Supporting Information: CO₂ Conversion in a Gliding Arc Plasmatron: Elucidating the Chemistry through Kinetic Modelling

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Detailed description of the model

The 0D model is based on solving equation (1):

$$\frac{\partial n_s}{\partial t} = \sum_{i=1}^{j}[(a_{s,i}^R - a_{s,i}^L)R_i] \tag{1}$$

where n_s is the density of species s (in m^{-3}) , j the total number of reactions, $a_{s,i}^L$ and $a_{s,i}^R$ the stoichiometric coefficients at the left hand side and right hand side of the reaction and R_i the rate of reaction (in m^{-3} s^{-1}), given by:

$$R_i = k_i \prod_s n_s^{\alpha_{s,i}} \tag{2}$$

where k_i is the rate constant (in m^3 s^{-1} or m^6 s^{-1} for two-body or three-body reactions, respectively). The rate constants of the heavy particle reactions are either constant or dependent on the gas temperature, whereas the rate constants of the electron impact reactions depend on the electron temperature T_e or the reduced electric field E/N (i.e., the electric field E divided by the number density of all neutral species N, usually expressed in Td = 10^{-21} V m^2). The rate constants of the electron impact reactions are generally calculated according to the following equation:

$$k_i = \int_{\varepsilon_{th}}^{\infty} \sigma_i(\varepsilon)v(\varepsilon)f(\varepsilon)d\varepsilon \tag{3}$$

with ε the electron energy (usually in eV), ε_{th} the minimum threshold energy needed to induce the reaction, $v(\varepsilon)$ the velocity of the electrons (in m s^{-1}) , $\sigma_i(\varepsilon)$ the cross section of collision i (in m^2), and $f(\varepsilon)$ the (normalized) electron energy distribution function (EEDF; in eV^{-1}) calculated using a Boltzmann solver.

In this work we use the ZDPlaskin code to solve the balance equations (1) of all species, which also has a built-in Boltzmann solver, called BOLSIG+ [1], to calculate the EEDF and the rate constants of the electron impact reactions [2] based on a set of cross sections, the plasma composition, the gas temperature and the reduced electric field (E/N). The electric field (E; in V m^{-1}) is calculated from a given power density, using the so-called local field approximation [3]:

$$E = \sqrt{\frac{P}{\sigma}} \tag{4}$$

with P the input power density (in W m^{-3}) and σ the plasma conductivity (A V^{-1} m^{-1}). The plasma conductivity is estimated at the beginning of the simulations as [3]:

$$\sigma = \frac{e^2 n_{e,init}}{m_e v_m} \tag{5}$$

with e the elementary charge (1.6022x10^{-19} C), $n_{e,init}$ the initial electron density (in m^{-3}), m_e the electron mass (9.1094x10^{-31} kg) and v_m the collision frequency (in s^{-1}) calculated using BOLSIG+ [1]. During the simulation the plasma conductivity is calculated as [3]:

$$\sigma = \frac{e v_d n_e}{\left(\frac{E}{N}\right)_{prev} n_0} \tag{6}$$

with v_d the electron drift velocity (in m s^{-1}), which is calculated using BOLSIG+ [1] implemented in ZDPlaskin, and $\left(\frac{E}{N}\right)_{prev}$ the reduced electric field at the previous time step (in V m^2).

The balance equation for the gas temperature T_g (in K) is also solved:

$$N \frac{\gamma k}{\gamma - 1} \frac{dT_g}{dt} = P_{e,el} + \sum_j R_j \Delta H_j - P_{ext} \qquad (7)$$

where $N = \sum n_i$ is the total neutral species density, γ is the specific heat ratio of the total gas mixture, k is the Boltzmann constant (in J K^{-1}), $P_{e,el}$ is the gas heating power density due to elastic electron-neutral collisions (in W m^{-3}), R_j is the rate of reaction j (in m^{-3} s^{-1}), ΔH_j is the heat released (or consumed when this value is negative) by reaction j (in J) and P_{ext} is the heat loss due to energy exchange with the surroundings (in W m^{-3}). The specific heat ratio of the total (ideal) gas mixture is calculated from the specific heat ratios of the individual species in the model, γ_i, using the formula:

$$N \frac{\gamma}{\gamma - 1} = \sum_i n_i \frac{\gamma_i}{\gamma_i - 1} \qquad (8)$$

