well below the millisecond timescale of the plasma.

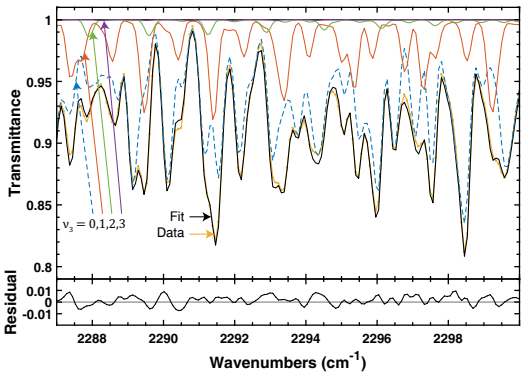

Fig. 1: IR transmittance data and fit of CO_2 at 0.5 ms after plasma-on, at 50 mA and 6 mbar. Absorptions from transitions with ν_3 = 0, 1, 2, and 3 are shown separately.

For the analysis we developed an algorithm to calculate and fit the transmittance spectra of CO_2 and CO, using the HITEMP-2010 database. Fit parameters include the rotational temperature, T_{rot}, the temperature of the fermi-coupled symmetric stretch (ν_1) and bending (ν_2) modes of CO_2, $T_{1,2}$, and the temperature of the asymmetric (ν_3) mode, T_3.

3. Analysis results, related to Raman spectroscopy

Fig. 1 shows a fit at 0.5 ms after plasma-on, giving T_{rot} = 437 K, $T_{1,2}$ = 459 K, and T_3 = 913 K. Hence, a clear asymmetric stretch excitation of CO_2 is observed, with respect to the other temperatures. Details on a kinetic model used to study these experiments are given in [1]. Furthermore, details on the important role and kinetics of O atoms in these discharges are given in [2]. Additional experiments are planned, to study the link between the measured vibrational excitation and CO_2 dissociation.

Time and spatially-resolved rotational Raman measurements are done to study the assumption made in the FTIR analysis, i.e. no temperature variations along the line-of-sight. Spatially, the measured T_{rot} does not significantly change, while temporally, it corresponds well to the IR fits. This affirms the validity of both measurement techniques and the reliability of vibrational temperatures resulting from the infrared absorption experiments.

4. References

[1] T. Silva *et al.*, abstract submitted to ICPIG 2017.
[2] A.S. Morillo-Candas *et al.*, abstract submitted to ICPIG 2017.