where n_i are the densities of the individual species i. The individual specific heat ratios, γ_i, can be calculated from the specific heat capacity at constant pressure $c_{p,i}$ (in J K^{-1} kg^{-1}) using the relation:

$$c_{p,i} = \frac{\gamma_i}{\gamma_i - 1} \frac{k}{M} \qquad (9)$$

where k is the Boltzmann constant and M is the molar weight of CO_2 (in kg). Since the vibrational levels are treated as separate species, only the heat capacity due to translational and rotational degrees of freedom and, in the case of CO_2, also the heat capacity due to the symmetric vibrational modes, which are not treated as individual species, should be taken into account [4,5]. A classical partitioning between the translational and rotational degrees of freedom is assumed, which gives a value for the specific heat ratio, at room temperature and above, of 1.67 for the atomic species and 1.40 for the diatomic molecules (CO, O_2 and C_2).

For O_3, a value of 1.27 was taken [4,6]. Details about the calculation of the total heat capacity and the resulting specific heat ratio for CO_2, calculated using equation (9), can be found in [4].

Vibrational levels included in the model

Table S.1: Notation of the different vibrational levels included in the model with their corresponding state and energy, following the model developed in [7].

Notation	States	Energy (eV)
Ground state (g)	(000)	0.00
Va	(010)	0.08
Vb	(020)+(100)	0.17
Vc	(030)+(110)	0.25
Vd	(040)+(120)+(200)	0.33
V1	(001)	0.29
V2	(002)	0.58
V3	(003)	0.86
V4	(004)	1.14
V5	(005)	1.43
V6	(006)	1.70
V7	(007)	1.97
V8	(008)	2.24
V9	(009)	2.51
V10	(0010)	2.77
V11	(0011)	3.03

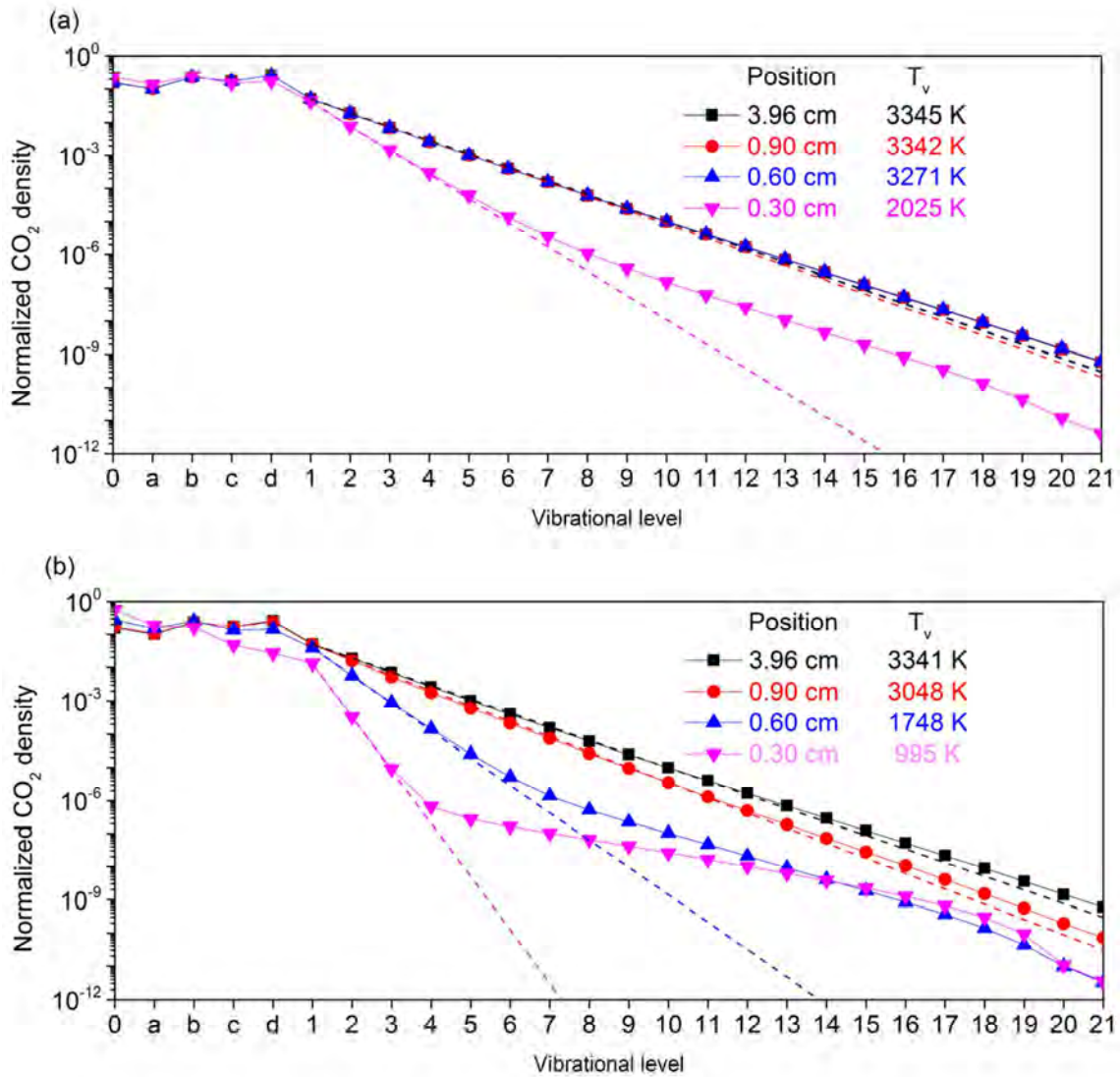|		
V12	(0012)	3.29
V13	(0013)	3.55
V14	(0014)	3.80
V15	(0015)	4.04
V16	(0016)	4.29
V17	(0017)	4.53
V18	(0018)	4.77
V19	(0019)	5.01
V20	(0020)	5.24
V21	(0021)	5.47

Calculated vibrational distribution functions

Figure S.1: Vibrational distribution functions (VDFs) of CO_2 at a flow rate of 10 L/min (a) and 22 L/min (b) for a plasma power of 650 W, at different positions in the arc column. The vibrational temperature is also indicated in the legend for each case. It is calculated from the slope, indicated with dashed lines.

Effect of flow rate on the CO$_2$ conversion and energy efficiency
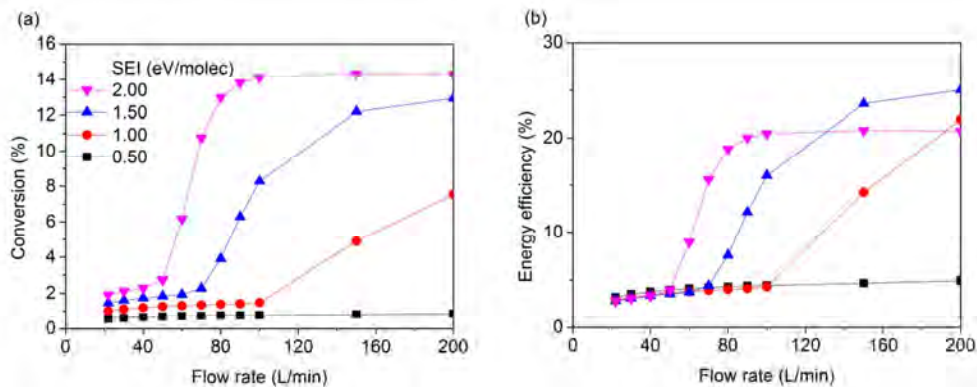
Figure S.2: CO$_2$ conversion (a) and energy efficiency (b) as a function of flow rate for different SEI values and at a maximum gas temperature of 500 K. Note that for each curve the power will also increase with the flow rate, to keep the SEI constant.
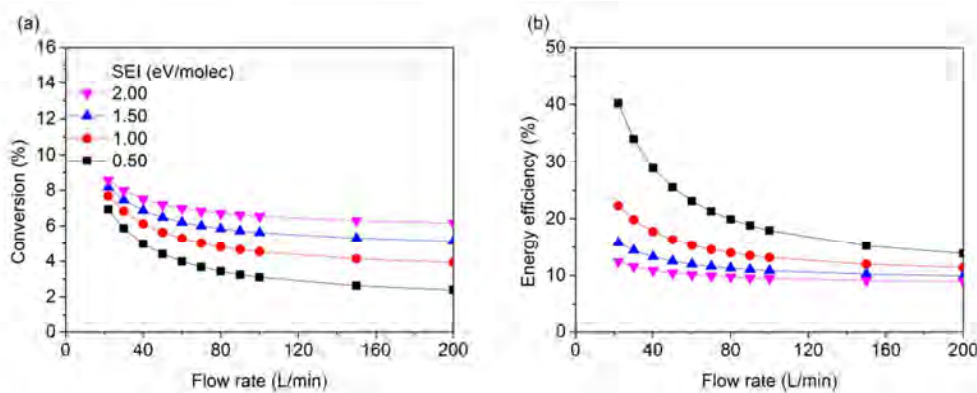
Figure S.3: CO$_2$ conversion (a) and energy efficiency (b) as a function of flow rate for different SEI values and at a maximum gas temperature of 3500 K.

Contribution of the different vibrational levels towards dissociation
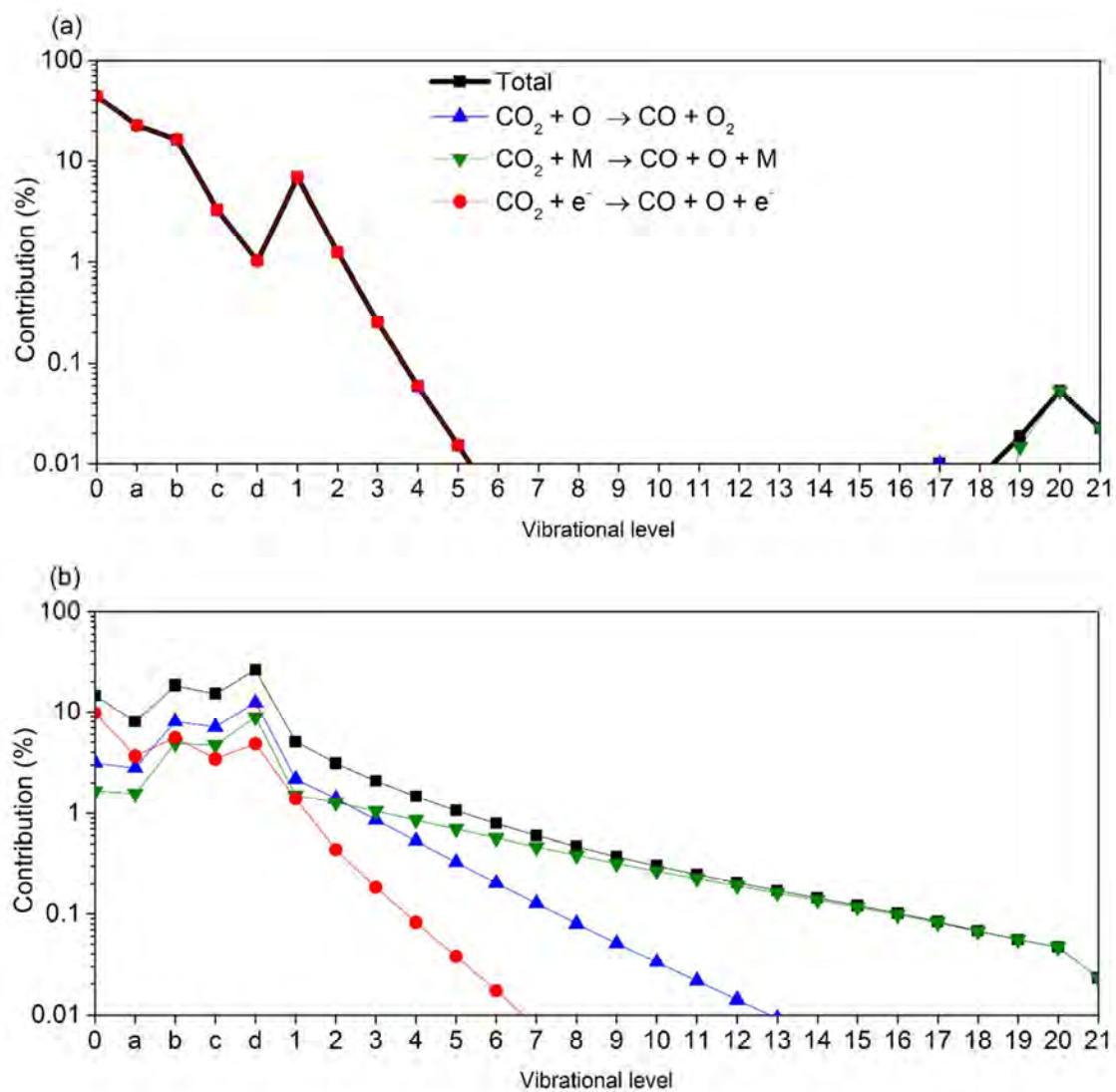
Figure S.4: Contribution of the different vibrational levels of CO_2 to the total dissociation of CO_2 at a flow rate of 22 L/min and a maximum gas temperature of 500 K (a) and 3500 K (b) at a SEI of 2.5 eV/molec.
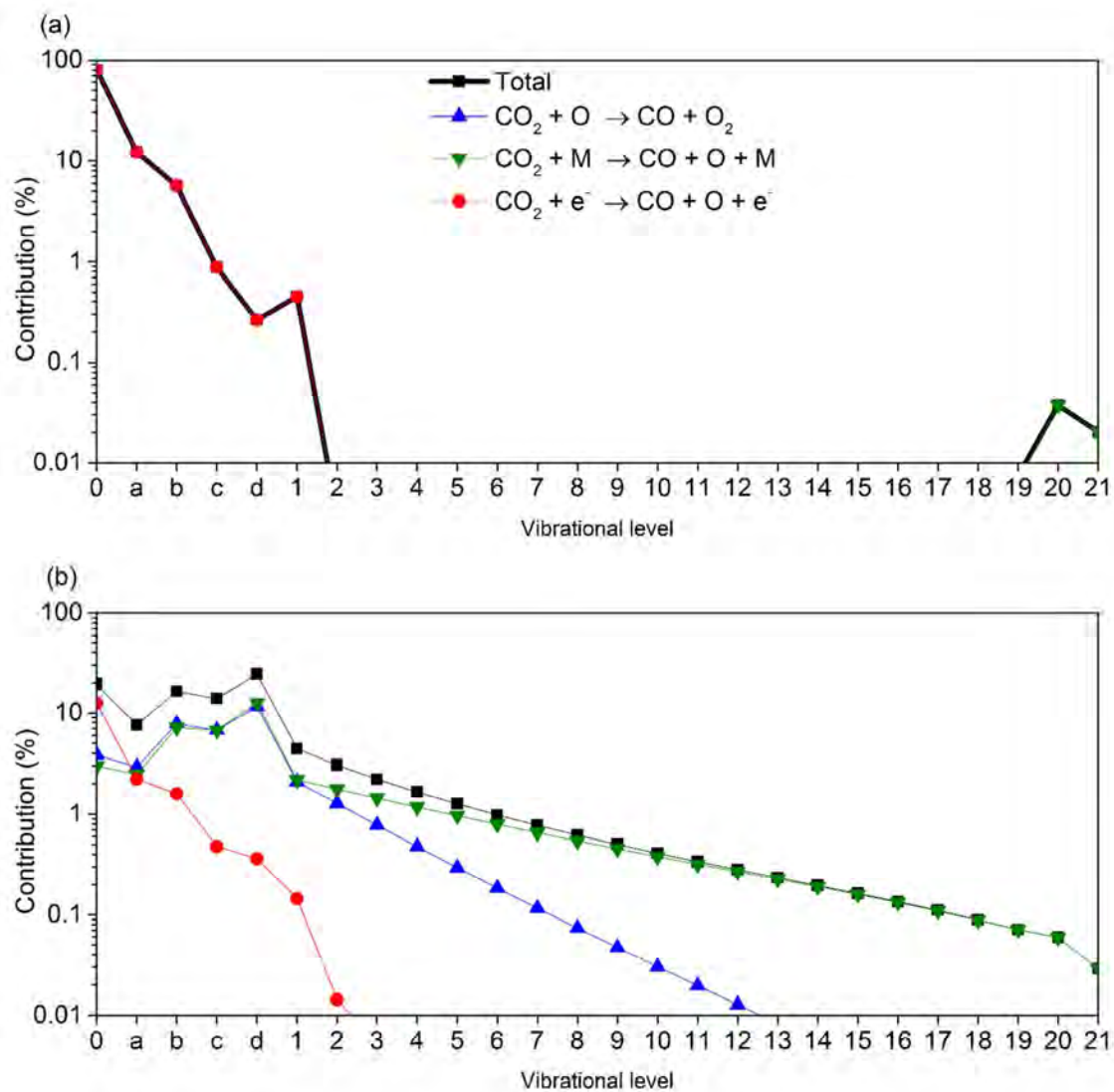
Figure S.5: Contribution of the different vibrational levels of CO_2 to the total dissociation of CO_2 at a flow rate of 22 L/min and a maximum gas temperature of 500 K (a) and 3500 K (b), at a SEI of 0.2 eV/molec, where the maximum energy efficiency is reached (see Figure 8(b) from the main text).
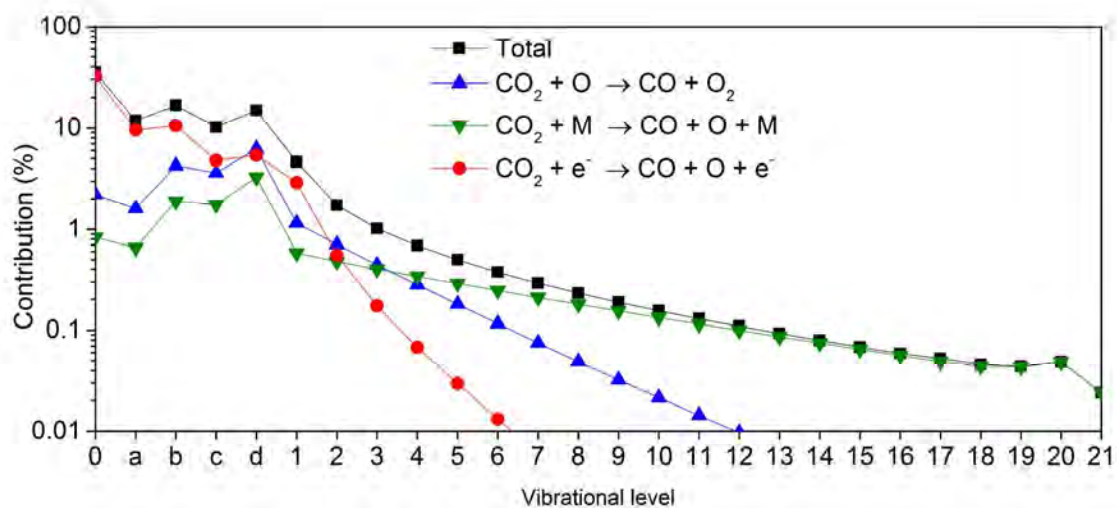
Figure S.6: Contribution of the different vibrational levels of CO_2 to the total dissociation of CO_2 at a flow rate of 200 L/min and a maximum gas temperature of 3500 K, at a SEI of 0.34 eV/molec, where the maximum energy efficiency is reached in case of 3500 K (see Figure 8(d) from the main text).
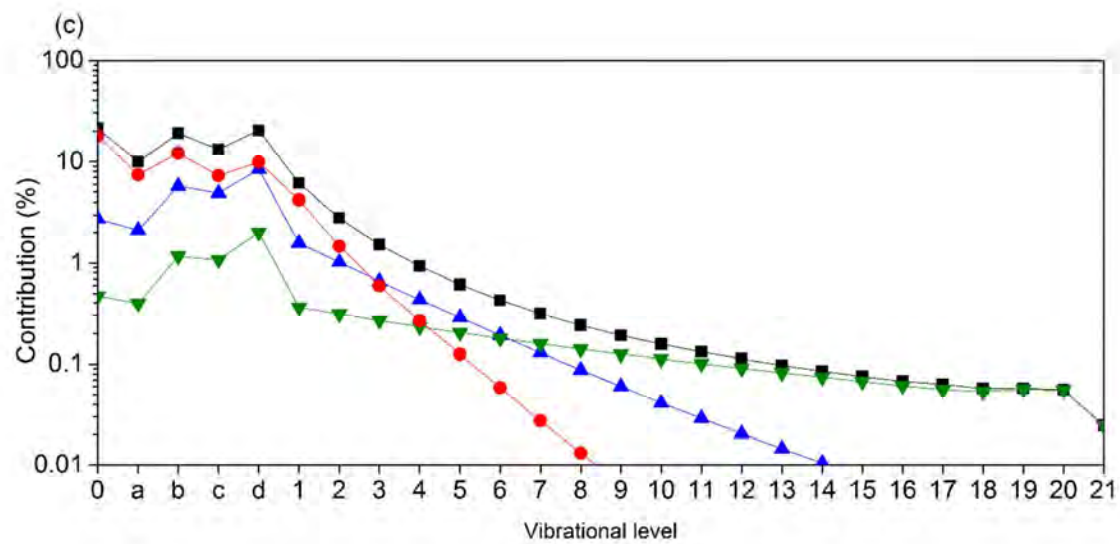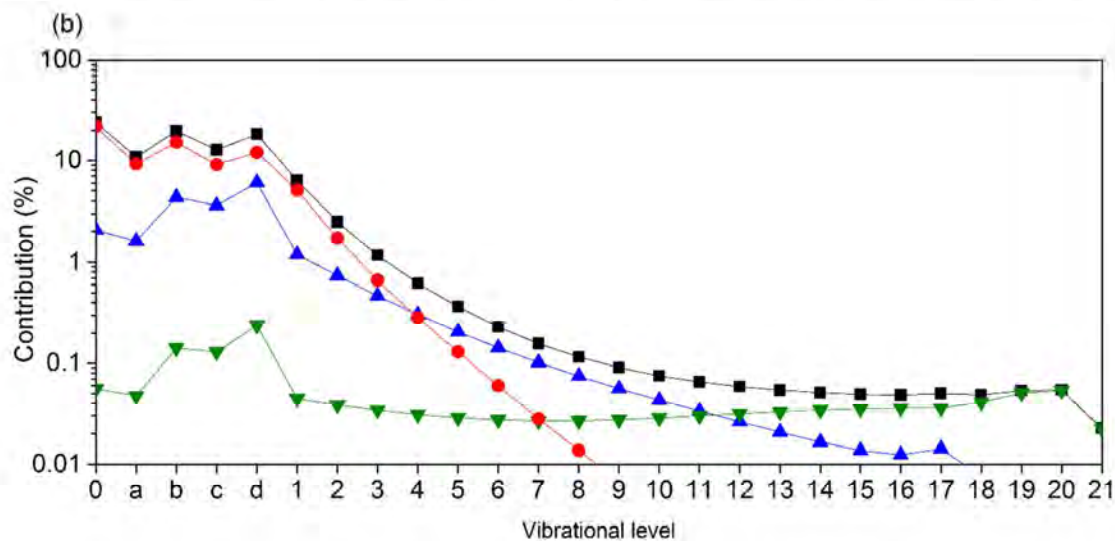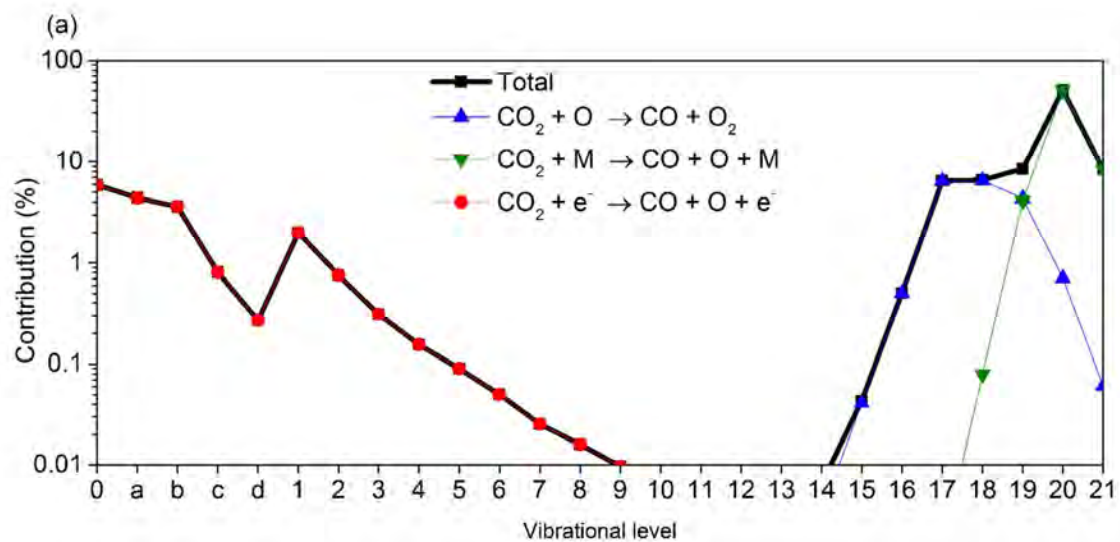
Figure S.7: Contribution of the different vibrational levels of CO_2 to the total dissociation of CO_2 at a flow rate of 200 L/min and a maximum gas temperature of 500 K (a), 3000 K (b) and 3500 K (c), at a SEI of 1.4 eV/molec, where the maximum energy efficiency is reached in case of 500 K (see Figure 8(d) from the main text).

References

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